Cleanup of Extracts Using Sweep Co-distillation Adapted to Gas Chromatograph

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The sweep co-distillation method of STORHERR and WATTS /1/ has proved very efficient in cleanup of plant extracts before the quantitative determination of organophosphorus pesticide residues. In combination with gas chromatography, the sweep co-distillation provides a very useful method for quantification of multiple parent organophosphorus pesticides.

This paper reports an adaptation of the gas chromatograph as an integrate apparatus for the sweep co-distillation cleanup and quantitative analysis of extracts from crops and milk fortified prior to cleanup with a mixture of diazinon, fenitrothion, malathion and trichloronat at total levels of 0.25 and 5 ppm. The crops selected for this study were gourds, kale, carrots, sugar beet tops, cauliflower, tomatoes, lettuce, apples, plums, and pears.

METHOD

Equipment and Reagents

Gas chromatograph. - Varian Aerograph Model 205-1 equipped with CsBr-thermionic detector, modified Storherr tube /see Fig. 1/, and a glass column 180 cm x 3 mm /o. d./ packed with 5 % DC 200 on Vara-

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port 30 /100-200 mesh/; the first 25 cm after injection were packed with Pyrex glass wool.

Vacuum rotary evaporator.

Siloxid^{R}. - Precipitated active silica, 170-300 mesh. Available from TONASO n. p., Czechoslovakia.

Solvents. - Analytical grade benzene, acetone, and ethyl acetate.

Pesticide standards. - Diazinon, fenitrothion, malathion, and trichloronat. The purity of pesticides was checked by GLC. Solutions of selected concentrations were prepared in ethyl acetate.

Extraction

The preparation of extracts from crops and milk was based on the column extraction method developed by KOVÁČand BÁTORA /2/. According to this procedure 100 g of the sample was homogenized with Siloxid^{R} and eluted in a glass column with a mixture of benzene and acetone /1:1/; 200 ml of the eluate was collected. In the case of milk the same procedure was used but the column was eluted first with 100 ml of petroleum ether /B. p. 40-60 ^{o}C/ and then with the benzene-acetone mixture.

A part of the extract corresponding to 2 g of sample was evaporated just to dryness using a gentle stream of nitrogen at 40 ^{o}C. The residue was dissolved in 0.5 ml of ethyl acetate containing a mixture of diazinon, fenitrothion, malathion, and trichloronat at the total concentration level of 0.25 and 5 ppm.

Sweep Co-Distillation Cleanup and Gas Chromatography

Two 0.25 ml portions of the fortified extract immediately followed by 2 x 0.25 ml and 4 x 0.5 ml of ethyl acetate were injected at 3 min intervals in-

to the modified Storherr tube packed with Pyrex glass wool and heated to 185 °C at nitrogen flow of 600 ml. $min.^{-1}$. To the distillate in a graduated receiving tube an ethyl acetate solution of parathion methyl as an internal standard was added. After suitable concentration under a nitrogen jet, the pesticides were determined by GLC method /2/ in an appropriate aliquot of the extract.

The following operating conditions were maintained: temperatures, column 180 °C, detector 210 °C, injector 200 °C; flow rates, nitrogen 18 ml. min^{-1}, hydrogen 15 ml. min^{-1}, and air 170 ml. min^{-1}. The column was conditioned 48 hours at 250 °C.

DISCUSSION AND RESULTS

The adaptation of the gas chromatograph detector oven for sweep co-distillation cleanup is wery simple /Fig. 1/. All parts of the all-glass apparatus are removable; the medified Storherr tube with glass ground joints is easy to exchange. Two openings in the wall of the detector oven of the gas chromatograph serve for inlet and outlet of the modified Storherr tube.

The technique is rapid, versatile, and inexpensive, it elimantes the need for adsorbents and large volumes of organic solvents. When combined with thin layer chromatography it is suitable especially for screening fo samples with unknown history of chemical treatment as it presents one of the simplest ways for routine identification of multiresidues before quantitative analysis by gas chromatography.

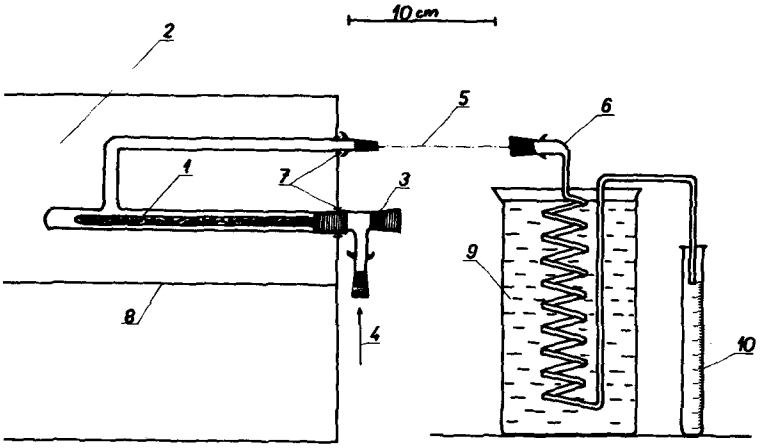

Fig. 1. Gas chromatograph adapted to the sweep co-distillation cleanup. 1-Modified Storherr tube packed with Pyrex glass wool. 2-Detector oven of the gas chromatograph. 3-Injection type septum. 4-N_2-inlet. 5-Connection for the condenser with the Sorherr tube. 6-Condenser. 7-Openings in the wall of the detector oven. 8-A wall between the detector and column ovens of the chromatograph. 9-Ice bath. 10-Graduated collection tube.

Temperature control and reading is common for both the Storherr tube and the gas chromatograph. Temperature operating conditions are the same as for GLC determination. If necessary, the Storherr tube can be heated in a wide range over the vorking temperature of the chromatographic column.

The recoveries of four organophosphorus pesticides added as a mixture to extracts from ten crops and milk are summarized in Table 1.

TABLE 1

Per Cent Recoveries of a Mixture of Organophosphorus Pesticides from Fortified Crop and Milk Extracts

	Diazinon	Fenitro-thion	Mala-thion	Trichlor-onat
Gourds	101	97	90	92
Kale	97	101	104	96
Carrots	104	98	102	98
Sugar beet tops	96	95	94	85
Cauliflower	108	100	100	95
Tomatoes	96	81	80	75
Lettuce	82	76	75	80
Apples	87	79	84	87
Plums	70	62	68	80
Pears	107	74	79	75
Milk	107	97	96	96

The results were obtained by using GLC with the CsBr-thermionic detector. Each result represents a single determination. The coefficient of variation of the GLC determinative step was in the range of $\pm$ 2.5 - 7.9 %. As may be observed from Table 1, the individual pesticide recovery was satisfactory with the exception of the plum extract where substantially lower results were found. This phenomenon could not be explained so far. Radiometric recovery studies using ^{32}P-fenitrothion have shown that about 5 % of the radioactivity was held back by the modified Storherr tube packing, probably due to the thermal breakdown

of the pesticide. For this reason a new Storherr tube should be used for each analysis.

SUMMARY

An adaptation of the Varian Aerograph gas chromatograph to the sweep co-distillation cleanup using the modified Storherr tube is described. The recoveries of this cleanup technique were evaluated for the mixture of four organophosphoru pesticides added to extracts from ten crop and milk. Pesticides were analyzed by gas chromatography with a cesium thermionic detector.

REFERENCES

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2. KOVÁČ, J. and BÁTORA, V., Proc. 3rd Analytical Conference, Budapest, 1970, p. 313-318.