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Note

Novel, polymer-deactivated adsorbents as supports in gas–liquid chromatography

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We have recently described the production and properties of non-extractable, ultrathin layers of Carbowax 20M on gas chromatographic (GC) supports. These GC phases allow extremely fast, efficient separations. Furthermore, they perform unexpectedly well in the chromatography of polar and/or relatively unstable organics: The support has apparently been well "deactivated"[1].

This aspect of deactivation —in addition to the bonded nature of the Carbowax film— made such materials good candidates for a role as GC supports, carrying the conventionally much heavier loads of desired liquid phases. There exist many analytical problems where the deactivation inferred by the polymer film would be desirable, while its separation pattern, or speed, would interfere with analytical objectives.

Thus, we decided to coat Carbowax-modified Celite with conventional loads of common liquid phases, and to test the resulting materials for chromatographic utility. Two questions were apparent: Would deactivation be preserved? and: Would the separation pattern resemble that of the Carbowax layer or that of the chosen liquid phase? Answers to both were, of course, fairly easy to predict.

Since the Carbowax layer has been shown resistant to continuous extraction with methanol and other solvents, coating it with another polymer was unlikely to cause its demise.

And it seemed equally unlikely that it would significantly influence the retention pattern: Most polar compounds elute from the Carbowax layer much faster than they do from regular liquid phases, indicating that their interaction with the bulk polymer rather than with an ultrathin film would dominate. Experimental proof, however, was lacking.

EXPERIMENTAL

A batch of Celite 545 was acid-washed as described earlier[1], dedusted, and portioned into halves. One half was modified by Carbowax 20M[1] and the other half was used bare.

These supports were covered with 1%, 3% and 10% loads of Apiezon L (Applied Science Labs., State College, Pa., U.S.A.) and OV-210 (Analabs, North Haven, Conn., U.S.A.) by the conventional rotary evaporation technique. The 3% OV-101 (Analabs) packings were similarly prepared.

To test for deactivation, phases were paired (*e.g.* 3% Apiezon L on bare Celite was paired with 3% Apiezon L on modified Celite), packed into 180 cm by 4 mm I.D. glass U-tube columns, and run side-by-side in a Mikrotek 220 gas chromatograph. The instrument was equipped with a high-temperature switching valve (Valco, Houston, Texas, U.S.A.), which allowed the effluent of either column to be routed to the ^{63}Ni electron capture detector (ECD).

After conditioning overnight, the same small amounts of chlorinated hydrocarbon mixtures were injected onto both columns for testing. If no response was obtained on the non-modified columns, larger solute amounts were used for doping both columns, and smaller amounts were again injected for testing.

The 1%, 3% and 10% loads of Apiezon L and OV-210 were thus evaluated. For a definition of elution patterns, only the 3% loads of Apiezon L, OV-210, and OV-101 were used.

These were packed into 1.5 m × 2 mm I.D. glass U-tube columns and tested singly in a Bendix Model 2500 gas chromatograph equipped with a ^{63}Ni ECD. Doping was used as necessary and the oven temperature was adjusted to yield approximately the same retention time for lindane, at a constant nitrogen carrier gas flow-rate of 20 ml/min.

RESULTS

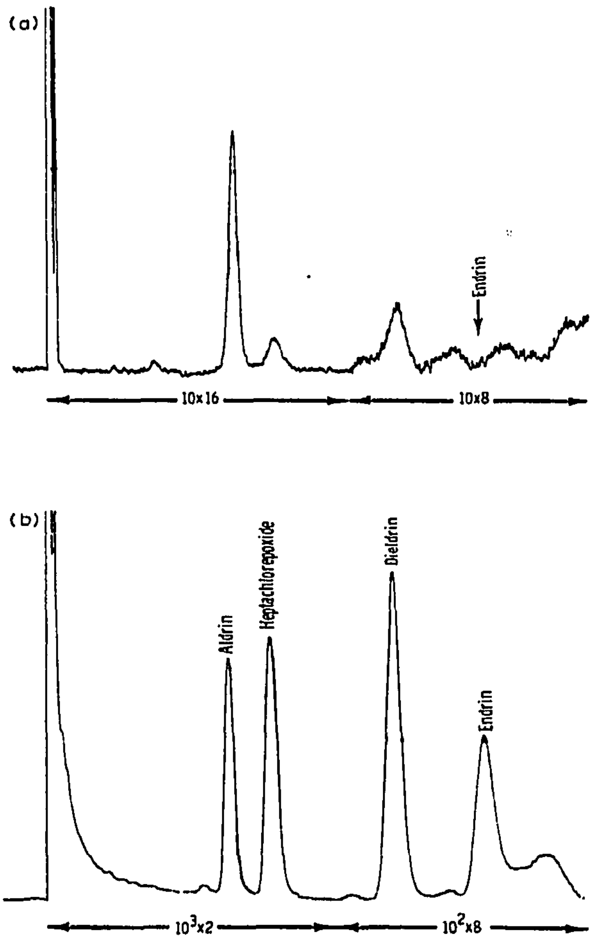
As expected, the attributes of deactivation remained with the support through the coating with the two bulk liquid phases. Similarly to be expected, the differences between the two members of a pair, *i.e.* the difference between bare and modified supports, became less pronounced as load and/or polarity of the liquid phases increased.

Fig. 1 shows a typical pair, 3% Apiezon L on bare and modified Celite, after several injections of insecticides. The first injection brought no response at all from the former phase, but acceptable chromatography from the latter. Even after several injections, a much lower attenuation had to be used to show any insecticides surviving the contact with the Celite surface. Under these conditions (and within the confines of the experiment, involving only three liquid phases and one type of test compounds), the desired deactivation effect could be clearly observed on 1%, 3% and 10% Apiezon L and OV-210.

The presence of these confines, imposed by the scarcity of test situations, should be even stronger emphasized in the question of separation patterns. Table I shows that elution data, as expected, pinpoint the bulk liquid phase rather than the Carbowax film as the location where solute retention primarily takes place: The much more abundant liquid phase determines the separation pattern.

This is visually re-emphasized in Fig. 2, where the chromatography of insecticides on the modified support —at a significantly lower temperature— appears clearly different from the two, almost identical chromatograms obtained on 3% Apiezon L phases.

Thus, the presence of an ultrathin, non-extractable film of Carbowax 20M on



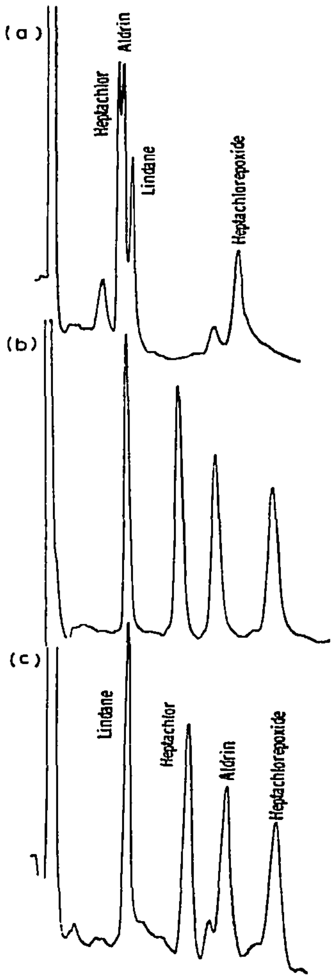


Fig. 1. Decomposition of chlorinated hydrocarbons on comparably treated and doped phases: (a) 3% Apiezon L on bare Celite and (b) 3% Apiezon L on modified Celite. The columns were conditioned overnight at 210°, followed by one injection of 5 μl test mixture. The test mixture contained 100 pg/μl each of aldrin, heptachlorepoxide, and dieldrin, 200 pg/μl of endrin, and 300 pg/μl of *p,p'*-DDT. Mikrotek 220 gas chromatograph; 6 ft. × 4 mm I.D. Pyrex U-tube columns at 210°; ^{63}Ni ECD; nitrogen flow-rate, approx. 80 ml/min.

Fig. 2. Comparison of the separation patterns of chlorinated hydrocarbons using (a) Carbowax 20 M-modified Celite, 143°, (b) 3% OV-101 on Carbowax 20 M-modified Celite, 186°, and (c) 3% OV-101 on bare Celite, 187°. Amounts injected were 30–60 pg each of the compounds. Bendix Model 2500 gas chromatograph; 5 ft. × 2 mm I.D. Pyrex U-tube columns at the temperatures indicated above; ^{63}Ni ECD; nitrogen flow-rate, 20 ml/min.

a support used in typical gas–liquid chromatography (GLC) exerts a strong effect on the state of deactivation, but does not significantly influence the separation pattern prescribed by the liquid phase.

TABLE I

RETENTION OF CHLORINATED HYDROCARBONS ON VARIOUS GC PHASES

Retention in cm recorder chart at 30 in./h.

Column	*Oven (°C)*	*Retention*			
		Lindane	*Heptachlor*	*Aldrin*	*Heptachlorepoxide*
Modified Celite	143	2.5	2.1	2.3	5.8
3% Apiezon L–modified Celite	224	2.5	3.3	4.3	5.3
3% Apiezon L–bare Celite	220	2.5	3.3	4.5	5.6
3% OV-101–modified Celite	186	2.4	4.0	5.1	6.8
3% OV-101–bare Celite	187	2.5	4.2	5.4	6.8
3% OV-210–modified Celite	170	2.5	2.5	2.9	6.3
3% OV-210–bare Celite	167	2.4	2.4	2.8	6.7

DISCUSSION

The conclusion above is certainly valid for some, but definitely not valid for all chromatographic conditions. We had obviously chosen experimental parameters so as to sustain or deny our assumptions in a demonstrable manner. Ample precedent for these assumptions existed: It is a long-known and widespread practice in GLC to add small amounts of polar compounds to relatively unpolar liquid phases in order to suppress undesirable support effects.

Clearly, then, it depends on the relative amounts of deactivator and liquid phase, and on their polarities or respective interactions with the solute, which one will determine separation patterns. Under typical conditions, it will be the liquid phase.

Carbowax 20M is not the only type of polymer which we have used for producing modified supports[2]. However, the other phases —involving hydrocarbons, silicones, and polyesters— have never been tested as supports for regular liquid loads as in the context of this note. One could expect that the degree of deactivation would increase with the polarity of the polymer film and possibly also that certain films may be incompatible with certain liquid phases, *e.g.* that the bulk liquid phase would coalesce rather than form a layer of uniform thickness. However, certain combinations could be of practical value.

One could argue that it may be more practical to produce supports modified by a (in terms of separation) desirable polymer, rather than to use this polymer as liquid phase on a support modified by another substance. However, not all polymers are equally suited for producing modified supports and, while the very short retention times obtained on the latter may be desirable for high boilers, low boilers may be short-changed.

If the few experiments described in this note should be indicative of a wider range of chromatographic conditions —as we believe they might well be— such modified materials could prove valuable as supports in GLC.

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