Journal of Chromatography, 93 (1974) 217–220

CHROM. 7393

Note

Kaolinite, an adsorbent in gas–solid chromatography

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(First received July 31st, 1973; revised manuscript received February 6th, 1974)

Very little work has been carried out on the utility of kaolinite in gas chromatography[1,2]. This note describes briefly some important results obtained during our evaluation of this mineral as a potential adsorbent in gas–solid chromatography.

EXPERIMENTAL

A sample of mineral, as received from a commercial Indian source, was characterized by chemical, thermal and X-ray analyses and identified as kaolinite.

TABLE I

GAS–SOLID CHROMATOGRAPHIC SEPARATIONS USING KAOLINITE

Mixture separated	*Carrier gas and flow-rate (ml/min)*	*Temperature of column (°C)*	*Detector**	*Fig. No.*
He, O_2, N_2, CH_4, CO	H_2, 70	−78	TCD	1
(O_2 + N_2 + Ar), (CO_2 + N_2O), C_2H_2, H_2S	He, 60	30	TCD	2
CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, 1-butene, *i*-butene, 1,3-butadiene	H_2, 60	50	TCD	3
C_5–C_9 *n*-paraffins	N_2, 75	180	FID	4
C_5–C_{13} *n*-paraffins	N_2, 75	250	FID	5
CH_4, CH_3Cl, CH_2Cl_2 (CCl_4)**, $CHCl_3$	H_2, 45	150	TCD	6
Benzene, toluene	N_2, 75	180	FID	7

* TCD = thermal conductivity detector; FID = flame ionization detector.
** CCl_4 has a retention time close to that of CH_2Cl_2 and less than that of $CHCl_3$.

A 6 ft. × ⅛ in. I.D. copper tube was filled with 30–50 mesh kaolinite which had been dried at 110° for about 3 h. Qualitative gas chromatographic studies were then carried out in order to evaluate the ability of the stationary phase to separate gaseous and liquid mixtures, using a home-made gas chromatograph equipped with thermal conductivity and flame ionization detectors. The experimental conditions under which the different separations were carried out are specified in Table I.

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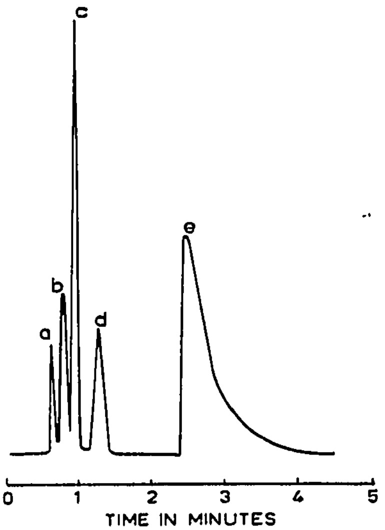


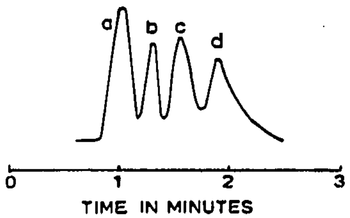
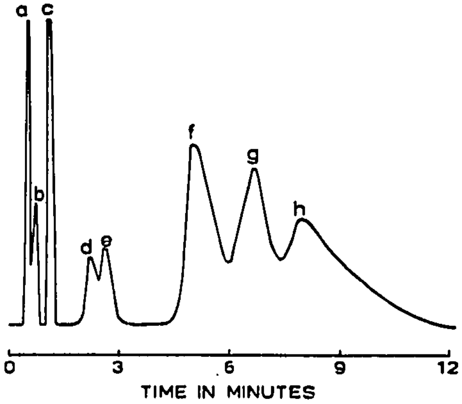


Fig. 1. Separation of permanent gases on kaolinite at −78°. (a) He; (b) O_2; (c) N_2; (d) CH_4; (e) CO.

Fig. 2. Separation of permanent gases on kaolinite at 30°. (a) $O_2 + N_2 +$ Ar; (b) $N_2O + CO_2$; (c) C_2H_2; (d) H_2S.

RESULTS AND DISCUSSION

The experimental results in Table I and Figs. 1–7 clearly demonstrate the utility of kaolinite for a wide variety of separations. The separation of helium, oxygen, nitrogen, methane and carbon monoxide is achieved at −78° (Fig. 1). Carbon dioxide, which is retained at −78°, is eluted at room temperature. It is worth noting that synthetic molecular sieves give a more efficient separation of the above five components



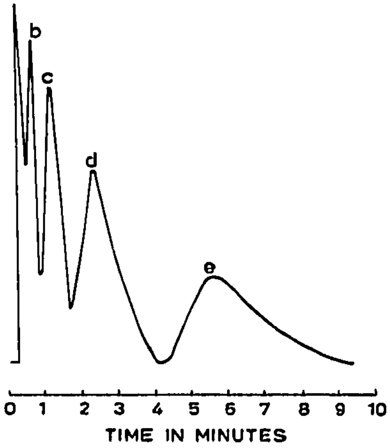


Fig. 3. Separation of some saturated and unsaturated hydrocarbons on kaolinite at 50°. (a) CH_4; (b) C_2H_6; (c) C_3H_8; (d) *i*-C_4H_{10}; (e) *n*-C_4H_{10}; (f) 1-butene; (g) *i*-butene; (h) 1,3-butadiene.

Fig. 4. Separation of C_5–C_9 *n*-paraffins on kaolinite at 180°. (a) to (e): C_5H_{12} to C_9H_{20} in sequence.

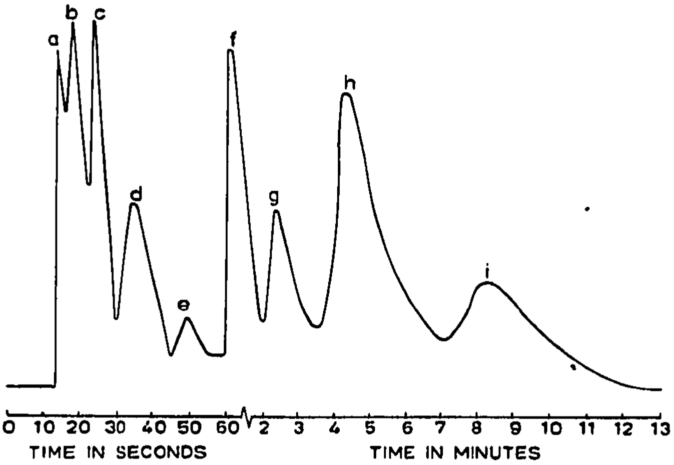
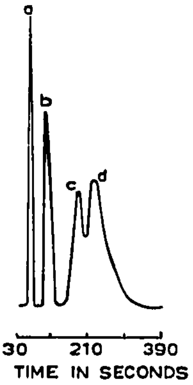


Fig. 5. Separation of C_5–C_{13} *n*-paraffins on kaolinite at 250°. (a) to (i): C_5H_{12} to $C_{13}H_{28}$ in sequence.

with little tailing at room temperature, while carbon dioxide, which is retained at room temperature, is eluted at higher temperatures. In some of the characteristics of the elution profiles (*e.g.*, tailing of carbon monoxide in Fig. 1), kaolinite behaves in a manner similar to silica gel.

Nitrous oxide and carbon dioxide exhibit similar adsorption characteristics on kaolinite at room temperature (Fig. 2). The unsaturated hydrocarbons are eluted after the corresponding saturated hydrocarbons with the same carbon number, as found in the case of the C_4 hydrocarbons at 50° (Fig. 3). Figs. 4 and 5 point out to the possibility of separating C_1–C_{13} paraffins using this mineral and adopting the programmed temperature technique.

In the case of the separation of methane and chloromethanes, it can be seen that the retention time increases with increasing number of chlorine atoms up to chloroform (Fig. 6) and then falls, leading to a retention time for carbon tetrachloride



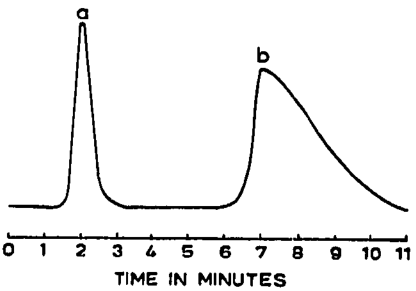


Fig. 6. Separation of methane and chloromethanes on kaolinite at 150°. (a) CH_4; (b) CH_3Cl; (c) CH_2Cl_2; (d) $CHCl_3$.

Fig. 7. Separation of benzene and toluene on kaolinite at 180°. (a) Benzene; (b) toluene.

that is almost the same as that of dichloromethane. The study of the separation of benzene and toluene (Fig. 7) was not extended to higher homologues, as the retention time of toluene was found to be 7 min.

The studies carried out so far have shown that kaolinite is a very promising stationary phase for use in gas–solid chromatography, with possible applications in air pollution studies, and in petroleum refineries and other chemical laboratories. The investigations on this mineral are continuing.

ACKNOWLEDGEMENTS

Shri A. G. Datar is grateful to the Department of Atomic Energy for the Junior Research Fellowship under the Bombay University–B.A.R.C. Collaboration programme. The authors express their appreciation of the critical comments offered by Dr. Ch. Venkateswarlu during the preparation of this manuscript.

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