CHROM. 13,717

Note

Effects of hydrogen treatment on typical gas chromatographic supports*

PALITHA P. WICKRAMANAYAKE and WALTER A. AUE*

5637 Life Sciences Building, Dalhousie University, Halifax, Nova Scotia B3H 4J1 (Canada)

(Received February 9th, 1981)

Iron found on the surface of gas chromatographic (GC) supports is considered detrimental[1]; hence the higher price one pays for acid-washed (AW) materials. Iron is not the only deleterious element (aluminium is another major one[1,2]) but, because of the color of its compounds, it is the most obvious. One may formally ascribe the negative effects of any contaminating metal to two factors: The general inhomogeneity of the surface it produces, and the specific interactions it undergoes with the solute and/or the liquid phase.

In contrast to iron contamination of a silicic surface, pure iron oxide —whether in supported[2] or unsupported[3,4] form— is not a bad separation medium; especially when it is covered by a polar liquid phase[5,6]. "Reduced" iron is even better[2].

Why this should be so is not immediately clear. But it has been established that a reduced iron layer of several ångstroms thickness, carrying a bonded layer derived from Carbowax 20M, yields gas chromatograms of the same quality as a similarly covered pure silica surface would have done[2].

If iron oxides present on the surface of typical diatomaceous supports are indeed to blame for inferior chromatographic performance, and if a layer of "reduced" iron behaves indeed better in chromatography than the iron oxide layer from which it originated, then it may be possible to improve regular supports by changing the iron (and perhaps other elements) on the surface from an "oxide" to a "reduced" state. In this case the surface would still be heterogeneous in an elemental sense, but some highly active surface sites might then have lost some of that activity and become more similar, chromatographically speaking, to other adsorption centers.

Perhaps the easiest and most often pursued path in reducing surfaces is to expose them to hydrogen at elevated temperature. This approach is common to a variety of disciplines. In chromatography, however, it is relatively rare: The best known example here is the treatment of graphitized carbon to render it non-polar[7]. In some of our studies, we attempted to reduce bonded ferric oxide and did observe the expected color change from brick-red to grey[2]. Now, if one treats typical GC supports such as Chromosorb W (W for white) and Chromosorb P (P for pink) with hydrogen at 700°C, both also turn grey. If these grey materials are oxidized, *e.g.* by

---

* Taken from thesis research of P.P.W.

exposure to air at 700°C, both take on again their former white and pink appearances.

Though photoelectron spectra (of plain and reduced iron oxide layers) were equivocal on the question, it would be reasonable to presume that the observed color change from pink to grey reflected a change in the valence state of iron. In addition, changes may have occurred that were not immediately visible. Since hydrogen treatments are cheap and easy to perform, it may be worthwhile to use them routinely on conventional GC supports, provided one could demonstrate some beneficial effects.

Just of what kind such potential effects may be, is open to speculation. For instance: Oxidizing —but not reducing— conditions are generally avoided in GC. Often an analyst fights ppm levels of oxygen in his gas supply while, on other occasions, he employs pure hydrogen as carrier. It is not unusual to hear the premature degradation of both stationary liquid phases and GC solutes being attributed to the unwanted presence of an oxidizing agent. By using a "reduced" support, one could perhaps counteract such deterioration in chromatographic performance.

Other speculative effects concern the solid surface: It is often blamed for tailing and "irreversible adsorption" of solutes. Reducing it could change its adsorptive and catalytic properties. It may also alter the solid–liquid interface region by re-arranging the orientation of liquid phase molecules in respect to the surface.

A final bit of speculation deals with "bonded" phases: Any attempt at bonding a liquid phase depends critically, and in ways not well understood, on the chemical state of the surface. The better these reactions function the better "deactivated" is the surface and the more satisfying will be its chromatographic performance.

Speculations aside now, it is this "chromatographic performance" that decides whether or not there is an advantage in the hydrogen treatment of supports. To show any potential effect as clearly as possible, we started out with *non*-acid-washed (NAW) materials. These were used (as received) for the synthesis of thin, bonded layers based on Carbowax 20M (ref. 8), as well as for the preparation of conventional gas–liquid chromatographic (GLC) packings from the popular liquid phases Apiezon L, OV-17 and Carbowax 20M. We wanted to compare hydrogen-treated with non-treated materials in two respects: Whether bonded phases showed any differences in chromatography, and whether regular GLC phases showed any change in bleed rates.

EXPERIMENTAL

Chromosorbs W and P, NAW, 45–60 and 60–80 mesh, respectively, were filled into a cylindrical quartz reservoir and, after flushing with nitrogen, were heated for 4 h at 700°C in a tubular furnace, while a *ca.* 10 ml/min hydrogen stream passed through. Hydrogen was shut off only when the supports had again reached room temperature.

The "bonding" with Carbowax 20M was carried out in boiling hexadecane[8], and non-bonded material was removed by extracting for 10 h with methanol at boiling point temperature in a continuous extractor[9].

Regular GLC phases were prepared in 5% load by conventional rotary evaporation. All materials were packed into 100 × 0.2 cm I.D. borosilicate glass U-tubes and tested with mixtures of *n*-alkanes and *n*-alkanols in an 8°C/min temperature

program. "Bleed" was evaluated —after conditioning the columns at 220°C for 48 h—by measuring the rise in the baseline reflecting a 40 to 220°C, 8°C/min temperature program followed by an isothermal hold at the upper temperature (until the baseline current had become constant).

Elemental analysis of bonded phases was done by Guelph Chemical Labs., Guelph, Canada.

RESULTS AND DISCUSSION

Table I lists the carbon content of bonded phases and the relative bleed rate of regular phases. Elemental analysis shows the amount of bonded material to be higher on hydrogen-treated than on untreated supports: Slightly so on Chromosorb W, decidedly so on Chromosorb P.

TABLE I

CARBON CONTENT OF BONDED PHASES AND BLEED RATE OF REGULAR PHASES

Chromosorb	Bonded phase: % C	Regular phase: bleed*		
		Apiezon L	Carbowax 20M	OV-17
W, NAW, untreated	0.18	100	100	100
hydrogen-treated	0.23	77	38	77
P, NAW, untreated	0.22	100	100	100
hydrogen-treated	0.76	42	44	88

* At 220°C, relative (untreated = 100).

The chromatograms of alkanols demonstrate that the bonded phases based on hydrogen-treated supports are better "deactivated"; i.e. they give rise to larger, sharper, and more symmetrical peaks. Part of this effect on Chromosorb P is caused, no doubt, by the higher organic load. But it is also obvious, at least in the case of Chromosorb W where loads are comparable, that the hydrogen treatment itself had done some good. Fig. 1 shows some typical chromatograms. (It must be noted, however, that the chromatographic performance shown here is still not as good as that obtainable from a scrupulously cleaned Chromosorb W (ref. 8) or P (ref. 10) taken through the same reaction with Carbowax 20M.)

Chromatographic performance was also routinely checked on the regular GLC phases but, as expected, their comparatively heavy liquid loads prevented any significant differences from showing up. Rather, the noteworthy aspect of regular phases is their bleed rate. The data of Table I show that hydrogen treatment of the support reduces the bleed rate of each of the three representative liquid phases coated on it.

Interestingly enough, reduction in bleed appears to correlate roughly with the phases' susceptibility to oxidation. (Carbowax 20M consists of two polyethyleneglycol chains linked by a diepoxide; Apiezon L can be characterized as a molecular distillate of hydrocarbons with some unsaturation present; and OV-17 is a linear methylphenylpolysiloxane.)

It would be interesting to know how long the reduction in bleed lasts through conventional chromatographic usage and, should the effect vanish after some time,
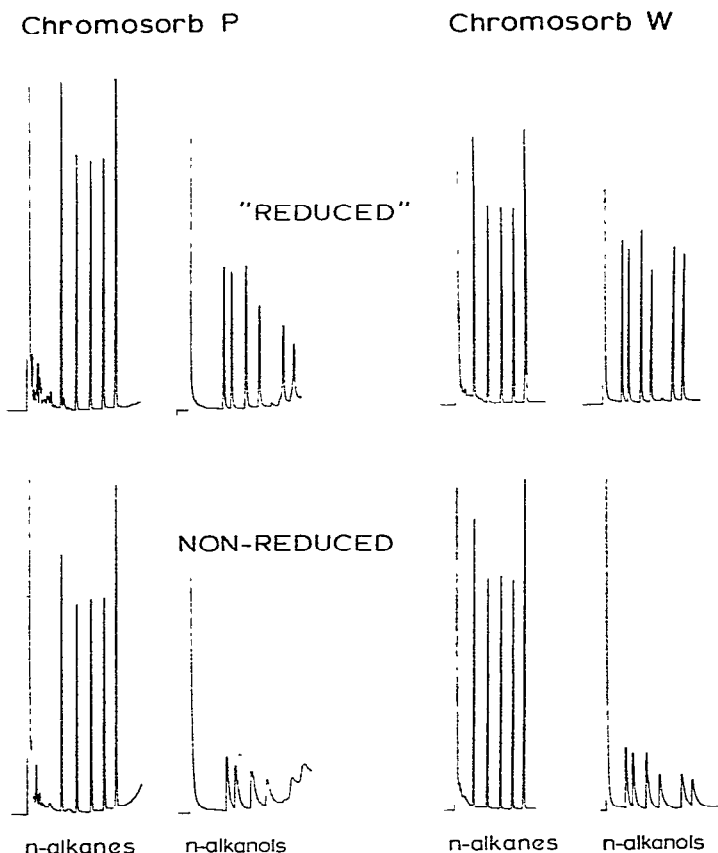
Chromosorb P   Chromosorb W

Fig. 1. Temperature-programmed chromatography of *n*-alkanes (C$_{12}$, C$_{14}$, C$_{16}$, C$_{18}$, C$_{20}$) and *n*-alkanols (C$_7$, C$_8$, C$_{10}$, C$_{12}$, C$_{16}$, C$_{18}$) on bonded phases from Carbowax 20M, on hydrogen-treated and non-hydrogen-treated Chromosorbs P and W.

whether it can be prolonged by, say, doping the carrier gas with minute amounts of hydrogen. It would also be interesting to see if phases of the hydrogen-treated variety behaved differently toward easily decomposed solutes; or if hydrogen treatment also brings about changes in those highly cleaned diatomaceous supports that have little iron left on their surface. Such studies could prove lengthy, however, and that puts them beyond our present designs.

REFERENCES

1 D. M. Ottenstein, *J. Gas Chromatogr.*, 1 (1963) 11.
2 W. A. Aue, M. M. Daniewski and E. E. Pickett, *J. Chromatogr.*, 189 (1980) 13.

3 Kilarska and Zielinski, *Chem. Anal. (Warsaw)*, 10 (1965) 403; as cited by G. E. Baiulescu and V. A. Ilie, *Stationary Phases in Gas Chromatography*, Pergamon, Oxford, Toronto, 1975, p. 270.
4 W. R. Moore and H. W. Ward, *J. Phys. Chem.*, 64 (1960) 832.
5 A. Betti, G. Lodi, C. Bighi and F. Dondi, *J. Chromatogr.*, 106 (1975) 291.
6 Cs. Horváth, *Inaugural Dissertation*, J. W. Goethe University, Frankfurt/M., 1963, as cited by L. S. Ettre and J. E. Purcell, *Advan. Chromatogr.*, 10 (1974) 35.
7 F. Bruner, G. Bertoni and P. Ciccioli, *J. Chromatogr.*, 120 (1976) 307.
8 M. M. Daniewski and W. A. Aue, *J. Chromatogr.*, 147 (1978) 119.
9 W. A. Aue, M. M. Daniewski, J. Müller and J. P. Laba, *Anal. Chem.*, 49 (1977) 1465.
10 M. M. Daniewski and W. A. Aue, *J. Chromatogr.*, 150 (1978) 506.