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Note

Gas-solid chromatographic studies using beryl as adsorbent

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There seems to be no reference in the literature to the use of beryl (the most important economically workable beryllium ore with the formula $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) as an adsorbent in gas-solid chromatography (GSC). This paper describes the results of GSC studies carried out to evaluate this aspect in detail.

EXPERIMENTAL

The samples of beryl (of Indian origin) used for these investigations were characterized by chemical and X-ray analyses. They contained BeO in the range 12.8–13.4%.

The experimental conditions under which the different separations were carried out are included in Table I. Some typical chromatograms are given in Figs. 1–6.

RESULTS AND DISCUSSION

Separation capabilities of beryl

The results in Table I indicate that a narrow range of members in many homologous series can be separated on beryl in appropriate temperature ranges.

A mixture of hydrogen, oxygen, nitrogen, carbon monoxide and carbon dioxide is not separated on beryl, even at -78° , and in this respect the separation capability of beryl is inferior to that of attapulgite¹ and kaolinite². It is worth pointing out that many polar compounds are separated on beryl in the temperature range $0-30^\circ$, while they are not eluted from columns of silicate minerals such as attapulgite, kaolinite and bentonite under comparable conditions.

Elution profiles

Almost all classes of compounds exhibit tailing on beryl, the extent of which depends, amongst other things, on the nature of the compound and the temperature of the column. An interesting type of unsymmetrical elution profile (of the type shown for C_9 and C_{10} *n*-paraffins in Fig. 3c) is encountered in many instances when

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TABLE I

GSC SEPARATIONS OBTAINED ON BERYL

Beryl dried at 110° for 2 h before loading it in the column; column, copper, 5 ft. \times 1/8 in.; mesh size, 30-50; injection port temperature, 180°; carrier gas, (a) N₂ at 45 ml/min for separations of organic mixtures, (b) H₂ at 45 ml/min for separations of mixtures involving inorganic gases; detector, flame ionization detector for organic mixtures and thermal conductivity cell for mixtures with inorganic gases.

Mixture separated	Temperature of column (°C)	Figure
Methane-ethane-propane, butane-isobutane, butene, pentane, hexane and heptane	-78	1a
Pentane, hexane, benzene, heptane, toluene, octane and xylene	0	1b
2-Methylpentane-hexane, 2,2,4-trimethylpentane and <i>n</i> -octane	0	2a
	30	—
C ₅ -C ₉ <i>n</i> -paraffins	0	—
Benzene, toluene and xylene	0	—
	30	—
Diethyl ether, diisopropyl ether and di- <i>n</i> -butyl ether	0	—
Diethyl ether-diisopropyl ether and di- <i>n</i> -butyl ether	30	2b
Acetone, ethyl methyl ketone and butyl methyl ketone	0	—
	30	2c
Methanol, ethanol-isopropanol, <i>n</i> -propanol and <i>n</i> -butanol	0	2d
Benzene and chlorobenzene	0	3a
	30	—
Benzene and pyridine	0	3b
C ₅ -C ₁₀ <i>n</i> -paraffins	30	3c
Benzene, pyridine and α -picoline	30	4a
C ₁ -C ₅ <i>n</i> -alkanols	30	4b
Air, H ₂ S-water vapour	30	5a
Air, NH ₃ -water vapour	30	5b
Methanol and water vapour	30	5c
C ₇ -C ₁₂ <i>n</i> -paraffins	50	6a
C ₉ -C ₁₃ <i>n</i> -paraffins	100	6b

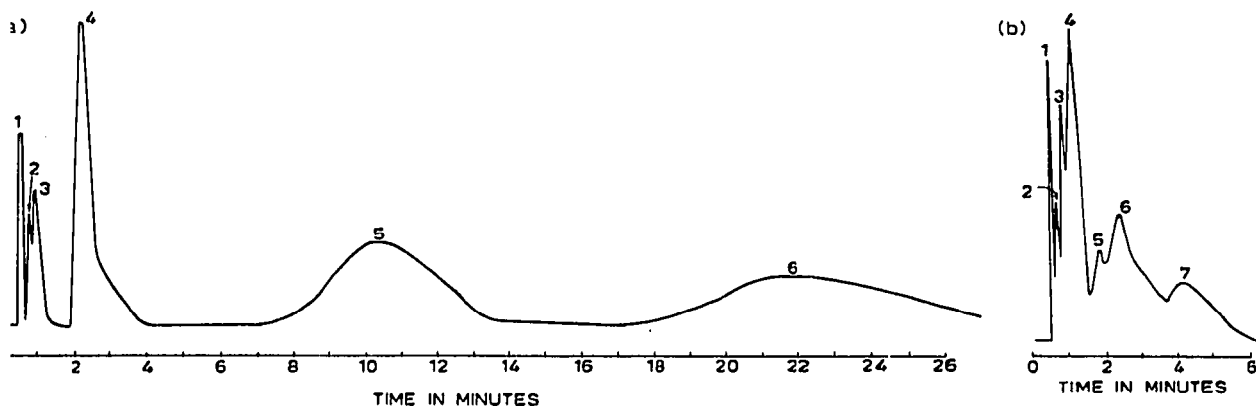


Fig. 1. (a) Separations on beryl at -78° . 1, Propane; 2, butane; 3, butene; 4, pentane; 5, hexane; 6, heptane. (b) Separation of aliphatic and aromatic hydrocarbons at 0° . 1, Pentane; 2, hexane; 3, benzene; 4, heptane; 5, toluene; 6, octane; 7, xylene.

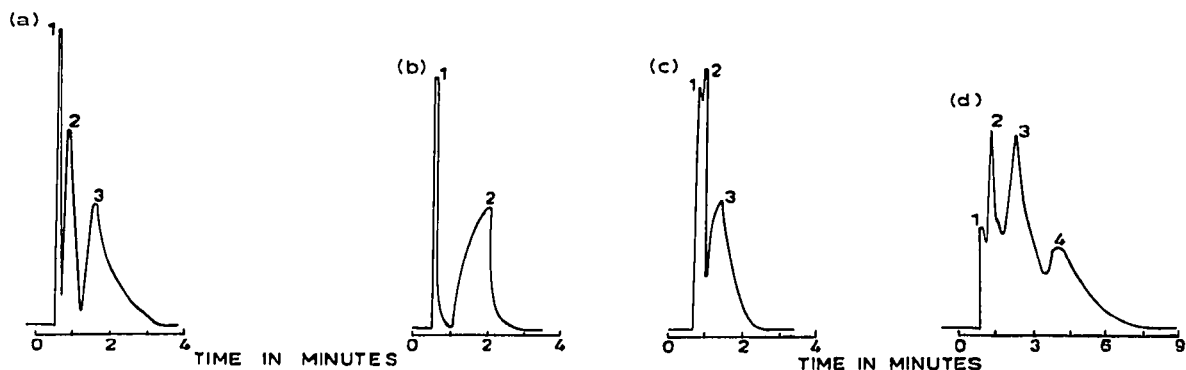


Fig. 2. (a) Separation of branched- and straight-chain hydrocarbons at 0° . 1, 2-Methylpentane-hexane; 2, 2,2,4-trimethylpentane; 3, octane. (b) Separation of ethers at 30° . 1, Diethyl ether-diisopropyl ether; 2, di-*n*-butyl ether. (c) Separation of ketones at 30° . 1, Acetone; 2, ethyl methyl ketone; 3, butyl methyl ketone. (d) Separation of aliphatic alcohols at 0° . 1, Methanol; 2, ethanol-isopropanol; 3, *n*-propanol; 4, *n*-butanol.

the concentration is increased beyond certain values. This threshold concentration also depends on the nature of the substance and the temperature of the column. A decrease in the temperature of the column decreases the carbon number and concentration at which these peaks appear. The concentration dependence of the nature

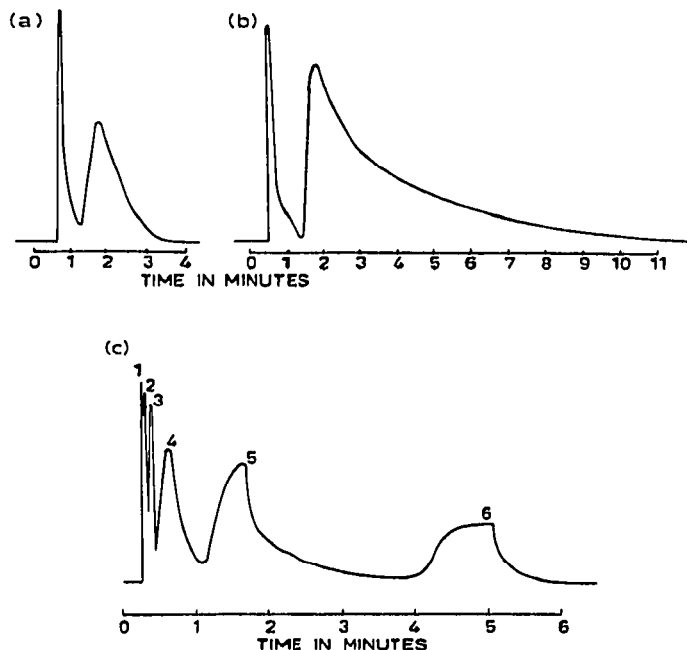


Fig. 3. (a) Separation of benzene and chlorobenzene at 0° . 1, Benzene; 2, chlorobenzene. (b) Separation of benzene and pyridine at 0° . 1, Benzene; 2, pyridine. (c) Separation of C_5 - C_{10} *n*-paraffins at 30° . 1, C_5 ; 2, C_6 ; 3, C_7 ; 4, C_8 ; 5, C_9 ; 6, C_{10} .

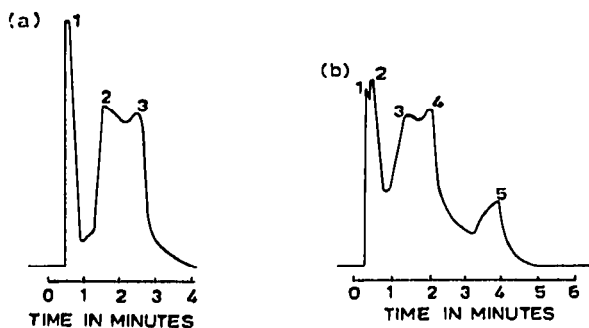


Fig. 4. (a) Separation of benzene, pyridine and α -picoline at 30° . 1, Benzene; 2, pyridine; 3, α -picoline. (b) Separation of C_1 - C_5 n -alkanols at 30° . 1, C_1 ; 2, C_2 ; 3, C_3 ; 4, C_4 ; 5, C_5 .

of the elution profile of amyl alcohol at 30° is illustrated in Fig. 7a. When the amount of amyl alcohol is increased above $1.0 \mu\text{l}$, the height of the peak remains steady (*i.e.*, the peak height becomes virtually independent of concentration) while the peak width at base increases fairly linearly with concentration. With large amounts ($20 \mu\text{l}$) the nature of the elution profile changes further (curve 7, Fig. 7a).

Similar chromatograms and behaviour were reported by Belayakova *et al.*³ in studies of the adsorption of water on the uniform surface of graphitized carbon black. They also gave a set of corresponding adsorption isotherms (which were convex to the pressure axis). In these instances, the non-specific interaction with the solid is very weak, while the adsorbate molecules interact more strongly among themselves, resulting in isotherms convex to the pressure axis (and chromatograms that have a broad leading edge). Benzene³ and methanol⁴ give chromatograms on graphitized carbon black comparable (but not identical) with those of water, under appropriate experimental conditions.

Fig. 7b represents the chromatograms for different amounts of pyridine at 0° . The peak maximum continuously shifts to the left with increase in amount of pyridine. Identical behaviour was reported for benzene on graphitized carbon black³ under appropriate conditions. These chromatograms correspond to isotherms convex to the uptake axis.

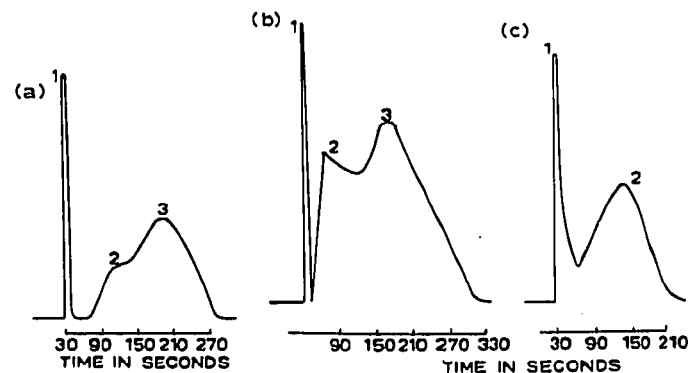


Fig. 5. (a) Separation of air, hydrogen sulphide and water vapour at 30° . 1, Air; 2, hydrogen sulphide; 3, water vapour. (b) Separation of air, ammonia and water vapour at 30° . 1, Air; 2, ammonia; 3, water vapour. (c) Separation of methanol and water vapour at 30° . 1, Methanol; 2, water vapour.

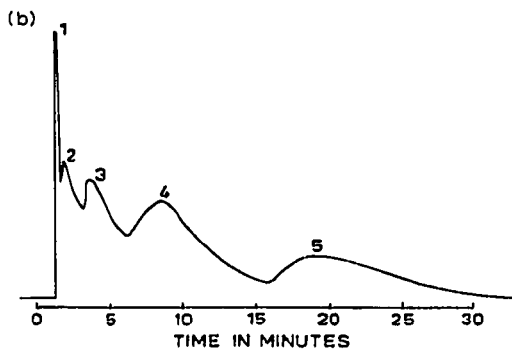
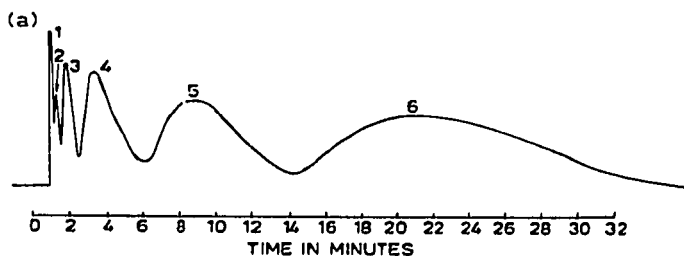


Fig. 6. (a) Separation of C_7 - C_{12} *n*-paraffins at 50° . 1, C_7 ; 2, C_8 ; 3, C_9 ; 4, C_{10} ; 5, C_{11} ; 6, C_{12} . (b) Separation of C_9 - C_{13} *n*-paraffins at 100° . 1, C_9 ; 2, C_{10} ; 3, C_{11} ; 4, C_{12} ; 5, C_{13} .

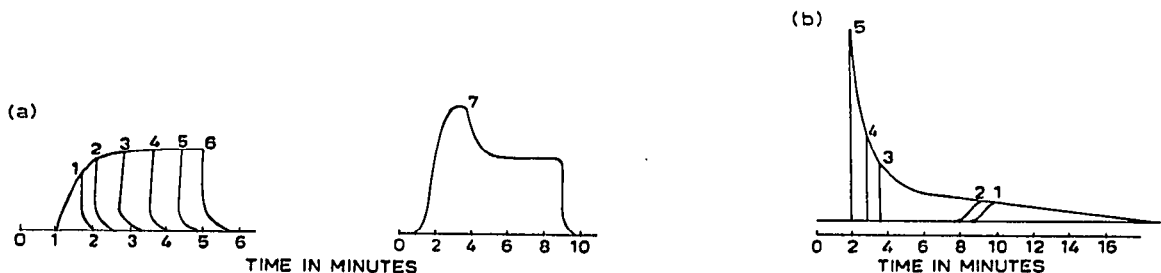


Fig. 7. (a) Effect of concentration on the elution profile of amyl alcohol at 30° . Amount of amyl alcohol present (μ l): 1, 0.5; 2, 1.0; 3, 1.5; 4, 2.5; 5, 4.0; 6, 5.0; 7, 20.0. (b) Effect of concentration on the elution profile of pyridine at 0° . Amount of pyridine present (μ l): 1, 0.1; 2, 0.2; 3, 0.5; 4, 1.0; 5, 2.5.

In Fig. 8, the uncorrected retention times (at 30°) are plotted against the boiling points of the different compounds used as adsorbates. It is found that the aliphatic hydrocarbons, aromatic hydrocarbons, cycloparaffins, ethers and ketones almost fall on a single curve (a). The compounds that do not fit on this curve are

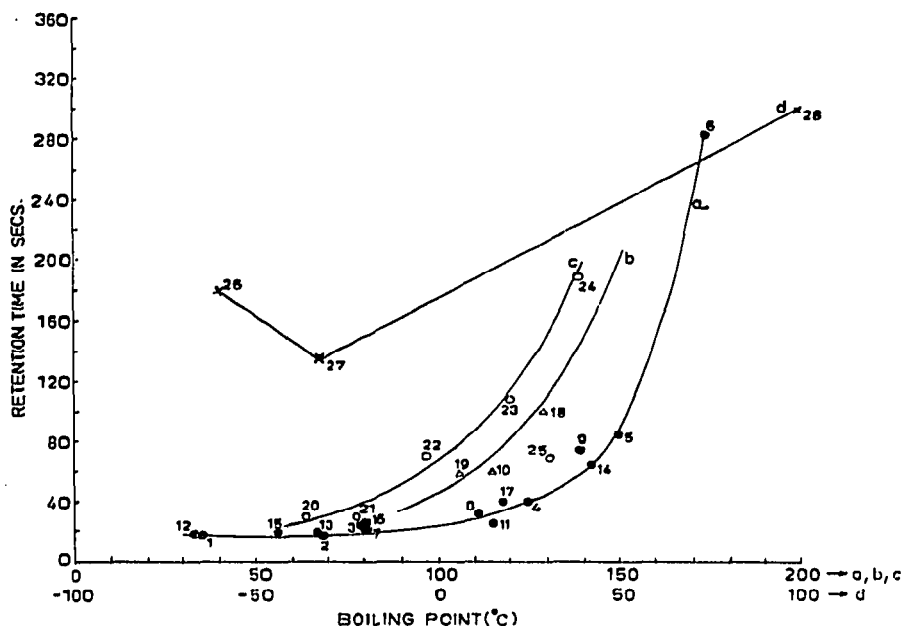


Fig. 8. Plots of retention time at 30° against boiling point. 1, *n*-Pentane; 2, *n*-hexane; 3, *n*-heptane; 4, *n*-octane; 5, *n*-nonane; 6, *n*-decane; 7, benzene; 8, toluene; 9, xylene; 10, pyridine; 11, 2,2,4-trimethylpentane; 12, diethyl ether; 13, diisopropyl ether; 14, dibutyl ether; 15, acetone; 16, ethyl methyl ketone; 17, butyl methyl ketone; 18, α -picoline; 19, piperidine; 20, methanol; 21, ethanol; 22, *n*-propanol; 23, *n*-butanol; 24, *n*-pentanol; 25, chlorobenzene; 26, hydrogen sulphide; 27, ammonia; 28, water.

piperidine, pyridine, α -picoline, C_1 - C_5 *n*-alkanols, water, hydrogen sulphide and ammonia. The first three compounds and the alcohols give two independent (continuously rising) curves (b and c), while the last three give a completely different curve (d) with a minimum at ammonia. A very similar set of curves was also obtained at 0°. These results show that basic compounds and compounds that can form hydrogen bonds are more preferentially retained on beryl, although the affinity is still considerably less than that exhibited by other silicate minerals such as attapulgite, kaolinite and bentonite (from which they are not eluted at ordinary temperatures^{2,5,6}).

The GSC results discussed above indicate that beryl exhibits behaviour similar to that of non-specific (Type I) adsorbents⁷.

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