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Note

Preparation and use of surface-modified adsorbents in clean-up techniques for pesticide residue analysis

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One of the main problems in residue analysis is the clean-up of the first crude extract. The numerous other plant substances that are extracted simultaneously can, in many instances, mask the presence of pesticide residues. Even with more specific analytical techniques such as gas–liquid chromatography (GLC) with electron capture detection for organochlorine compounds, clean-up procedures are necessary in order to obtain reliable results. The nature of the co-extracted plant materials depends on the extraction solvent; in most instances this is a non-polar organic solvent, so the impurities are generally lipophilic.

Adsorption column chromatography and thin-layer chromatography are often used for the clean-up of such extracts. These techniques generally result in separations by compound type and give very good results when the contaminants and the pesticides differ considerably in their polarity. In most instances in residue analysis, however, these differences are minor, and hence overlapping of spots or peaks in the developed chromatograms occurs.

In order to overcome the above disadvantage, the procedure described by Abel *et al.*[1] and adopted by Stewart and Perry[2] was examined and modified. It was considered that, if the active adsorptive sites of a porous material are replaced with aliphatic chains of different lengths, the resolving properties of the material will differentiate between lipophilic compounds in the extract. It would be expected that the modified material will separate the different compounds in the extract not adsorptively, but according to their partition coefficient between the aliphatic chains attached to the surface of the porous particles (stationary phase) and the eluent (mobile phase).

EXPERIMENTAL

Materials

Aluminium oxide: Camag MFC (Hopkin & Williams, Chadwick Heath, Great Britain) was dried by heating for 11 h at 550°. Silica gel: For Chromatographic Adsorption (BDH, Poole, Great Britain) and MFC (Hopkin & Williams) were dried by heating for 11 h at 480°.

Preparation of modified adsorbents

The dry powders were poured into a solution of 11.7 g of octadecyltrichloro-

silane (Aldrich, Milwaukee, Wisc., U.S.A.) in about 500 ml of sodium-dried light petroleum (boiling range 60–80°). The suspension was shaken for 5 h and the light petroleum was then removed by filtration. The powder was dried and placed in a round-bottomed flask. The flask was fitted to a rotary evaporator (Fig. 1) modified so that hot air saturated with water vapour was continuously passed through the powder while the powder was agitated. Fumes of hydrochloric acid were evolved for at least 24 h. The air stream was stopped when no further hydrochloric acid was detected (wet litmus paper) in the exit stream of air.

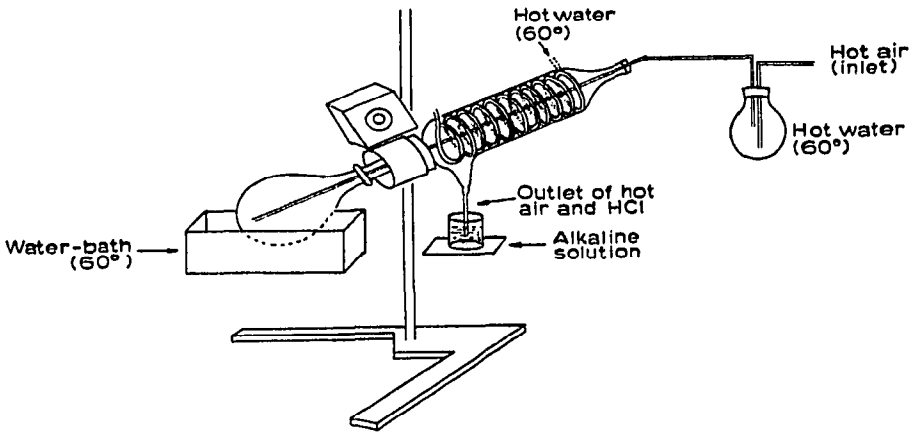

Fig. 1. Modified rotary evaporator used for the dehydrochlorination of the adsorptive material.

The resultant material was dried for 12 h at 60° and 0.1 mmHg. The powder, yellowish in colour, was washed successively with redistilled *n*-hexane, acetone and absolute ethanol and dried. The final fractions of each of the washing solvents were examined by GLC using both electron capture and flame ionization detectors. No peaks other than those due to the pure solvents were observed.

The same procedure was followed for the preparation of powders modified with dimethyldichlorosilane (11.8 g).

Use of modified adsorbents

A 2.5-g amount of the adsorbent was packed in a chromatographic column (15 cm × 0.5 cm I.D.). A 15-cm long extension was fitted on each column and the adsorbent washed with 20 ml of 5% acetone in *n*-hexane (one drop per second) followed by 20 ml of *n*-hexane. Then 2 ml of an *n*-hexane extract from tomatoes to which DDT, DDE and γ-BHC had been added were introduced into the column. The column was eluted with 10 ml of *n*-hexane, and the eluate was collected and concentrated to 1 ml on a water-bath (60°), employing a steam of dry air for evaporation. A 1-μl volume of the concentrate was examined by GLC.

RESULTS AND DISCUSSION

The results obtained from modified alumina or coarse silica gel columns were not very satisfactory. Those obtained from fine-grade silica gel (Hopkin & Williams) were much better.

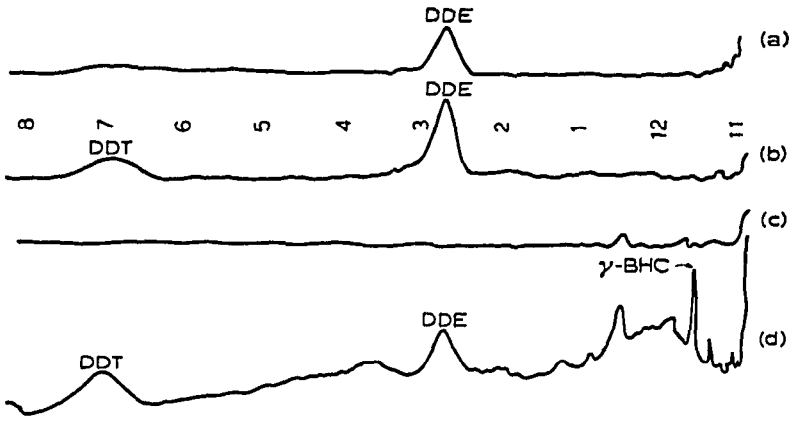

Fig. 2. Gas–liquid chromatograms obtained on the first 10 ml of *n*-hexane eluate from columns containing the modified adsorptive material. Traces: (a) silica gel modified with octadecyltrichlorosilane; (b) silica gel modified with dimethyldichlorosilane; (c) silica gel untreated; (d) *n*-hexane extract with no clean-up.

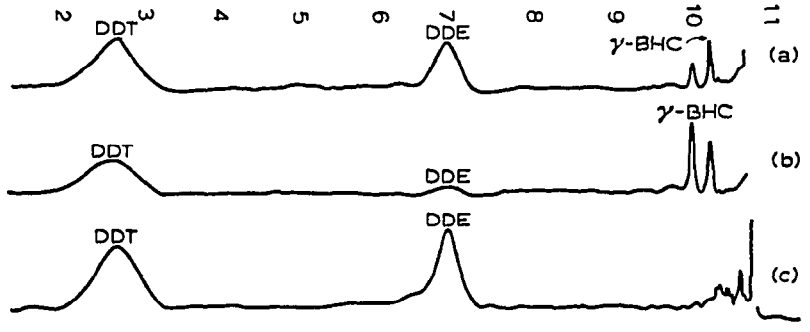

Fig. 3. Gas–liquid chromatograms obtained on the second 10 ml of *n*-hexane eluate from columns containing the modified adsorptive material. Traces: (a) silica gel modified with octadecyltrichlorosilane; (b) silica gel modified with dimethyldichlorosilane; (c) silica gel untreated.

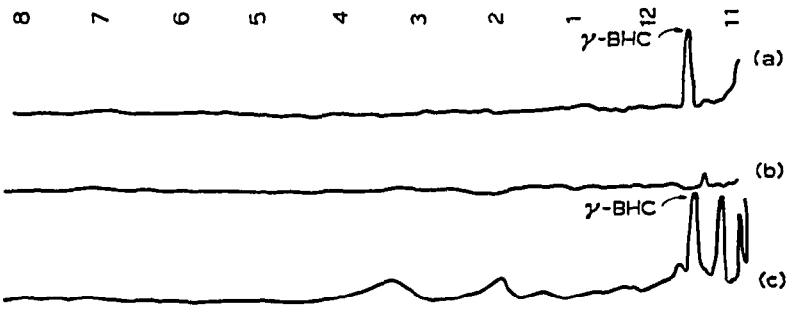

Fig. 4. Gas–liquid chromatograms obtained on the first 10 ml of acetone–*n*-hexane eluate from columns containing the modified adsorptive material. Traces: (a) silica gel modified with octadecyltrichlorosilane; (b) silica gel modified with dimethyldichlorosilane; (c) silica gel untreated.

Figs. 2, 3 and 4 show the chromatograms obtained with such columns. In each case, trace (a) is from silica gel modified with octadecyltrichlorosilane; (b) from silica gel modified with dimethyldichlorosilane; (c) untreated; and (d) with the *n*-hexane extract without any clean-up. It is obvious from Fig. 2 that in order to obtain easily identifiable peaks, it is necessary that the first extract be cleaned up (compare traced with traces a, b and c), and that the untreated silica gel (trace c), with its strong adsorptive sites, retards the elution of the interfering plant compounds (trace d) in addition to the γ-BHC, DDE and DDT when *n*-hexane is used as the eluent. The first millilitre of eluate shows a clear baseline in trace c. However, with modified adsorbents, the results are different (compare trace c with traces b and a).

In trace b, from the adsorbent modified with dimethyldichlorosilane, it seems that DDE is more soluble in the *n*-hexane than in methyl groups attached to the powders. For this reason, DDE is eluted quantitatively and in the first 4 ml of the *n*-hexane eluate. DDT is retained more strongly and only a trace amount is eluted in the first 4 ml of eluate.

In trace a, the result is the same except that DDT does not appear in the chromatogram, probably because of its strong lipophilic properties.

Fig. 3 shows the nature of the next 10 ml of *n*-hexane eluate. The untreated column (trace c) permits both DDE and DDT to be eluted but γ-BHC is retained completely. The dimethyldichlorosilane-modified column permits γ-BHC and DDT to be eluted, plus an unknown compound (first peak) and a trace amount of DDE. However, the octadecyltrichlorosilane-modified column (trace a) permits the remainder of the DDE to be eluted together with the DDT (quantitatively) and a small amount of γ-BHC. The unknown compound (first peak) is also present with the same area as in trace b.

Fig. 4 shows more obviously the selective and differential function of the three columns. The eluent in this instance was 10 ml of a 5% solution of acetone in *n*-hexane. The untreated column results in quantitative elution of the γ-BHC (trace c), but at the same time this peak is accompanied by three unknown peaks due to plant compounds. The dimethyldichlorosilane-treated column (trace b) gives trace amounts of the unknown compound (first peak), while the octadecyltrichlorosilane-treated column (trace a) gives quantitatively a very clear peak of γ-BHC. The next 10 ml of eluate from both the columns with the modified silica gel and the untreated column, containing the pigments of the plant material, are, as a consequence, coloured without the presence of any of the added compounds (γ-BHC, DDE and DDT).

The results obtained are difficult to explain on the basis of the affinities of the pesticides between the compounds used to modify the adsorptive material and the eluent. Nevertheless, it is clear that the compounds are separated not on the basis of their polarity but according to their affinity towards the modified material (compare the results in Fig. 4, traces a and b).

Much more work must be done in order to attain a better understanding of the mechanism of function of these modified columns. Nevertheless, it is obvious that the above technique may have potential in modifying the resolution of certain adsorptive materials. It may be more useful in TLC techniques. The main advantage is the number of parameters that can be changed in order to improve the resolution: the untreated adsorptive material; the number of methyl groups in the aliphatic chain;

and the combination of different eluents. We hope in the future to be able to present more convincing results for both GLC and TLC.

REFERENCES

1 F. W. Abel, F. H. Pollard, P. C. Uden and G. Nickless, *J. Chromatogr.*, 22 (1966) 23.
2 H. N. M. Stewart and S. G. Perry, *J. Chromatogr.*, 37 (1968) 97.