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## SYNTHESIS AND GAS CHROMATOGRAPHIC USE OF METAL-CONTAINING SURFACES\*

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### SUMMARY

A variety of volatile metal halides were used in the gas phase to produce layers with thicknesses in the monomolecular range on Chromosorb W. The final layers result from subsequent treatment with H<sub>2</sub>O, NH<sub>3</sub> or H<sub>2</sub>. They could be considered to be of the "oxide", "nitride" or "reduced" type, although no evidence for particular surface structures has been obtained. Layers were tested by gas chromatography directly and after attempted synthesis of an additional "bonded" Carbowax 20M layer. These procedures were successful (in terms of achieving inorganic layers in the monomolecular range and good chromatography with Carbowax 20M) in some but not all cases. The best materials were about equal in chromatographic performance to the best comparable phases containing no metals. "Bonding" of Carbowax could be achieved on several types of layers. For example, those containing Fe or Cr performed noticeably better than those containing Al or B. General uses of such materials are suggested.

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### INTRODUCTION

Metal compounds can play a role in, on, under or as chromatographic phases. If they are present by design, their effects are considered beneficial. This is perhaps clearest seen in complexation chromatography (for a review see ref. 1; some recent papers are cited as refs. 2-10). For this technique, metals are used in the form of salts, ions (on an ionexchange matrix) or chelates.

Somewhat different from this application is the role of metal oxides. Aside from silica (and, on occasion, alumina), they have but rarely served as gas chromato-

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graphic (GC) phases or supports. Hydrated ferric oxide has been used for the analysis of gases<sup>11,12</sup> and so has chromia<sup>13</sup>. Ferric oxide has also carried thin films of Carbowax 20M<sup>14</sup> and heavier loads of the liquid phase triethylene glycol<sup>15</sup>. Several other materials, e.g., antimony pentoxide<sup>16</sup>, have also been investigated.

If metals are present on chromatographic supports owing to natural or, unwittingly, industrial processes, their influence is considered detrimental. The presumably macromolecular forms of iron and aluminum on the surface of diatomaceous earth supports may serve as the most common example.

To decrease their concentration, extraction with HCl is the most often-used procedure. Although the commercial treatment removes only a very small percentage of Fe and Al<sup>17</sup>, it is definitely beneficial as evidenced by the broad acceptance which the much higher-priced acid-washed supports have found. Less decomposition of solutes (possibly also of the liquid phase) occurs and chromatographic efficiency is generally better.

The detrimental influence of metals can be seen as part chemical reactivity, part surface inhomogeneity. The latter effect appears to be the more difficult to define, but not much is known about either of them. (The great difficulties associated with characterizing inhomogeneity even in pure materials have been pointed out well in recent studies by Waksmundzki *et al.*<sup>18</sup>. In our case, several metals on the surface, present in unknown concentrations and chemical states, complicate the matter further.)

We were interested in defining the effects of particular metals present on a diatomaceous support, notably iron and aluminum. To study these effects, a diatomaceous surface covered by only one type of metal, preferably in the oxide or silicate form, had to be available. We were also interested in exploring whether or not our method of "bonding" ultrathin polymer layers on silicic supports could be extended to various types of metal-containing surfaces. (Apparently, it is possible in the case of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (ref. 14).) Finally, we were interested in comparing the chromatographic properties of such surfaces without a modifying polymer layer, *i.e.*, in pure gas-solid chromatography.

A variety of methods can be used to obtain a metal-containing surface. It would be possible, in the case of several metals, to use their oxides in neat form. However, their pore structures may be less than ideal for chromatographic purposes, and phases of different pore structures would be difficult to compare.

It is also possible to coat soluble metal salts onto supports similar to the coating of liquid phases<sup>1</sup>. These can be further reacted to yield the desired compounds. Or the desired surface compound can be produced by precipitating it on the support<sup>8,12</sup>. However, it is apparently very difficult to achieve a homogenous layer with this technique and small, isolated deposits are to be expected<sup>8</sup>.

For our purpose, one promising approach toward the synthesis of fairly "homogenous" layers seemed to be the chemical reaction between surface silanol groups and metal halides in vapor form. This reaction is, in a way, the reverse of our purification technique for GC supports, in which HCl gas reacts at high temperature with the metal oxides and/or silicates and metal chlorides distill off<sup>17</sup>.

The reaction of metal halides with surface silanols is not new; such compounds as BCl<sub>3</sub>, AlCl<sub>3</sub>, etc., have been used for characterizing silanol groups and the water content of silica gels (for a review see ref. 19). Presumably chemical bonding occurred

and an even distribution must have been achieved, reflecting the distribution of silanol groups on the surface.

The skeleton of diatoms consists essentially of silica. Chromosorb, *i.e.*, diatomaceous earth for gas chromatography, should be capable of similar reactions as silica gel. However, Chromosorbs, even in their AW (acid-washed) form, contain significant amounts of Fe, Al and other metals still on their surface. These would render them unusable for the purposes of this study. The clean-up method for Chromosorbs mentioned above removes most of this surface contamination by reaction with hydrogen chloride at 850°<sup>17</sup>. The remaining, "clean" silicic surface can be reacted with a particular metal halide and, once a surface layer (possibly with residual, reactive halide) is formed, subsequent reactions can be attempted, *e.g.*, with water to give "oxide", with ammonia to give "nitride" or with hydrogen to give "reduced" type structures. We realized from the beginning that this approach was likely to result in materials whose precise surface structures were impossible to determine by means available to us. Although reactions as cited above are well known in bulk phase, extrapolation to processes occurring in the monomolecular layer region of a silicic substrate, with little-characterized pore geometry and chemical reactivity, is fraught with peril.

Thus, while it is easy to tell that *some* reaction has occurred (say by the evolution of HCl), its exact nature may be uncertain. There may also be the possibilities of incomplete coverage, reaction with the silica network (opening of Si-O-Si), reaction of one average halide molecule with a fractional number (between 0 and 2, generally) of silanol groups, metal valence changes, formation of multiple layers (in a series of reactions alternating metal halide and water, or even with some residual water around) and others more. These ambiguities in mind, we intended this study to serve as a scouting trip into a little-explored field, with chromatography as the main, but not the only, point of interest.

## EXPERIMENTAL

Chromosorb W (45-60 mesh in early experiments and 100-120 mesh in later ones) was purified as previously described<sup>17</sup> by a pre-wash with 6 *N* HCl, a treatment with HCl gas at 850°, again a wash with 6 *N* HCl and a final wash with distilled water to neutrality. Then the material was dried overnight at  $\approx 150^\circ$  in vacuum.

This Chromosorb (thereafter designated "RW") was filled into a vertically standing quartz tube (about 1 in. diameter, about 1 ft. high) with indentations (to hold the lower quartz wool plug) and ground quartz joint terminals. The upper terminal formed a "T" with the side entrance admitting nitrogen and the main entrance (through a septum) allowing injections, *e.g.*, of water, or permitting a little quartz vessel containing halide to be lowered into the heated region of the quartz tube. The quartz tube was heated by a large aluminum block with cartridge heaters. This oven was supported in a lab-made hood and the exit line from the bottom terminated inside the hood's exhaust duct. It could be easily opened to check for HCl evolution, etc.

The metal halides used in this study were AlCl<sub>3</sub>, BCl<sub>3</sub>, CrO<sub>2</sub>Cl<sub>2</sub>, FeCl<sub>3</sub>, MoCl<sub>5</sub>, NbCl<sub>5</sub>, TaCl<sub>5</sub>, SnCl<sub>4</sub>, TiCl<sub>4</sub>, WCl<sub>6</sub> and VOCl<sub>3</sub>. Two non-metal halides processed by the same techniques were POCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, the former to produce an acidic phase<sup>49</sup>, the latter to produce a pyrolytic carbon layer<sup>20</sup> for purposes of comparison and for

bonding studies. Depending on the volatility of the halide, it was either used as gas or vapor carried by the nitrogen stream or, more often, introduced neat into the top portion of the heated zone where it evaporated. All metal halides were taken through procedures (a) and (b) outlined below; only some of the resulting materials were further processed by (c) or (d).

(a) *Initial reaction with metal halides.* After the tube had been charged with Chromosorb W RW (kept in place by two large quartz wool plugs), nitrogen was turned on to about 30 ml/min for the whole of the experiment. The aluminum block was kept at elevated temperature (the same temperature as used for the subsequent reactions) for 2–6 h, mainly to remove water. Then the little quartz vessel containing the metal halide was lowered into the heated zone (or the nitrogen flow was charged with halide vapor or gas). Hydrogen chloride evolution began and after some time excess metal halide began to appear at the tube exit. This first step was considered complete when the nitrogen stream contained only traces of HCl (usually after 2–4 h). The temperature chosen for this experiment represented a compromise among various considerations involving mainly the volatility and reactivity of the halide and the number and nature of silanol groups on the surface. The resulting material was then treated in one of several ways.

(b) *Further reaction with water.* Keeping the same temperature, an excess of water was injected into the tube ( $\approx 0.5$  ml). Hydrogen chloride evolved and excess water condensed in the exit. It usually took 1–2 h until the HCl content of the exiting  $N_2$  stream was down to trace levels. Then the reaction with metal halide and the subsequent injection of water was repeated. If there was substantially less HCl evolved in the repeated sequence, the procedure was considered complete and the material was left at the elevated temperature overnight and then allowed to cool down. If considerable amounts of HCl were evolved in the second cycle, a third one was added. The nitrogen was kept flowing until the coated material was removed. This type of phase is hereafter called "oxide", although it should be realized that the true structure (which is not known) may not always be fully consistent with this name.

(c) *Further reaction with ammonia.* Starting with material from (a) above, the temperature was raised to the desired level (chosen from ref. 22 for nitride formation from metal halides and  $NH_3$ ) and approximately 20 ml/min ammonia gas added to the nitrogen stream for about 12 h. Then the ammonia was turned off and the material allowed to cool under nitrogen.

(d) *Further reaction with hydrogen.* This reaction started with the (a) or the (b) type material as described above. In each case, the material was brought to the desired temperature in a suitable quartz tube oven and then  $\approx 15$  ml/min of hydrogen were added (to the usual 30 ml/min  $N_2$  flow) for 6 h. This type of material is sometimes termed "reduced" in this paper. As in the above cases, the precise state of the surface is unknown.

(e) *Additional heat treatment.* Some phases, especially those that were tested neat rather than be used in polymer bonding experiments, were heated under the usual nitrogen flow to 850° for 12 h in a suitable quartz tube furnace.

### *Analyses*

Due to matrix effects and the extremely small amounts involved, not all materials could be successfully analyzed. In several cases, analyses were performed in

duplicate and on more than one sample. Al, Cr, Fe and Sn were determined by nitrous oxide/acetylene flame emission after extraction with boiling 6 *N* HCl; B, Mo, Nb, P, Ta, Ti, V and W were done by arc spectroscopy. Nitrogen was determined by the Kjeldahl method. These analyses were performed at the University of Missouri Experiment Station's Spectrographic Laboratory (E. E. Pickett) and Chemical Laboratories (C. W. Gehrke). In addition, some analyses of Fe by  $\text{KMnO}_4$  titration were done at Dalhousie. A nominal layer thickness was calculated by using the BET surface of the Chromosorb and the bulk density of the compound assumed closest in chemical composition to the layer (e.g.,  $\text{Al}_2\text{O}_3$ , CrN, etc.)

### *Chromatographic tests*

All materials were tested as gas chromatographic phases, first neat and then after the attempted synthesis of a bonded Carbowax 20M layer<sup>21</sup>. The chromatographies were done in 1 m  $\times$  1.9 mm I.D. borosilicate columns, with 30 ml/min  $\text{N}_2$  flow and FID detection in a Shimadzu 4BM gas chromatograph.

## RESULTS AND DISCUSSION

As noted in the Experimental section, some elemental analyses were difficult to perform on samples based on Chromosorb W with its low surface area ( $\approx 1 \text{ m}^2/\text{g}$ ). However, in a subsequent investigation involving Porasil A ( $\approx 400 \text{ m}^2/\text{g}$ ) and liquid chromatography<sup>23</sup>, more reliable layer thickness values could be obtained. These are comparable to (though, as expected, somewhat lower than) the values obtained on Chromosorb, thus supporting the results of this study.

Following are some values for nominal layer thicknesses with, in parentheses, the colors of the materials, and formulae of the compounds whose densities and element ratios were used for calculation. It should again be noted, though, that the surface layers are not to be equated with these bulk compounds nominally used for computation; the procedure simply reflects reasonable chemical similarities devoid of any experimental corroboration.

Iron was determined in different forms (pink,  $\text{Fe}_2\text{O}_3$ ; grey, Fe) and on different samples. All values obtained were in the 1–5 Å range. Chromium gave layer thicknesses of 12 Å (dark reddish brown,  $\text{CrO}_3$ ) and 9 and 10 Å (green, CrN; values for N and Cr, respectively). It should be stressed at this point, however, that we do not know how well the Kjeldahl method was able to cope with this type of sample and that the green color suggests  $\text{Cr}_2\text{O}_3$ . Aluminum showed 6 Å ( $\text{Al}_2\text{O}_3$ ). Smaller amounts were found of Ti, Sn, P, V, Mo and B (oxide forms, no obvious color). These most likely reflect layers in the 0.1–1 Å range; with the possible exception of Sn which might have been incompletely extracted, and B, which occurred in the matrix (from the extraction of Chromosorb with 6 *N* HCl in borosilicate soxhlets prior to use). No significant evidence was found for the presence of Nb, Ta and W. Later evidence<sup>23</sup> on silica gel, however, showed Nb and W to be present on that material at 0.04 Å ( $\text{Nb}_2\text{O}_5$ ) and about 0.01 Å (brown,  $\text{WO}_2$ ); Ta was not run. Thus, "layers" in the 0.01–0.1 Å range seem likely on Chromosorb. (The layer terminology is kept here for purpose of comparison, even though it has now lost its physical meaning.)

The analyses for Fe, Cr and Al, however, and possibly those for Sn, Ti, V and Mo, also, support the initial assumption that layers in the monomolecular range can be ob-

tained in this fashion. The syntheses performed in this study were run at different temperatures. Temperature influences the number and kind of silanol groups (chemisorbed water), the reaction rate and, because of the quasicromatographic flow system, the contact time of the metal halide. The reaction conditions were chosen as being "reasonable" but none was optimized. If one assumes a  $1 \text{ m}^2/\text{g}$  Chromosorb surface comparable to a fully hydroxylated silica ( $\approx 6$  silanol groups per  $100 \text{ \AA}^2$ ), and calculates the nominal layer thickness of, say,  $\text{Fe}_2\text{O}_3$  (bulk density  $\approx 5 \text{ g/cm}^3$ ) arising from a load of one metal atom per silanol group, it turns out to be  $1.5 \text{ \AA}$ . This compares with measured values from  $1\text{--}5 \text{ \AA}$ . One also needs to realize that not all types of silanol groups are apt to react with all types of metal halides, that certain halide molecules may react with more than one silanol group and that, to start with, the surface is not likely to be fully hydroxylated. All these effects would tend to decrease "layer thickness" below its theoretical value. On the other hand, the number of metal atoms bound has been found to be larger in certain cases than the number of silanol groups<sup>24</sup>. Furthermore, some metal hydroxide structures are undoubtedly formed in the subsequent reaction with water and, again depending on temperature, can react themselves with more metal halide introduced in the second or third cycle. This formation of "multiple layers", and the likely presence of residual adsorbed water as well as the possible presence of residual adsorbed metal halide at different steps in the procedure, all represent effects which would tend to increase "layer thickness" above its theoretical value.

It is obvious that a thorough investigation of these parameters would far exceed the confines of a simple chromatographic study. Fortunately, however, some tentative conclusions can be derived from even the scant evidence available.

The major impurities found on the surface of Chromosorbs are iron and aluminum. Both pure iron and aluminum "oxide" could be coated onto pure Chromosorb in relatively thick layers. Throughout the chromatographic tests, the phases based on Fe performed significantly better than the one based on Al; in fact, they were generally comparable to pure Chromosorb itself. Thus the experiments suggest that the presence of Al on the surface of a support is of a considerable greater detriment than the presence of Fe; at least in the context of the tests carried out.

The tests of the metal-containing surfaces themselves, by pure gas-solid chromatography, proved unexciting. Some materials behaved slightly better or just about as well as the pure Chromosorb, others performed considerably worse. Fig. 1 shows a temperature-programmed separation of hydrocarbons on  $\text{H}_2$ -treated ("reduced") type layers.

In order to obtain better chromatography, a thin layer of Carbowax 20M can be "bonded" to the surface<sup>14,21</sup>. We felt that this procedure provided a more interesting test for the various surfaces than the use of standard-load liquid phases. To provide good chromatography it is necessary that Carbowax chains are capable of (a) bonding to the surface and (b) deactivating it. In the case of surfaces with low metal content, "bonding" could occur to the silicic structure (presumably via multipoint hydrogen bonding to the silanol groups), while with high metal content (assuming homogeneous distribution) it would have to involve the surface layer. It is possible, of course, that a particular surface may be capable of good performance with regular (non-bonded) typical GLC liquid phases, but would fail to show such performance in this test because the Carbowax would not bond (= would prove extractable).

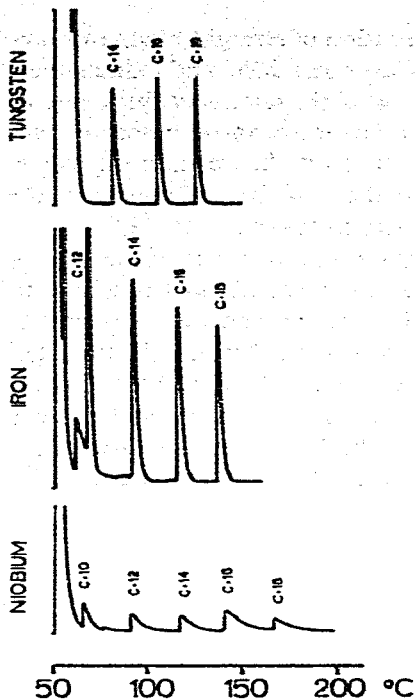


Fig. 1. Temperature-programmed gas chromatographies of *n*-alkanes on Chromosorb W, reacted with metal chlorides and treated with hydrogen as described in the text.

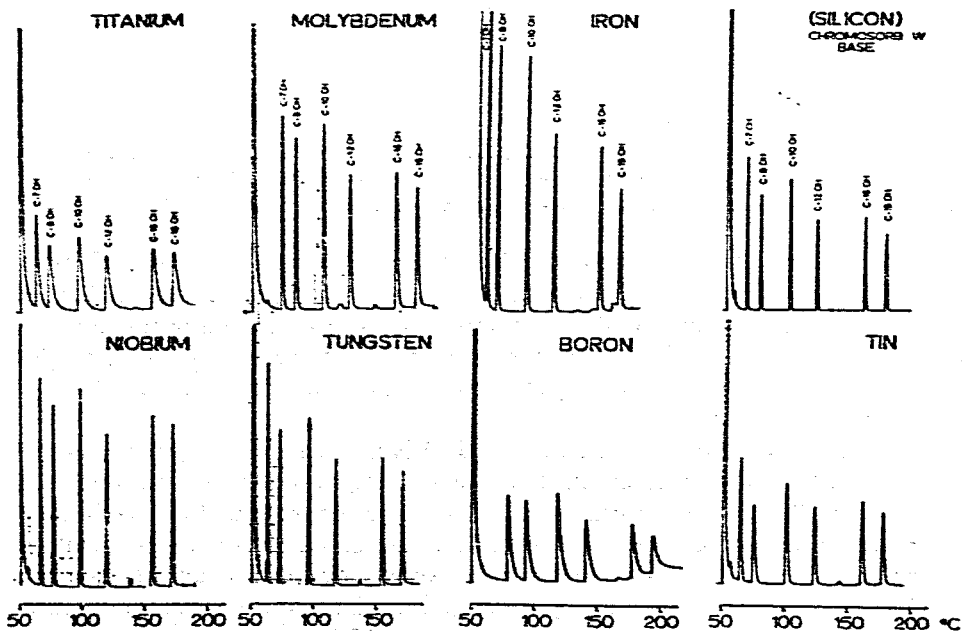


Fig. 2. Temperature-programmed chromatographies of 1-alkanols on Chromosorb W that has been reacted with indicated metal chlorides and water, and has been modified with Carbowax 20M as described in the text.

Fig. 2 shows the temperature-programmed separation of straight-chain primary alcohols on various "oxide" type layers modified by Carbowax 20M and exhaustively extracted with methanol. Some layers, among these the pink, relatively thick one of iron, show acceptable chromatography. Particularly inferior are those based on titanium and boron, and a similar one based on aluminum (not shown) is even worse. This is not completely unexpected in view of the position of these elements in the periodic table and what is known about their surface structures (*e.g.*, ref. 19).

It is not quite clear whether the presence of very small amounts of metals has helped chromatography, but in some cases like tungsten it has at least not hurt it. Fig. 3 shows an isothermal separation of some hydrocarbons and alcohols on the Carbowax-modified surface of Chromosorb W doped with "reduced" tungsten (reaction with  $WCl_6$ , then with  $H_2$ ). The performance is as good as the best of these types of columns (without metals) can provide; *i.e.*, over 5000 plates per metre, close to the theoretical limit for a 100–120 mesh support. (The flow used is considerably higher than the HETP minimum would suggest; however, the Van Deemter curves for such phases show very low  $C$  terms.)

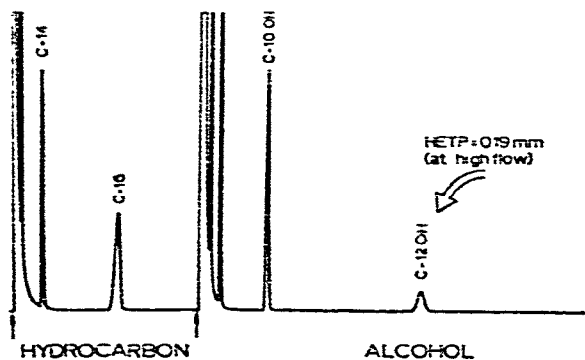


Fig. 3. Comparison of peak shape and efficiency of alkanes and alkanols in isothermal gas chromatography on a 1-m column. Stationary phase: Chromosorb W, 100–120 mesh, doped with  $WCl_6$ , treated with  $H_2$ , and modified with a non-extractable layer from Carbowax 20M.

The performance of a modified, much heavier layer of the "reduced" type, namely the grey layer of iron (reaction with  $FeCl_3$  and  $H_2O$ , twice repeated, then treatment with  $H_2$ ), is shown in Fig. 4 with temperature-programmed separations of two "polarity" test mixtures. It shows that the support is well deactivated and, similar to a bonded layer of Carbowax 20M on pure Chromosorb, considerably less "polar" than a regular Carbowax GLC phase<sup>25</sup>.

It has been shown before that Carbowax 20M is not the only polymer that can be "bonded" to silicic surfaces<sup>26</sup>. Even materials as unlikely to bond as Apiezon L can form non-extractable layers on Chromosorb<sup>21</sup>. Now it appears that Carbowax 20M not only bonds to silicic surfaces but also to surfaces which contain various metals in different chemical states. (Even pyrolytic carbon showed a certain affinity for this liquid phase.) Here as there, obviously, particular polymers and particular surfaces are clearly favored over others in terms of chromatographic performance. No attempt has been made to correlate such behavior to, say, the number and reactivity of surface hydroxyls and their steric "fit" to the non-extractable polymer.





## NOTE ADDED

Most of this manuscript had been written some time ago and, while literature that has appeared since then does not require any significant change, we would like to add for the convenience of the reader a recent review<sup>27</sup> and a few interesting papers<sup>28-48</sup> to the list of references.

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