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INERTON —A NEW SUPPORT FOR GAS CHROMATOGRAPHY

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SUMMARY

The physical characteristics and the separation, adsorption and catalytic properties of new commercial supports, Inerton and Inerton AW-DMCS, were investigated and compared with the properties of functionally corresponding supports, Chromosorb G and Chromosorb G AW-DMCS. The results of the measurements provide evidence that the physical and chromatographic properties of both types of supports are very similar, but the bulk density is twice that of the white diatomite equivalents.

INTRODUCTION

Chromosorb G, the support for gas chromatography produced by Johns-Manville (Denver, Colo., U.S.A.), combines conveniently in its properties the adsorption inertness of white diatomite supports (*e.g.*, Chromosorb W and Chromaton N) with the hardness of pink diatomite supports of the firebrick type (*e.g.*, Chromosorb P and Chezasorb). New supports have now been developed and produced by Lachema, Brno, Czechoslovakia: a basic support (Inerton), an acid-washed support (Inerton AW) and a support silanized by dimethyldichlorosilane (Inerton AW-DMCS) or by hexamethyldisilazane (Inerton AW-HMDS).

In this paper, both the physical and chromatographic properties of Inerton and Inerton AW-DMCS are reported and compared with the properties of corresponding supports based on Chromosorb G.

EXPERIMENTAL

Materials

The Lachema supports, Inerton and Inerton AW-DMCS, had particle sizes in the range 0.16–0.20 mm; Chromaton N AW-DMCS had a similar particle size. Other supports, obtained from Carlo Erba (Milan, Italy) and Johns-Manville, were Chromosorb G and Chromosorb G AW-DMCS, particle size range 80–100 mesh (0.149–0.177 mm).

Methods

The specific surface of the supports was measured by the method of heat de-

sorption of nitrogen[1] using as a standard aluminium oxide with a specific surface of 202 m^2/g, measured by the B.E.T. method.

Porosimetric measurements of the pore size distribution and the total pore volume were carried out using a mercury pressure porosimeter (Carlo Erba, Model 70H).

The separation efficiency was measured using supports coated with 5% squalane in a U-shaped glass column 800 mm long and I.D. 4 mm, at a nitrogen flow-rate of 25 ml/min and a temperature of 80°. The testing mixture of benzene, toluene and cyclohexane was injected in 0.7-μl portions. The shape of the Van Deemter plots of the height of the theoretical plates *versus* the linear flow-rate of carrier gas, $H = f(\bar{u})$, was investigated for toluene using supports coated with 10% squalane under otherwise identical conditions at nitrogen flow-rates in the range $\bar{u}$ = 2–13 cm/sec.

The separation efficiency was measured by means of supports coated with 5% Carbowax 20M in the same column at a nitrogen flow-rate of 25 ml/min using the following mixtures of test compounds: cyclohexanol, benzene, *n*-butanol, isobutanol and *n*-amyl alcohol (injection 0.7 μl); methyl acetate, isopropyl acetate, isobutyl acetate and amyl acetate (injection 0.7 μl), at temperatures of 80° and 100°; and ethanol, cyclohexanol, decanol, undecanol, ethylene glycol and diethylene glycol (injection 0.8 μl) at a temperature of 140°.

The separation efficiency was expressed as the shape of the Van Deemter curves and by the number of theoretical plates of the column for toluene[2].

In addition to the number of theoretical plates, the separation efficiency for alcohols and esters was also expressed by the number of theoretical plates related to 1 min of retention time of a given compound, n/t_R. Because the weights of the column fillings for all the supports tested were virtually the same (6.1–6.2 g), it was not necessary to introduce corrections to the retention times for identical weights of filling.

The separation efficiency was further expressed by the percentage separation of benzene and cyclohexane peaks[3].

The adsorption inertness was tested with the supports loaded with 5% squalane in the glass column at a nitrogen flow-rate of 25 ml/min and a temperature of 80° using the polar compounds acetone, methanol, ethanol, amyl alcohol and triethylamine, injected separately in 0.5-μl portions. The column was conditioned before testing for 2 h at 100° in a slow flow of nitrogen. The extent of the adsorptive effects of the supports was expressed as the peak width measured at one tenth of the peak height at a chart speed of 20 mm/min.

The catalytic effects of the supports were determined from the decomposition of *n*-butanol on an uncoated support pre-warmed to 320°. The method used was taken from a paper by Pospíchal[4], and was slightly modified for the purpose of the present work. A stainless-steel column with internal dimensions of 110 × 6 mm was filled with the support and maintained at a temperature of 320 ± 0.5°. This column was coupled with the analytical glass column, 800 × 4 mm, filled with Chromaton N AW (particle size 0.16–0.20 mm), coated with 15% Tridox (tridecanol–polyethylene oxide), maintained at a temperature of 80°. Then 0.5-μl portions of *n*-butanol were injected into the column at a nitrogen flow-rate of 20 ml/min. The decomposition products were separated from the undecomposed *n*-butanol on the Tridox column and the extent of catalytic decomposition was expressed as a percentage from the equation

$$K\,(\%) = \frac{\text{area under the peaks of decomposition products}}{\text{area under the peaks of decomposition products} + \text{undecomposed } n\text{-butanol}} \cdot 100$$

Chromatographic separations were carried out using a Chrom 2 chromatograph (Laboratorní přístroje, Prague), except for the separation of a mixture of C_2–C_{10} alcohols with temperature programming, which was carried out using a DC-1 chromatograph (Carlo Erba).

RESULTS AND DISCUSSION

Basic support, Inerton

Inerton is a support with a silica (SiO_2) content of *ca.* 90% and, as is evident from Table I, the physical characteristics of loose and bulk density, specific surface

TABLE I

PHYSICAL AND CHROMATOGRAPHIC CHARACTERISTICS OF INERTON AND CHROMOSORB G SUPPORTS

Parameter	*Inerton*	*Chromosorb G**
Support colour	White	Oyster white
Loose weight (g/cm³)	0.44	0.47
Bulk density (g/cm³)	0.54	0.58
Specific surface (m²/g)	0.4–0.65	0.5
Specific surface (m²/cm³)	0.22–0.35	0.29
pH of 5% aqueous suspension	7.0–8.5	8.5
Maximum capacity for stationary phase	up to 10%	up to 10%
Optimum coating of stationary phase	5–10%	up to 5%
Range of particle size supplied	6 grades covering the range 0.1–0.63 mm	10 grades within the range 140–30 mesh

* Figures supplied by the producer, Johns-Manville.

and loading capacity for the stationary phase are very similar to those of Chromosorb G. In its mechanical hardness, Inerton is equivalent to pink supports, *e.g.*, Chromosorb P and Chezasorb, and has a hardness and high abrasion resistance equal to those of Chromosorb G.

In Fig. 1, the porograms of three batches of Inerton (Batch Nos. 159-1, 149 and 155 B) and porograms of two batches of Chromosorb G obtained from Carlo Erba and Johns-Manville are plotted. The total pore volume in the Inerton varies between 0.40 and 0.48 cm³/g, while the total pore volume in the Chromosorb G varies in the range 0.36–0.45 cm³/g. The pore size distribution of Inerton is narrower compared with that of Chromosorb G; the maximum pore size distribution of Inerton is at r = 24 000 Å, whereas for Chromosorb G the maximum is at r = 17 000 Å. The similar porosities of the two supports and their very similar specific surfaces provide good evidence for the similar geometry of porous structure and for the suitability of the surface for coating with a uniform film of stationary phase.

The other factors that influence the separation efficiency are the microstructure of the support surface, *i.e.*, the presence of micropores that cannot be detected with a

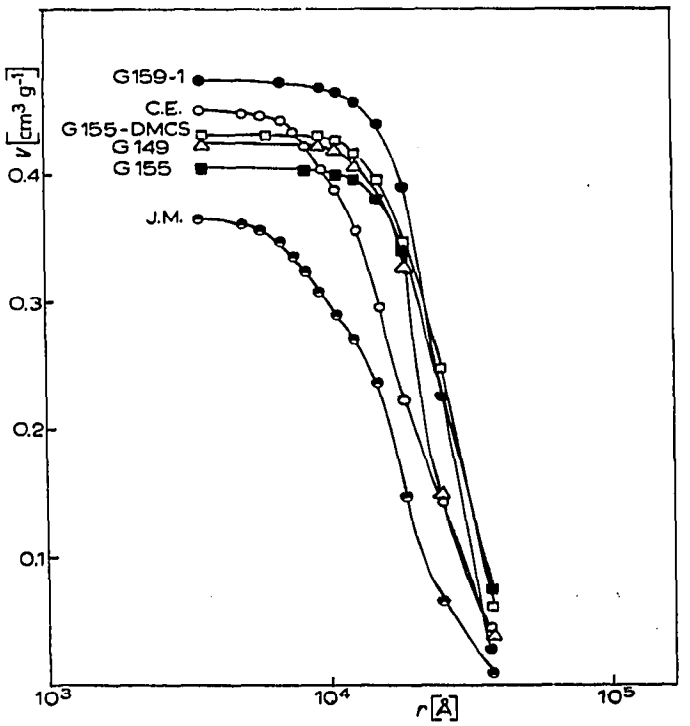

Fig. 1. Porograms of supports: ■, △, ●, different batches of Inerton; □, Inerton AW-DMCS; ◓, Chromosorb G (Johns-Manville); ○, Chromosorb G (Carlo Erba).

porosimeter, and also the adsorption capacity of the support surface. Both factors lead to the broadening and tailing of peaks. A good support should not contain micropores and the adsorption capacity of its surface should be minimal. Because both of these factors have a considerable negative influence on the chromatographic separation, the supports were examined in the chromatographic tests for their separation efficiency and adsorption activity. The results of these experiments, summarized in Table II, indicate the high separation efficiency of the Inerton.

Fig. 2 shows the chromatographic separation of an alcohol mixture on Inerton (Batch No. 159-1) and Chromosorb G (Johns-Manville). These chromatograms were used for the calculation of the number of theoretical plates (n) and n/V_R values given in Table II. It is evident from Fig. 2 that the separations on both supports are good and very similar.

In order to check the applicability of the Inerton for use in rapid analysis at higher and, from the point of view of separation efficiency, non-optimum flow-rates of the carrier gas, the Van Deemter function was measured for toluene with 10% squalane on the support.

The experimental curves measured with two batches of Inerton (Batch Nos. G 159-1 and G-146) and with two batches of Chromosorb G are plotted in Fig. 3. From these results, it is evident that the separation efficiencies of both groups of supports are very similar. The 10% loading of the supports was chosen intentionally as it is the highest loading with stationary phase at which the separation efficiency of the

Fig. 2. Separation of an alcohol mixture on (a) Inerton and (b) Chromosorb G at 100°. Peaks: 1 = benzene; 2 = cyclohexane; 3 = isobutanol; 4 = *n*-butanol; 5 = isoamyl alcohol; 6 = amyl alcohol.

Inerton is not reduced. It is interesting to note that as a consequence of the Inerton having a bulk density approximately twice that of Chromosorb W or Chromaton N, the 10% loading with stationary phase on Inerton corresponds to 20% loading on Chromosorb W or Chromaton N.

The other important indicator of the suitability of supports for use in gas chromatography is the adsorption inertness of their surface, which is shown during the separation of polar compounds on a non-polar phase by peak tailing.

The peak widths of a number of polar testing compounds on seven different batches of Inerton and three different packings of Chromosorb G are summarized in

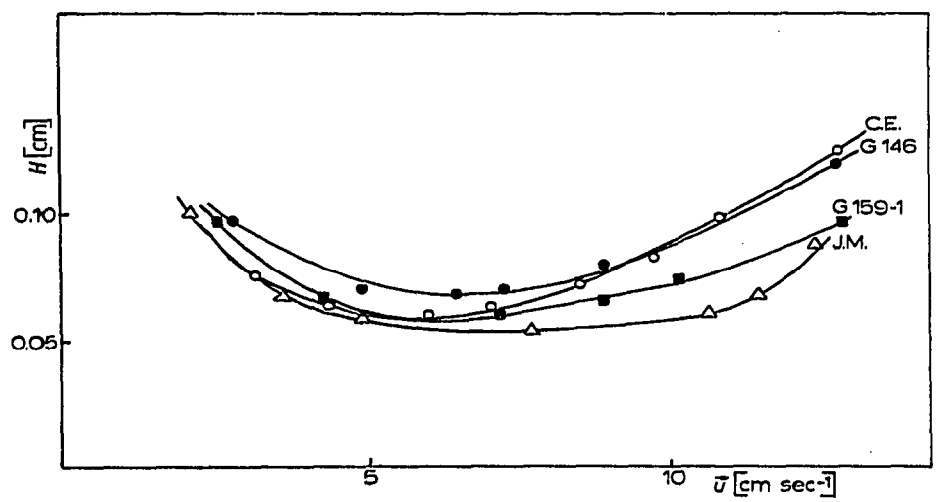

Fig. 3. Van Deemter plots on Inerton and Chromosorb G for toluene (10% squalane coating temperature 80°). ■, ●, Inerton, Batch Nos. 146 and 159; ○, Chromosorb (Carlo Erba); △ Chromosorb G (Johns-Manville).

TABLE II

SEPARATION EFFICIENCIES OF INERTON AND CHROMOSORB G SUPPORTS

Support	*Toluene (n)*	*Separation of benzene and cyclohexane peaks (%)*	*Test temperature (°C)*	*n-Butanol*		*Isobutanol*		*Isobutyl acetate*		*Amyl acetate*		*Decanol*		*Ethylene glycol*	
				n	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})
Inerton, Batch No. 155	900	84.5	100	710	405	610	450	920	680	446	249	298	51.4	266	102
Inerton, Batch No. 159-1	1039	89.0	100	866	516	857	657	1050	805	822	483	527	62.5	224	50.3
Chromosorb G (Johns-Manville)	1070	87.0	100	850	430	710	465	655	436	391	194.5	282	33.2	202	41.2
Inerton, Batch No. 146	1050	89.3	80	884	289	710	314	936	411	–	–	306	38.4	169	38.3
Inerton, Batch No. 139-4	1042	87.9	80	900	272	710	336	871	357	–	–	307	41.3	152	36.7
Chromosorb G (Carlo Erba)	990	87.2	80	1070	298	870	352	1088	382	–	–	288	47.4	315	69.8

TABLE III

ADSORPTION ACTIVITIES OF INERTON AND CHROMOSORB G SUPPORTS

Support	*Peak width at 1/10th of its height (mm)*				
	Acetone	*Methanol*	*Ethanol*	*Amyl alcohol*	*Triethylamine*
Inerton, Batch No. 155	3.0	3.3	3.4	20.0	8.0
Inerton, Batch No. 139-4	3.8	4.6	4.0	36.0	9.0
Inerton, Batch No. 143-2	3.8	3.9	3.9	26.5	9.1
Inerton, Batch No. 146	3.9	4.0	4.0	33.1	10.4
Inerton, Batch No. 148	3.8	4.0	4.0	24.9	11.1
Inerton, Batch No. 133	4.0	4.0	3.9	22.0	8.9
Inerton, Batch No. 149	4.0	4.5	4.5	42.0	9.9
Average	3.75	4.04	4.10	29.18	9.50
Chromosorb G	3.5	3.3	4.0	20.0	8.9
(Carlo Erba)	4.0	4.0	4.3	41.3	10.1
(3 separately prepared packings)	3.8	4.0	4.0	41.1	9.9
Average	3.77	3.77	4.10	35.20	9.64

Table III. The completely comparable measurements can be carried out only with the column packing conditioned in the same way; any subsequent conditioning or further use of the column is accompanied by a decrease in the peak width of polar compounds and hence also with an apparent improvement in the adsorption inertness of the support. From a comparison of the average values of peak widths measured on Inerton and Chromosorb G, it follows that these supports have very similar adsorption properties. The peaks of polar compounds are narrow, which is evidence for the good adsorption inertness of both groups of supports.

The chromatograms obtained in studies of the catalytic properties of Inerton (Batch No. 154-1) and Chromosorb G (Johns-Manville) are demonstrated in Fig. 4.

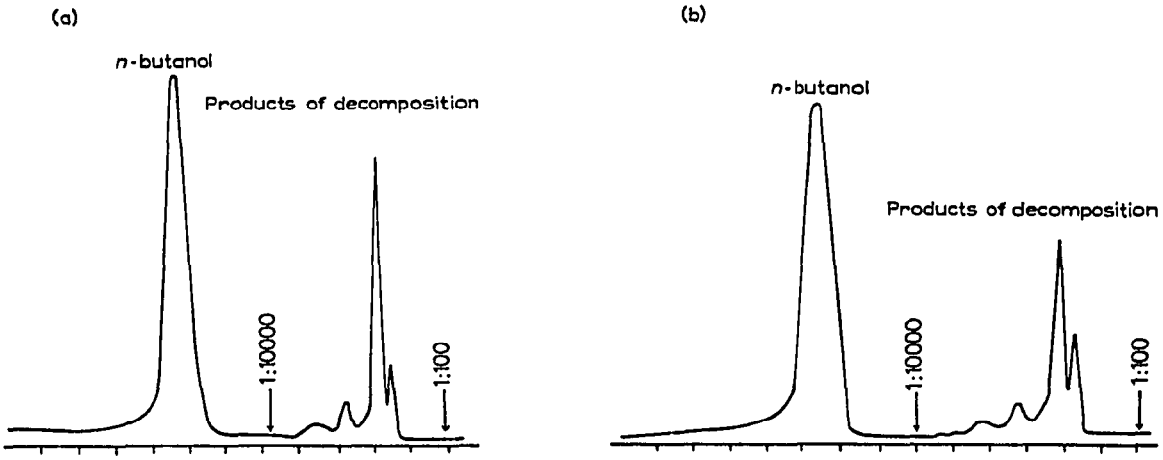

Fig. 4. Catalytic decomposition of *n*-butanol at 320° on uncoated supports (1:100 and 1:10 000 refer to the chromatograph sensitivity). (a) Inerton; (b) Chromosorb G.

TABLE IV

SEPARATION EFFICIENCIES OF INERTON AW-DMCS AND CHROMOSORB G AW-DMCS SUPPORTS

Support	*Toluene (n)*	*Separation of benzene and cyclohexane peaks (%)*	*Test temperature (°C)*	*n-Butanol*		*Isobutanol*		*Isobutyl acetate*		*Amyl acetate*		*Decanol*		*Ethylene glycol*	
				n	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})	*n*	n/V_R (min^{-1})
Inerton AW-DMCS, Batch No. 155	890	86.5	100	764	382	605	388	980	670	745	390	594	67.2	328	68.6
Inerton AW-DMCS, Batch No. 160	1165	90.0	100	966	449	740	456	1130	690	665	304	550	55.0	394	72.4
Chromosorb G AW-DMCS (Johns-Manville)	1100	94.0	100	821	385	633	394	1140	724	676	322	500	51.6	343	66.6

Apparently the decomposition of *n*-butanol is equal on both supports; the extent of decomposition expressed quantitatively is 1.53% on Inerton and 2.19% on Chromosorb G. For comparison, the extent of decomposition of *n*-butanol on the white support Chromaton N under identical conditions is 0.5% and on the pink support Chezasorb it is 33%.

Silanized support, Inerton AW-DMCS

The properties of the silanized support, Inerton AW-DMCS, were investigated by the same methods. This support is acid-washed Inerton silanized with dimethyldichlorosilane.

The porosimetric measurements (Fig. 1) indicate that, as expected, successive washing and silanization do not substantially change either the total pore volume or the pore size distribution. Also, other physical and chromatographic properties, *e.g.* the loose and bulk density and loading capacity (Table I) remain unchanged. The acid washing leads to a slight increase in the specific surface, while the silanization, on the contrary, decreases the specific surface by about 0.1 m^2/g. As shown in Table I, the basic support has a specific surface of 0.4–0.65 m^2/g. Measurements of the specific surface of silanized supports gave values of 0.3–0.55 m^2/g for Inerton AW-DMCS and 0.45 m^2/g for Chromosorb G AW-DMCS (Johns-Manville).

The results on the separation efficiency of Inerton AW-DMCS given in Table IV (the number of theoretical plates of an 800-mm column for toluene, polar compounds and for the separation of benzene and cyclohexane) are comparable with similar results obtained on Chromosorb AW-DMCS. Also, the numbers of theoretical plates generated within 1 min of the retention time for a given test compound are of the same order for both supports.

The separation of cyclohexanol, ethylene glycol, decanol, undecanol and diethylene glycol on Inerton AW-DMCS (Batch No. 160) and Chromosorb G AW-

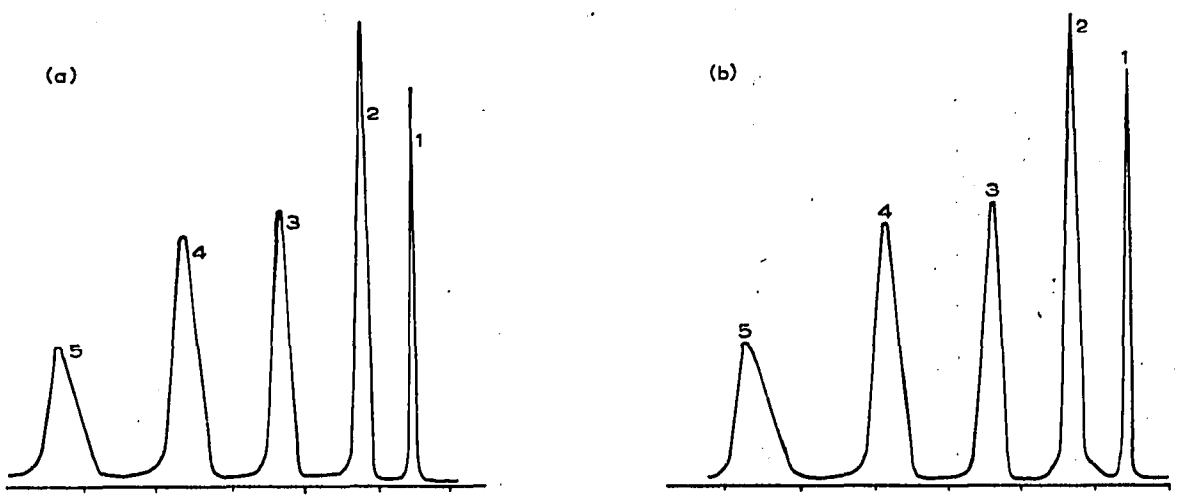

Fig. 5. Separation of an alcohol mixture on (a) Inerton AW-DMCS and (b) Chromosorb G AW-DMCS (temperature 140°). Peaks: 1 = cyclohexanol; 2 = ethylene glycol; 3 = decanol; 4 = undecanol; 5 = diethylene glycol.

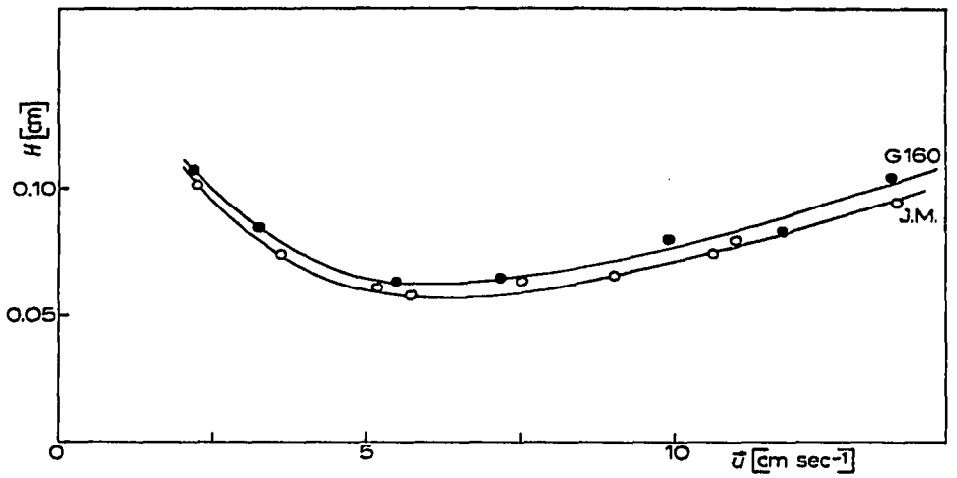

Fig. 6. Van Deemter plots measured on Inerton AW-DMCS and Chromosorb G AW-DMCS for toluene (10% squalane coating, temperature 80°). ●, Inerton AW-DMCS, Batch No. 160; ○, Chromosorb G AW-DMCS (Johns-Manville).

DMCS (Johns-Manville) both coated with 5% Carbowax 20M is illustrated in Fig. 5. The quality of the separation is the same on both supports.

The Van Deemter function plotted in Fig. 6 has the same shape for both supports and is characterized by a low value of the theoretical plate height in the mini-

TABLE V

ADSORPTION ACTIVITIES OF INERTON AW-DMCS AND CHROMOSORB G AW-DMCS SUPPORTS

Support	*Peak width at 1/10th of its height (mm)*				
	Acetone	*Methanol*	*Ethanol*	*Amyl alcohol*	*Triethylamine*
Inerton AW-DMCS, Batch No. 155	2.5	3.2	3.0	10.5	7.8
Inerton AW-DMCS, Batch No. 154	2.5	4.2	3.0	12.5	8.2
Inerton AW-DMCS, Batch No. 146-3	2.5	2.8	2.5	9.8	9.2
Inerton AW-DMCS, Batch No. 146-7	2.4	3.0	2.8	10.1	9.5
Inerton AW-DMCS, Batch No. 159-1	2.5	4.0	2.9	12.0	7.6
Inerton AW-DMCS, Batch No. 160-3	2.5	3.1	3.0	10.5	8.0
Inerton AW-DMCS, Batch No. 160-7	2.5	3.5	3.0	11.5	7.6
Average	2.5	3.4	2.9	11.0	8.28
Chromosorb G AW-DMCS (Johns-Manville) (3 separately prepared packings)	2.5	4.0	3.1	13.0	8.0
	2.8	3.5	2.9	12.9	10.0
	2.6	3.4	2.8	11.8	9.9
Average	2.63	3.63	2.93	12.63	9.3

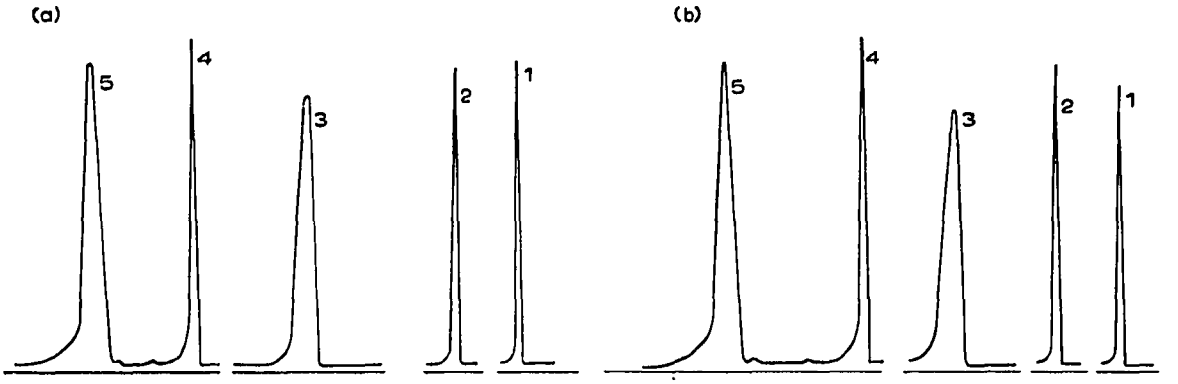

Fig. 7. Shapes of peaks of polar compounds on (a) Inerton AW-DMCS and (b) Chromosorb G AW-DMCS (5% squalane coating, temperature 80°). Peaks: 1 = acetone; 2 = ethanol; 3 = triethylamine; 4 = methanol; 5 = amyl alcohol.

mum of the curve: $H_{min.}$ at a flow-rate of nitrogen of 5–6 cm³/min is 0.60–0.63 mm. The very low shape of the curve in the region of higher flow-rates enables rapid analyses to be carried out with a negligible loss in separation efficiency. An increase in the number of analyses by a factor of two is accompanied by the loss of only one third of the separation efficiency.

The adsorption inertness of silanized supports expressed as the peak widths of polar compounds obtained on the non-polar phase squalane is shown in Table V. The average values of the peak widths for the seven batches of Inerton AW-DMCS investigated agree with the values obtained on three separately prepared packings of Chromosorb G AW-DMCS. The slight differences in the average peak widths on both types of support are negligible.

The shapes of the peaks of polar compounds shown in Fig. 7 are uniform for both of the supports compared. The peaks are sufficiently narrow and reveal only slight tailing, which is evidence of the good adsorption inertness of both supports.

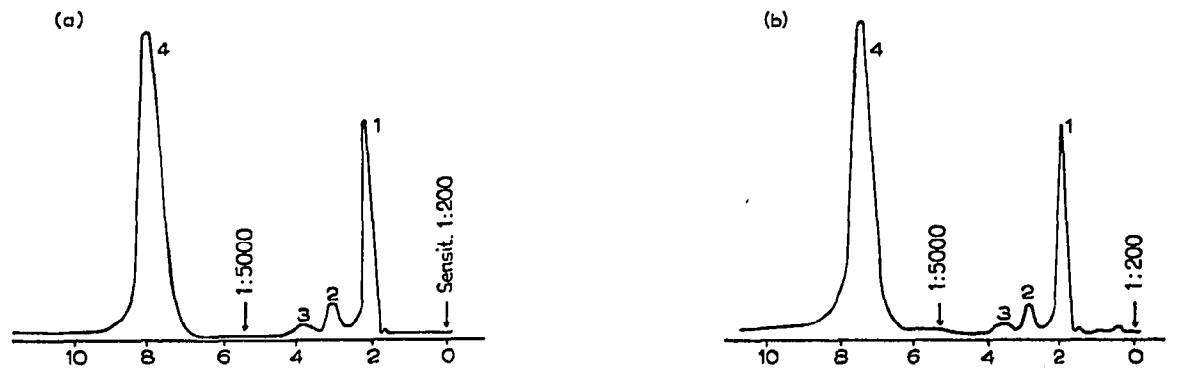

Fig. 8. Catalytic decomposition of *n*-butanol on uncoated silanized supports at 320° (1:200 and 1:5000 refer to the adjusted sensitivity of the chromatograph). (a) Inerton AW-DMCS; (b) Chromosorb G AW-DMCS (Johns-Manville). Peaks: 1, 2, 3 = C_4H_8 hydrocarbons; 4 = undecomposed *n*-butanol.

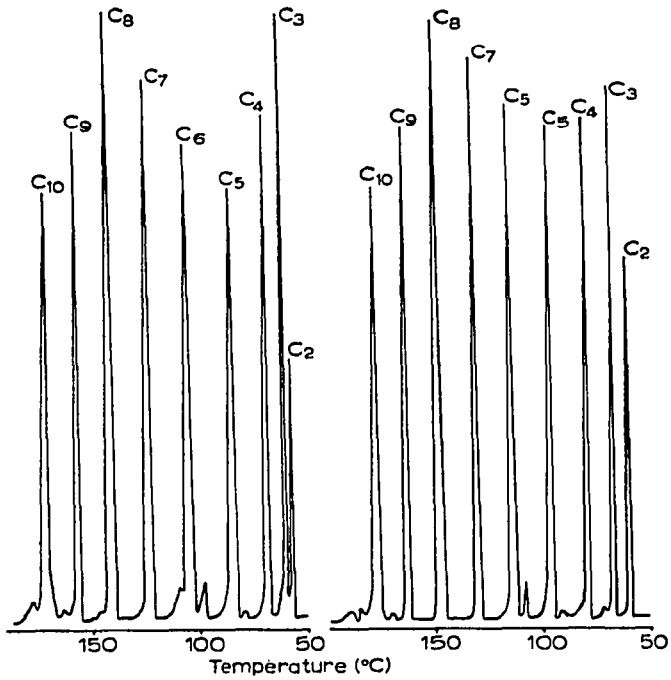

Fig. 9. Chromatogram of an *n*-alcohol mixture on Inerton AW-DMCS and Chromaton N AW-DMCS. Column 1400 × 4 mm; temperature 50–180°; nitrogen flow-rate 25 ml/min; amount injected 1 μl.

The catalytic activity, expressed as for the basic supports by the percentage thermal decomposition of *n*-butanol, is, as shown in Fig. 8, approximately the same for both supports. Its value for Inerton AW-DMCS is 1.18%, whereas for Chromosorb G AW-DMCS it is 1.15%. For comparison the decomposition of *n*-butanol detected under the same conditions was 0.1% on silanized Chromaton N and 2.73% on silanized Chezasorb.

Fig. 9 demonstrates the chromatographic separation of a mixture of C_2–C_{10} *n*-alcohols with temperature programming on Inerton AW-DMCS and Chromaton N AW-DMCS, loaded with 5% and 8% silicone oil DC-200, respectively. The loading with stationary phase was selected such that the amount of the phase in the column was the same in both instances (0.35 g). Under isothermal conditions (155°), the separation efficiency for octanol is 1250 theoretical plates on Inerton AW-DMCS and 1000 theoretical plates on Chromaton N AW-DMCS. From these results, it is evident that Inerton is equivalent to the white diatomite support Chromaton N, the properties of which are described in the literature[5], but the mechanical properties are much better.

CONCLUSION

The measurements of specific surface, total pore volume, pore size distribution and the results of chromatographic measurements of separation efficiency, adsorp-

tion and catalytic activities indicate that the basic white support Inerton and its silanized derivative Inerton AW-DMCS are, in terms of their physical and functional properties, very similar to Chromosorb G and Chromosorb G AW-DMCS from Johns-Manville. Their hardness is comparable with that of pink supports (*e.g.* Chromosorb P and Chezasorb) and their separation efficiencies, adsorption and catalytic properties are very similar to those of white diatomite supports (*e.g.* Chromosorb W and Chromaton N), but the bulk density is twice as high.

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