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"SYNACHROM", A MACROPOROUS COPOLYMER, AS A SORPTION MATERIAL FOR GAS CHROMATOGRAPHY

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SUMMARY

A chromatographic sorbent called "Synachrom" based on a styrene-divinylbenzene bead copolymer has been developed. The chromatographic separation properties of this material were investigated for mixtures of gases and a number of other materials, for which the Kováts' elution indices were measured. The elution of several near boiling substances from different homologous series was investigated in order to elucidate the separation properties of "Synachrom" and it was found, that the elution order corresponds to the increasing value of the polarizability of substances. From this it is evident, that Synachrom behaves not only as an adsorbent but also as a liquid phase of non-polar character. The properties of Synachrom correspond to analogous types of unmodified polymer sorbents, which are available on the world market at present.

In recent years macroporous copolymers have been used frequently as packings for gas chromatography columns; especially copolymers of styrene with divinylbenzene or ethylvinylbenzene and divinylbenzene, respectively. They are usually prepared by means of pearl copolymerization; the preparation, and some of the properties of the bead polymer have been described by LLOYD AND ALFREY^{1,2}, the preparation being claimed by a number of patent specifications, including some from Czechoslovakia³.

The use of these materials for gel permeation chromatography was described by MOORE⁴, and by HOLLIS⁵ who followed the work of the former, using, for the first time, macroporous copolymers of the styrene-divinylbenzene type for gas chromatography. At present the material is available from a number of firms (in particular Waters Associates), and is designated by different trade-marks, such as Porapak Q-PAR, Polypack etc. Further development was pursued especially by Waters Associates, who now offer further types of Porapak (S, R, T, N) which, again, are copolymers based on styrene and divinylbenzene with a certain quantity of a polar monomer, containing different groups, *e.g.* carboxylic groups. Another type of porous polymer based on polyphenylethers has been described by TRANCHANT⁶.

As a result of earlier experience in the preparation of macroporous ion exchangers at the Research Institute for Synthetic Resins and Lacquers we tried to prepare an analogous type of styrene-divinylbenzene copolymer having suitable properties for use as a sorption material for gas chromatography. The bead copolymer was prepared by suspension copolymerization of styrene and divinylbenzene in the presence of an inert substance producing a porous structure and which was removed after the end of the polymerization. A three-dimensional both inter and intramolecular network is produced during polymerization. The microstructure of the bead copolymer is shown in Fig. 1. The structure and properties, *i.e.* swelling capacity, particle size, specific surface, distribution and diameter of pores, are characterized by:

- (a) the type of the inert substance and its quantity;
- (b) the quantity of divinylbenzene;
- (c) the conditions of the pearl polymerization (temperature, polymerization time, suspension stabiliser, mixer revolutions, etc.).

The size of the specific surface of the copolymer, measured by the BET method, varies according to the preparation conditions, within the limit of 10^2 – 10^3 m²/g; with Synachrom the specific surface size was found to be 520 m²/g. Using the thermal desorption method, a value of 620 m²/g was found for the same sample. The volume of the inside pores per g of material was found to be 2.34 ml/g from the measured densities of helium ($\rho = 1.038$ g/ml). If one assumes that the pores have the form of infinite cylinders, the mean diameter of the pores can be calculated, which, in case of the given Synachrom sample, was 45 Å.

Another part of our work was devoted to the evaluation of the macroporous copolymer as the sorption packing for a chromatographic column. Like any solid



Fig. 1. Microstructure of Synachrom: a section under an electron microscope.

material with a large and rough surface the copolymer has the character of an adsorbent. Furthermore, especially when vapors of organic substances are separated, not only adsorption can occur, but also the molecules of the sorbate can penetrate into the structure of the copolymer, *i.e.* absorption, which depends upon the character

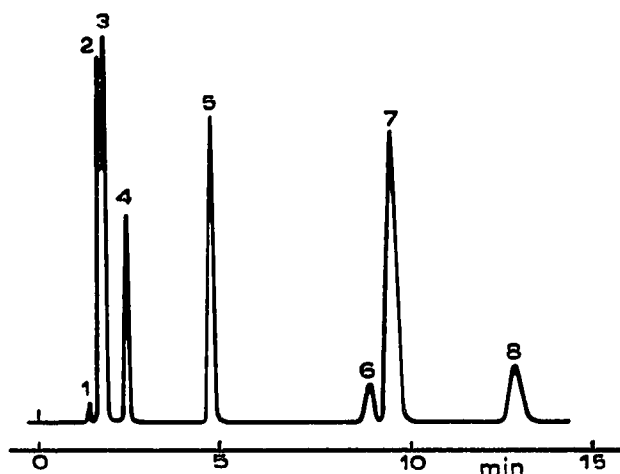
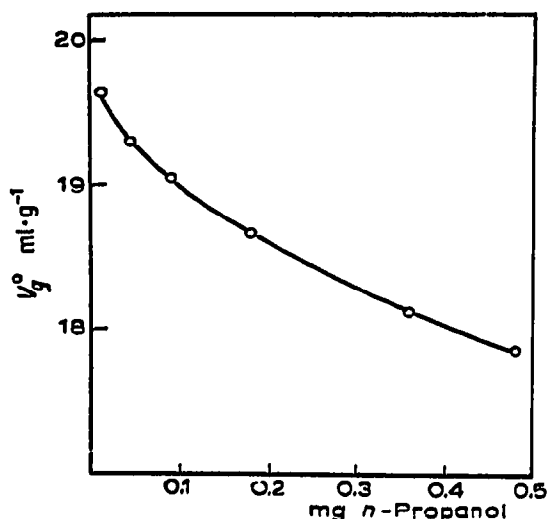


Fig. 2. Dependence of specific retention volume V_g^0 on the sample size of *n*-propanol.

Fig. 3. Fractovap GV (Carlo Erba), thermal conductivity detector, Synachrom 60/80 mesh, column 5 m × 2 mm, stainless steel, temperature 26°, carrier gas He, 25 ml/min. 1 = H₂; 2 = N₂ + O₂; 3 = CO; 4 = CH₄; 5 = CO₂; 6 = C₂H₄; 7 = C₂H₂; 8 = C₂H₆.

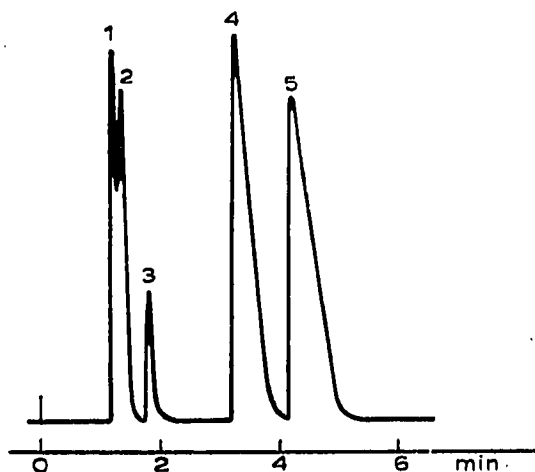
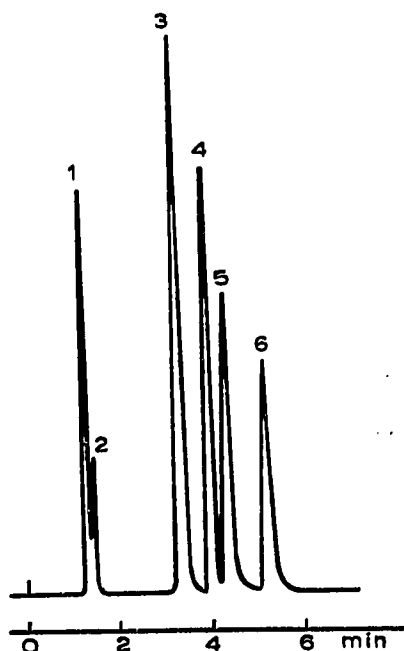


Fig. 4. Synachrom 60/80 mesh, column 5 m × 2 mm, stainless steel, temperature -78°, carrier gas He, 40 ml/min. 1 = H₂; 2 = Ne; 3 = N₂; 4 = O₂; 5 = Ar; 6 = CO.

Fig. 5. Synachrom 60/80 mesh, column 5 m × 2 mm, stainless steel, temperature 24°, carrier gas H₂, 27 ml/min. 1 = N₂; 2 = CO; 3 = CH₄; 4 = CO₂; 5 = N₂O.

of the sorbate or on its relation to the sorbent. Consequently, the final separation effect of the copolymer is a result of combined adsorption and absorption.

The adsorption influence can be distinguished quite easily in the shape of the peaks especially of substances which due to their polarity do not diffuse into the skeleton, and are separated primarily on the adsorption principle. Their peaks are asymmetric to a certain extent which is an indication of a non-linear separation isotherm. In addition, the working temperature of the chromatographic column has to be about 50° higher than that of a conventional gas chromatography arrangement in order to obtain acceptable retention times. Last but not least the shape of the chromatographic peak and the position of the peak maximum depends upon the sample size. Fig. 2 shows the dependence of the specific elution volume on the sample size of *n*-propanol. An interesting example of the separation effect of Synachrom as compared with classical adsorbents such as active charcoal and silica gel, is the separation of C₂-hydrocarbons. Their separation together with other gases is illustrated in Fig. 3. Another example of a separation of a mixture of gases can be found in Figs. 4 and 5.

As mentioned above, the molecules of the sorbate penetrate into the copolymer structure during the absorption, so that the whole of the mass of the copolymer can behave like a liquid non-polar phase of a polyaromatic character. To compare the polarity of the packing, ROHRSCHEIDER's⁷ process was used, and the polarity was expressed as the difference of the Kováts' index for benzene on squalane and Synachrom at 150°. Teflon was used as solid support in the case of the column filled with squalane. From the value found $\Delta I_{Bz}^{Sq/Syn.} = -38$ it is evident that the copolymer behaves like a phase of even a lower polarity than squalane. Evidently we have here a non-polar column packing; the elution of individual substances will be determined first of all by means of the dispersion forces between the sorbent and the molecules of the substances to be separated, *i.e.*, by the total polarizability of the substances. In Table I a series of several substances with similar boiling points from various homologous series, along with indications of their boiling points, total polarizability α , and corresponding Kováts' indices is shown. It is evident from Table I that the order of elution is in agreement with the increasing values of the polarizability of substances. This phenomenon is still more obvious in strongly polarized substances like water, lower aliphatic acids, diols, etc. It is above all this very fact which has made polymeric column packings extremely popular. Their use means a substantial solution of troubles during the analysis of *e.g.* aqueous solutions, because water, as evident from Table II,

TABLE I

RELATION BETWEEN THE KOVÁTS' RETENTION INDICES AND THE TOTAL POLARIZABILITY OF SUBSTANCES

Compound	B.p. (°C)	$\alpha \cdot 10^{-24}$	Kováts index
Ethyl alcohol	78.4	5.06	412
Acrylonitrile	81.8	6.11	488
Methyl ethyl ketone	79.5	8.19	559
Ethyl acetate	76.8	8.82	582
1-Chlorobutane	77.8	10.09	612
Benzene	80.1	10.36	622
Cyclohexane	80.7	10.99	625

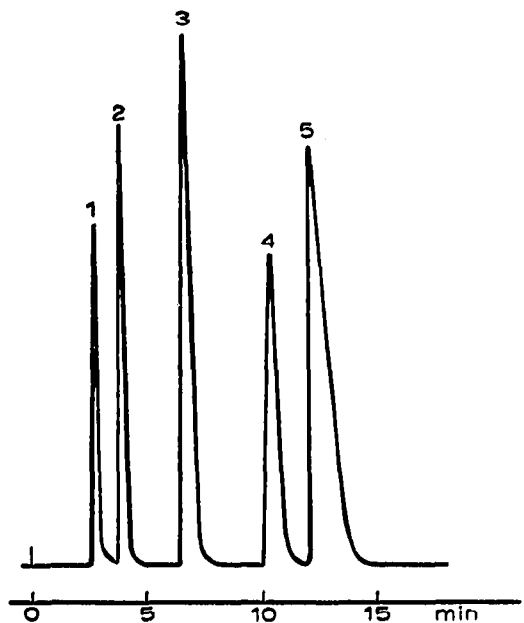


Fig. 6. Synachrom 80/100 mesh, column 1.5 m × 5 mm, glass, temperature 150°, carrier gas He, 60 ml/min. 1 = water; 2 = methyl alcohol; 3 = ethyl alcohol; 4 = acetone; 5 = ethyl ether.

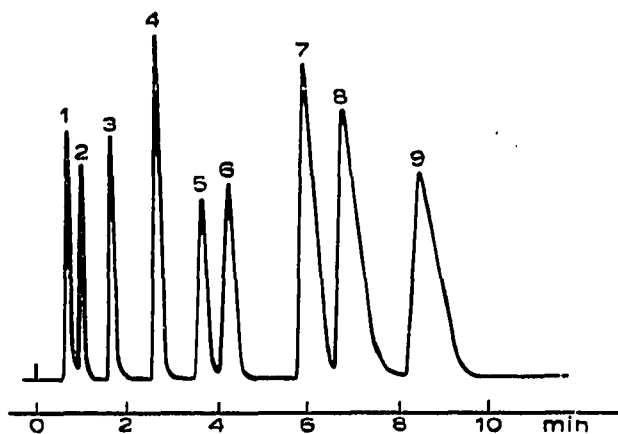


Fig. 7. Synachrom 80/100 mesh, column 1.5 m × 5 mm, glass, temperature 150°, carrier gas He 50 ml/min. 1 = water; 2 = methyl alcohol; 3 = ethyl alcohol; 4 = isopropyl alcohol; 5 = propyl alcohol; 6 = *tert.*-butyl alcohol; 7 = *sec.*-butyl alcohol; 8 = isobutyl alcohol; 9 = butyl alcohol.

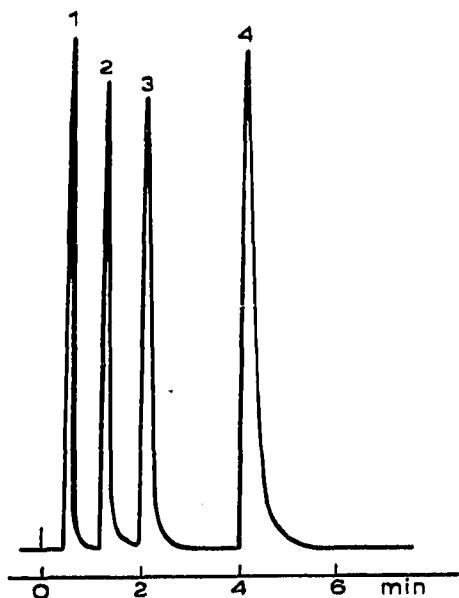


Fig. 8. Synachrom 80/100 mesh, column 1.5 m × 5 mm, glass, temperature 175°, carrier gas He, 60 ml/min. 1 = water; 2 = formic acid; 3 = acetic acid; 4 = propionic acid.

is eluted between ethane and propane in a relatively symmetrical peak. Examples of several separations are shown in Figs. 6-8, and the Kováts' indices of these and some other substances are given in Table II.

TABLE II

KOVÁTS' RETENTION INDICES ON SYNACHROM

Column conditions: Synachrom 60/80 mesh; Fractovap GV (Carlo Erba); Column 1.5 m × 5 mm, glass, temperature 150°; Thermal conductivity detector, 150 mA, temperature 200°; Carrier gas, He, 60 ml/min.

Compound	B.p. (°C)	Kovats index
Water	100.0	250
Methyl alcohol	64.7	319
Acetaldehyde	20.2	365
Ethyl alcohol	78.4	412
Formic acid	100.6	444
Acetonitrile	81.8	446
Acrolein	52.5	459
Acetone	56.5	468
Isopropyl alcohol	82.5	472
Dichloromethane	40.7	480
Acrylonitrile	78.5	488
Ethyl ether	34.6	493
Methyl acetate	56.9	494
Allyl chloride	44.6	495
Propyl alcohol	96.6	501
Cyclopentane	97.8	510
Acetic acid	118.1	526
<i>tert.</i> -Butyl alcohol	82.9	531
Vinyl acetate	72.3	551
Methyl ethyl ketone	79.5	559
Trichloromethane	61.3	569
<i>sec.</i> -Butyl alcohol	99.5	570
Tetrahydrofuran	66.0	572
2-Methylpentane	60.3	580
Ethyl acetate	76.8	582
Isobutyl alcohol	108.0	586
3-Methylpentane	63.3	595
1,2-Dichloroethane	82.4	595
Methylcyclopentane	71.8	604
Butyl alcohol	117.5	609
1-Chlorobutane	77.8	612
Carbon tetrachloride	76.7	618
Benzene	80.1	622
Cyclohexane	80.7	625
Propionic acid	141.1	631
Ethyleneglycol	197.3	641
Cyclohexene	83.0	643
Acrylic acid	141.1	645
Isopropyl acetate	88.9	655
Propyl acetate	101.6	682
Pyridine	115.2	699
Ethylcyclopentane	103.5	711
Toluene	110.6	721

Because of their frequently exceptional properties the macroporous copolymers have become a popular material not only for analysis of aqueous solutions, but also for trace analysis. A shift in the elution pattern of the trace impurities can be made possible in many cases whereby it elutes before the main component. Apart from this they are suitable not only for gas chromatography, but also as sorbents for thin-layer chromatography⁸, and as column packing materials for liquid chromatography.

From the results quoted above it is evident, that Synachrom materials can be used successfully and added to the list of other macroporous materials used so far as sorbents in gas chromatography.

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