Determination of chloroorganic pesticide residues in meat by gas chromatography technique

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There are many specific methods known at present for determining the pesticides, but the majority — as a rule — are very complicated as well as labour and time consuming. Very often their specificity is also very doubtful. The modern procedures, however, require — before all — techniques which are universal, quick, simple and ready to be applied in serial control analyses. Specific methods may be used in certain cases as supplementary tests, or tests confirming the presence of given pesticides.

It is generally known that the main difficulties encountered when analysing any foodstuff for the presence of pesticides is connected practically with the problem of proper preparation of samples. The widely used techniques for separation detection and estimation of pesticides such as thin layer, paper and vapour chromatography require more or less through cleanup. It is obvious that the cleanup method is so much more useful for the purpose of practical control of contamination of various foodstuffs with pesticides as it extends over a wider scope of pesticides and their metabolities as well as over the tested matter.

At present there is still a demand in the world science for simple and quick cleanup techniques when dealing with the pesticide residues prior to submitting them to quantitive or qualitative analyses.

Judging by the results obtained by J. Kim and C. Wilson (1) and also by the author (2,3,4) it is believed that cleanup of pesticides in vapour phase has precisely all the features of simple, quick and universal technique for a whole group of chloroorganic pesticides in biological matters of various origin.

The present paper deals with the problem of adapting a technique consisting in extraction of pesticides in vapour phase prior to analysing their residues in meat by applying a gas-liquid chromatographic method with a recombination detector (Ni—63). This detector reacts selectively to chemical compounds containing atoms of strongly negative elements.

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in meat by applying the gas-liquid chromatographic method. Detailed results will be presented at a later date.

METHODS

Apparatus

1. Vapour phase cleanup apparatus — constructed in the Institute's Workshop.
2. Laboratory mechanical stirrer model Ws 2 — produced by Warszawskie Zaklady Aparatury Laboratoryjnej i Pomiarowej.
3. High vacuum pump — Edwards High Vacuum Ltd.
4. Gas chromatograph — W. G. Pye Series 104 Mod. 84 complete with accessories.

Reagents

1. Argon — produced by PPH Gazy Techniczne, Poland
2. Acetone p.a. and p. grades — produced by Zaklady Chemiczne, Oświecim. The p.a. reagent redistilled over silver nitrate (1 g) (1 b).
3. Silver nitrate, p. grade — POCh Gliwice.
4. Benzene, p.a. grade — produced by Zaklady Koksochemiczne Hajduki; redistillted over silver nitrate.
5. Medium filtrating paper — POCh Gliwice.
6. Munktell filtrating paper — extracted with benzene in Soxhlet apparatus.
7. E — 30 — W. G. Pye and Co. Ltd.
8. Gas-Chrom Z 60/80 mesh — Applied Science Laboratories, Inc.
9. n-Hexane — T. Schuchardt; redistilled over silver nitrate.
10. Xylene, p.a. grade — produced by Zaklady Koksochemiczne Hajduki; redistilled over silver nitrate.

11. p, p' DDT
12. p, p' DMDT
13. p, p' — DDE
14. γ — HCH

Standards received from Food and Drug Administration, Ottawa, Canada

15. Anhydrous sodium sulphate, p.a. grade — heated for 2 hours at 150° C; before using as packing of microcolumn it was extracted with benzene in Soxhlet apparatus.
16. Cotton-wool — before using in microcolumn extracted with benzene in Soxhlet apparatus.
17. Silica gel G according to Stahl (5—25 μ) — Merck; extracted with benzene in Soxhlet apparatus and heated for 1 hour at 90° C.

Separation of Pesticides

Extraction

Raw meat or meat products intended for testing were minced 4 times using a mechanical mincer provided with a 2 mm mesh screen. Out of the obtained mass 1.5 g was weighed and put together with 3.0 g of anhydrous sodium sulphate and 10 ml of n-hexane into a 50 ml. Erlenmeyer flask; the flask was then shaken for 30 minutes on mechanical stirrer. After that time the mixed contents was transfered onto a 363 filter on which a 5 g. compact layer of anhydrous sodium sulphate had been already placed. The Erlenmayer flask was rinsed with four 2.5 ml portions of n-hexane; each portion was transfered onto the filter. Next the filter was rinsed thrice with 2 ml portions of n-hexane. The filtate was collected in a special vessel in shape of a test tube with ground joint and a conical calibrated bottom (2).

Cleanup in vapour phase

The obtained meat extract was concentrated under vacuum conditions by means of microfractional concentrator (1) to the volume of 1.5 ml. Next 1 ml, i.e. the equivalent of 1 g. meat, was taken by means of a syringe and injected directly into the described by the author (3) apparatus for cleanup of pesticides in vapour phase.

The pesticides were extracted with 16 ml of n-hexane passed at a rate of 2 ml/min (as liquid) at 245° C.

At the beginning of the cleanup process the extraction tube outlet was immersed to a depth of 4 cm in n-hexane with which the vapour trap was filled. The vapour trap (in shape of a test tube with ground joint) was cooled in an ice bath. After all n-hexane vapour was distilled the trap was lowered. so that the extraction tube outlet was no longer immersed in the distillate. Next 0.2 ml of xylene was injected in order to rinse that part of the extraction tube, which being outside the thermostate, could have some of the pesticides deposited on its surface. The mentioned part of the extraction tube was also rinsed on the outside with appr. 1 ml of n-hexane which was then added to the distillate.

Cleanup in microcolumn using the silica gel

The obtained distillate was next cleaned in microcolumn packed from the bottom with: cotton-wool plug, 0,5 g of anhydrous sodium sulphate, 0,4 g of silica gel G, 0,5 g. of anhydrous sodium sulphate and round Munktell filtating paper. Pesticides were eluted with a mixture of n-hexane and benzene (3: 2) in quantity of 13.5 ml, out of which the first 3 ml were used for removing the air and rinsing the microcolumn contents.

The distillate condensed to a volume of 1 ml was transfered quantitatively

on top of the microcolumn and the vapour trap was rinsed four times with 1 ml of the eluant waiting every time until the meniscus of the solvent reaches the layer of anhydrous sodium sulphate. Similarly, the walls of the microcolumn were rinsed thrice with 0.5 ml of eluant. Only then the remaining 5 ml of eluant were poured on the top of the column. The silica gel layer was compacted to such an extent as to adjust the dissolvent flow rate from 12 drops per minute to 8 drops per minute at maximum and minimum liguid column, respectively. The eluate was collected in a vessel of the same shape as for collecting the meat eluate.

Determination of pesticides

Determination of pesticides as dealt with within the scope of the present work was carried out by a gas chromatography technique using the Pye apparatus Series 104 Mod. 84 complete with recombination detector (Ni-63).

Glass columns 3 feet in length and 4 mm in internal diameter were filled with 8 % methyl silicone (E-30) placed on Gas-Chrom Z 60/80 mesh. Argon, flowing at a rate of 120 ml/min, was used as a carrier. Temperature of the column thermostate was maintained at 195° C while that of the detector thermostate at 220° C. The detector voltage was set to pulsation, the pulse width being 0.75 μs and cycle 500 μs.

From the eluate obtained from the column and next reduced to a volume of 2 ml under vacuum conditions 0.001—0.002 ml were transfered to the chromatographic column. The time of a single analysis was limited to 18 minutes.

Quantitative interpretation was accomplished by comparing the respective peaks obtained from the tested matter and those obtained from the standard solution.

RESULTS AND DISCUSSION

Fig. 1 shows a chromatogram obtained from the extract corresponding to 1 g of raw pork. Fig. 2 illustrates the result of a chromatographic analysis of identical meat sample with an appriopriate quantity of pesticide standard solution added before the cleanup in vapour phase.

In tests on the recovery of solution the pesticides was added to the extract obtained from larger quantity of pork. From the strengthened extract obtained in the manner described, volumes equivalent to 1.5 g of meat were taken for analysing; the procedure was exactly the same as discussed before. The obtained results are presented in Table 1.

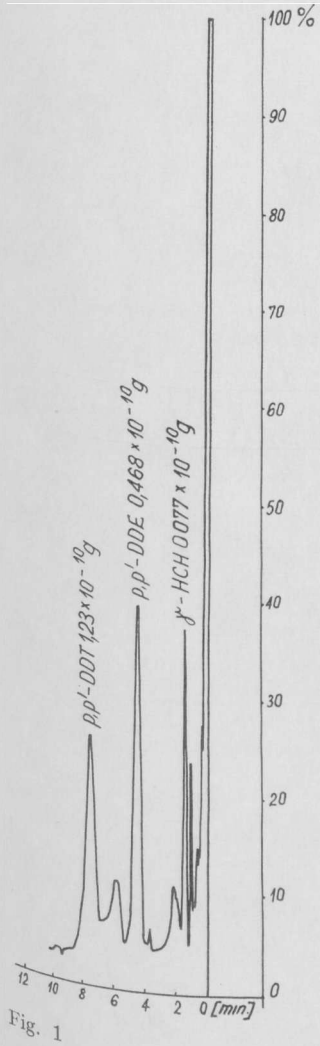

Fig. 1

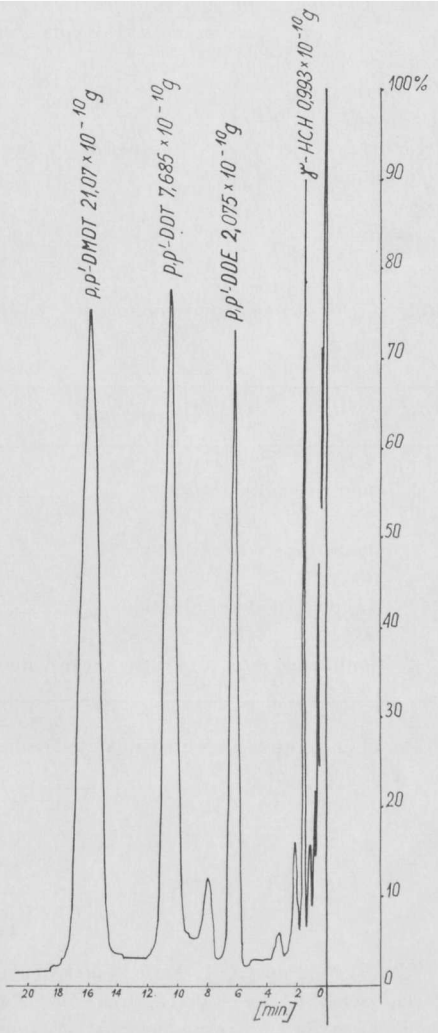

Fig. 2

Explanations to figures

Fig. 1. *Chromatogram of chloroorganic pesticide residues in raw pork*

Conditions:

a. *column — glass, length 3 feet, internal diameter 4 mm, filled with 8 % E 30 on Gas-Chrom Z — 60/80 mesh, temp. 195° C*
b. *detector — recombination (Ni-63), pulsation 500 μs, temp. 220° C*
c. *carrier gas — argon, flow rate 120 ml/min*
d. *injection volume — 2 μl*
e. *paper — 10"/h*
f. *sensitivity — 5×10^{-10} A*

Fig. 2. *Chromatogram of chloroorganic pesticides obtained from raw pork extract with addition of standard pesticide solution.*

Conditions:

a. column
b. detector
c. carrier gas
d. injection volyme
e. paper
f. sensitivity — 1×10^{-9} *A*

} *same as in fig. 1*

Table 1. *Results of determination* γ*—HCH; p, p'—DDE; p, p' — DDT and p,p' — DMDT in raw park*

Item	*Chemical compound*	γ*-HCH*	*p,p'-DDE*	*p,p'-DDT*	*p,p'-DMDT*
1	Quantity added (μg)	0.14	0.21	1.05	3.0
2	Quantity recovered (μg)	0.075	0.14	0.65	2.0
3	Number of determinations	7	6	7	7
4	Confidence interval for the mean value	0.008	0.01	0.05	0.1

Confidence intervals were calculated using the t —Student schedule for the significance level $1 - a = 0.95$

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