Journal of Chromatography, 91 (1974) 545–547

CHROM. 7315

THE USE OF AN ELECTRON CAPTURE DETECTOR FOR THE DETERMINATION OF PESTICIDES IN WATER

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SUMMARY

The use of an electron capture detector for the determination of chlorinated insecticide residues in water is described. A linear response of the detector was found for BHC and DDT isomers and metabolites in the range 0.03–1.20 μg/ml.

Results for the determination of chlorinated insecticide (γ-BHC; α- + β- + δ-BHC; DDT + DDE) residues in waters in Slovakia (for the years 1971–72) are given. BHC and DDT contents in Slovakian rivers ranging from 0.01 to 0.80 μg/l, in the Danube from 0.01 to 0.60 μg/l and in ground waters from 0.02 to 0.30 μg/l were found. The DDT content was lower than the content of BHC residues.

The results agree well with the actual consumption of chlorinated insecticides in agriculture in the area studied.

INTRODUCTION

The increasing use of chemical compounds in agriculture has led to contamination of both superficial water and ground water. Appropriate analytical methods for the identification and determination of pesticide residues are required in order to estimate the toxicological risks and to take hygienic measures for protection of the hydrosphere.

Highly sensitive analytical methods are required in order to determine chlorinated insecticides in water when the concentration of these substances is extremely low. Multi-detectional analysis by means of gas–liquid chromatography (GLC) with the use of a sensitive detector is suitable for this purpose. An electron capture detector[1] with tritium or nickel-63 as the electron source has proved to be the most efficient device for the determination of organochlorine insecticides.

When using this detector, one must take into account that it is possible to distinguish between even very similar compounds that differ only in the positions of substituents on the benzene ring. Gaul[2] has shown the lower electron affinity of the β-isomer of BHC in comparison with the other isomers. We found their electron affinities to decrease in the order $\alpha > \gamma > \delta > \beta$ (1:0.66:0.50:0.20)[3].

A column packed with 3–5% SE-30 on Chromosorb W, 80–100 mesh, is suitable for the separation of certain chlorinated insecticides, *e.g.*, γ-BHC, heptachlor, heptachlor epoxide, DDT, DDE and DDD[4]. This column is not suitable for the sepa-

ration of BHC isomers, but it can be replaced by a column packed with 5% Dow Corning 11 on Aeropack 30, 80–100 mesh, for this purpose[3]. However, this column cannot be used for the simultaneous separation of DDT metabolites and isomers. The simultaneous determination of BHC and DDT isomers and their metabolites can be achieved on a packing composed of liquid phases of different polarity, *e.g.*, 1.5% OV-17 + 2% QF-1 on Chromosorb W, 80–100 mesh[3,5].

EXPERIMENTAL

The water samples were extracted with low-boiling light petroleum and the extract was concentrated on a vacuum rotary evaporator and purified by column chromatography on an appropriate adsorbent. The eluate was then used for GLC on a Carlo Erba (Milan, Italy) Type 452 GI gas chromatograph equipped with a nickel-63 detector operated under the following conditions: glass column, 180 × 0.4 cm, packed with 2% QF-1 + 1.5% OV-17 on Chromosorb W, 80–100 mesh; temperature of the column, 200°; temperature of the injection space, 210°; temperature of the detector, 220°; carrier gas, nitrogen at a flow-rate of 80–100 ml/min; detector voltage, 10 V; recorder speed, 5 mm/min.

The concentration range of a standard mixture to which the detector responded linearly was measured so that calibration curves could be used for the evaluation of the chromatographic records. The following concentration ranges fulfilled this requirement:

α-BHC: 0.03–0.12 μg/ml	*p,p'*-DDE: 0.15–0.60 μg/ml
β-BHC: 0.15–0.60 μg/ml	*o,p'*-DDT: 0.30–1.20 μg/ml
γ-BHC: 0.04–0.18 μg/ml	*p,p'*-DDD: 0.30–1.20 μg/ml
δ-BHC: 0.03–0.12 μg/ml	*p,p'*-DDT: 0.30–1.20 μg/ml

The concentration of the substances studied in the samples under analysis was adjusted to be within the above range.

The identification of the chromatographic peaks was confirmed by thin-layer chromatography on Silufol plates[6].

RESULTS AND DISCUSSION

More than 150 samples of superficial water and ground water taken in 1971–72 were examined for chlorinated insecticide residue contents. In the waters of Slovak rivers (except the Danube), the γ-BHC content ranged from 0.03 to 0.81 μg/l, while the other BHC isomers were found in total concentrations between 0.01 and 0.52 μg/l. Both the DDT and DDE contents in the rivers (from 0.01–0.60 μg/l) were lower than the total BHC content.

The γ-BHC content in the Danube ranged between 0.03 and 0.31 μg/l, while the other BHC isomers were found at levels between 0.01 and 0.52 μg/l, and the DDT and DDE concentrations varied from 0.01 to 0.60 μg/l.

The BHC concentration is lower in ground water than in superficial water. For γ-BHC, values from 0.02–0.34 μg/l were found; the total concentration of the other isomers was found to be between 0.03 and 0.30 μg/l. Similarly, the DDT and DDE content is lower in ground water than in superficial water (from 0.05–0.39 μg/l). As in superficial water, in the West-Slovakian district the BHC residues are

higher than the DDT residues, and in the East-Slovakian district the ratio is reversed.

Similar results for DDT and γ-BHC were obtained by Edwards[7]. In the U.S.A., the DDT concentration in superficial water ranged between 0.102 and 0.720 μg/l while the BHC content varied between 0.004 and 0.120 μg/l; in Great Britain, the γ-BHC contents were in the range 0.098–0.180 μg/l.

Faust and Suffet[8] found 0.005–16.0 μg/l of DDT and 0.007–1.0 μg/l of γ-BHC in superficial water in the U.S.A.

Wolter[9] reported higher DDT concentrations (0.5 mg/l) in drinking water reservoirs after dispersion of these substances in the air to fields near to Güstrov Island and near to Lake Schwerin in the G.D.R. He found a concentration of 0.1 mg/l of lindane in superficial water and 0.05 mg/l in drinking water.

Our results agree well with the actual consumption of chlorinated insecticides in agriculture, where more BHC is applied than DDT. In this connection, the differences between DDT and BHC levels in Slovak rivers can be mentioned. The finding that both the DDT and DDE concentrations in the rivers in the East-Slovakian district are still higher agrees well with the observation that DDT consumption in this district is declining more slowly than in other parts of the country. This dependence was also found for chlorinated insecticide concentrations in butter made from milk originating from these areas[10].

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