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Commercial propane and butane — Analysis by gas chromatography

Propanes et butanes commerciaux — Analyse par chromatographie en phase gazeuse

Reference number
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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 7941 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

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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Commercial propane and butane — Analysis by gas chromatography

WARNING: Safety precautions — When testing LPG it is essential to observe suitable safety precautions and any regulations applicable to installations, apparatus and storage. Particular attention shall be given to the following.

a) LPG can cause serious burns from the cold, and the liquid should not be allowed to contact the skin. When sampling LPG, goggles and gloves must be worn.

b) Discharge of LPG can give rise to static electricity and it is essential to connect containers to "earth" prior to and during discharge.

If hydrogen is used as a carrier gas, special safety precautions shall be taken. More particularly, the hydrogen line shall be carefully tested for leaks, especially in the oven.

1 Scope and field of application

This International Standard specifies a gas chromatographic method for the quantitative determination of hydrocarbons in liquefied petroleum gas (LPG), excluding components whose concentrations are below 0,1 % (*m*/*m*). It is applicable to the analysis of propane, butane and their commercial mixtures, which may include saturated and unsaturated C_2, C_3, C_4 and C_5 hydrocarbons. It does not apply to "on-line" chromatography.

2 References

ISO 565, *Test sieves — Woven metal wire cloth, perforated plate and electroformed sheet — Nominal sizes of openings.*

ISO 4257, *Liquefied petroleum gases — Method of sampling.* [1)]

3 Principle

Physical separation by gas chromatography. Identification of the components by passing a standard reference mixture or pure hydrocarbons through the column, or by comparison with relative retention volumes of typical chromatograms. Calculation of concentrations of components by measuring peak areas and applying correction factors.

4 Definitions

4.1 correction factor: A factor applied to account for the fact that equal amounts of different components produce unequal signals in the detector.

4.2 peak: The portion of the chromatogram recording the detector response while a component is eluted from the column.

4.2.1 peak area: The area bounded by the peak and the baseline.

4.2.2 peak height: The distance between the peak maximum and the baseline.

4.2.3 peak width: The segment of the baseline intercepted by the tangents drawn at the inflection point of each side of the peak.

The **peak width at half height** is the segment of a line drawn parallel to the baseline at half the peak height which is intercepted by the peak sides.

If the baseline is seen to be sloping from the horizontal, both measurements are of the projection of these segments onto the horizontal axis.

4.2.4 peak resolution: The extent to which the peaks of two components overlap or are separated. It is expressed by means of the equation in 6.3.3. Values below 1 imply overlapping; values above 1 imply separation of the components.

4.3 Retention

4.3.1 adjusted retention time [or **volume**]: The time elapsed [or the volume of gas emerged from the column] between the moment of elution of unretained components (e.g. air or methane) and the moment of elution of the component in question, both referring to peak maxima.

1) To be published.

When a flame ionization detector is used, the air peak time may be calculated from uncorrected retention times of three consecutive normal paraffins as follows:

$$t_0 = \frac{t_1 t_3 - t_2^2}{t_1 + t_3 - 2t_2}$$

where

t_0 is the retention time for the unretained component;

t_1 is the retention time for component 1;

t_2 is the retention time for component 2;

t_3 is the retention time for component 3.

4.3.2 relative retention: The ratio of the adjusted retention time [or volume] of a component to that of a standard reference component.

4.4 internal normalization technique: The technique by which the concentration of a component is found by comparing its corrected peak area (the product of its peak area and correction factor) with the sum of the corrected peak areas of all components.

5 Materials

5.1 Carrier gas

Hydrogen (see **warning** on page 1), helium or nitrogen, free of hydrocarbons, oxygen and water impurities.

5.2 Reference gases

Pure gases or a mixture of gases with certified compositions, boiling in the LPG range.

6 Apparatus

6.1 General

Apparatus for gas phase chromatography, or chromatograph, containing the following main elements and satisfying the requirements defined in 6.2 to 6.7:

a) device for the control of the flow of carrier gas;

b) injection device (see 6.2);

c) oven with suitable column or columns;

d) detector (see 6.4);

e) recorder and, generally, integrator or computer (see 6.5).

6.2 Injection device

A liquid sample valve capable of delivering a liquid test portion of 0,5 to 1 µl, or a gaseous sample valve capable of delivering a gaseous test portion of up to 0,5 ml.

6.3 Column

The types of column described in this clause have been found suitable and are recommended. Other columns may be used provided that the resolution performance quoted in 6.3.3 is achieved and provided that the relative retentions of other hydrocarbons are well known.

6.3.1 Column material

The column should be made from glass, copper, stainless steel or aluminium tubing and have the following dimensions and form.

6.3.1.1 Dimensions

a) For commercial propane, 8 m of di-*n*-butyl maleate packing + 3 m of $\beta\beta'$-oxy-dipropionitrile packing.

b) For commercial butane, 8 m of di-*n*-butyl maleate.

c) For both applications, alternatively 6 m of sebaconitrile (1,8-dicyano-octane) packing.

Tubing with an internal diameter between 2 mm and 5 mm is recommended. The external diameter of the tubing should be appropriate to the chromatograph.

6.3.1.2 Form

Any suitable coil shape that will fit into the oven without acute bends.

6.3.2 Packing

6.3.2.1 Solid support

Chromosorb P[1)], acid washed and sieved to obtain the portion between 180 µm and 250 µm (see ISO 565).

6.3.2.2 Stationary phase

Chemical identity:

— di-*n*-butyl maleate and $\beta\beta'$-oxy-dipropionitrile [see 6.3.1.1 a) and 6.3.1.1 b)]

— sebaconitrile (1,8-dicyano-octane) [6.3.1.1 c)]

1) Chromosorb P is the trade-name of a commercially available product. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Level of loading:

— 25 g of stationary phase per 75 g of support for columns 6.3.1.1 a) and 6.3.1.1 b)

— 20 g of stationary phase per 80 g of support for column 6.3.1.1 c).

Solvent:

— pentane for columns 6.3.1.1 a) and 6.3.1.1 b)

— dichloromethane or toluene for column 6.3.1.1 c).

Procedure for coating:

— Dissolve 25 g [or 20 g for column 6.3.1.1 c)] of the stationary phase in a quantity of solvent such that the 75 g [or 80 g for column 6.3.1.1 c)] of support are covered entirely by the solution.

— Cover the solid support with the solution and stir the mixture with a clean glass rod until excess solvent has evaporated or been absorbed. Transfer the mixture to a rotary evaporator and remove the remaining solvent so that the packing becomes dry and free-running.

— Screen the support thus prepared gently, and preserve the 180 µm to 250 µm fraction.

6.3.2.3 Method of packing

Use a method of packing that allows reproducible columns to be prepared. The flow of packing into the column may be assisted by applying a vacuum to the column outlet, and regular packing ensured by tapping or by applying gentle vibration to the column.

6.3.2.4 Column conditioning

The column should be maintained at a temperature of 40 °C for 5 h with the carrier gas flowing but with the detector disconnected. The column outlet should be disconnected from the detector.

6.3.3 Resolution in the recommended experimental conditions

The following resolution should be obtained between propane and propene in commercial propane and between propene and isobutane in commercial butane (see figure 1):

$$R_{AB} = 2\frac{[d'_{R(B)} - d'_{R(A)}]}{w_A + w_B} \geqslant 1,5$$

where

A and B are the components propane and propene or propene and isobutane respectively;

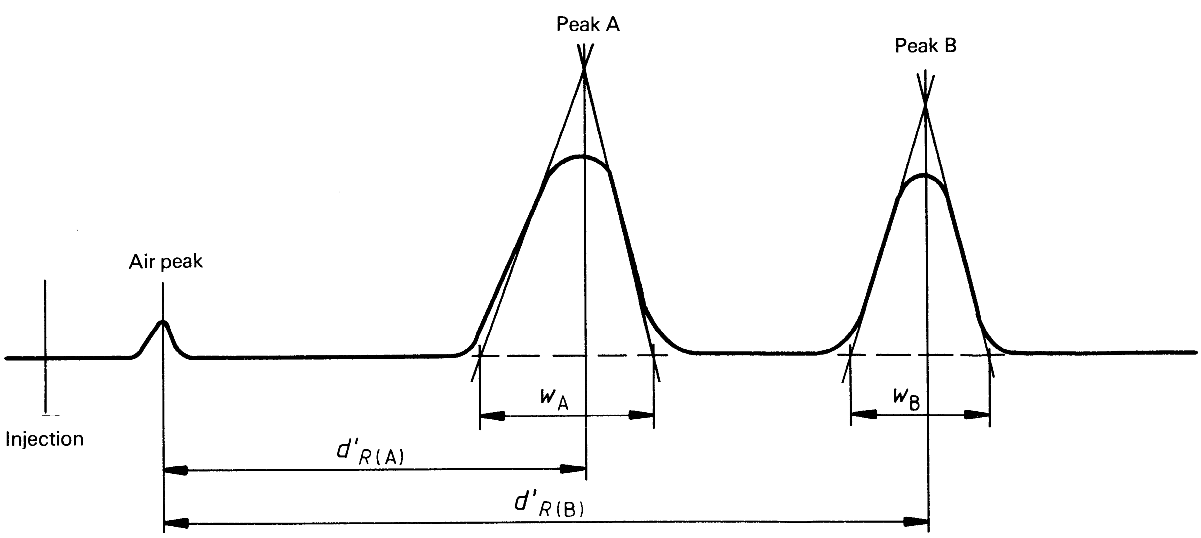
R_{AB} is the resolution for the two peaks A and B;

$d'_{R(A)}$ and $d'_{R(B)}$ are the adjusted retention times for components A and B respectively, the times being expressed as chart distances in millimetres;

w_A and w_B are the peak widths of components A and B respectively.

6.4 Detector

The detector may be a thermal conductivity type (hot-wire type or thermistor type) or a flame ionization type. The system should be capable of detecting 0,1 % concentration of any



NOTE — The diagram shows an air peak, but this would not be seen with a flame ionization detector.

Figure 1 — Measurements for determination of resolution

component that is resolved. If a recorder is used and the peaks are measured subsequently, the peak height for this concentration should be at least 5 chart divisions above the noise level on a 0 to 100 division chart. The noise level should be restricted to a maximum of 1 chart division. If electronic integration is employed, the signal for a component present at 0,1 % should be measurable with a repeatability of not greater than 20 % relative when the sample is analysed.

Check the linearity of response of the apparatus by injecting a series of reference gas mixtures with widely varying but known concentrations or by injecting mixtures of pure gases at different known partial pressures.

6.5 Recorder and optional integrator or computer

The potentiometric recorder should have the following characteristics:

a) a maximum full scale response time of 1 s;

b) an available chart speed such that the first peak width to be measured will be at least 3 mm at half height.

Peak areas are measured either manually, as described in 8.4.3, or by using electronic integration. Both techniques have been used to establish the precision quoted in clause 10.

The integrator should have the following characteristics:

a) wide range (0-1 V) input;

b) capable of baseline tracking and of measuring peaks on a sloping baseline.

6.6 Attenuator

If peak areas are to be measured from the recorder chart, a multistep attenuator for the amplified detector output should be used to maintain the peak maxima on the recorder chart.

6.7 Sintered metal filter

If a liquid sample valve (6.2) is used, it is recommended that a suitable sintered metal filter should be inserted before the injector, to prevent the introduction of solid particles into the injector. This filter should be located just after the outlet valve from the sampling container or cylinder.

7 Sampling

See ISO 4257.

8 Procedure

8.1 Control of the apparatus

8.1.1 Injector port

For liquid injection, adjust the injection port temperature to 40 ± 5 °C but maintain the liquid sample valve at ambient temperature. For gaseous injections, the sample valve and loop may be warmed (e.g. to 70 °C) to avoid condensation of higher boiling components at the column pressure.

8.1.2 Oven

Depending on the choice of column, maintain the oven temperature at

— 40 ± 1 °C for columns 6.3.1.1 a) and 6.3.1.1 b);

— 20 ± 1 °C for column 6.3.1.1 c).

8.1.3 Flowrate

Adjust the flow to a value such that the conditions required for the resolution (see 6.3.3) are obtained.

8.1.4 Detector

Thermistor type conductivity detectors should be operated at 40 to 50 °C.

Hot-wire type conductivity detectors should be operated at 100 to 150 °C.

The flame ionization detector should be operated at 100 to 150 °C.

8.1.5 Recorder

Select the chart speed to obtain the conditions set out in 6.5.

8.2 Calibration

8.2.1 Qualitative analysis

The identification of components may be obtained by passing through the column a standard reference mixture or pure hydrocarbons, or by comparison with typical chromatograms and relative retentions (see 4.3.2) shown respectively in figures 2, 3 and 4 and table 1.

8.2.2 Quantitative analysis

8.2.2.1 Thermal conductivity detector

The calibration method is an internal normalization method. The peak area correction factors used[1)] are given in tables 2

1) The peak area correction factors used have been taken from the following publication:

KAISER, *Gas phase chromatography,* vol. III, p. 91, Butterworths (1963), the values in which were taken from:

VAN DE CRAATS, *Gas chromatography 1958*, Butterworths (1958) (for hydrogen gas vector);

MESSNER and ROSIE, *Analytical chemistry*, 1959, vol. 31, p. 230 (for helium gas vector).

The precision given in clause 10 was based on the use of these correction factors.

and 3. They should be used only as a guide or approximation; laboratories who have both the equipment and the experience to prepare calibration gas mixtures should determine their own correction factors.

8.2.2.2 Flame ionization detector (FID)

If the linearity is satisfactory for FID detection (see 6.4), peak area correction factors F_i for component masses are calculated according to the following formula:

$$F_i = \frac{(12{,}01\ n_{Ci} + 1{,}008\ n_{Hi}) \times 0{,}826\ 5}{12{,}01\ n_{Ci}}$$

where

n_{Ci} is the number of carbon atoms in component i;

n_{Hi} is the number of hydrogen atoms in component i;

0,826 5 is the mass factor of carbon in butane, its use serving only to make F_i (butane) = 1; the factors for other components are given in table 4.

8.3 Introduction of test portion

Volume of test portion injected: 0,5 to 1 µl for liquid injection; up to 0,5 ml for gaseous injection.

The size of test portion chosen for the test should be such that linear response is ensured (see 6.4).

8.3.1 Liquid injection (preferred method)

Place the sampling container or the gas cylinder in an upright position, with the outlet valve at the bottom. Connect this valve through the metal filter (6.7) to the injector, using a non-plasticized or plastic, transparent, armoured or pressure-resisting tube which should be earthed (see figure 5).

Downstream of the purge system of the injection device, use a pressure-reducing valve to avoid any vaporization upstream when the flow equilibrium is reached.

Open the outlet valve and control the flow through the transparent tube so that the latter becomes completely filled with liquid.

Inject the test portion into the column.

Close the outlet valve.

8.3.2 Gaseous injection (less desirable)

Use one of following alternative procedures:

8.3.2.1 Connect a sampling container of 2 ml capacity (see figure 6) in an upright position, with the inlet valve at the bottom, directly to the liquid sample source or to a larger sampling container containing the liquid sample. Purge the 2 ml container until liquid appears at the outlet. Close the outlet valve, and after approximately 10 min (to establish equilibrium), close the inlet valve. Close the sample source valve and disconnect the 2 ml sample container. Support the container in the upright position, open the bottom valve, and run off approximately 20 % of the contents.

Vaporize the sample completely into an empty vessel of a sufficient capacity to contain the sample at a pressure slightly greater than atmospheric pressure. Mix the sample thoroughly. Connect this vessel to the injection device, flush the loop and then inject the test portion into the column.

8.3.2.2 Use a normal sampling container, in a vertical position with the ullage tube at the top. Connect a Drechsel bottle, containing sufficient water to give a 6 mm seal, to the outlet of the sample loop of the injector. Connect the bottom sampling container valve to the inlet of the sample loop, open it slightly and allow the vapour to purge the loop at the rate of two bubbles per second (as indicated at the Drechsel bottle). Care should be taken not to open the valve on the sampling container excessively, or the lighter hydrocarbons will vaporize at a faster rate than the heavier ones and the test portions injected will not be representative of the liquid in the sampling container. Purge the sample loop with about ten times its volume, and then close the valve on the sampling bomb. Allow the vapour in the loop to come to atmospheric pressure and inject the test portion into the column. Disconnect the Drechsel bottle to prevent water being sucked back into the chromatograph.

8.4 Examination of the chromatograms

8.4.1 Typical chromatograms

Figures 2, 3 and 4 represent typical chromatograms obtained with samples of commercial propane, commercial butane and a reference mixture containing LPG components. The columns used are those described in 6.3.1.1 a), 6.3.1.1 b) and 6.3.1.1 c) respectively and under the conditions as described in 8.3.1.

8.4.2 Qualitative analysis

8.4.2.1 Identification of components

Identify the components by comparison with a reference mixture or by relative retention times (see 8.2.1).

8.4.2.2 Interferences

Under the conditions recommended in this International Standard, there is no separation between the following pairs of components:

— air and methane, with the columns 6.3.1.1 a), b) and c);

— ethane and ethene, with the columns 6.3.1.1 a), b) and c);

— butane and isobutene, with the columns 6.3.1.1 a) and b).

8.4.3 Quantitative analysis

Evaluate the peak area for each component (A_i) as follows, depending on whether a recorder or an integrator or a computer is used.

8.4.3.1 Using a recorder

Measure each peak height and peak width at half height (see 6.3.3) and calculate the product for each peak to give the recorded peak area; correct the recorded peak areas all to the same attenuation to give the peak areas.

8.4.3.2 Using an integrator or a computer

Note the reading corresponding to each peak and use it in place of the peak area in the calculation (clause 9).

9 Expression of results

Calculate the concentration of each component in the sample using the following equations.

9.1 Thermal conductivity detector

The mass percentage, x_i % (m/m), of component i in the sample is given by the equation

$$x_i = \frac{K_i A_i}{\sum_{i=1}^{i=n} K_i A_i} \times 100$$

where

K_i is the peak area mass correction factor for component i given in table 2;

A_i is the peak area of component i;

n is the number of components in the mixture.

The molar percentage, x_i % (molar), of component i in the sample is given by the equation

$$x_i = \frac{K'_i A_i}{\sum_{i=1}^{i=n} K'_i A_i} \times 100$$

where

K'_i is the peak area molar correction factor for component i given in table 3;

A_i is the peak area of component i;

n is the number of components in the mixture.

Round off the values to one-tenth of the reproducibility (see table 5).

9.2 Flame ionization detector

The mass percentage, x_i % (m/m), of component i in the sample is given by the equation

$$x_i = \frac{F_i A_i}{\sum_{i=1}^{i=n} F_i A_i} \times 100$$

where

F_i is the FID peak area mass correction factor for component i given in table 4;

A_i is the peak area of component i;

n is the number of components in the mixture.

The molar percentage, x_i % (molar), of component i in the sample is given by the equation

$$x_i = \frac{A_i / n_{Ci}}{\sum_{i=1}^{i=n} (A_i / n_{Ci})}$$

where

n_{Ci} is the number of carbon atoms in component i;

A_i is the peak area of component i;

n is the number of components in the mixture.

Round off the values to one-tenth of the reproducibility (see table 5).

10 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows.

10.1 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown in table 5 only in one case in twenty.

10.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown in table 5 only in one case in twenty.

11 Test report

The test report shall contain at least the following information:

a) the type and identification of the product tested;

b) a reference to this International Standard;

c) the result of the test;

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.

Table 1 — Relative retention (relative to *n*-butane)

Component	Relative retention		
	di-*n*-butyl maleate column	di-*n*-butyl maleate + *ββ'*-oxy-dipropionitrile column	sebaconitrile column
Air + methane	0	0	0
Ethane	0,11	0,16	0,11
Ethene	0,11	0,16	0,11
Propane	0,33	0,37	0,32
Propene	0,42	0,59	0,52
Isobutane	0,68	0,69	0,64
n-butane	1	1	1
1-butene	1,20	1,44	1,50
Isobutene	1,20	1,44	1,61
2-*trans*butene	1,55	1,75	1,95
2-*cis*butene	1,77	2,05	2,31
1,3-butadiene	1,96		3,17
Isopentane	2,21		2,19
n-pentane	2,86		2,83

NOTE — These values are not applicable when standard blends are used, and should be confirmed by the use of carefully prepared known mixtures.

Table 2 — Thermal conductivity detector — Peak area correction factors for component mass

Component	Peak area correction factor	
	Hydrogen carrier gas	Helium carrier gas
Methane	0,56	0,65
Ethane	0,74	0,86
Ethene	0,74	0,84
Propane	0,89	0,97
Propene	0,90	0,94
Isobutane	1,03	1,02
n-butane	1	1
1-butene	1,00	1,00
Isobutene	1,01	1,00
2-*trans*butene	0,99	0,96
2-*cis*butene	0,99	0,94
1,3-butadiene	1,01	0,99
Isopentane	1,14	1,05
n-pentane	1,10	1,01

NOTE — These values are not applicable when standard blends are used, and should be confirmed by the use of carefully prepared known mixtures.

Table 3 — Thermal conductivity detector — Peak area correction factors for component molar fraction

Component	Peak area correction factor	
	Hydrogen carrier gas	Helium carrier gas
Methane	2,03	2,37
Ethane	1,44	1,66
Ethene	1,52	1,74
Propane	1,17	1,28
Propene	1,24	1,29
Isobutane	1,03	1,02
n-butane	1	1
1-butene	1,03	1,03
Isobutene	1,04	1,04
2-*trans*butene	1,02	1,00
2-*cis*butene	1,02	0,98
1,3-butadiene	1,08	1,07
Isopentane	0,92	0,85
n-pentane	0,89	0,82

NOTE — These values are not applicable when standard blends are used, and should be confirmed by the use of carefully prepared known mixtures.