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GAS CHROMATOGRAPHY ON MODIFIED SUPPORTS

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SUMMARY

Four gas chromatographic phases —consisting of ultrathin, non-extractable polymer layers on diatomaceous earth supports— were tested with a variety of gas chromatographic problem mixtures. The phases proved to be well deactivated and capable of some interesting isomer separations.

INTRODUCTION

We have recently described the syntheses of a number of modified supports, *i.e.* diatomaceous earth particles that carry non-extractable layers of polymers ranging in polarity from polyethylene to polydiethylene glycol succinate[1]. These modified supports were corollaries to a similar material based on Carbowax 20M, which proved to be a well-deactivated, fast and efficient phase in gas chromatography. The typical Carbowax load was between 0.1 and 0.2% (ref. 2).

In many cases, this extremely thin film allows fast and efficient chromatography of polar compounds. Although the support appears well deactivated, surface forces can be assumed to contribute significantly to retention. In this regard, modified supports resemble the stationary phases of gas–solid chromatography (GSC) which are particularly effective for isomer separations.

On the other hand, these modified supports resemble stationary phases used in gas–liquid chromatography (GLC) in their degree of deactivation and the visual appearance of their chromatograms. Retention times or temperatures can be quite a bit lower for polar compounds than those of either typical GSC or GLC; a feature which adds to the deactivation aspect in facilitating the chromatography of labile solutes.

Various chromatographies at trace levels corroborated these two significant characteristics for the modified support based on Carbowax 20M. The chromatogra-

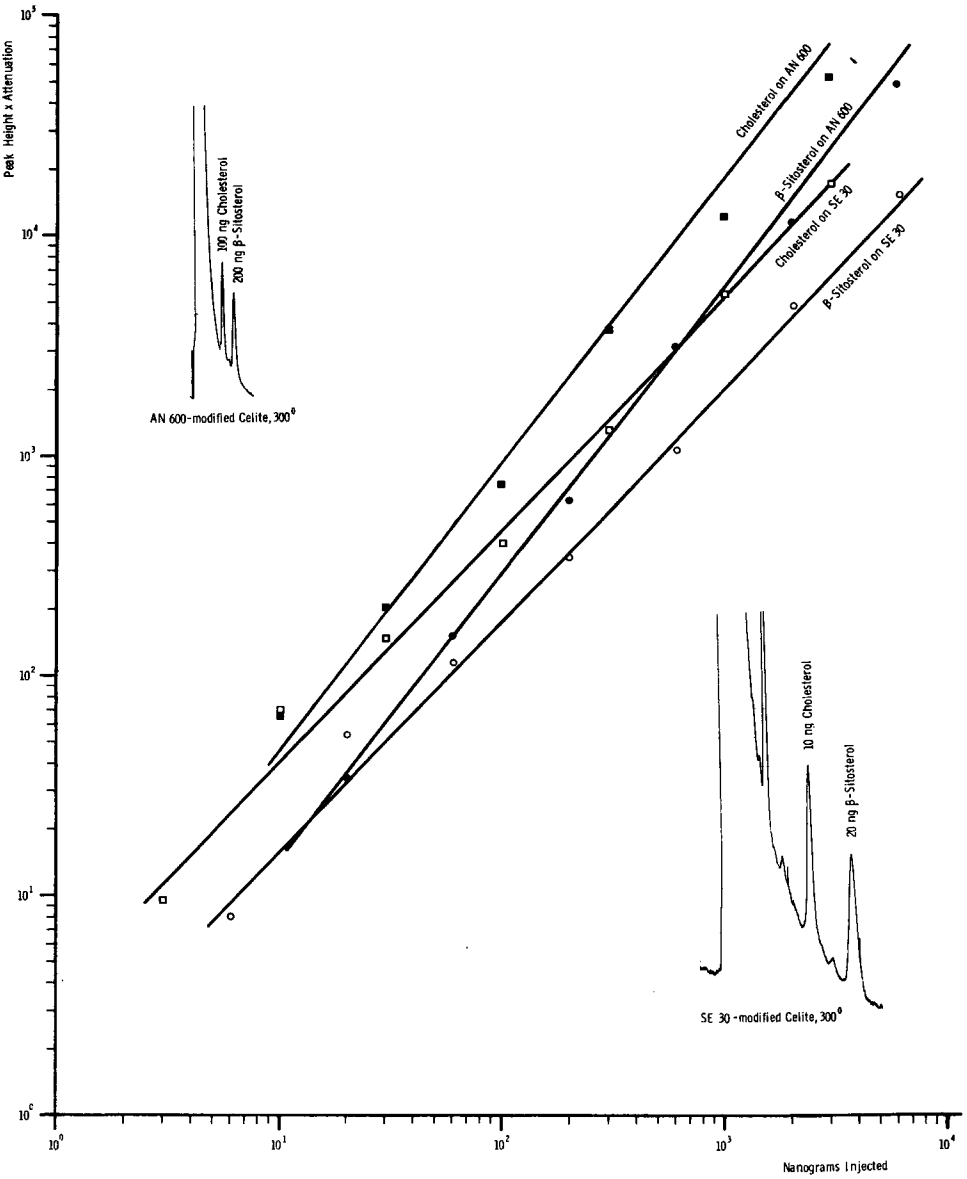

Fig. 1. Calibration curve and gas chromatography of sterols on phases[1] obtained by heat treatment of 6% AN-600 at 350° and 6% SE-30 at 400°, both on 100–120 mesh, acid-washed Celite 545, followed by exhaustive extraction with chloroform; in a 5 ft. × 2 mm I.D. Pyrex glass tube at 300°. Nitrogen flow-rate, 50 ml/min; Bendix 2500; FID.

phies included separations of benefin and trifluralin, of the *n*-butyl esters of citric and nitrilotriacetic acids, of the N-trifluoroacetyl *n*-butyl esters of protein amino acids, of the *n*-butyl esters of various metabolic hydroxy acids, and of chlorinated hydrocarbon insecticides and pollutants. The comparatively low bleed proved an added advantage.

This paper combines three rather disparate examples of chromatography on

different polymer layers, chosen to demonstrate two characteristic capabilities of the modified supports: (a) isomer separation and (b) chromatography of labile compounds. The layers were a linear polyethylene glycol (linear Carbowax 20M), a linear polyethylene (NBS standard), a dimethyl polysiloxane (SE-30), and a 2-cyanoethyl(methyl) polysiloxane (AN-600).

EXPERIMENTAL

The four modified supports were materials produced during an earlier study[1]. They were packed into U-tube, borosilicate glass columns, 1.5 to 1.8 m long with an inner diameter of 2 mm; and used in either a Bendix Model 2500 or a Microtek Model 220 gas chromatograph. The test mixtures contained compounds of current interest, whose conditions of chromatography are noted in the respective figures.

RESULTS AND DISCUSSION

Fig. 1 shows the isothermal chromatography of two sterols on two silicones. Although some decomposition is apparent on AN-600 (the calibration curve deviates from a 45° line), the low nanogram ranges are reached. Chromatographies of free

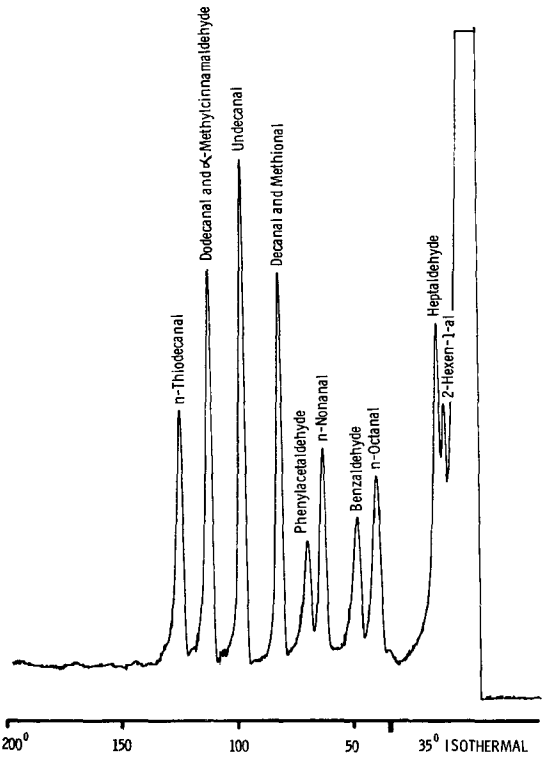

Fig. 2. Separation of free aldehydes, about 45 ng each, on a phase[1] obtained by heat treatment at 270° of 6% "linear Carbowax 20M" on 100–120 mesh, acid-washed Chromosorb W, followed by exhaustive extraction with methanol; in a 6 ft. × 2 mm I.D. Pyrex U-tube. Nitrogen flow-rate, 11 cm/sec; Microtek 220; FID.

sterols can, of course, be achieved on regular GLC phases —although most analysts prefer to derivatize the hydroxyl groups— but it is surprising that such minute amounts would elute at all from a modified support.

Fig. 2 shows the temperature-programmed chromatography of a number of aldehydes. Aldehydes are of importance in quite a number of fields from air pollution to food flavors, and the fact that this particular separation was obtained on an ultra-thin film of Carbowax 20M at low solute concentrations makes it noteworthy. In this case, the relative speed of analysis on modified supports becomes a disadvantage, because the lower aldehydes elute too fast to be separated at ambient temperature.

While Figs. 1 and 2 demonstrate the relative inertness of the modified supports, Fig. 3 illustrates their capability for isomer separations. Polynuclear aromatics, especially in environmental samples, present a challenge to the analyst; and gas chromatography has been repeatedly employed to separate, to some degree, these complex mixtures. The separations shown in Fig. 3 —*e.g.* anthracene–phenanthrene or chrysene–benzanthracene— are of interest because they were achieved on a mere 5 ft. of column. In regular GLC, capillaries or long packed columns are generally necessary to obtain

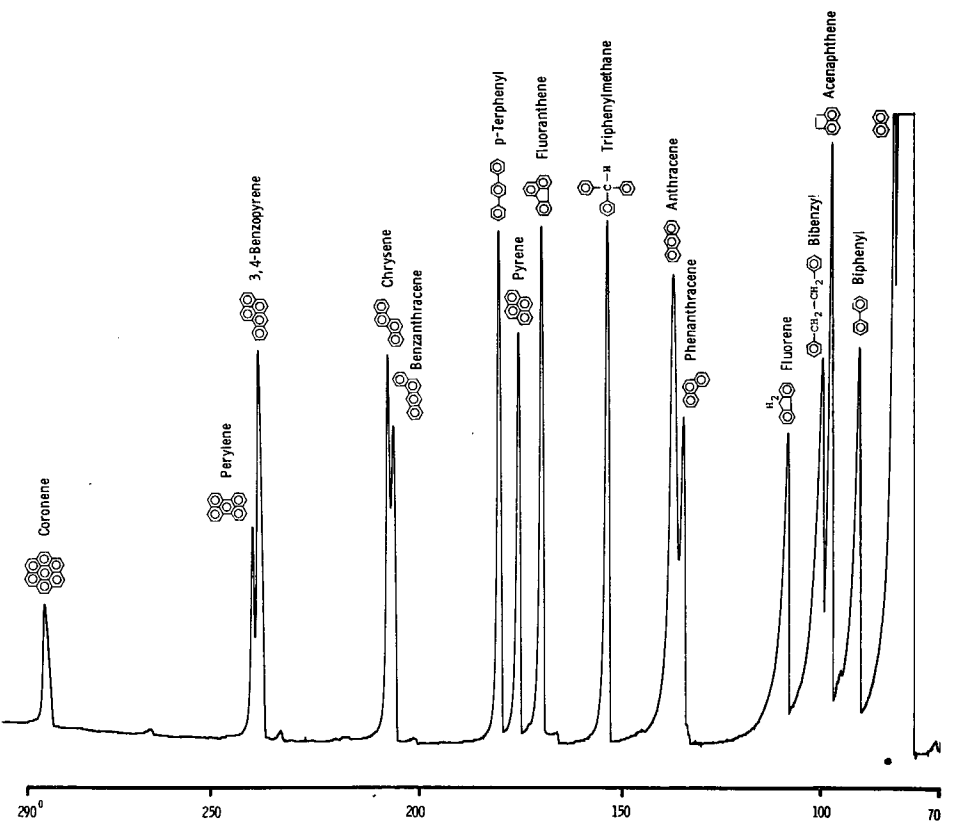

Fig. 3. Gas chromatography of polynuclear hydrocarbons, *ca.* 300 ng each. Column: Celite 545, acid-washed, 100–120 mesh, surface modified with linear polyethylene heated at 280°, followed by exhaustive extraction with toluene[1]; in a 5 ft. × 2 mm I.D. Pyrex U-tube. Nitrogen flow-rate, 9 cm/sec; Microtek 220; FID.

similar chromatograms; while GSC, which can give superior separations, is often avoided for other reasons (compare, for instance, refs. 3–6). Fig. 3 also demonstrates nicely the desirably low bleed from the film of linear polyethylene.

Judged from the rather desultorily selected chromatographies shown above, it appears that well-chosen modified supports —*i.e.* particular combinations of support surfaces and bonded polymers designed for a particular separation— may find applications in various analytical problems of current interest. These problems would most likely involve the separation of higher-boiling, closely related substances and/or the separation of polar, chromatographically labile compounds.

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