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Note

Natural magnetite as an adsorbent in gas-solid chromatography*

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Although the introduction of porous polymers in gas-solid chromatography (GSC) has solved many analytical problems, there is still considerable interest in inorganic adsorbents and in their practical and theoretical applications. Particular interest is devoted to metal oxides, which are temperature stable, with surface properties covering a wide range of basicity, homogeneity and specific surface area. They can also be easily modified by heat, special chemical treatment, inorganic salts or organic compounds, leading to the different adsorptive properties of their surfaces. Such treatment generally lowers retention times, eliminates tailing and improves separations.

The application of modified alumina, silica and alumina-silica adsorbents was well described over 10 years ago by Phillips and Scott¹, and most subsequent papers dealt with those oxides. Aue *et al.*² examined the deactivation of silica surfaces using monomolecular polymer films. Cook *et al.*³ used several transition metal salts for modification of silica gel. Lykourghiotis *et al.*⁴ described the chromatographic properties of antimony pentoxide, while Kolasnitsyna and Petrova⁵ used rutile for a similar purpose. Of the iron oxides, to our knowledge, only haematite (α -Fe₂O₃) has been used as an adsorbent in GSC⁶, mainly for analytical applications.

In this work we studied natural magnetite modified in several ways and considered its possible application in GSC.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 881 gas chromatograph equipped with dual hydrogen flame-ionization detectors was employed. The flow-rate of the carrier gas (nitrogen) was 20 ml/min in all experiments. The carrier gas was dried prior to entering the chromatograph. A Hitachi/Perkin-Elmer Model 159 strip-chart recorder with a chart speed of 10 mm/min and 2-mV full-scale response was used to record the chromatograms. Adsorbate samples were injected as vapours using a 10- μ l Therumo UMS-10 syringe. Retention times were determined to within ± 0.2 sec using a stop-watch.

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Materials

The experiments were performed with natural magnetite kindly supplied by the Baljevci na Ibru coal mines, Serbia. The magnetite was ground and sieved, the 60–80-mesh fraction being used. The fraction was washed with water and dried for 24 h at 110°.

The composition of the initial natural magnetite used in the work was determined by chemical analysis to be as follows: Fe₂O₃·FeO 80.10%; SiO₂ 8.40%; Al₂O₃ 0.79%; CaO 1.02%; NiO 0.16%; and MgO 0.99%.

The surface area of the fraction used was determined by the B.E.T. nitrogen adsorption method and a value of 2.0 m²/g was obtained.

All organic compounds (obtained from various commercial sources) were of analytical -reagent grade.

Column preparation

All of the columns used (2 m × 2.2 mm I.D.) were made of stainless steel. They were filled with magnetite treated in five different ways. Also, for comparison, a column with initial (untreated) magnetite was prepared.

Column 1 was filled with 18.62 g of untreated magnetite.

Column 2 contained 17.20 g of material coated with Carbowax 20M (1% from chloroform).

Column 3 was packed with 17.85 g of magnetite silanized with DMCS in the usual way.

Column 4 contained 19.80 g of material treated as follows: 25 g of Fe₃O₄ was equilibrated with 100 ml 3 M hydrochloric acid for 24 h, then the magnetite was washed until neutral with deionised water and dried for 24 h at 110°.

Column 5 was filled with 17.80 g of magnetite treated by the following procedure: 20 g natural magnetite were equilibrated with 100 ml of 3 M hydrofluoric acid in a polyethylene bottle for 72 h, then the product was washed until neutral with deionised water and dried for 24 h at 110°.

Column 6 was packed with 14.25 g of magnetite re-treated as follows: column 2 was heated under a stream of nitrogen at 300° for 15 h, then the contents were transferred into a polyethylene bottle and 100 ml of carbon tetrachloride were added in order to extract Carbowax 20 M. After several washings with carbon tetrachloride, the material was dried at room temperature.

After packing, the columns were conditioned overnight in a stream of nitrogen at 200°.

Procedure

The corrected retention volumes were measured by injecting each adsorbate at least three times on to the column. The corrected retention volume, V_R , was calculated from the relation

$$V_R = t_R \cdot \frac{T_C}{T_A} \cdot j \cdot f \quad (1)$$

where t_R is the corrected retention time, T_C and T_A are the column and flow meter temperatures (°K), respectively, j is the James–Martin gas compressibility correction factor and f is the volume flow-rate at ambient temperature and pressure.

The corrected retention volume can be converted into specific retention volume at a given temperature, V_S^T , by dividing V_R by the total surface area of the adsorbent in the column, A_s . The specific retention volume at a given column temperature for a given adsorbate-adsorbent pair is also equal to the distribution constant³, K_d :

$$\frac{V_R}{A_s} = V_S^T = K_d = \frac{C_{(S)}}{C_{(G)}} \text{ (ml/m}^2\text{)} \quad (2)$$

where $C_{(S)}$ and $C_{(G)}$ are the concentrations of adsorbate in the solid and gaseous phases, respectively. The variation of K_d from adsorbent to adsorbent for the same adsorbate molecule indicates differences in distribution behaviour, due solely to changes in the properties of the adsorbent.

RESULTS AND DISCUSSION

In Table I the specific retention volumes for a number of adsorbates at 100° on all of the columns used are reported.

TABLE I

V_S^T VALUES (ml/m²) AT 100° ON VARIOUS TREATED NATURAL MAGNETITE

Compound	B.p. (°C)	Column no.					
		1	2	3	4	5	6
<i>n</i> -Pentane	36.2	0.115	0.154	0.165	0.518	0.178	0.233
<i>n</i> -Hexane	69.0	0.222	0.171	0.165	1.266	0.214	0.233
<i>n</i> -Heptane	98.4	0.471	0.197	0.174	2.527	0.365	0.233
<i>n</i> -Octane	125.8	—	0.249	0.183	11.54	0.436	0.233
Cyclohexane	81.4	—	0.214	0.165	—	0.240	0.241
Isooctane	116.0	0.187	0.188	0.165	—	0.347	0.249
Benzene	80.1	—	0.446	0.192	0.657*	0.347	0.257
Toluene	110.6	—	0.677	0.218	1.715*	0.780	0.342
<i>m</i> -Xylene	139.1	—	1.072	—	4.253*	2.447	0.467
Carbon tetrachloride	76.8	—	0.334	—	0.310*	0.231	0.233
Chloroform	61.3	0.177	0.548	—	0.339*	—	0.257
Methylene chloride	40.1	—	0.368	—	0.281*	0.249	0.233

* At 150°.

The influence of the chemical treatment is evident from the results. The largest values of the specific retention volumes are obtained on column 4 (magnetite treated with 3 *M* hydrochloric acid). Also, it is evident that V_S^T increases with increase in the number of carbon atoms in *n*-alkanes, with the exception of column 6.

Cycloalkanes are generally retained longer than the corresponding *n*-alkanes in gas-liquid chromatography (GLC), but shorter than in GSC⁷. This generality is not valid in all instances; thus, at 100° cyclohexane is more retained than *n*-hexane. However, with column 4 cyclohexane is eluted prior to *n*-hexane. This behaviour is discussed later.

TABLE II

 V_s^T VALUES (ml/m²) AT DIFFERENT TEMPERATURES ON COLUMN 4

Compound	B.p. (°C)	μ (D)	Temperature of column (°C)			
			120	135	150	170
Carbon tetrachloride	76.8	0	1.314	0.488	0.310	0.274
Chloroform	61.3	1.0	0.818	0.555	0.339	0.286
Methylene chloride	40.1	1.6	0.574	0.411	0.281	0.257

The retention of representative chlorinated hydrocarbons on several forms of natural magnetite was studied. It can be seen (Table I) that the specific retention volumes increase with increasing number of chlorine atoms up to chloroform, and then decrease. The same results were obtained by Datar *et al.*⁸, who examined the retention of chlorinated compounds on kaolinite.

The effect of temperature on the retention of chlorinated hydrocarbons is shown by the results, in Table II, which were obtained with column 4. Only at 120° do the retentions follow the order of boiling points and the reverse order of dipole moments (Fig. 1). At all other temperatures, the results obtained are in agreement with those obtained on the other columns examined (Table I).

The aromatic hydrocarbons have retention volumes higher than those of aliphatic and alicyclic hydrocarbons with the same number of carbon atoms (Table I), as they interact with the adsorbents specifically.

In general, magnetite treated with 3 *M* hydrochloric acid (column 4) shows the greatest interaction with all of the examined adsorbates, in comparison with the other materials used. This result may be due to a change in the acid-base surface properties of magnetite. Treatment of magnetite with 3 *M* hydrochloric acid leads to a decrease in the point of zero charge (z.p.c) from $\text{pH}_{\text{z.p.c.}} = 6.5$ to 3.8 (ref. 9). Such a

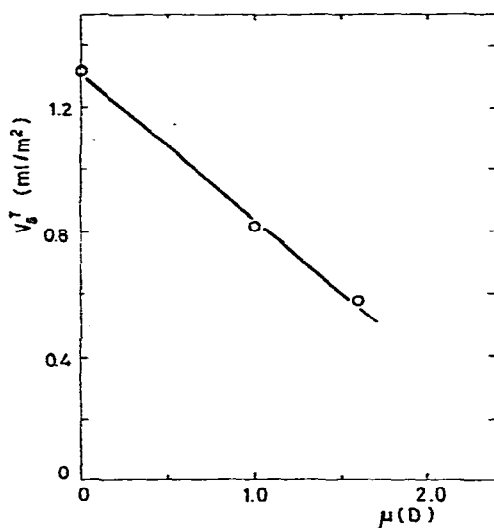


Fig. 1. Specific retention volumes of chlorinated hydrocarbons as a function of their dipole moment (μ).

decrease in z.p.c. values is caused by a change in the coordination of the Fe^{3+} ion in magnetite. According to Kittaka¹⁰, a value of $\text{pH}_{\text{z.p.c.}} = 4.0$ corresponds to tetrahedrally coordinated Fe^{3+} , while higher values of z.p.c. are ascribed to octahedrally coordinated Fe^{3+} and Fe^{2+} .

A good separation of *n*-alkanes and isooctane is achieved on column 4 (magnetite treated with 3 *M* hydrochloric acid) at 170°. However, untreated magnetite (column 1) did not separate the corresponding components in a trial mixture. Using magnetite treated with 1% Carbowax 20M (column 2), *n*-alkanols (methanol to 1-butanol + 3-methyl-1-butanol) were separated without significant tailing at 100°.

The above results indicate that iron oxides containing primarily tetrahedrally coordinated Fe ions deserve further analytical study.

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