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Note

The modification of a firebrick-type support for the gas chromatography of polar molecules

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The overwhelming majority of gas chromatographic (GC) analyses is conducted today on diatomaceous earth supports of the "white" variety, *e.g.*, Chromosorbs W or G. These flux-calcined materials have a lower surface area (1 and 0.5 m^2/g, nominally) than supports of the "pink" variety, *e.g.*, Chromosorb P (3–4 m^2/g). Their surfaces, moreover, show much less interaction with polar solute molecules and the undesirable but not uncommon effects of tailing, irreversible adsorption, catalyzed rearrangement, *etc.*, are consequently suppressed. The firebrick-type supports like Chromosorb P (they truly were ground firebrick in the past, but are nowadays based on diatomaceous earth) are much less "deactivated", though potentially capable of higher GC efficiency. The prevalent view of their characteristics is perhaps best expressed in a recent review by McNair, who states about Chromosorb P that "because its surface is more adsorptive than that of other Chromosorb grades, it is used primarily for hydrocarbon fractionation. It produces the greatest column efficiencies, but cannot be used with polar samples"[1].

The pink color of firebrick is presumably due to oxides of iron, but compounds of other metals are present as well. When Chromosorb P is acid-washed commercially, some of the iron, aluminum, calcium, etc. is removed from its surface[2]. The support becomes noticeably less "active", although the overall reduction in metal content is minor. This "Chromosorb P AW" is, in fact, still pink although its albedo has somewhat increased.

In a recent study we managed to remove some 98% of the iron contained in Chromosorb P as well as less dramatic percentages of other materials[3]. Apparently, most of the iron had been present in a surface layer. Marine sediments, *e.g.* clays, are difficult to remove from diatom skeletons and we assume (although we are unaware of the particulars of producing Chromosorb P) that the iron-containing sediment layer is simply glazed onto the relatively pure diatomaceous silica during calcination in the commercial production of the support. It was this pink layer that we had apparently removed in our clean-up, resulting in a gleaming white material. At that point, one could be tempted to assume that some of the less desirable properties of Chromosorb P had been removed as well.

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Thus it became interesting for us to coat this material with a thin, non-extractable polymer layer[4] as well as a regular 10% load, and to test its performance as a GC support with polar solutes.

EXPERIMENTAL

Chromosorb P NAW, 80–100 mesh, was purified as described[3]. This purification included a preliminary wash with 6 *M* hydrochloric acid in a Soxhlet apparatus, the main clean-up with hydrogen chloride gas at *ca.* 850°, and subsequent washes with 6 *M* hydrochloric acid and distilled water. Since Carbowax 20M was to be used as the coating polymer, the purified Chromosorb P was further washed with a dilute potassium hydroxide solution and with distilled water to neutrality, followed by drying in vacuum at 110°. To produce the bonded layer, this material was coated with Carbowax 20M in refluxing hexadecane[5] (this is a faster variant of the original coating method described in ref. 4). The hexadecane was decanted and the material leached for three days with methanol near boiling point temperature in a highly efficient continuous extraction apparatus. To produce the 10% phase, common rotary evaporation was used.

The resulting phases were filled into short, 1 m × 3 mm I.D. borosilicate glass columns and tested in a Shimadzu 4B gas chromatograph with suitable mixtures of varying polarity and propensity for peak tailing and solute rearrangement.

RESULTS AND DISCUSSION

Fig. 1 shows temperature-programmed chromatographies of *n*-alkanes and *n*-alkanols. The phases are efficient but comparison of hydrocarbon and alkanol peaks reveals tailing of the latter. However, the extent of tailing can be considered minor.

Fig. 2 shows a temperature-programmed separation of leaf oil from *Abies sibirica*. The pattern strongly suggests the virtual absence of catalyzed rearrangements[6] that have been known to plague the GC of terpenes[7]. This is remarkable since the deactivating layer of Carbowax 20M is extremely thin. It is also noteworthy that no signs of overload occur with a 0.5-μl injection of pure sample (bottom chromatograms).

Fig. 3 shows a chromatography of fatty acid methyl esters. As evident from the trio of C-18 acids, the "polarity" of the bonded layer as compared with that of the regular GC phase is decreased as expected[8].

From these all too few examples, it would appear that the phase under test is indeed capable of serving in the GC separation of polar compounds with a minimum of adverse side effects. This might not have been expected in view of the notorious behaviour of pink supports. Although it is still somewhat more prone to produce tailing peaks than a similarly treated Chromosorb W, a cleaned and deactivated Chromosorb P may be a good choice for several types of analysis. It should also be possible to use this material as a GC support for carrying heavier loads of other polymers[9].

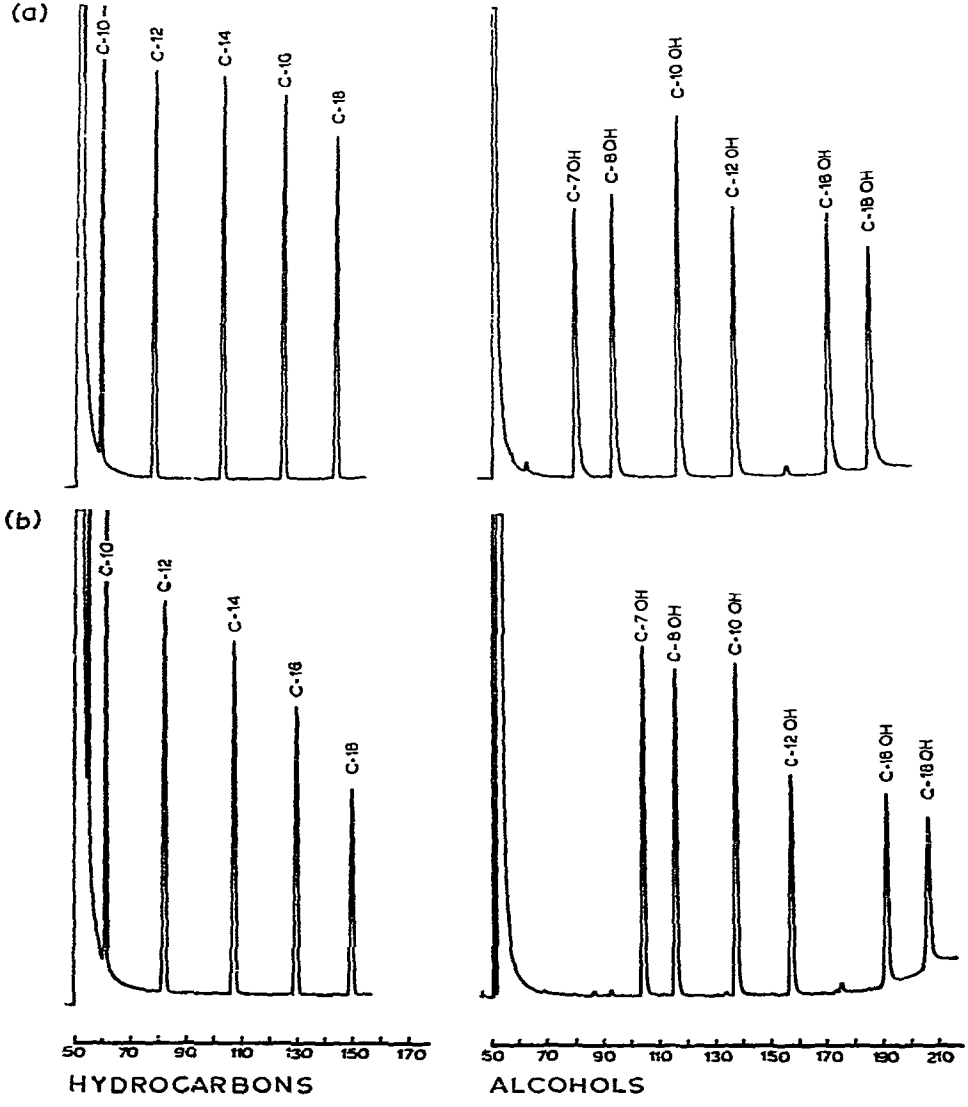

Fig. 1. Temperature-programmed gas chromatographies of *n*-alkanes and *n*-alkanols as listed by carbon number on (a) Chromosorb P modified by a non-extractable layer of Carbowax 20M and (b) purified Chromosorb P coated with 10% Carbowax 20M.

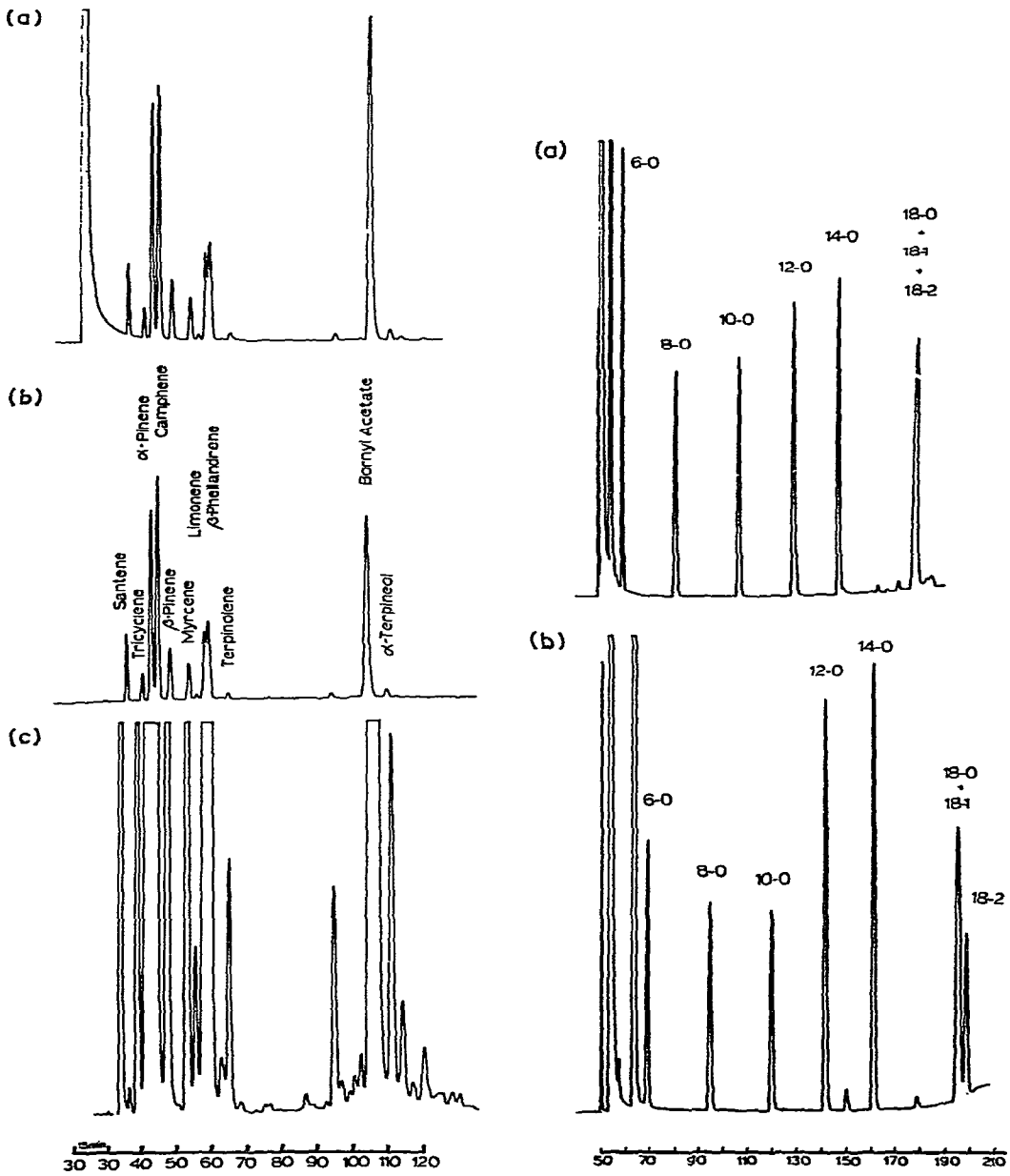

Fig. 2. Temperature-programmed gas chromatographies of neat and diluted *Abies Sibirica* leaf oil on purified Chromosorb P modified by a non-extractable layer of Carbowax 20M. (a) 1:100 diluted oil; attenuation, $4 \cdot 10^3$. (b) Neat oil; attenuation, $128 \cdot 10^3$. (c) Neat oil; attenuation, $4 \cdot 10^3$.

Fig. 3. Temperature-programmed gas chromatographies of fatty acid methyl esters on (a) Chromosorb P modified by a non-extractable layer of Carbowax 20M and (b) regular phase of 10% Carbowax 20M on purified Chromosorb P.

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