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PROPERTIES OF ACID-WASHED AND SILANIZED CZECHOSLOVAK SUPPORTS: CHROMATON N AND CHEZASORB

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SUMMARY

The separating efficiency as well as the adsorptive and catalytic properties of the new Czechoslovak acid-washed Chromaton N-AW and Chezasorb AW supports, as well as silanized Chromaton N-AW-DMCS, Chromaton N-AW-HMDS, and Chezasorb AW-HMDS supports for gas chromatography, were studied. The results were compared with data obtained in the same manner with untreated supports and functionally corresponding supports of the Chromosorb W and P types. The pore size distribution was measured in the acid-washed supports.

It has been found that the separating efficiency of Chromaton N type supports is similar to that of the Chromosorb W type. The separating efficiency of Chezasorb type supports is slightly better than that of Chromosorb P type products. The catalytic properties are the same with all mutually corresponding supports, but is considerably reduced by acid washing and silanization. The adsorptive properties are least with Chromaton N-AW-DMCS and Chromosorb W-AW-DMCS, are slightly greater with Chezasorb AW-HMDS and Chromaton N-AW-HMDS and are relatively greatest with Chromosorb W-AW-HMDS and Chromosorb P-AW-DMCS.

INTRODUCTION

In recent years, new Czechoslovak supports for gas chromatography have been developed; these supports, treated by acid washing and silanization, have appeared on the market this year. The physical and chemical characteristics of the untreated supports, as well as separating efficiency, and catalytic and adsorptive activity tests of treated supports, are described here. The results are compared with values measured in the same manner for untreated as well as functionally corresponding supports of the Chromosorb W and P types.

SUPPORTS BASED ON CHROMATON N

Chromaton N is a diatomaceous earth support which is white colored and according to OTTENSTEIN's classification¹ belongs to type II. It is obtained by calcinating physically and chemically purified diatomaceous earth (from the Borovany deposit) with an alkaline flux and, prior to the final step of production, working it up into spherical beads. For physical and chemical data concerning this support see Table I.

TABLE I

PHYSICAL AND CHEMICAL DATA OF CHROMATON N (see ref. 2)

Approximate chemical composition	SiO ₂	93 %
	Al ₂ O ₃	3.3 %
	Fe ₂ O ₃	0.04 %
	TiO ₂	0.01 %
	CaO + MgO	0.1 %
	Na ₂ O + K ₂ O	3.4 %
Specific surface	approximately 1 sq. m/g	
Bulk weight	0.235 g/cm ³	
Specific weight of the skeleton	2.3 g/cm ³	
pH of a 5% water suspension	9-10	
Capacity for stationary phases	20-25 %	
Appearance	snow white regular spheres up to ellipsoids	
Particle size	7 varieties covering the scale from 0.1 mm to 0.63 mm	

The acid-washed support Chromaton N-AW is obtained by leaching Chromaton N with acid, washing and floating with water and further washing with alcohol. The alkalis are thus washed off the surface of the support and, consequently, the pH value of a 5 % water suspension is between 6 and 8. Fine powder particles which decrease the separating efficiency of the column and increase the column resistance to the carrier gas are removed from the support at the same time. The other properties of the support remain the same as those of untreated Chromaton N.

The silanized supports Chromaton N-AW-DMCS and Chromaton N-AW-HMDS are obtained by treating the acid-washed Chromaton N-AW with dimethyldichlorosilane (DMCS) or hexamethyldisilazane (HMDS) respectively; this treatment results mainly in removing the undesirable catalytic and the adsorptive activity of the support.

SUPPORTS BASED ON CHEZASORB

Chezasorb is a pink diatomaceous earth support which, according to OTTENSTEIN'S classification¹, belongs to type I, *i.e.* the Firebrick type. It is obtained by calcinating chemically purified diatomaceous earth (the Kučlín deposit) with additives and crushing the mass formed. The mechanical strength of this support is far greater than that of Chromaton N. Physical and chemical data of this support are shown in Table II.

Acid-washed Chezasorb AW is obtained by leaching Chezasorb with acid, washing and floating with water to neutral reaction. The purpose of this treatment is not to change the surface reaction as it was with Chromaton N, but the removal of R₂O₃ type oxides showing catalytic and adsorptive activity. The leaching of a certain amount of ferric oxide from the surface is indicated by some fading of the initial pink coloring. In the flotation process undesirable powder particles are removed from the support, while the other properties are retained.

The silanized support, Chezasorb AW-HMDS, is obtained by treating Chezasorb AW with hexamethyldisilazane.

TABLE II
PHYSICAL AND CHEMICAL DATA OF CHEZASORB³

Approximate chemical composition	SiO ₂	90-95%
	Al ₂ O ₃	3.5%
	Fe ₂ O ₃	1.5%
	TiO ₂	0.09%
	CaO + Mg	0.3-0.5%
	Na ₂ O + K ₂ O	0.5-1.0%
Specific surface		3.0 ± 0.5 sq. m/g
Medium pore radius		0.5-0.9 μ
Total pore volume		0.5-0.6 cm ³ /g
Bulk weight		0.6-0.7 g/cm ³
Specific weight of the skeleton		approximately 1.9 g/cm ³
pH of a 5% water suspension		6.0-7.4
Capacity for stationary phases		up to 20%
Appearance		pink particles of irregular shape
Particle size		5 varieties covering the scale from 0.1 mm to 0.58 mm

EXPERIMENTAL

The pore size distribution and the total pore volume of the supports were measured on a mercury pressure porosimeter in the Adsorption and Gas Chromatography Laboratory, Department of Chemistry, Lomonosov University, Moscow, U.S.S.R.

The separating efficiency was expressed by the number of theoretical plates N of an 800 mm column⁴ for toluene and by the resolution R of an 800 mm column for *o*-xylene and *p*-xylene, where:

$$N = 16 \left(\frac{V_R'}{w} \right)^2$$

and

$$R = \frac{2(V_{R2} - V_{R1})}{w_1 + w_2}$$

A glass column, 4 mm I.D., packed with the support under study and coated with 3% Apiezon L was used for these measurements. The temperature used was 70°, the flow rate of the nitrogen carrier gas was 40 ml/min and 0.5 μl of a mixture consisting of benzene, toluene, *o*-xylene, and *p*-xylene was injected.

In addition, graphs of the Van Deemter functions for benzene and isopropyl ether were plotted, and from these plots the minimum height equivalents to a theoretical plate ($HETP_{min.}$) were obtained. The measurement was carried out using a metal column, 880 mm length and 0.2826 cm² cross section, packed with the support under study and coated with 15% squalane; the temperature was 100° and the charge of benzene and isopropyl ether mixture 0.5 μl. In these measurements, it was arranged that approximately the same particle size of the supports to be compared was used: 0.16-0.20 mm for Chromaton N-AW-DMCS, 80-100 mesh for Chromosorb W-AW-DMCS, 0.20-0.25 mm for Chezasorb AW-HMDS, and 60-80 mesh for Chromosorb P-AW-DMCS.

The catalytic properties of the supports (K) were determined according to POSPÍCHAL⁵ and expressed as the degree of catalytic decomposition of n -butanol on the uncoated support being studied, when it was heated to $290 \pm 1^\circ$ in a 110×4 mm metal column. The undecomposed n -butanol was separated from its decomposition products in an 800×4 mm glass column packed with Chromaton N coated with 10% Tridox (tridecanol-polyethyleneoxide). The temperature of the separating column was 100° , the flow rate of the nitrogen carrier gas 25 ml/min and the sample quantity, 1 μ l. The degree of decomposition was expressed in % and was determined by measuring the areas of the peaks of n -butanol and its decomposition products planimetrically. n -Butanol was injected repeatedly, till the area of the peaks compared did not change in the course of three tests following one after another.

The adsorptive properties of the supports were determined from the peak width of n -amyl alcohol ($S_{1/10}$) measured at one tenth of its height. The measurement was carried out under the conditions described for the determination of N and R , 1 μ l quantities of 20% n -amyl alcohol solution in ether were injected and the shift speed of the chart was 12.5 mm/min.

The supports of Chromaton N and Chezasorb types examined were supplied by the Research Institute of Pure Chemicals, Lachema Natl. Corp., Brno, from current production and sale, while the supports of the Chromosorb W and P types were supplied by Becker, Delft (The Netherlands).

With the exception of the Van Deemter functions, for the measurement of which a Chrom II chromatograph with flame ionization detector (Laboratory Apparatus Natl. Corp.) was used, all other measurements were carried out with a Fractovap chromatograph, DACI model (Carlo Erba, Milan, Italy) with a flame ionization detector.

RESULTS AND DISCUSSION

The pore size distribution and total pore volume of the acid-washed supports are evident from Fig. 1. The total pore volume of Chromaton N-AW amounts to 1.34 cm^3/g , while the value found for Chezasorb AW, 0.61 cm^3/g , is slightly higher than

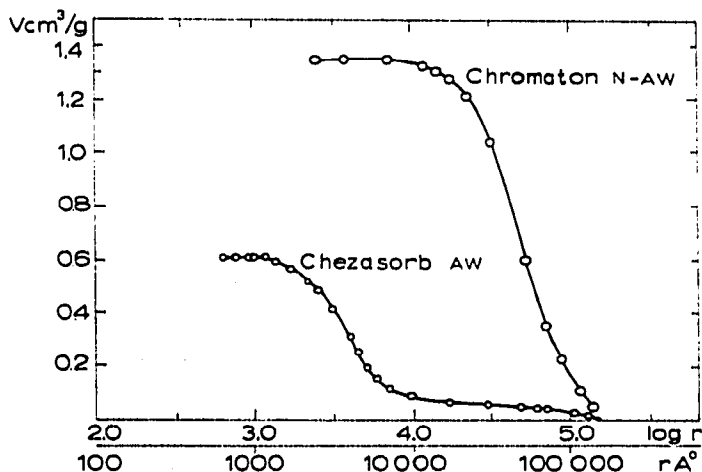


Fig. 1. Pore size distribution of Chromaton N-AW and Chezasorb AW.

the range indicated for an unwashed support by the manufacturer. The slope of both curves up to their horizontal portions and towards smaller pores suggests a narrow pore size distribution as well as the absence of undesirable micropores. The medium pore radius of Chromaton N-AW is about 4μ , while the value found for Chezasorb AW, 0.4μ , is somewhat lower than the range indicated for an untreated support by the manufacturer.

TABLE III

SEPARATING EFFICIENCIES, CATALYTIC AND ADSORPTIVE ACTIVITIES OF CHROMATON, CHEZASORB, AND CHROMOSORB SUPPORTS

Supports	Particle size	N	R	K (%)	S _{1/10} (mm)
<i>White supports, type II</i>					
	(mm)				
Chromaton N	0.20-0.25	420	1.0	0.5	—
Chromaton N-AW	0.20-0.25	460	1.1	0.4	—
Chromaton N-AW-DMCS	0.16-0.20	490	1.1	0.2	3.2
Chromaton N-AW-HMDS	0.20-0.25	440	1.1	0.2	4.0
	(mesh)				
Chromosorb W	60-80	450	1.1	0.4	—
Chromosorb W-AW	60-80	460	1.1	0.3	—
Chromosorb W-AW-DMCS	80-100	430	1.1	0.2	3.2
Chromosorb W-AW-HMDS	60-80	420	1.0	0.2	11.5
<i>Pink supports, type I</i>					
	(mm)				
Chezasorb	0.10-0.20	750	1.3	28.1	—
Chezasorb AW	0.10-0.20	870	1.5	9.7	—
Chezasorb AW-HMDS	0.10-0.20	780	1.3	1.2	4.0
	(mesh)				
Chromosorb P	80-100	570	1.24	27.1	—
Chromosorb P-AW	80-100	670	1.5	12.6	—
Chromosorb P-AW-DMCS	60-80	750	1.3	0.47	10.0

Table III gives the separating efficiency of the new Czechoslovak supports and the Chromosorb products (Johns-Manville). The separating efficiency of Chromaton N type supports is similar to that of Chromosorb W products. When comparing the pink supports with one another, it must be remembered that these are commercial products and that the particle size does not correspond accurately. Though the range of the particle size of Chezasorb supports is broader than that of corresponding Chromosorb P products, the separating efficiency of the former is slightly better. Under column conditions, the separating efficiency of the pink supports is greater than that of the white products; this is due to their having approximately twice as great a specific surface and more than double bulk weight.

The separating efficiency can be compared more precisely according to the HETP_{min.} values. The course of the Van Deemter function on Chromaton N-AW-DMCS and Chromosorb W-AW-DMCS can be seen in Fig. 2. The value of the minimum height equivalent for Chromaton N-AW-DMCS to a theoretical plate for benzene is 3.2 mm and 1.9 mm for isopropyl ether. The corresponding HETP_{min.} value found for isopropyl ether on Chromosorb W-AW-DMCS is 2.3 mm. No conclusions regarding

superior properties for Chromaton N-AW-DMCS can be drawn from the difference between these values.

The course of Van Deemter function on Chezasorb AW-HMDS is similar (see Fig. 3), but the minima of the curves lie lower. A value of 0.90 mm HETP_{min.} was obtained for benzene and 0.70 mm for isopropyl ether. The corresponding values of minimum height equivalent to a theoretical plate for isopropyl ether on Chromosorb P-AW-DMCS is 1.10 mm, suggesting a better separating efficiency with silanized Chezasorb.

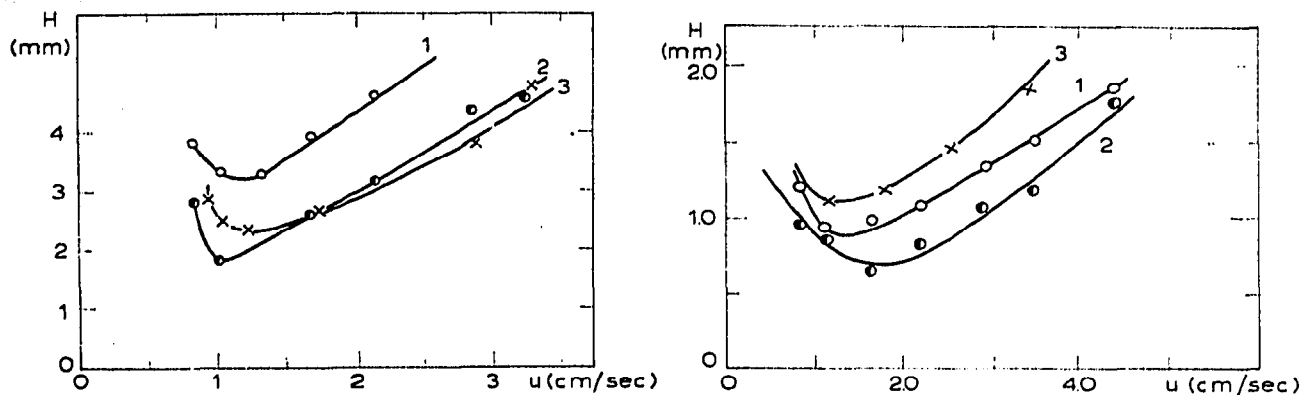


Fig. 2. Plot of the Van Deemter function for Chromaton N-AW-DMCS (1 = benzene; 2 = isopropyl ether) and for Chromosorb W-AW-DMCS (3 = isopropyl ether).

Fig. 3. Plot of the Van Deemter function for Chezasorb AW-HMDS (1 = benzene; 2 = isopropyl ether) and for Chromosorb P-AW-HMDS (3 = isopropyl ether).

It can be seen from Table III that under the conditions of the test, the white supports only show a very slight catalytic activity and that this is reduced to practically zero by silanization. The considerable degree of decomposition of *n*-butanol which takes place on the surface of untreated pink supports may be accounted for by ferric oxide and aluminium oxide, the removal of which from the surface of the supports by acid washing is accompanied by a considerable decrease in catalytic activity. This is further reduced by silanization and drops approximately to the level of the untreated white supports.

The test for adsorptive activity ($S_{1/10}$), in the modification applied by us, is only suitable for silanized supports, as with the other supports such a deformation of the *n*-amyl alcohol peak occurs that the results cannot be evaluated. From the results of measurements summed up in Table III, it may be concluded that the adsorptive activity is most reduced in the white supports treated with dimethyldichlorosilane. Chromaton N-AW-DMCS is equivalent to Chromosorb W-AW-DMCS, while Chromosorb W-AW-HMDS does not attain the level of Chromaton N-AW-HMDS. Thus, for white supports, dimethyldichlorosilane is a more efficient silanizing agent than hexamethyldisilazane, which is in good agreement with reports in literature^{6,7}. The adsorptive activity of pink supports is in some degree higher than that of the white ones. Chezasorb-AW-HMDS appears to be better than Chromosorb P-AW-DMCS, as its adsorptive activity is reduced to a similar extent to that of Chromaton N-AW-HMDS.

Numerically expressed results may be documented in a more illustrative manner by the shape of *n*-amyl alcohol peaks on white (see Fig. 4) and pink supports (see Fig. 5).

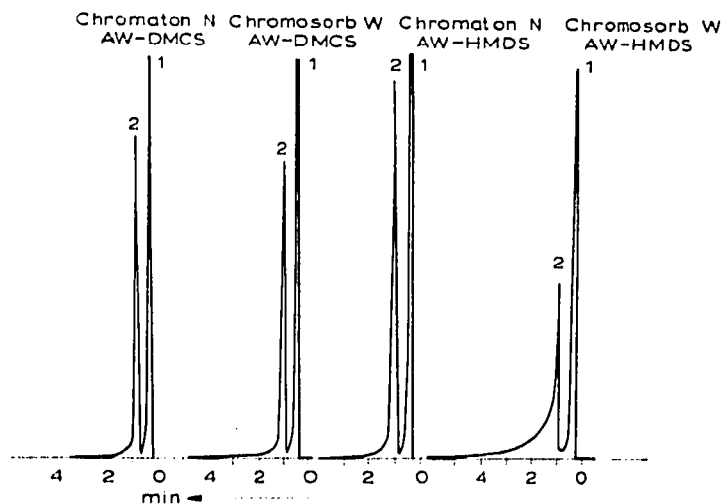


Fig. 4. Tailing of the peaks of *n*-amyl alcohol on silanized white supports. 1 = ether; 2 = *n*-amyl alcohol.

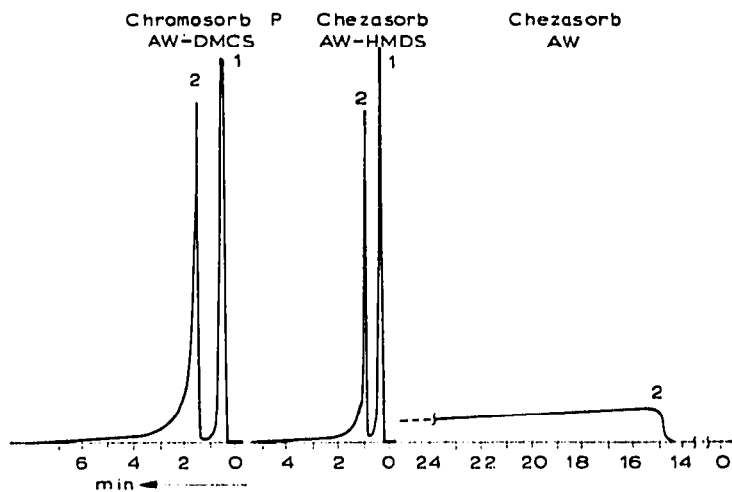


Fig. 5. Tailing of the peaks of *n*-amyl alcohol on silanized pink supports and on untreated Chezasorb AW. 1 = ether; 2 = *n*-amyl alcohol.

The remarkable effect resulting from silanization is also very clearly shown from the comparison with an untreated support in Fig. 5. If a more polar phase, di-*n*-decylphthalate (see Fig. 6), is used, the difference between a silanized and a non-silanized support is manifested rather by the longer elution times of alcohols on a non-silanized support than by the tailing of their peaks.

CONCLUSIONS

From the results of the measurements quoted and also from our experience we can conclude that treated supports of the Chromaton N and Chezasorb type are

mutually matching products, owing to their properties. It is recommended that white supports are used for the analyses of substances sensitive to catalytic decomposition or for the separation of polar, strongly adsorptive substances when the supports are coated with low amounts of non-polar or medium polar stationary phases. The properties of Chromaton N-AW-DMCS are most advantageous in this respect.

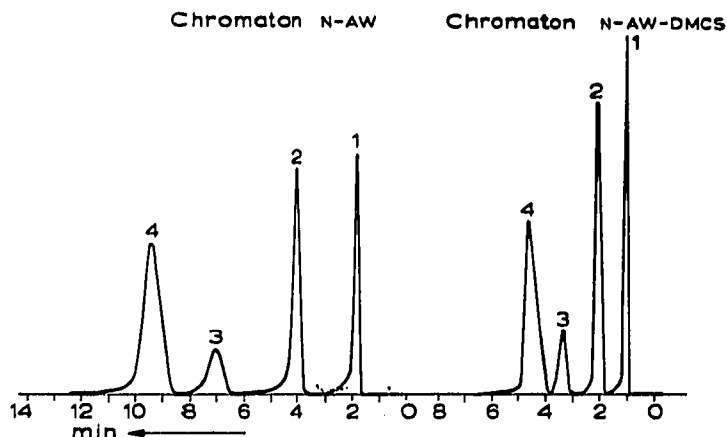


Fig. 6. Extension of elution times of alcohols in consequence of the adsorptive effect of the support. Coating 3% di-*n*-decylphthalate. 1 = propanol; 2 = *n*-butanol; 3 = isoamyl alcohol; 4 = *n*-amyl alcohol. $T = 80^\circ$, flow rate $N_2 = 40$ ml/min.

Treated pink supports based on Chezasorb are preferable in all cases when maximum separating effect is to be attained. These supports are of particular use in the separation of non-polar and medium polar substances, which are not too sensitive to catalytic decomposition. Chezasorb AW-HMDS even permits the separation of strongly polar substances with low coating of the support with non-polar stationary phases.

Acid-washed and silanized supports based on Chromaton N and Chezasorb broaden the scale of applicability of basic supports, their properties being equivalent to those of acid-washed and silanized Chromosorb W and P products.

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