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PREPARATION OF DIATOMACEOUS SURFACES FOR THE SYNTHESIS OF BONDED PHASES AND TRACE ANALYSIS

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SUMMARY

The treatment of chromatographic supports with acid is of crucial importance for the subsequent bonding of polymers, as well as for certain types of analysis on conventional gas-liquid chromatographic coatings. This paper reports on the efficiency of treatments with acid for the removal of various cations from the silicic surfaces of Chromosorb W, G and P. While the commercial acid-washing process removes only negligible amounts of iron, the procedure reported here can remove over 95% of the iron initially present.

INTRODUCTION

The difference in price between non-acid-washed (NAW) and acid-washed (AW) brands of diatomaceous Chromosorb is substantial, representing a 30-150% increase in price for this surface treatment. However, acid-washed supports sell well, which attests to the advantages that a clean-up of the surface brings to gas chromatographic analysis.

The value of acid treatments has been well recognized and emphasized (refs. 1-3 and references therein), although disagreement with this assessment occasionally surfaces. For our particular interests, which involve bonded stationary phases (*e.g.*, ref. 4) and trace analysis, washing with acid is essential. Having decided to purchase the less expensive NAW supports and to perform the clean-up ourselves, the question arose to what extent the operation should be pursued.

It seemed simple to choose an efficient acid-treatment procedure and to consider clean-up to be complete when most of the non-silicic materials had been removed from the surface. Thus, we used a Soxhlet extraction with the thimble at the boiling temperature of hydrochloric acid. When, after extraction for several hours with a fresh batch of acid, the acid remained free of a yellow tinge, the treatment was considered to be complete. This arbitrary approach produced the desired chromatographic results, but extraction times became excessively long in certain instances.

While a few days would normally suffice for most batches of Chromosorb, one particular batch required 3 months of continuous extraction in order to meet the above criterion. Needless to say, this extraction was continued beyond the few initial days for general interest rather than for chromatographic utility.

PRELIMINARY WORK

This "3-months" support, together with other extracted and non-extracted Chromosorbs and also extracts, were analyzed by conventional procedures. For solid materials, these procedures involved arc spectroscopy, and digestion with hydrofluoric acid followed by atomic-absorption or flameemission spectrometry. Table I lists some of the results obtained and compares them with figures taken from the literature^{3,5}. Although one would not consider these values to be generally reproducible owing to batch-to-batch variations, they do raise some questions with regard to the extraction efficiency of commonly used procedures. Further, it appeared that some cations, notably iron, occur mainly at, or close to, the surface of the Chromosorb.

TABLE I
RESULTS OF PRELIMINARY WORK

Source	Chromosorb	Treatment	Fe (%)	Al (%)	Surface area (m ² /g)
Present work	W	—	1.08	1.60	1.09
	W	3 days in Soxhlet	1.00	1.18	—
	W	3 months in Soxhlet	0.34	0.26	2.25
Johns-Manville ^{3,5}	W	—	1.14	2.12	1.0 (nominal)
	W	AW	0.99	1.90	—

The 3-months' extraction doubled the surface area (from 1.09 to 2.25 m²/g) and added *ca.* 4% to the pore volume, effectively dissolving approximately 10% of the interior material. This dissolution increased the contribution of small pores to the total pore volume (and consequently increased the surface area), as shown by porosimetry in Fig. 1. (All of these measurements were carried out by Micromeritics, Norcross, Ga., U.S.A.)

Although the results for the "3-months" support were of general interest, there are obvious reasons for considering them to be irrelevant from a practical point of view. Thus, a relatively fast, efficient method of clean-up was still to be desired.

EXPERIMENTAL

Various types of NAW Chromosorb were washed for 1 day in a Soxhlet apparatus with 6 *N* hydrochloric acid in order to remove some of the easily soluble material and then packed into a laboratory-made substitute for a tubular oven, which consisted of a heavy-walled quartz tube (25 mm I.D., 31 mm O.D. and approximately 120 cm long) with ground-quartz ball-joint terminals. Nichrome wire was wound around

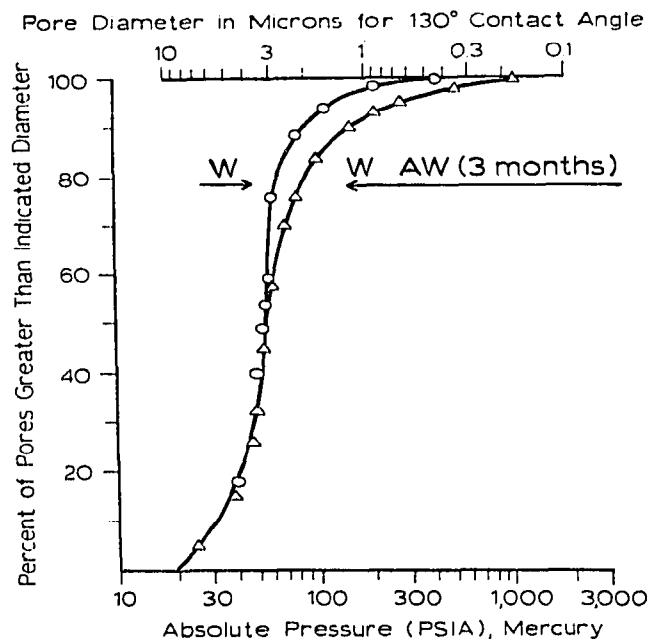


Fig. 1. Porosity of Chromosorb W, non-acid-washed w. acid-washed for three months (analysis by Micromeritics).

the tube, its loops being separated and held in place by tiny quartz protrusions. Layers of asbestos were wrapped around this core and the whole rod was placed into 1-in. Marinite insulation (basically an elongated box with open ends and a square cross-section). Power to the heater winding was controlled with a variable auto-transformer.

After packing the evenly heated sections of the tube with pre-cleaned Chromosorb held by plugs of quartz-wool, a nitrogen flow of *ca.* 100 ml/min was directed through the tube and its contents were heated to 850–900°. Small amounts of hydrogen chloride gas (*ca.* 5 ml/min) added to the stream of nitrogen served to produce chlorides from the various surface materials, some of which distilled out of the tube and solidified in its cooler exit portion, displaying zones of various colors. The gaseous effluents were routed to the fume-hood intake.

The time required for the treatment of Chromosorb under these conditions depends on a variety of parameters, notably the temperature. No exact study was made, but the time periods used varied between 1 and 3 days. Afterwards, the Chromosorb was allowed to cool in a stream of pure nitrogen.

It was then washed once again with 6 *N* hydrochloric acid in the Soxhlet apparatus for 1 day (mainly to remove any soluble, non-volatile chlorides), and then with distilled water in a Büchner funnel to neutrality before drying. These supports are designated "RW" in this paper.

It should be noted that some of the precautions generally observed for AW supports should likewise be taken with these materials: *e.g.* if it is intended to use Carbowax 20M as a liquid phase at high temperatures, then washing of the support with alkali prior to the final washing with water is advantageous, especially when

TABLE II
EFFECTS OF TREATMENTS WITH HCl

Source	Chromosorb	Treatment	Fe (%)	Al (%)	Surface area (m ² /g)
Present work	W	—	0.79	1.66	1.06
	W	AW (J.-M.)	0.86	1.49	—
	W	RW (our laboratory)	0.008	1.21	0.92
	G	—	0.77	1.72	0.62
	G	AW (J.-M.)	0.74	1.69	—
	G	RW (our laboratory)	0.10	1.35	1.10
	P	—	0.89	1.73	3.14
	P	AW (J.-M.)	0.80	1.83	—
	P	RW (our laboratory)	0.02	1.32	3.08
Johns-Manville ^{3,5}	W	—	1.14	2.12	1.0 (nominal)
	W	AW	0.99	1.90	—
	G	—	—	—	0.5 (nominal)
	P	—	1.14	2.32	4.0 (nominal)
	P	AW	0.99	2.17	—

Chromosorb P or a similar fire-brick type of support is involved.

The supports were then analyzed as described under Preliminary work.

RESULTS AND DISCUSSION

The results of the elemental and surface area analyses as given in Table II are largely self-explanatory. Data listed under NAW and RW (our laboratory) refer, of course, to the same (manufacturer's) batch, while those under NAW and AW most likely do not. Hence it is not surprising that the iron and aluminum contents of two supports that were washed with acid by the manufacturer are actually higher than those of the non-acid-washed material. Data from the manufacturer show that differences in cations between AW and NAW versions of the same batch are minor³; this agrees essentially with the results of our analyses.

It was therefore a considerable surprise to find that our clean-up procedure was capable of removing, on average, more than 95% of the iron present. This amount of iron must have been present on the surface (possibly from marine sediments) rather than in the bulk of the diatom skeletons. The aluminum content also decreased significantly, although not as dramatically as that of iron. An impression of the visual effects of the high-temperature clean-up can be gained from Fig. 2, where NAW and AW forms of Chromosorb P (P indicates pink) can be contrasted with the gleaming white RW product. The fourth material was added for color comparison; it is Chromosorb W (W indicates white) which we covered with a very thin layer of iron oxide.*

It should perhaps be emphasized that a high iron content *per se* does not necessarily imply inferior chromatographic performance under all circumstances. Rather, a high iron content may serve as an indicator that the acid-washing procedure

* Fig. 2 had to be deleted because of technical considerations. It showed Chromosorb P and Chromosorb P-AW in their usual brownish red, Chromosorb P-RW pure white, and Chromosorb W-Fe pink.

was not very efficient, that the surface is therefore inhomogeneous with a variety of chemically different adsorption sites present, and that iron oxide and the other non-removed materials might render the surface more prone to induce decomposition reactions in labile analytes and/or stationary liquid phases. It should be obvious that this statement is not intended to denigrate a reasonable product (which the Chromosorbs definitely are) but to direct attention to the fact that they also can be improved.

There is little doubt that the "purity" and homogeneity of the surface of a support is critically important in many types of trace analysis, while in others it hardly seems to matter. In any event, it would be interesting and may, in fact, prove advantageous, to try some of the more demanding types of analyses with supports from whose surface everything but the silicic network had been removed.

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