International Standard 6378

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

Butadiène 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.

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

Austria	Hungary	Portugal
Belgium	India	Romania
China	Italy	South Africa, Rep. of
Czechoslovakia	Korea, Rep. of	Switzerland
France	Netherlands	USSR
Germany, F.R.	Poland	

No member body expressed disapproval of the document.

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Butadiene 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 butadiene for industrial use.

The method is applicable to the determination of the impurities listed in annex B and principally to the determination of

— acetylene (ethyne) ($CH \equiv CH$) at concentrations greater than 5 ml/m³;

— propyne ($CH \equiv C - CH_3$) at concentrations greater than 5 ml/m³;

— 1-butyne ($CH \equiv C - CH_2 - CH_3$) at concentrations greater than 5 ml/m³;

— 3-buten-1-yne ($CH \equiv C - CH = CH_2$) at concentrations greater than 5 ml/m³;

— 1,2-butadiene ($CH_2 = C = CH - CH_3$) at concentrations greater than 10 ml/m³.

2 Reference

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

3 Principle

Selection of a gas chromatography column allowing the separation of the impurities to be determined.

Passage of a gaseous test portion through the column, 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 of the best available commercial quality, having oxygen and water contents each less than 5 ml/m³.

4.2 Standards

Prepare (or obtain) standard mixtures such that the concentration of each impurity to be determined is within the concentration limits which are encountered in the product to be analysed.

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 concentrations for each of the impurities as given in clause 1.

5.1.1 Injection device (see ISO 6377), permitting the introduction into the column of a test portion of about 1 ml, constant to within ± 1 %.

5.1.2 Columns

A number of columns which have been found suitable are described in annex A. Use, according to the desired aim, one of these columns, or several of them in succession, or any other columns giving satisfactory separation.

5.1.3 Detector, flame ionization type.

5.1.4 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.

6 Preparation of sample

See ISO 6377.

7 Procedure

7.1 Preparation of the apparatus

Select a column 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 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 (see annex A). Wait a sufficient time for these conditions to become stable (the production of a stable base line).

7.2 Injection of the test portion

See ISO 6377.

7.3 Preliminary test

Inject a preliminary test portion in order to establish that the separation of the peaks corresponding to the impurities to be determined is suitable. If the contents of the impurities are to be calculated from the peak heights, determine, taking into account the capability of the recorder, the attenuation at which these peaks will be as high as possible.

7.4 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.

7.5 Determination

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

7.6 Examination of the chromatograms

7.6.1 Typical chromatogram

See annex C.

7.6.2 Retention time

See annex B.

7.6.3 Calculation

See ISO 6377.

8 Expression of results

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

9 Test report

See ISO 6377.

Annex A

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

Column	Sebaconitrile[1]	Reoplex 400[2]	Flexol 8N8[3]
Length m	9	10	8
Internal diameter mm	4	4	4
Material	Stainless steel	Stainless steel	Stainless steel
Stationary phase	30 % Sebaconitrile	30 % Reoplex 400	30 % Flexol 8N8
Supporting phase	Chromosorb P-AW 60-80	Chromosorb P-NAW 30-60	Chromosorb P-NAW 30-60
Temperature °C	25	22	22
Carrier gas	Helium	Nitrogen	Nitrogen
Flow rate ml/min	30	50	50

Column	Squalane[4]	ββ′-iminodi-propionitrile[5]	Propylene carbonate
Length m	8	20	9
Internal diameter mm	4	4	2,4
Material	Stainless steel	Stainless steel	Stainless steel
Stationary phase	30 % Squalane	30 % ββ′-iminodipropionitrile	20 % propylene carbonate
Supporting phase	Chromosorb P-NAW 30-60	Chromosorb P-NAW 30-60	Chromosorb P-NAW 60-80
Temperature °C	22	22	4
Carrier gas	Nitrogen	Nitrogen	Helium
Flow rate ml/min	50	65	15

1) Sebaconitrile = decane-dinitrile, $NC-(CH_2)_8-CN$

2) Reoplex 400 = 1,2-propanediol-adipate

3) Flexol 8N8 = 2,2′ -(2-ethylhexanamido)-diethyl-di-2-ethylhexoate

4) Squalane $C_{30}H_{62}$ = 2,6,10,15,19,23-hexamethytetracosane

5) ββ′-iminodipropionitrile = $NC-CH_2-CH_2-NH-CH_2-CH_2-CN$

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

Column	Sebaconitrile and di-*n*-propyl phthalate (two columns in series)		Dimethyl phthalate, diethyl phthalate and di-*n*-propyl phthalate (two columns in series)	
Length m	9	1	12	1
Internal diameter mm	2	2	2	2
Material	Stainless steel	Stainless steel	Stainless steel	Stainless steel
Stationary phase	30 % Sebaconitrile	17 % di-*n*-propyl phthalate	17,5 % DMP and 7,5 % DEP	17 % di-*n*-propyl phthalate
Supporting phase	Chromosorb P-AW 60-80	Alumina 100-200	Chromosorb P 60-80	Alumina 100-200
Temperature °C	22	22	22	22
Carrier gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen
Flow rate ml/min	20	20	20	20

Annex B

Analysis of butadiene — Absolute retention times (in minutes)

Compounds	Column (see annex A)			
	Sebaconitrile	Reoplex 400	Flexol 8N8	Squalane
Methane	3,1	2,6	2,6	2,8
Ethane	4,0*	2,9*	3,3*	4,3
Ethene	4,0*	2,9*	3,2*	3,6
Ethyne	6,4*	6,0*	4,5	3,2
Propane	4,9	3,4	5,2	8,8*
Propene	5,9	4,0*	5,6	7,8
Cyclopropane	8,6	—	8,5*	13,5
Propadiene	9,7	7,3*	8,5*	10,2
Propyne	14,8	—	10,2	8,8*
Isobutane	6,5*	4,0*	8,5*	16,4
n-butane	8,0	4,7	11,1	24,3
1-butene	10,2	6,0*	11,9*	—**
Isobutene	10,8	6,0*	11,9*	—**
trans-2-butene	12,4	7,0*	14,2	26,2
cis-2-butene	14,1	7,9*	—**	29,2
1,3-butadiene	18,0	10,5	17,0	21,0
1,2-butadiene	22,5	14,9*	22,2*	33,2
1-butyne	29,4*	20,3	22,2*	—**
3-butene-1-yne	38,9	31,6	27,2	18,0
2-butyne	—	35,4	39,0	48,9*
2,2-dimethylpropane	8,2	—	—	28,2
2-methylbutane	13,4	7,0*	22,2*	55,6
n-pentane	16,2	7,9*	28,5	75,0*
1,4-pentadiene	27,9*	14,9*	—	48,9*
1-pentene	21,4	—	29,1	60,3
trans-2-pentene	24,0	—	34,8	75,0*
cis-2-pentene	27,2*	—	37,4	78,9

* Overlapping peaks.

** Eluted with 1-3 butadiene.

Compounds	Column (see annex A)			
	$\beta\beta'$-iminodipropionitrile	Propylene carbonate	Sebaconitrile + di-*n*-propyl phthalate	DMP and DEP + di-*n*-propyl phthalate
Methane	8,2	—	—	—
Ethane	8,8	—	—	—
Ethene	9,3	—	—	—
Ethyne	16,9*	—	—	—
Propane	9,8	—	9	9
Propene	11,7	7,8*	11	11
Cyclopropane	16,0*	—	—	—
Propadiene	20,5*	15,3*	28	28
Propyne	38,1	32,0	44	44
Isobutane	10,9	7,8*	19	19
n-butane	12,1*	9,1	24	24
1-butene	16,0*	13,0	30*	30*
Isobutene	16,9*	14,2*	30*	30*
trans-2-butene	18,1	15,3*	35	35
cis-2-butene	20,5*	18,0	41	41
1,3-butadiene	30,0	26,3	48	48
1,2-butadiene	36,5	34,8	67	67
1-butyne	58,9	84,0	80	80
3-butene-1-yne	—	124,0	100	100
2-butyne	—	—	—	—
2,2-dimethylpropane	12,1*	—	—	—
2-methylbutane	15,3	14,3*	—	—
n-pentane	17,3	21,8	—	—
1,4-pentadiene	—	—	—	—
1-pentene	24,8	—	—	—
trans-2-pentene	—	—	—	—
cis-2-pentene	—	—	—	—

* Overlapping peaks.

Annex C

Typical chromatogram from a Sebaconitrile column