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Note

Behaviour of 23 persistent organochlorine compounds during sulphuric acid clean-up on a solid-matrix column

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The most frequently used methods for the determination of organochlorine pesticide (OCP) residues in fatty samples involve adsorption chromatography on Florisil[1–3], alumina[4,5] or silica gel[6,7] as a clean-up step before determination by gas chromatography (GC) with electron-capture detection (ECD).

During analyses of lipid-rich samples such as human milk, cow milk and vegetable oils for OCP residues with Florisil clean-up[3], we frequently observed in the GC–ECD trace negative peaks which interfere with, and in some instances prevent, the determination of some OCP residues. Further, some large negative peaks, observed especially with vegetable oils, elute very late and their removal is very useful for decreasing the analysis time. Treatment with concentrated sulphuric acid has already been reported as the sole[8,9] or supplementary[10,11] clean-up of fatty extracts for the determination of OCP residues by GC–ECD. The treatment has been carried out either by shaking the sample extract dissolved in hydrocarbon solvents with concentrated sulphuric acid[8,10] or by passing it through a column of acid-impregnated Celite[11,12] or silica gel[9]. However, both approaches have some drawbacks. Shaking is not a safe procedure because sputtering of sulphuric acid may occur and, further, it requires centrifugation for clear separation of the phases. Impregnation by thoroughly mixing concentrated sulphuric acid with granular materials such as Celite is time consuming and also not safe because of the possible volatilization and inhalation of acid-charged particles. Both approaches involve the recovery of reusable glassware.

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This paper describes a sulphuric acid treatment for removing negative peaks from extracts of fatty samples which are insufficiently cleaned up by adsorption methods. The treatment is carried out on disposable solid-matrix columns in a simple, safe and efficient manner. The behaviour of selected OCPs toward this treatment has been studied.

EXPERIMENTAL

Reagents and materials

Analytical-reagent grade chemicals were used. Light petroleum (b.p. 40–60°C) and isooctane were redistilled from an all-glass apparatus. Sulphuric acid (95%, density 1.824 g/ml) was used. Organochlorine pesticide reference standards were from the collection in this laboratory.

Apparatus

Extrelut-1 columns (E. Merck, Darmstadt, F.R.G.; code 15371) are ready-to-use, disposable columns filled with a macroporous Kieselghur-type material with a nominal volume of 1 ml. Remove the upper paper disk before use and attach the supplied needle (Luer Lock 0.65/32) at the column end as a flow regulator in the elution step.

The analyses were carried out on a DANI 6800 gas chromatograph equipped with an electron-capture detector. A glass column (1.8 × 4 mm I.D.) was packed with OV-17 + QF-1 (1.5% + 1.95%) on Chromosorb W HP (100–120 mesh). The temperatures were oven 210, inlet block 230, outlet block 250 and detector 250°C. The carrier gas was nitrogen at a flow-rate of 55 ml/min.

A rotatory evaporator (bath temperature 40°C; reduced pressure) was used to concentrate solutions.

Procedure

Pipette 1 ml of sulphuric acid onto the Extrelut column, avoiding touching the inner walls. Allow the acid to drain and wait 10 min to obtain an even distribution into the filling material. Transfer onto the Extrelut column the sample extract cleaned up by Florisil adsorption chromatography, *e.g.*, according to Suzuki *et al.*[3] with three 1-ml portions of light petroleum. Wait 5 min, then elute the OCP residues with 10 ml of light petroleum. Collect the eluate and concentrate it carefully to dryness, dissolve the residue in 1 ml of isooctane and analyse the solution by GC–ECD.

RESULTS AND DISCUSSION

Some applications of solid-matrix columns and their advantages in pesticide residue analysis over conventional techniques have been reported previously[13–15]. In this application, the columns were used as a solid support to carry out a sulphuric acid clean-up of fatty extracts for the determination of OCP residues by GC–ECD.

The proposed procedure overcomes the problems mentioned in the Introduction because the acid is held in a solid matrix, the columns are prepared just prior to use with simple and safe operation and there is no need to recover reusable glassware. It is noteworthy that with this treatment emulsions do not occur, the elution is accom-

TABLE I

RECOVERIES OF ORGANOCHLORINE COMPOUNDS USING THE DESCRIBED PROCEDURE

Extrelut columns with 1 ml of 95% or 90% sulphuric acid, eluted with 10 ml of light petroleum.

Compound	*Amount present (μg)*	*Average recovery ±S.D. (n = 6) (%)*	
		95% H_2SO_4	*90% H_2SO_4*
HCB	0.01	76 ± 18	89 ± 7
α-HCH	0.01	90 ± 14	99 ± 6
τ-HCH	0.01	89 ± 10	98 ± 9
β-HCH	0.02	84 ± 16	94 ± 9
δ-HCH	0.01	100 ± 9	117 ± 20
Aldrin	0.01	91 ± 12	104 ± 15
Dieldrin	0.05	n.r.[a]	n.r.[a]
Endrin	0.05	–[b]	–[b]
HEPO	0.01	95 ± 8	102 ± 13
τ-Chlordane	0.03	95 ± 8	93 ± 9
α-Chlordane	0.03	95 ± 7	89 ± 8
τ-Chlordene	0.02	61 ± 12	–[c]
α-Chlordene	0.02	68 ± 15	–[c]
p,p'-DDE	0.03	98 ± 6	98 ± 10
o,p'-TDE	0.05	92 ± 8	94 ± 9
o,p'-DDT	0.05	88 ± 7	88 ± 9
p,p'-TDE	0.05	95 ± 5	92 ± 9
p,p'-DDT	0.05	86 ± 8	90 ± 11
Mirex	0.11	94 ± 7	95 ± 11
Metoxychlor	0.15	19 ± 17	49 ± 12
Oxychlordane	0.02	97 ± 8	–[c]
trans-Nonachlor	0.02	77 ± 10	–[c]

[a] Not recovered.

[b] Recovered as endrin ketone, which appears as a peak with a retention time longer than that of the parent compound.

[c] Not investigated.

plished in a few minutes with a reduced volume of solvent and the eluate is neutral and does not need to be centrifuged, washed and dried as in shaking methods[8].

The performance of the method was studied with respect to the recovery of selected OCPs, the quality of the GC–ECD trace and the weight of lipidic material left in the extract after the treatment.

In Table I are reported the average recoveries and standard deviations for 23 organochlorine compounds subjected to the described procedure in amounts ranging from 0.01 μg for HCB to 0.15 μg for metoxychlor. Acceptable recoveries were observed for most of the compounds. Exceptions included α-chlordene, τ-chlordene and metoxychlor, which were recovered only partly and with high variability; dieldrin was not visible in the GC–ECD trace at the sensitivity used; endrin, according to the published data[16], is converted to the ketone, which appears as a peak with a retention time longer than that of the parent compound.

With respect to the quality of the GC–ECD trace, Fig. 1 shows the substantial improvement in the gas chromatogram of a human milk extract obtained according to the method of Suzuki *et al.*[3] after the described treatment. Similarly, tissues from

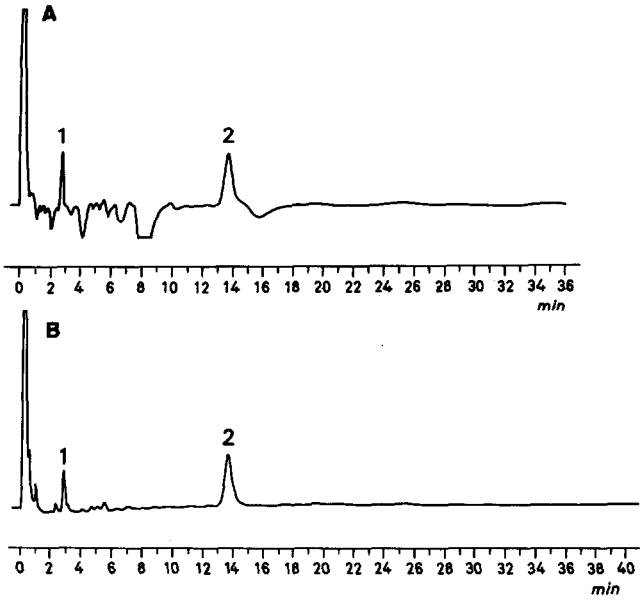

Fig. 1. Gas chromatogram of human milk extract obtained according to the method of Suzuki *et al.*[3], (A) before and (B) after the sulphuric acid clean-up. Peaks: 1 = HCB; 2 = *p,p'*-DDE. For conditions, see text.

marine organisms such as mussels and seal liver could be analysed for OCP residues only after applying the described sulphuric acid clean-up. The blank of the method is satisfactory under the GC–ECD conditions used, allowing the determination of OCP residues in milk at ppb (μg/kg) levels.

With respect to the ability of the described clean-up method to destroy unwanted lipidic material, it was found that extracts from ham, milk, mussels and seal liver and muscle after Florisil chromatography[3] normally contain 10–50 mg of lipidic material, which was reduced to just a few milligrams after the sulphuric acid clean-up. This is very important when capillary GC, especially with on-column injection, is used.

CONCLUSIONS

The described method offers a simple, rapid and safe method for a supplemental clean-up of difficult fatty extracts which are insufficiently cleaned up by adsorptive methods. As the procedure requires only disposable items and almost unattended operation, it offers a means of improving the throughput of residue laboratories with significant savings of reagents, glassware and time.

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