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SIEVING EFFECTS OF HORMITES IN GAS-ADSORPTION CHROMATOGRAPHY

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SUMMARY

Sepiolite, a clay mineral of the hormite group characterized by a porous lattice, was tested as a stationary phase in gas chromatography. The adsorbent is homogeneous and is able to separate molecules on the basis of steric factors.

Oxygen, nitrogen, methane and carbon monoxide are easily separated at -78° ; carbon dioxide is eluted with a symmetric peak at room temperature. A simple ballistic programme is able to perform the complete resolution of all the above components with a short column (80 cm long).

As the specific interactions are weak, sepiolite may be applied to the separation of liquid hydrocarbons on the basis of their geometric configurations. The elution order for the paraffins is: doubly branched alkanes, singly branched alkanes, straight-chain alkanes.

The resolution between *cis* and *trans* forms of disubstituted cycloalkanes is very high.

The values for the efficiency and symmetry are such that the use of sepiolite in gas-solid chromatography is considered to be practical.

INTRODUCTION

In gas-solid chromatography (GSC), selectivity is related to the geometrical structure of the solid adsorbent. KISELEV AND YASHIN¹ classified adsorbents in order of their decreasing pore size and mode of distribution. At the present time, type III adsorbents are of interest. These are defined as homogeneous microporous adsorbents; the openings of the holes of the porous crystals are identical so that they are particularly useful for molecular sieve separation. Zeolites A and X are well known examples of such adsorbents.

We decided to investigate the GC behaviour of hormites (attapulgite, pali-gorskyte, sepiolite), a group of clay minerals² characterized by a porous lattice with rectangular holes (the dimensions of the cross-section of the channels being 3.7 by 6.0 Å for attapulgite and 3.7 by 9 Å for sepiolite³). Such holes, as in molecular sieves, are normally filled with zeolitic water that may be reversibly removed at 150–200°; this material is stable up to at least 300°.

According to the structural patterns proposed, hormites would be expected

to behave in a similar manner to zeolites, except for the smaller intensity of the specific cation-dipole interactions owing to the lower cation-exchange capacity of hormites (3-15 mequiv./100 g compared with up to 300 mequiv./100 g for molecular sieves).

EXPERIMENTAL AND RESULTS

We tested a sepiolite sample, namely the Vallecás sepiolite (Ward's Natural Science Establishment, Inc., Rochester, N.Y., U.S.A.), purified by decantation and made homo-ionic with sodium and used as column packing as a 60-80 mesh fraction.

The column was conditioned at 200° overnight. Owing to the high selectivity, short columns (0.8-1 m) were used for the separations.

Separation of inorganic gases

According to the results for the adsorption of gases on attapulgite reported by BARRER AND MACKENZIE⁴, we predicted the possibility of separating inorganic gases in a very simple way.

The channels of hormites are not equally available to nitrogen, oxygen and carbon dioxide, and the results are governed by polarity rather than by molecular dimensions. In fact oxygen, nitrogen, carbon monoxide and methane are separated in this order at -78°; carbon dioxide is eluted with a symmetric peak at room temperature.

An example of the separation of a mixture of such components by a ballistic programme is shown in Fig. 1. It can be seen that the order of elution of carbon-monoxide and methane is the same as that reported⁵ for molecular sieves 5 A containing 9.5 % of water, that is, reversed with respect to the same molecular sieves

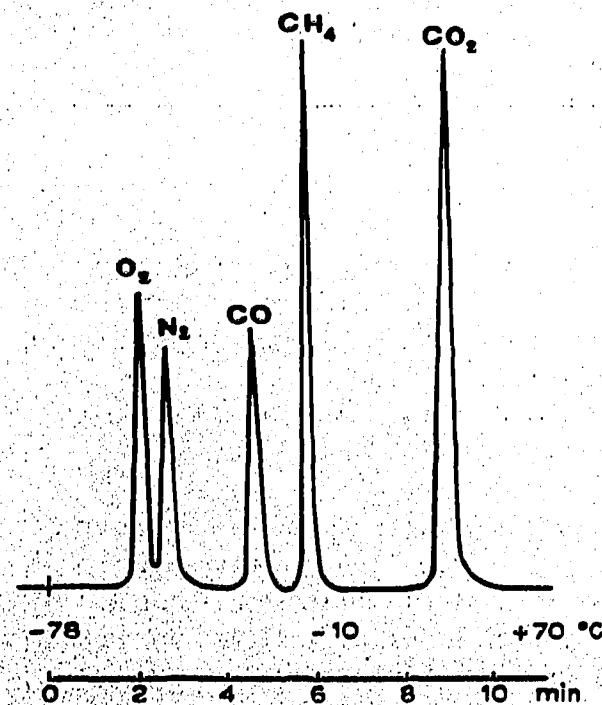


Fig. 1. Separation of oxygen, nitrogen, carbon monoxide, methane and carbon dioxide on sepiolite. Column: 80 × 0.4 cm; sepiolite: sodium Vallecás, 60-80 mesh; ballistic programme.

containing up to 4 % of water. It appears that this separation could be of practical interest owing to the short analysis time and the ease of operation. Molecular sieves, which are the most popular adsorbents used for the permanent gases, adsorb carbon dioxide irreversibly unless temperature programming up to 400° is used. Conventional analyses of carbon dioxide-air mixtures are carried out with two columns joined in series, carbon dioxide being eluted on silica gel.

Separation of liquid hydrocarbons

Even if the estimated cross-section of the holes of hormites is smaller than the van der Waals thickness of the alkyl chains, studies based on the preferential adsorption of some paraffins⁶ indicated that some aliphatic chains are adsorbed in the open channels or in the gutters around the edges of particles. It has also been found⁷ that attapulgite and sepiolite selectively adsorb various normal paraffins.

The results we obtained by GC are in good agreement with these results, as shown in Table I, where the retention indices of all the C₅-C₇, and some C₈ alkanes are given.

It can be seen that *gem*-substituted alkanes have exceptionally low retention indices (I_r) and the retention times are all similar, and independent of the increasing boiling points of the hydrocarbons.

Alkanes that are doubly branched in different positions and the singly branched alkanes have higher values of I_r . It is interesting to observe that the straight-chain alkanes that are strongly retained are eluted with symmetric peaks.

The data in Table I can be used to predict separations of mixtures of isomeric hydrocarbons. For example, the C₆ paraffinic isomers are all separated with the exception of 3-methylpentane, which is eluted together with 2,3-dimethylbutane (on non-polar stationary phases 2,3-dimethylbutane is eluted together with 2-methylpentane).

By coupling a sepiolite column with a non-polar stationary phase or by simply modifying the sepiolite with squalane, it is possible to separate all the C₆ paraffinic isomers with a short column.

TABLE I
RETENTION INDICES (I_r) OF NORMAL ALKANES ON SEPIOLITE
Temperature, 155°.

Hydrocarbon	I_r
2-Methyl butane	394
2,2-Dimethylpropane	217
2-Methylpentane	480
3-Methylpentane	432
2,3-Dimethylbutane	432
2,2-Dimethylbutane	283
2-Methylhexane	602
3-Methylhexane	540
3-Ethylpentane	457
2,3-Dimethylpentane	437
2,4-Dimethylpentane	416
2,2-Dimethylpentane	359
3,3-Dimethylpentane	354
2,4-Dimethylhexane	497
2,2-Dimethylhexane	432
2,2,4-Trimethylpentane	415

It may be noted that some straight-chain paraffins and olefins (*n*-pentane, pentene-1; *cis*-pentene-2; *trans*-pentene-2) are eluted almost together, regardless of the presence or the position of the double bond and of the steric configuration.

Separation of cycloparaffins

As shown in Table II, there is a complete separation of saturated and unsaturated cycloparaffins (cyclopentane-cyclopentene; cyclohexane-cyclohexene) and the last ones are more strongly retained. Methylcyclopentane is eluted after cyclohexane, although the latter has the higher boiling point.

The sieving action of the adsorbent is evident from the values of I_r , which are almost the same for cyclopentane and cyclohexane.

As an example of the excellent ability of sepiolite to achieve separations based on steric factors, Fig. 2 gives a chromatogram showing complete separation of all the dimethylcyclopentanes. It can be seen that the *cis* isomers are eluted before

TABLE II
RETENTION INDICES FOR CYCLOALKANES ON SEPIOLITE
Temperature, 155°.

Hydrocarbon	I_r	Boiling point (°C)
Cyclopentane	420	49.26
Cyclohexane	434	80.74
Methylcyclopentane	466	71.81
Methylcyclohexane	481	100.93
Cyclopentene	441	44.21
Cyclohexene	482	82.98

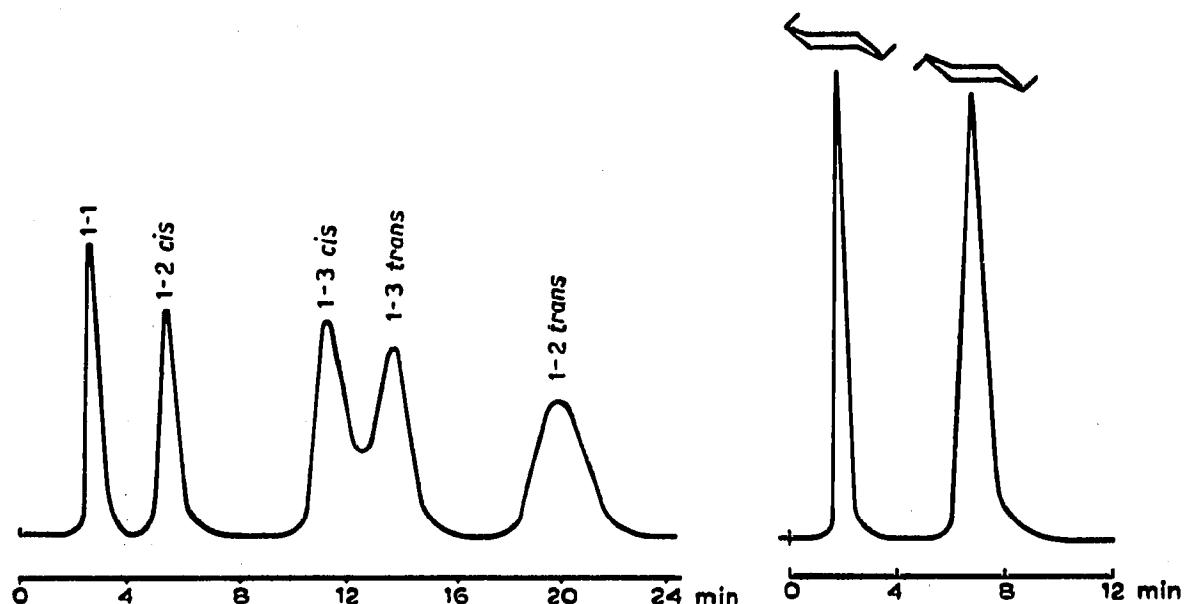


Fig. 2. Resolution of the dimethylcyclopentane isomers. Column: 100 × 0.4 cm; sepiolite: sodium Vallecas, 60-80 mesh; temperature, 170°.

Fig. 3. Separation of *cis*- and *trans*-1,4-dimethylcyclohexanes. Column as in Fig. 1 at a temperature of 195°.

the *trans* isomers and that the retention times are lower than those of normal paraffins.

Relative volatilities of dimethylcyclohexanes at 195° are reported in Table III. The elution order is the same as that observed on graphitized carbon black¹, but the relative volatilities are higher.

TABLE III
RELATIVE VOLATILITIES OF CYCLOALKANES ON SEPIOLITE

Hydrocarbon	Temperature (°C)	Relative volatility
<i>Dimethylcyclohexanes</i>		
1,2- <i>trans</i> /1,2- <i>cis</i>	195	3.9
1,3- <i>cis</i> /1,3- <i>trans</i>	195	3.9
1,4- <i>trans</i> /1,4- <i>cis</i>	195	8.7
<i>Dimethylcyclopentanes</i>		
1,2- <i>trans</i> /1,2- <i>cis</i>	176	4.7
1,3- <i>trans</i> /1,3- <i>cis</i>	176	1.2

DISCUSSION

The use of sepiolite, as an adsorbent in GSC appears to be limited to permanent gases and non-polar liquids, as aromatic hydrocarbons are so strongly retained even at high temperatures that their separation is not of practical interest.

Multi-branched alkanes are eluted with tailed peaks, but singly branched alkanes and straight-chain alkanes show, at a convenient elution temperature, peaks of good symmetry (A_s values 1.1-1.3) even when the retention times are very long.

The efficiency is not very high: the height equivalent to a theoretical plate (HETP) values are about 2-3 mm. It is possible that by choosing the appropriate particle size or by removing the powder, as has been done with other adsorbents, the efficiency could be improved. However, when steric differences exist, the separation factors are so high that the use of a low-efficiency column is not a problem.

Disadvantages due to the broadening of the peaks can be overcome in particular cases by the use of temperature programming.

For the above reasons, we think that the practical use of sepiolite is to be recommended. Furthermore, it is possible that other hormites (attapulgite, paligorskite) or samples of the same mineral from different origins could also be used.

It may be interesting to investigate further the adsorption mechanism and the actual sizes of the pores.

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