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Note

Deactivation of glass open-tubular columns with PEG 20M via the gas phase

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Much progress has been made in the development of glass open-tubular columns, especially for apolar stationary phases. However, current methods of deactivation of the column wall are open to criticism, particularly for high-temperature analyses (above 200°) and trace analyses at the picogram level. As a workable alternative, we advocated the use of relatively thick films of the stationary phase, so as to mask rather than eliminate the activity of the column wall[1]. However, the separation times on these columns are quite long and the need for well-deactivated columns of high-phase ratio ($\geqslant 500$) is obvious.

Aue *et al.*[2] described the formation of an ultra-thin film of chemically bonded PEG 20M on diatomaceous earth supports, and in a subsequent paper[3] they showed that these surfaces were highly inert. Cronin[4] applied this method to glass open-tubular columns in order to achieve a compatible surface for subsequent coating with PEG 20M. Blomberg[5], Schomburg *et al.*[6] and Grob and Grob[7] used variants of the method primarily to effect a deactivation, rather than to obtain a retentive film of chemically bonded phase. In all of these variants the PEG 20M was applied as a solution in dichloromethane. However, in 1970 Ives and Giuffrida[8] showed that vapours of PEG 20M, bled from a short pre-column on to a ready-to-use column, were considerably more effective in reducing tailing than was treatment of the support with solutions of PEG 20M.

We have examined the procedure of Ives and Giuffrida for the deactivation of non-coated glass open-tubular columns.

EXPERIMENTAL

A glass tube (8 × 0.25 in O.D., 2 mm I.D.), packed over a length of 3 in. with 5% PEG 20M on Chromosorb W AW, was inserted in the hot zone of the injection port of a gas chromatograph. In the oven compartment the exit end of this pre-column tapered off to 1.2 mm to match the outer diameter of the Duran 50 glass capillary

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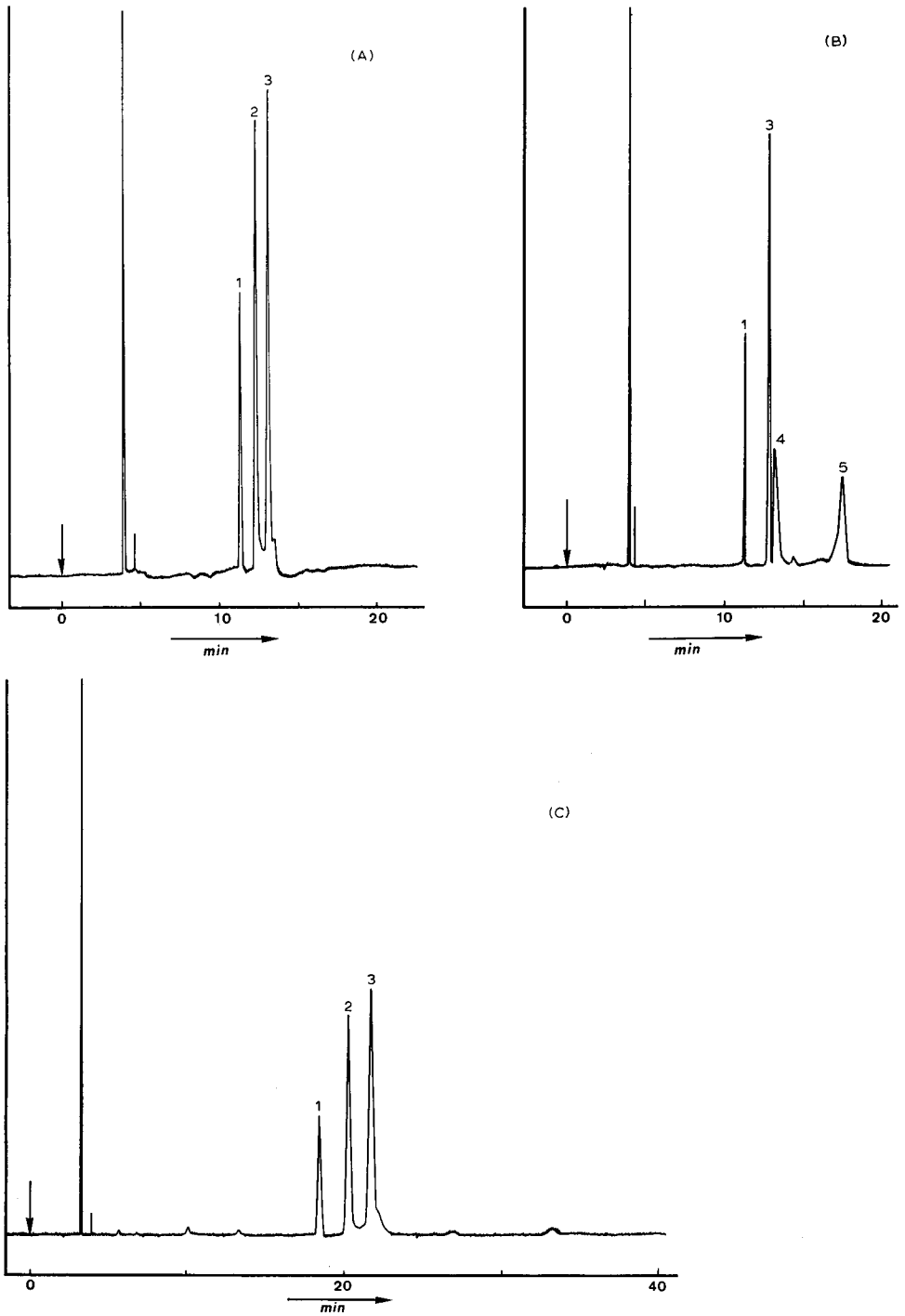

Fig. 1. (A) Test mixture (1 μl) on a thin film PEG 20M deactivated column coated with SE-30. Peaks: 1 = dieldrin; 2 = endrin; 3 = *p,p'*-DDD. (B) Test mixture (1 μl) on a thin film non-deactivated column coated with SE-30. Peaks: 1 = dieldrin; 3 = *p,p'*-DDD; 4 = endrin decomposition product 1; 5 = endrin decomposition product 2. (C) Test mixture (1 μl) on a thick-film non-deactivated SE-30 column. Peaks as in (A). For conditions and compositions of the test mixtures, see text.

column. The connection between the two columns was made with shrinkable PTFE tubing. The temperature of the pre-column was *ca.* 5–10° higher than that of the capillary column. The exact temperatures do not seem to be very critical and were *ca.* 250°. The PEG 20M was allowed to bleed through the capillary column overnight, at a nitrogen flow-rate of 1–3 ml/min. In order to test the deactivation of the resulting column wall, a deactivated Duran column (30 m × 0.4 mm) was coated with a film of 0.2 μm SE-30 (phase ratio 500) according to the static method of Bouche and Verzele[9]. For comparative purposes, a second similar column was prepared but without deactivation. SE-30 was chosen as the stationary liquid, because a thin layer of this apolar phase does not contribute substantially to the deactivation of the column wall[1], whereas a polar phase exerts a deactivating effect of its own.

Both columns were conditioned overnight at 235° and then kept at 220° for 4 weeks. An aliquot of 1 μl of a test mixture, containing 1.5 pg of dieldrin and 7.5 pg each of endrin and *p,p'*-DDD, was injected using a solids injection system[10]. The gas chromatograph was a Pye Series 104 Model 84, equipped with a 10-mCi ^{63}Ni electron capture detector (ECD). The oven temperature was 217°, and the detector was kept at 300°. Carrier gas, argon–methane (95:5); pre-pressure, 0.2 atm. Detector purge gas, argon–methane (95:5); flow-rate, 25 ml/min.

RESULTS AND DISCUSSION

Endrin is known to be very sensitive to the adsorptive and catalytic activity of the column wall. Fig. 1a shows the elution pattern of the test mixture on a PEG 20M deactivated column. Endrin is eluted between dieldrin and *p,p'*-DDD, as is the case on a thick film (phase ratio 190) non-deactivated SE-30 column (Fig. 1c). Hence, the elution sequence in Fig. 1a is not affected by the presence of the deactivating agent. As shown in Fig. 1b, endrin is not eluted from a thin film non-deactivated column. The compound decomposes to yield two products, which elute after *p,p'*-DDD and show reduced plate numbers. We presume that complete decomposition takes place in the first few meters of the column, since a gradual breakdown over the entire column length would give rise to an increased noise level, rather than to two distinct peaks.

The absence of decomposition products in the chromatograms a and c shows that the decomposition is indeed due to the column wall activity and not to decomposition in the injection system.

CONCLUSIONS

We have described a new simple method for deactivation of the column wall. The surfaces obtained even allowed the analysis of labile (*e.g.*, endrin) compounds at the picogram level. A more detailed study on the properties of the surfaces obtained will be published in a subsequent paper. A comparison will be made between the thermal stability of columns deactivated by the above method and by other methods involving PEG 20M. The compatibility of these surfaces with polar stationary phases will also be discussed. Preliminary results suggest that the gas-phase PEG 20M deactivation method will be generally applicable.

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