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GAS AND LIQUID CHROMATOGRAPHY ON SILICA-SUPPORTED CHROMIA LAYERS*

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SUMMARY

Gas-solid and liquid-solid chromatography have been performed on chromia layers bonded to silica gel 62 and to LiChrosorb Si 100, 10 μm , respectively. Compared to gas chromatography on plain silica gel 62, aliphatics are much stronger, aromatics much less retained on the chromia layers. There occurs a peculiar cross-over between homologous series: 1-olefins are less retained at low, but more retained at high molecular weight than are 2-olefins. When Carbowax 20M is "bonded" to the chromia surface, this retention behaviour is somewhat moderated but remains still distinctly different from that of silica.

LiChrosorb-supported chromia shows the same high efficiency as the bare silica gel in high-performance liquid chromatography, but differs in selectivity. Generally, chromia is more retentive than silica towards a variety of organic structures, but shows the opposite behavior towards free phenols.

INTRODUCTION

Apart from the popular phases based on SiO_2 , Al_2O_3 and C, a variety of other inorganic materials have been used in chromatography. Some served in neat form; others, mainly due to problems of friability and undesirable pore structure, were coated onto the chromatographically more suitable silicas or aluminas. The field of metal-containing phases has been well reviewed by Szczepaniak *et al.*¹

Recently we reported the synthesis of certain inorganic layers and multilayers on chromatographic supports. We used such materials to define the advantages and disadvantages brought about by the presence of metal in the surface layer, and characterize the role they can play as supports for organic layers in gas chromatography (GC)². It was also established that such layers can serve as selective adsorbents in liquid chromatography (LC), where they can bring about pronounced changes in retention patterns³. At that stage it was probable but not yet established that multilayers, *i.e.* layers thicker than the nominally "monomolecular" one, could indeed be produced. We therefore ascertained this fact for oxides of iron, chromium, aluminum

* Material taken from Ph.D. thesis of P.P.W.

and titanium bonded to both diatomaceous earth and silica gel. The data strongly supported, though they did not prove, our initial hope that these layers would be homogeneous⁴.

If these metal oxide layers were indeed homogeneous, chromatography on them may be as good as that of the base silica gel. Thus we decided to take one of the more interesting bonded layers, namely that of chromia [chromium(III) oxide], and apply it to areas of chromatography where silica [silicon(IV) oxide] excels: gas-solid chromatography of light hydrocarbons, and solid-liquid chromatography of the high-performance liquid chromatography (HPLC) variety. A further point of interest was how the presence of an additional, "bonded" organic layer would influence the chromatographic properties of the chromia surface.

The use of chromia has often been reported in the chromatographic literature. For instance, Van der Vlist and De Jong⁵ separated nitrogen from oxygen on Cr_2O_3 . Chromia deposited on alumina served in the separation of hydrogen isotopes⁶. For various catalytic reactions, chromia is often supported on alumina to prevent its decrease in surface area above 400°C ⁷. Ref. 7 provides also an extensive review of the catalytic qualities of chromia at low temperatures. Returning to GC, the use of a coordination polymer of Cr(III) has been reported⁸.

EXPERIMENTAL

Silica gel 62, 80–100 mesh, was modified by a nominal three layers of chromia as described earlier⁴. The product was treated with hydrogen at 800°C for 3 h to give the final, green phase.

LiChrosorb Si 100, 10 μm , served as the support for LC. It was washed with hot 6 *N* HCl until no further colour was noticed, rinsed with excess distilled water and dried in vacuum at 110°C . Then one nominal layer was produced by treatment with CrO_2Cl_2 at 280°C as described earlier⁴. After 45 min of reaction, NH_3 was introduced and the reaction tube heated to 500°C . This temperature and the flow of ammonia were maintained for 5 h, after which the product was allowed to cool down in a $\text{NH}_3\text{-N}_2$ stream. It was then transferred to a quartz tube and heated at 800°C for 6 h in a $\text{NH}_3\text{-N}_2$ stream; followed by a further 2 h in pure nitrogen.

Carbowax 20M was "bonded" to chromia-modified silica gel 62 as described earlier for Chromosorb W⁹.

GC materials were tested in 100×0.2 cm I.D. glass columns; LC materials were tested in 9×0.41 cm I.D. LiChroma stainless-steel tubes. Packing the 9-cm HPLC columns was done in a conventional tetrabromoethane-carbon tetrachloride slurry at 4500 p.s.i. The same pressure was used for conditioning; however, retention measurements were run below 2000 p.s.i.

Surface areas were measured by Micromeritics (Norcross, GA, U.S.A.) using the N_2 BET method; nitrogen was analyzed by the block digester-autoanalyzer method at the Experiment Station Chemical Laboratories of the University of Missouri, Columbia, MO, U.S.A.; carbon and hydrogen analysis was provided by Galbraith Labs (Knoxville, TN, U.S.A.). Chromium was determined by neutron activation analysis at the SLOWPOKE reactor, Dalhousie University.

RESULTS AND DISCUSSION

Gas chromatography

Fig. 1 shows sample chromatograms of two test mixtures on silica and chromia surfaces, both neat and covered by a *ca.* 5 Å thick "bonded" layer based on Carbowax 20M. (Layer thickness was approximately the same for silica and chromia). Two conclusions are immediately apparent: first, the retention patterns vary widely between silica and chromia; second, chromatographic efficiency is approximately the same for each of the two base packings and not much worse than for each of the two Carbowax 20M modified packings.

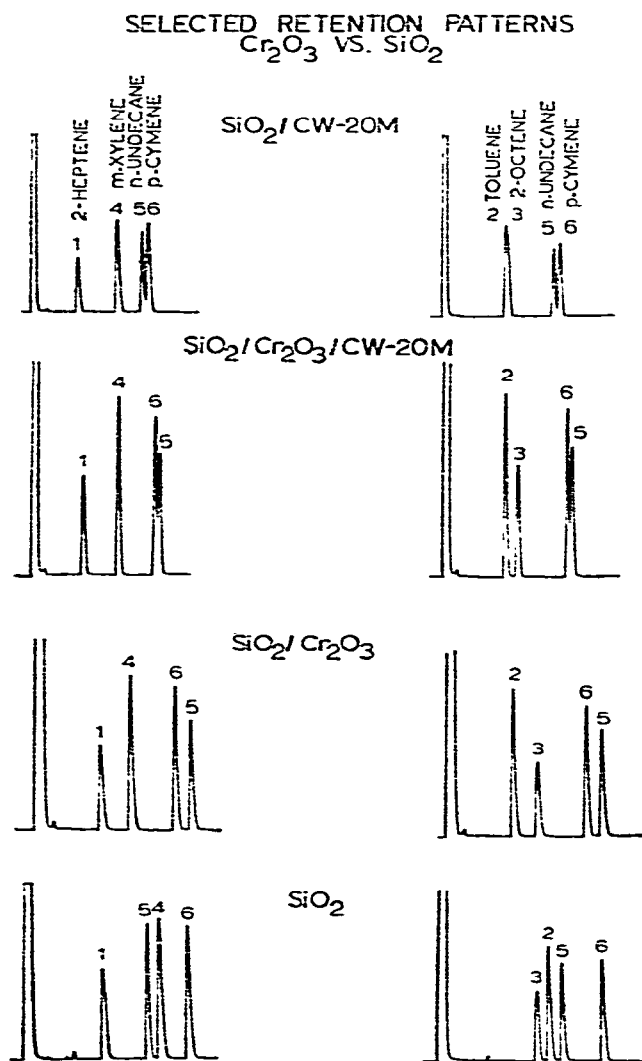


Fig. 1. Retention patterns of two test mixtures on silica and chromia surfaces, both bare and modified with Carbowax 20M (CW-20M), in temperature-programmed gas chromatography.

To wit, the reduced plate height ($HETP/d_p$, where $HETP$ = height equivalent to a theoretical plate, and d_p = particle diameter) for alkanes is typically 4 for silica and chromia-silica, and typically 3 for the same surfaces when modified by Carbowax. Isothermal tailing is more pronounced on the former than on the latter type of material. In comparison, the lowest reduced plate height we ever measured on a modified silica was 2.2; and that approached the theoretical minimum. The values generally expected of gas-solid chromatography are much higher¹⁰. Thus it is probably fair to consider these phases to be as good as they reasonably can be.

On closer inspection, the retention patterns provides a surprise. This is shown in Fig. 2, which lists retention temperatures for various compound classes. Compared to silica gel, chromia adsorbs aliphatics more strongly, aromatics less strongly. (It should be realized, however, that this comparison is made between two packings of slightly different surface areas.)

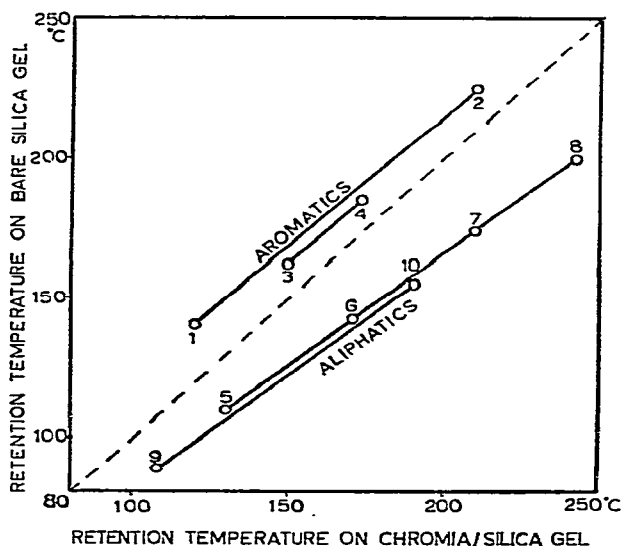


Fig. 2. Comparison of retention temperatures on silica vs. chromia. Temperature-programmed gas chromatography (but different program and flow than in Fig. 1). 1 = Benzene; 2 = naphthalene; 3 = toluene; 4 = *m*-xylene; 5 = *n*-heptane; 6 = *n*-nonane; 7 = *n*-undecane; 8 = *n*-tridecane; 9 = cyclohexane; 10 = decalin.

This difference between aliphatics and aromatics is quite surprising for a material whose general catalytic activity is attributed to surface coordinative unsaturation. We do not know, of course, the precise nature of our chromia. However, by analogy with data from catalysis⁷, one would assume it to be microcrystalline α - Cr_2O_3 , with Cr^{3+} and O^{2-} being the predominant surface species, perhaps augmented by some Cr^{2+} . Since chromium is a transition element and an excellent complex-former, one may have expected a stronger interaction with aromatic systems than is shown here.

Within the realm of aliphatics and aromatics, then, chromia turns out to be a relatively "non-polar" phase. (Its strong affinity for alkanes is not perhaps, as one might have conjectured, due to an increase in surface area brought about by formation

of a suitably structured layer; in fact, silica gel 62 has a surface area of approximately 300 m²/g and the chromia-coated material tested out at only 250 m²/g.) Somewhat surprisingly, too, cyclohexane and decalin appear "less polar" (in the representation of Fig. 2) than the straight-chain alkanes.

Why aromatics are less retained on chromia than on silica can be only a matter of speculation at present. For instance: because of the heat treatment it experienced, our chromia has likely much less (and different) hydroxyl groups on its surface than silica gel. And it is the hydroxyl groups on silica that are presumed to be responsible for the adsorption of aromatics¹¹.

Speculations aside, the retention properties of the chromia layer make for some interesting plots in comparison with chromatographies done on its bare carrier. Fig. 3 shows the retention of the homologous series of 1-olefins and 2-olefins on silica gel 62. Parallel curves are expected and this is indeed what is being observed. In Fig. 4, however, the same chromatography on the chromia surface looks quite different: the retention curves now cross each other.

The reason for this somewhat unusual behaviour is unclear at present. More than one retention mechanism may be at work; steric considerations may play a part; and one could think of a variety of other scenarios that could be made responsible for such a behaviour.

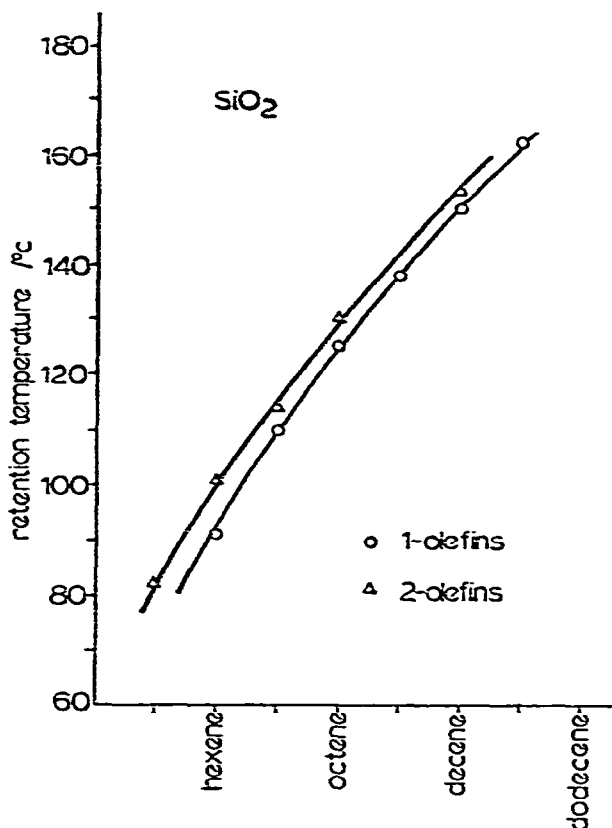


Fig. 3. Retention temperatures of 1- and 2-olefins on bare silica gel 62.

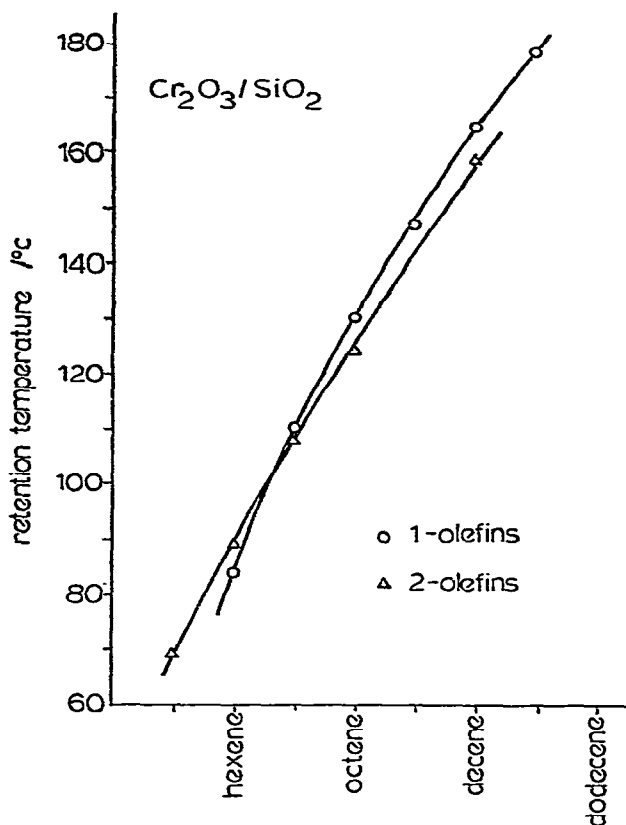


Fig. 4. Retention temperatures of 1- and 2-olefins on chromia (on silica gel 62).

When chromia is covered by an organic layer based on Carbowax 20M, the two curves move closer to each other. Crossover still occurs, though at a somewhat different chain length (Fig. 5).

Liquid chromatography

It was known from an earlier, exploratory study³ that different metal oxides coated on silica gel lead to different retention patterns in LC. However, establishing the difference of retention patterns was the only aim of that study. It was conducted on Porasil, high pressures were not involved, and high efficiencies were not sought.

Obviously, if there were to be any benefits to the use of layers of chromia—or, for that matter, of any other metal oxide—in modern LC, three conditions had to be met. First, the synthetic process had to be able to cope with typical, small-particle HPLC adsorbents. Second, the synthesized phases had to be stable under conditions of high flow and pressure. Third, these phases needed to perform at least as efficient as the silica gel on which they are based. These conditions were addressed in the present study.

The synthesis of chromia layers on LiChrosorb differed somewhat from that used for silica gel 62. The use of ammonia and nitrogen is quite common for the

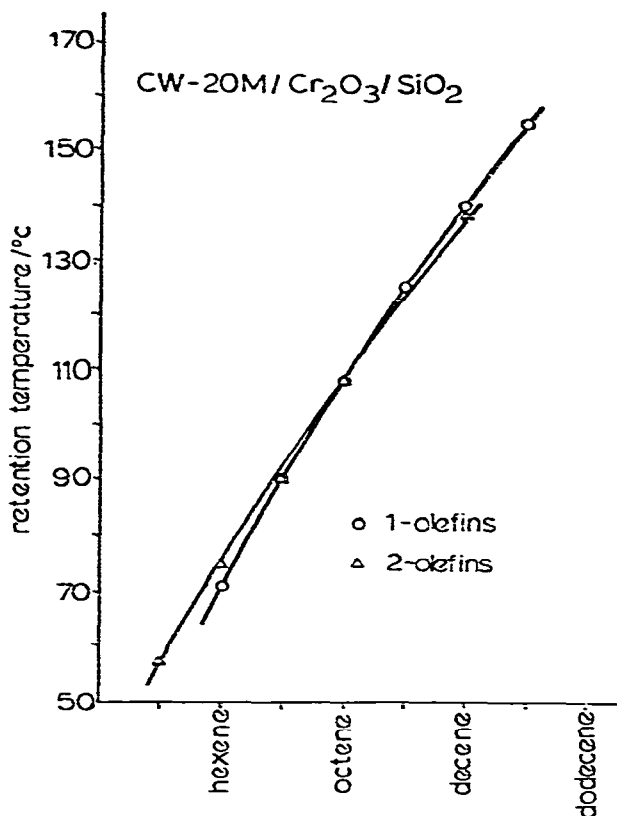


Fig. 5. Similar to Fig. 5, but chromia covered by a *ca.* 5 Å layer derived from CW-20M.

treatment of chromia catalysts⁷. However, in this case we have to admit to an attempt of producing a nitride-type structure. As the analysis showed (13.6% chromium vs. only 0.23% nitrogen), this objective was not met. Most likely we produced a similar α -Cr₂O₃ as on silica gel 62; the colours were also very much alike. Nitrogen does not necessarily have to be in nitride form; chemisorption of ammonia is well-known on chromia catalysts.

There were no unusual difficulties in working with LiChrosorb and we did not notice any chemical or mechanical instability in the coated product.

Differences in solute retention patterns on chromia vs. silica were expected and were found. Table I lists a number of *k'* values for different compounds run on the two columns. While silica-supported chromia is the somewhat more retentive phase (judged by the few compounds that were run), the two free phenols included in the list are exceptions. (2-Nitrophenol does not qualify here because of its intramolecular hydrogen bonding.) It could be presumed that the stronger retention of the phenols on silica gel is due to an increased opportunity for hydrogen bonding; however, no further study was made of this interesting aspect.

The chromatograms obtained from the two phases packed into 9-cm columns looked pretty much alike in terms of efficiency. Fig. 6 shows runs with a typical test

TABLE I
RETENTION (CAPACITY FACTORS, k') OF VARIOUS SOLUTES ON SILICA AND CHROMIA SURFACES

Solute	k'	
	Plain LiChrosorb	Cr ₂ O ₃ /LiChrosorb
<i>Solvent: chloroform-hexane (1:4)</i>		
Cinnamaldehyde	1.6	2.6
Salicylaldehyde	0.43	0.86
<i>p</i> -Quinone	2.1	3.0
Furfural	2.3	3.0
<i>m</i> -Dinitrobenzene	1.4	1.8
<i>o</i> -Nitroaniline	2.9	3.0
Phenol	9.6	5.1
<i>p</i> -Cresol	9.0	5.1
<i>o</i> -Nitrophenol	0.29	0.43
<i>Solvent: hexane</i>		
Anthracene	0.28	0.45
Anisole	0.93	1.1
Naphthalene	0.21	0.28
Nitrobenzene	2.1	2.9

mixture. The HETP of the nitrobenzene peak on chromia is 28 μm ; this can be considered quite good on a nominal 10 μm support. Since the corresponding number for LiChrosorb is similar (in fact, a bit larger), we presume that the difference of these numbers from the theoretical plate height minimum simply reflects our packing tech-

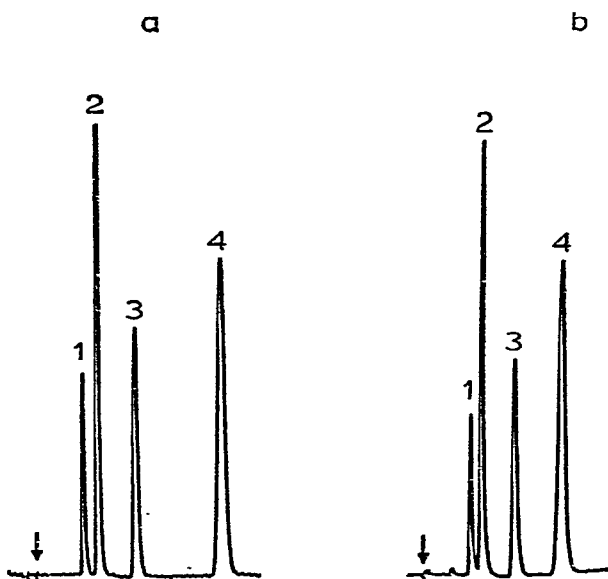


Fig. 6. Liquid chromatographies of a test mixture on 9-cm columns of LiChrosorb Si 100, 10 μm , bare (b) and with chromia layer (a). Mobile phase: hexane. Peaks: 1 = toluene; 2 = anthracene; 3 = anisole; 4 = nitrobenzene.

nique and the band broadening in our 10-year old liquid chromatograph, rather than some intrinsically detrimental influence of chromia.

One of the serious limitations of solid-liquid chromatography is the very small number of adsorbents available. If other metal oxide layers will perform as well as that of chromia—and we can see no reason why they should not—these would provide yet another tool for the liquid chromatographer to achieve his desired separations. Use of different metal oxides with the same mobile phase may also provide a convenient approach toward practical two-dimensional LC.

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