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LIQUID CHROMATOGRAPHY ON METAL OXIDES WITH SILICA GEOMETRY

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SUMMARY

A typical liquid chromatography silica can be reacted with vapors of various volatile metal halides such as $FeCl_3$, $AlCl_3$, $SnCl_4$, etc., to form thin, inorganic layers. These oxide-type layers retain the silica geometry and show different retention behaviour in liquid chromatography.

INTRODUCTION

There are available many (too many?) stationary phases for gas–liquid chromatography; there are but a few for liquid–solid chromatography (LSC), and fewer still that will withstand the high pressures of modern usage. The most widely used LSC adsorbents are of the silicic type, and the developments of recent years have focused mainly on physical aspects such as particle size, pore distribution and, related to it, column packing techniques.

The predominance of silica (and the second most important phase, alumina) is easily understood in terms of high-performance liquid chromatography (HPLC) prerequisites: suitable porous, small particles with great mechanical stability. It would obviously be interesting, both from an analytical and a fundamental point of view, to have available materials with active surfaces other than SiO_2 and Al_2O_3 which, however, would retain the porosity and attrition resistance of a good silica or alumina.

There have been numerous attempts to coat active metal ions like Ag^+ on silicic surfaces and some attempts to incorporate them into the silicic structure (see refs. 1–6, and literature cited therein). "Argentation" chromatography has become a standard technique for resolving *cis–trans* isomers; some other approaches have met with less success.

The obvious uncertainty about such chromatographic layers or packings

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relates to the distribution of the additive on or within the silicic base. Coarser or finer mechanical mixtures and/or more or less heterogeneous coatings can be obtained; and it is obviously difficult to arrive at a precise definition of a particular material. A thorough recent study provides a good case-in-point[3]. It is probably fair to assume that a *homogeneous* layer of a pure inorganic material on silica suitable for chromatography, has rarely been achieved.

The approach taken in this study came about by considering, in reverse, a recently developed technique for removing metal oxides from the surface of typical gas chromatographic (GC) supports[7]. These oxides are converted to chlorides in a stream of HCl at 850° and distilled off. In the reaction reversed, typical metal chlorides could react with silanol groups present on a silicic surface and "bond" to it. Residual chlorine can be hydrolyzed off with water, giving rise to oxide or hydroxide structures. The latter could, in certain cases, be reacted again with the metal chloride, yielding a second molecular layer, and so on. Whereas the metal oxides removed from the surface of a GC support would be of the mixed variety, the new layer(s) formed by the reversed procedure would contain only one kind of metal.

The crucial question for this approach is whether suitable metal chlorides, or similar materials, will react with the silanol groups. This question has been answered affirmatively a number of times, for instance by physicochemical studies designed to characterize the various forms of water occurring on a silicic surface[5].

We have therefore used this approach for producing GC supports and LC phases from low- and high-surface-area silicic materials, respectively. The earlier GC study used Chromosorb and was concerned primarily with surface activity and the "bonding" of organic polymers[9]. The LC study contained in this note was concerned only with the question whether these different surfaces would bring about different retention behavior. Since elution order (rather than high resolution) was the criterion, a low-priced, easily-handled porous silica was used as the base upon which the new surfaces were to be built.

EXPERIMENTAL

Preparation of phases

The phases were prepared in a manner similar to the treatment of GC supports[9]. Batches of 2 g of Porasil A, 35–75 μm (Waters, Milford, Mass., U.S.A.) were filled into a vertical quartz tube with ground joint terminals and a fine frit situated about 2/3 down the tube. The laboratory-made tubular oven was a drilled block of aluminium, heated by cartridge heaters (Watlow) and insulated by Marinite (Johns-Manville). It was used such that both the top and the bottom of the tube were accessible; the top for introducing nitrogen carrier and the halide reagent, the bottom for monitoring the effluents. Solid reagents were kept in a little beaker, dangling inside the tube from a wire leading through a septum on top. The beaker was lowered into the heated zone to start the reaction. Liquid reagents were injected through the septum.

The reaction with halide was considered complete when excess reagent collected in the cool bottom part of the apparatus. Then *ca.* 0.5 ml water was injected several times until the bottom condensate was neutral to pH paper.

Table I shows the approximate temperatures used and the color, if any, of the materials obtained.

TABLE I

REACTION TEMPERATURES AND COLORS OF COATED PORASIL

Reagent	Approximate temperature (°C)	Coated support
$FeCl_3$	350	Dark red
$AlCl_3$	210	White
$SnCl_4$	150–180	Off-white
WCl_6	400	White, yellow*
$TiCl_4$	170	White
$NbCl_5$	280	White
$POCl_3$	150	White
CH_2Cl_2	400	Black (see text)

* Yellow form can be converted to white by treating it again with H_2O at 400°.

It should be mentioned that the same apparatus can be used to produce a pyrolytic carbon layer from CH_2Cl_2 (compare refs. 10 and 11).

Testing of phases

The materials were dry-packed into 20 cm × 1.8 mm I.D. steel columns and capacity factors (k') determined of the following test compounds: benzene, diphenyl ether, 2-methoxynaphthalene, phenol, benzophenone, *o*- and *p*-diethoxybenzene, quinoline, 1,4-naphthoquinone, *p*-quinone, cinnemaldehyde and nitrobenzene [with chloroform, chloroform–hexane (1:4), and *n*-butylchloride], and caffeine, theobromine, nicotinic acid, aniline, N,N-dimethylanine, quinoline, and 8-hydroxyquinoline (with dioxane).

Analysis of phases

The coated Porasils were first examined at Columbia, Mo., by arc spectrography. In all but the case of W were significant amounts of the metals found; W was present only as a trace.

Then the Porasils were quantitatively analyzed as follows: Fe was extracted with boiling 6 *N* HCl; W and Ti were put in solution by volatilization of SiO_2 with H_2SO_4 and HF; all others were fused with NaOH in Ni crucibles, the melt dissolved in water and made to volume. Fe, Sn, and Al were done by flame emission using the standard additions method to correct for matrix effects. W and P were done colorimetrically, Nb was done by arc emission spectrography, Ti was done gravimetrically as TiO_2.

Several (different) batches were analyzed at Halifax for Fe by extraction with HCl, followed by atomic absorption spectrometry and $KMnO_4$ titration, and for Sn and W by dissolution in KOH and atomic absorption.

RESULTS AND DISCUSSION

The analytical data, similar to those obtained on Chromosorb for the preceding GC study, point to significant differences in the amount of metal bonded. Part of this effect is obviously due to the number and type of silanol groups available at the different temperatures at which the reactions were run. However, the chemical nature

of the element to be bonded, and the chemical state in which it is used, also play a role.

It is not too surprising that, where several batches were analyzed as in the case of the iron oxide layer, relatively large differences in metal content were observed. This effect may parallel the well-known difficulties in obtained silicagels with precisely the same number and type of silanol groups, and is obviously exacerbated by the day-to-day variation in synthesis conditions. At this stage, we felt it to be more important to demonstrate that layers on silica gel could be obtained by our approach and that these materials could be used to advantage in LC, than to strive for a high degree of reproducibility.

Following are the results of analyses performed on coated Porasils: 12.5% Fe (average from 4 batches), 0.3% W (3 batches), 2.5% Sn (2 batches), 6.3% Ti, 0.5% Nb, 5.1% Al, and 2.8% P. Pyrolytic carbon was not determined. A calculation of nominal layer thickness shows that Fe, Ti, Al (and P) are close to 1 Å; the rest, Sn, Nb and W, close to 0.1 Å. It would appear from these results that atomic size affects layer thickness (i.e. larger atoms are less likely to bond), and more detailed arguments could undoubtedly be made in regard to geometries involved in various types of silanol groups and, in the case of high-surface-area carriers, their accessibility. (Our calculations of nominal layer thickness are based on the N_2 BET surface of Porasil, and Porasil is known to contain significant numbers of very narrow pores). However, both syntheses and analyses would have to be repeated in a much more extensive and precise manner before correlations of this sort could be justified.

For the purpose at hand, a nominal layer thickness within an order of magnitude of that of the "monomolecular" layer seemed reasonable enough; and this result was indeed achieved with several elements.

No tests were performed to characterize the stability of the synthesized layers. With the mobile phases used (chloroform, dioxane, etc.), no instability was expected and none was immediately apparent. However, it is obvious that strongly acidic conditions would entail leaching of Fe, that water would remove P, etc. (It should be noted at this point that two of the reagents used, $POCl_3$ and CH_2Cl_2, are clearly different from the metal halides, and have been included in this study only because they could be easily handled and promised to produce a very different type of surface. The phosphorus-doped material was tested similar to the metal-containing surfaces; the carbon-coated material, which showed reversed-phase behavior as expected[11], was not.)

Little purpose would be served by listing all the k' values measured in this study and we are therefore including only Table II as a single example of runs with one solvent. It is interesting, however, to look at the trends displayed when all the data acquired in this study are put together.

First, there are large differences between the various packings in k' values for a particular solute–solvent combination. More important, the order of the columns, as listed from the most to the least retentive, depends strongly on the solute–solvent combination. In some cases, this order was almost reversed by a change in solute; i.e. the column which proved to be the most retentive for one solute turned out to be among the least retentive for another. In other words the packings did serve the purpose for which they were intended: to provide retention patterns different from those obtainable from silica gel.

TABLE II

k' VALUES ON DIFFERENT COLUMNS

Solvent: n-Butylchloride

Solute	Surface							
	Plain (Si)	Fe	W_{yellow}*	W_{white}*	Sn	P	Ti	Al
Benzene	0.0	0.2	0.25	0.3	0.1	0.1	0.1	0.2
Nitrobenzene	0.4	—	0.5	—	0.4	0.3	0.4	0.4
p-Quinone	7.0	7.3	7.7	9.6	7.6	3.0	6.7	6.3
1,4-Naphthoquinone	6.0	0.3	3.5	0.2	0.2	2.6	4.8	5.0
Cinnemaldehyde	4.6	5.3	5.9	6.1	5.2	3.6	4.7	3.8
Diphenyl ether	0.1	0.3	0.2	0.1	0.1	0	0.1	0.1
p-Diethoxybenzene	1.3	2.2	2.1	2.5	1.4	0.8	1.3	1.3
o-Diethoxybenzene	2.6	3.6	3.5	4.2	2.9	1.7	2.5	2.2
2-Methoxynaphthalene	0.1	0.3	0.3	0.2	0.1	0.1	0.1	0.1
Phenol	5.4	2.8	2.9	4.3	5.6	6.4	5.4	5.4

Retention order

p-Quinone: $W_{white} > W_{yellow} \approx Sn > Fe > Si > Ti > Al \gg P$

1,4-Naphthoquinone: $Si > Al \approx Ti > W_{yellow} > P \gg Fe \approx W_{white} \approx Sn$

Cinnemaldehyde: $W_{white} > W_{yellow} > Fe \approx Sn > Ti \approx Si > Al > P$

p-Diethoxybenzene: $W_{white} > W_{yellow} \approx Fe > Sn > Si > Ti \approx Al > P$

o-Diethoxybenzene: $W_{white} > Fe \approx W_{yellow} > Sn > Si \approx Ti > Al > P$

Phenol: $P > Sn > Si \approx Ti \approx Al > W_{white} > W_{yellow} \approx Fe$

* See footnote in Table I.

Second, the "acidic" type solutes would be preferentially retained by the "basic" type layers (Ti, Al) and vice versa. This is not unexpected when one considers the traditional roles of "acidic" SiO_2 and "basic" Al_2O_3 in LC. Obviously, the chemical history of the packing and the choice of solvent are also important in this context.

Effects other than those of the acid–base type appeared to be operative, as one would expect them to be. However, the limited context of this study does not justify any further, general conclusions.

It should be borne in mind that some of the layers were definitely less than "monomolecular", *i.e.* the observed retention behavior must have included a contribution of the bare Porasil surface. It is apparently possible to increase layer thickness in most cases on Chromosorb W (ref. 9) by repeated synthesis cycles, *e.g.* using the reagent sequence $FeCl_3$, H_2O, $FeCl_3$, H_2O, etc. A similar approach can be taken with silica gel, and should yield standard materials, which could be used with greater confidence in attempts to compare the behavior of chemically different surfaces with one and the same pore geometry.

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