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### Determination of aliphatic unsaturated hydrocarbons in hydrocarbon mixtures

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The determination of unsaturated hydrocarbons in hydrocarbon mixtures is one of the major tasks in petrochemistry and petroleum refining. In the method usually applied for the group analysis of unsaturated aliphatic hydrocarbons, they are absorbed from a mixture passed through a 20% solution of mercury(II) sulphate in a 20% solution of sulphuric acid, the mixture being chromatographed both before and after the reaction<sup>1,2</sup>. Disadvantages of this method are that the absorption system can be used for the sorption only of low-boiling compounds (boiling at temperatures of up to 100°C) as it is active at temperatures ranging from 20 to 40°C, special conditions are necessary to maintain the salt and acid concentrations strictly constant (when the water is entrained, more concentrated solutions also absorb aromatic hydrocarbons, whereas more dilute solutions do not provide complete absorption) and it is not very reliable as it absorbs *trans*-isomers of beta-olefins only extremely slowly<sup>3</sup>.

A possible means of identifying such components is to use the "subtraction" method, using a support with immobilized functional groups. In this work we studied the possibility of using a macroporous styrene-divinylbenzene copolymer with N,N-dichlorosulphonamide groups for the selective chemical adsorption of unsaturated aliphatic hydrocarbons<sup>4</sup>.

#### EXPERIMENTAL

The macroporous styrene-divinylbenzene copolymer with N,N-dichlorosulphonamide groups was synthesized at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences (Prague, Czechoslovakia) (specific surface area 336 m<sup>2</sup>/g; concentration of active groups 1.18 mg-equiv./g) from Synachrom E5 macroporous styrene-divinylbenzene copolymer (Lachema, Brno, Czechoslovakia).

The chemicals (see Table I) were obtained from commercially available sources. Silicone rubber SE-30 GC was obtained from Supelco (Bellefonte, PA, U.S.A.)

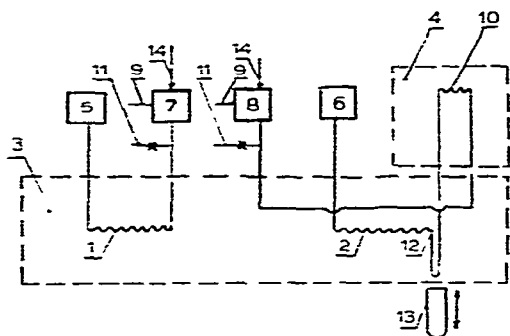


Fig. 1. Schematic diagram of apparatus. 1,2 = Chromatographic columns; 3 = thermostat for columns; 4 = thermostat for katharometer (the components housed in the thermostats are shown within broken lines); 5,6 = detectors; 7,8 = sample ports; 9 = carrier gas (nitrogen) port; 10 = column; 11 = discharge; 12 = trap (25 cm  $\times$  1.2 mm I.D. capillary filled with glass beads 0.2 mm in diameter); 13 = Dewar flask.

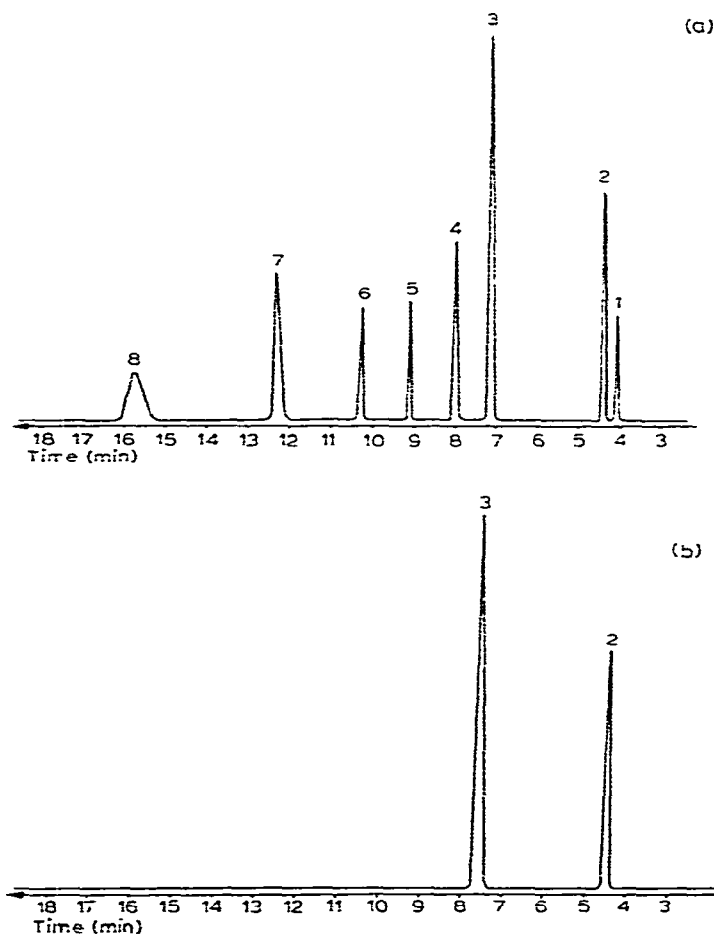


Fig. 2. (a) Chromatogram of separation of a mixture of hydrocarbons. 1 = 2-Methylpentene-2; 2 = *n*-hexane; 3 = *n*-nonane; 4 = decene-1; 5 = undecene-1; 6 = dodecene-1; 7 = tridecene-1; 8 = tetradecene-1. (b) Chromatogram of separation of the same mixture passed through the column containing the macroporous styrene-divinylbenzene copolymer with *N,N*-dichlorosulphonamide groups at 230°C.

and Chromaton NAW from Lachema. A Tsvet-3 gas chromatograph was used with two independent carrier gas lines, one serving as a reference line and the other as the working line incorporating a column (10, Fig. 1) containing the macroporous copolymer (60 cm  $\times$  1.2 mm I.D.). The sorption temperatures were 130 and 230°C. The chromatographic columns (1 and 2) (3 m  $\times$  1.2 mm I.D.) were packed with 5% SE-30 on Chromaton NAW (0.1–0.16 mm fraction). The tested mixtures of saturated and

TABLE I

## ADSORPTION OF ORGANIC COMPOUNDS BY THE COPOLYMER

Substance	Boiling point (°C)	Adsorption (%)	
		130°C	230°C
<i>n</i> -Hexane	69	0	0
<i>n</i> -Heptane	98	0	0
<i>n</i> -Nonane	150	0	0
<i>n</i> -Decane	174	0	0
<i>n</i> -Undecane	194	0	0
<i>n</i> -Dodecane	215	0	0
<i>n</i> -Tridecane	234	0	0
<i>n</i> -Tetradecane	253	0	0
Ethylene	-104	95	100
Butene-1	-5	98	100
Pentene-1	30	100	100
Pentene-2 ( <i>cis</i> - and <i>trans</i> -)	36	100	100
Hexene-1	66	100	100
Hexene-3	64	100	100
2,3-Dimethylbutene-2	73	100	100
2-Methylpentene	80	100	100
4-Methylpentene-2 ( <i>cis</i> - and <i>trans</i> -)	80	100	100
Heptene-1	95	100	100
Heptene-2 ( <i>cis</i> - and <i>trans</i> -)	99	100	100
Octene-1	120	100	100
2,4,4-Trimethylpentene-1	126	—*	100
Decene-1	172	—*	100
Undecene-1	188	—*	100
Dodecene-1	208	—*	100
Tridecene-1	233	—*	100
Tetradecene-1	248	—*	100
Acetylene	-84	100	100
Methylacetylene	-27	100	100
1,3-Butadiene	-4	100	100
Piperylene	42	100	100
Isoprene	32	100	100
Propylacetylene	48	100	100
Hexyne-1	63	100	100
Hexyne-3	64	100	100
Octyne-3	115	100	100
Cyclohexane	81	0	0
Cyclopentane	49	0	0
Benzene	80	0	0
Toluene	111	0	0
Ethylbenzene	136	0	0

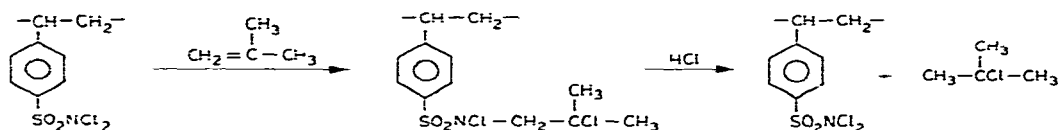
\* Not tested.

unsaturated hydrocarbons were injected through the sample port (8) into the column (10). The unadsorbed substances in this column were concentrated for 2 min (up to 20 min with aromatic hydrocarbons) in a trap (12) cooled with liquid nitrogen. At the end of the concentration period the Dewar flask was removed and the substances concentrated in the trap were injected into the separation column (2). After exposure for 2 min at room temperature (20°C) to defrosting the trap (12), the thermostat of the columns was heated to 95°C (with substances boiling below 100°C) or to 200°C (with higher boiling substances) at the rate of 15°C/min.

The test mixtures were also introduced into column 1, and a comparison was made of the chromatograms obtained on column 1 (initial mixture composition) and column 2 (composition of the mixture after adsorption). Fig. 2a shows as an example the chromatogram of the separation of one of the mixtures before adsorption and Fig. 2b the same mixture after adsorption. The separation conditions were as follows: carrier gas flow-rate, 4 ml/min; freezing-out time, 2 min; exposure at 20°C, 2 min; and subsequent heating, to 200°C.

## RESULTS AND DISCUSSION

The experiment involved 40 substances, including alkanes, naphthenes, olefins, dienes, acetylenes and aromatic hydrocarbons. The results in Table I show that only ethylene is not completely adsorbed by the copolymer at 130°C. Hence, the macroporous styrene-divinylbenzene copolymer with N,N-dichlorosulphonamide groups completely adsorbs olefins, dienes and acetylenes over a wide temperature range (the range from 130 to 230°C was tested). The sorption rate increases with increasing temperature. Alkanes, naphthenes and aromatic hydrocarbons are not adsorbed by the copolymer. After the copolymer has lost its activity, it can be reactivated by passing hydrogen chloride through it at 25–60°C for 10–2 h. The adsorption reaction yields an adduct. For example, the reactions of adsorption of isobutylene by the copolymer (first step) and regeneration of the sorbent (second step) are as follows:



Thus, the use of the copolymer makes it possible to extend substantially the range of adsorbable compounds, including higher-boiling ones (boiling at up to 250–280°C), with rapid and reliable sorption of *trans*-isomers of beta-olefins. The group analysis technique is simple and there is no need to use toxic mercury(II) compounds.

The results indicate the promising nature of porous supports with immobilized functional groups used as reagents in group analysis by the "subtraction" method.

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