

Note

Use of volcanic slag as a support in gas chromatography

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Usually in gas chromatography, solid supports based on natural diatomite are used. However, such supports contain oxides of the type R_2O_3 and hence they exhibit some catalytic and adsorption activity. The purpose of this work was to obtain a support based on volcanic slag containing the minimum of these oxides. Volcanic slags from a deposit in the Georgian S.S.R. were used as the source material.

Powdered rock (1 g) was suspended in sodium hydroxide solution (10 ml, 20%) and stirred on a water-bath at 90–100° for 15–16 h. The product was allowed to settle for 16 h, then the solution was separated from the solid phase. The solution was free of oxides of the type R_2O_3 . Hydrochloric acid (20%) was poured into the solution (1:1) and a loose, white, precipitate was formed, which was separated and washed with distilled water until neutral. The precipitate was dried in an oven and then calcined at 700° (supports 1 and 2) for 4 h and 1000° (support 3) for 8 h. The resulting white mass, consisting mainly of silica with small amounts of alumina and iron(III) oxide (Table I, supports 1 and 2), was ground and the fraction of the required particle size (0.25–0.315 mm) was taken for use as a solid support.

TABLE I

PERCENTAGE COMPOSITION OF SOLID SUPPORTS

Support	Moisture and calcination losses	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO	MgO	K ₂ O + Na ₂ O
Chromosorb W	0.3	88.9	4.0	1.6	0.2	6.2	0.6	0.6	3.6
1	3.7	94.6	0.17	0.12	—	—	0.4	0.14	0.53
2	2.8	96.5	0.10	—	—	—	Trace	Trace	0.3

Studies were conducted with an LXM-72 chromatograph equipped with a flame-ionization detector and a 1.5 m × 4 mm I.D. column at 140°, the carrier gas being nitrogen at a flow-rate of 30 ml/min. 1,2,3-Tris-(β-cyanoethoxy)propane (I) and Apiezon L (II) (10%, w/w) were used as stationary phases. Chromosorb W was studied under identical conditions for comparison with supports 1 and 2. Model sample mixtures were C₆–C₁₀ n-alkanes and aromatic hydrocarbons.

The heights equivalent to a theoretical plate (HETP) were measured for the various compounds (Table II) and compared with the values obtained using Chromo-

sorb W. The column packed with the volcanic slag support is as good as that packed with Chromosorb W, and when Apiezon L is used as the stationary phase it is superior.

TABLE II

HETP VALUES FOR HYDROCARBONS ON SOLID SUPPORTS CONTAINING 10% OF 1,2,3-TRIS-(β -CYANOETHOXY)PROPANE (I) AND APIEZON L (II).

Hydrocarbons	Chromosorb W		Support 1		Support 2: I	Support 3: II
	I	II	I	II		
<i>n</i> -Hexane	1.1	1.4	1.6	0.74	1.8	1.42
<i>n</i> -Heptane	2.2	1.4	1.48	0.97	3.6	1.52
<i>n</i> -Octane	1.5	1.8	1.2	0.98	2.2	1.05
<i>n</i> -Nonane	1.1	1.9	1.07	1.23	3.7	0.86
<i>n</i> -Decane	2.2	2.2	1.7	1.80	2.7	0.81
Benzene	0.93	1.2	1.3	0.74	2.6	1.88
Toluene	0.86	1.2	1.05	1.51	1.8	1.39
Ethylbenzene	1.07	1.2	1.3	1.22	2.5	0.93
Cumene	1.37	2.0	2.04	1.22	2.9	0.89
Pseudocumene	2.2	2.7	1.3	1.30	2.7	1.16

The separation factors (K)¹ for binary mixtures of hydrocarbons show the superior separating activity in comparison with Chromosorb W (Table III). $K = \Delta l / [\mu_{0.5(1)} + \mu_{0.5(2)}]$ where Δl is the distance between the maxima of two adjacent peaks and $\mu_{0.5(1)}$ and $\mu_{0.5(2)}$ are the peak widths at half height.

TABLE III

SEPARATION FACTORS (K) FOR BINARY MIXTURES OF HYDROCARBONS

Mixture	Chromosorb W		Support 1		Support 2: I	Support 3: II
	I	II	I	II		
<i>n</i> -Hexane- <i>n</i> -heptane	—	0.99	0.86	0.98	1.22	2.0
<i>n</i> -Heptane- <i>n</i> -octane	—	0.98	0.91	2.33	1.75	2.6
<i>n</i> -Octane- <i>n</i> -nonane	—	1.33	1.5	2.4	1.89	3.28
<i>n</i> -Nonane- <i>n</i> -decane	—	2.30	1.4	2.33	1.70	3.87
Benzene-toluene	0.73	2.0	1.33	2.0	0.51	3.25
Toluene-ethylbenzene	0.80	2.3	1.76	2.1	1.72	3.51
Ethylbenzene-cumene	—	1.2	1.6	1.43	1.36	2.85
Cumene-pseudocumene	0.98	2.42	1.5	2.3	1.61	3.52

To estimate the uniformity of separation of aromatic hydrocarbon mixtures, the uniformity criterion, Δ , was used¹, the value of which varied from 0 to 1. $\Delta = n_K \tau K_{\text{eff}} / t$, where n_K is the number of peaks on the chromatogram, τ is the base width of the narrowest peak, K_{eff} is the separation factor for the worst separated pair of components and t is the duration of analysis. The greater this value, the more compact is the chromatogram and the peak widths for different compounds differ little from one another. It is clear from Table IV that in the separation of aromatic hydro-

carbons, the uniformity criteria are larger on the volcanic slag supports than on Chromosorb W. The uniformity is greatest with 1,2,3-tris-(β -cyanoethoxy)propane as the stationary phase.

TABLE IV

UNIFORMITY CRITERIA, Δ , FOR THE SEPARATION OF MULTI-COMPONENT MIXTURES OF AROMATIC HYDROCARBONS (BENZENE-TOLUENE-ETHYLBENZENE-CUMENE-PSEUDOCUMENE) AND SATURATED HYDROCARBONS (n -HEXANE- n -HEPTANE- n -OCTANE- n -NONANE- n -DECANE)

Mixture	Chromosorb W		Support 1		Support 2: I	Support 3: II
	I	II	I	II		
Aromatic hydrocarbons	0.116	0.239	0.445	0.165	0.502	0.205
Saturated hydrocarbons	—	0.220	0.215	0.283	0.555	0.225

REFERENCE

- 1 M. S. Vigdergauz, *Calculations in Gas Chromatography*, Khimia, Moscow, 1978, pp. 23 and 30.