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Screening Procedures for Organophosphorus, Organochlorine and Carbamate Pesticide Residues on Tobacco*

by. E. Nesemann and F. Seehofer
Department of Research and Development, B·A·T Cigaretten-Fabriken GmbH, Hamburg, Germany

The attempt to replace long-lasting chlorinated hydrocarbon insecticides with less-persistent chemicals has led to increased use of phosphorus containing and carbamate pesticides.

Although numerous analytical procedures are available for determining residues of a particular organochlorine and organophosphate pesticide on food products, there are only a few methods for tobacco. There is a great need for a rapid, accurate, and sensitive procedure capable of determining any of a large number of such pesticide residues.

The *Mills-Onley-Gaither* (1) screening procedure for organochlorine pesticide residues has previously been adapted as a screening procedure for organothiophosphate pesticide residues in fruit and vegetables (2—5). Methods for carbamates are published (6, 7, 8, 9), two of them for tobacco. This paper describes the preliminary development of a general method for the organochlorine pesticides, water-insoluble and water-soluble organophosphorus pesticides, and metabolites derived from the latter.

PRINCIPLE

The procedure consists of the following steps. The sample is blended with acetonitrile and filtered. An aliquot of the acetonitrile is diluted with water. The organochlorine and some of the organothiophosphate pesticides are partitioned into petroleum ether. The aqueous-layer is reserved for water-soluble compounds.

The petroleum ether solution is purified by chromatography on a Florisil column, eluting with mixtures of petroleum ether, ethyl ether and dioxane. Residues in concentrated eluates are separated by gas chromatography and measured by the microcoulometric system for chlorine and by the thermionic detector for phosphorus.

The residual acetonitrile-water layer is extracted with methylene chloride. The extract is dissolved in water, filtered and an aliquot of the solution is extracted with methylene chloride. The concentrated solution is taken for gas chromatography with the phosphorus detector.

For detection of carbamates the sample is blended with methylene chloride in the presence of sodium sulfate and filtered. An aliquot is taken to near dryness, the residue is dissolved in an acid saline solution and filtered. The carbamate pesticide residues are partitioned into methylene chloride. The concentrated extract is subjected to thin-layer chromatography. The pesticides are located by chromogenic spray. The amount is estimated by visual comparison with standard solutions.

METHOD

Reagents

(a) Acetonitrile. B. p. 81—83° C, preferably redistilled.
(b) Petroleum ether. B. p. 40—60° C, Merck AR.
(c) Ethyl ether. Merck AR.
(d) Dioxane. Riedel, for chromatography, stabilized.
(e) Methyl ethyl ketone. Merck AR.
(f) Methylene chloride. Merck AR.
(g) Florisil. 60/100 mesh. Store in oven at 130° C for 5 hr, cool in desiccator and add 0.7 % water. Mix about 1 hr and let equilibrate for 24 hr.
(h) Eluting mixtures.
  (1) Ethyl ether: dioxane: petroleum ether, 10:1:89:
  (2) Ethyl ether: dioxane: petroleum ether, 15:5:80.
(i) Acetone. Merck AR.
(j) Coagulating solution. Dissolve 0.5 g NH_4Cl in 400 ml dist. water containing 1 ml H_3PO_4 (85 %).
(k) TLC-Plates. Pre-coated with aluminium oxide (Type E), F_{254}.
  Manufactured by E. Merck, Darmstadt, West Germany.
(l) Developing solvent. Hexane: acetone, 9:1.
(m) Chromogenic sprays.
  (1) Dissolve 100 mg Fast Blue B salt in 100 ml H_2O,
  (2) Dissolve 10 mg 2,6-dichloroquinonechloroimide in 100 ml acetone.
(n) Alcoholic potassium hydroxide. 1.0 N in ethanol.
(o) Mixed pesticide standard solutions.
  (1) Mixture of lindane, aldrin, dieldrin, endrin, p,p'-DDT, p,p'-TDE (DDD), thiodan. Prepare solution in methyl ethyl ketone in ratios 1:1:2:2:2:2, using 7.5 ng lindane/µl.

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(2) Mixture of DDVP, trichlorofon, Metasystox R, diazinon, dimethoate, malathion, parathion, Guthion (ethyl-). Prepare solution in methyl ethyl ketone in ratios 1:1:1:1:1:1:6, using 2.5 ng parathion/µl.
(3) Standard solutions in acetone containing carbaryl and Unden, resp., 80 ng/µl.

Apparatus

(a) Chromatographic tubes. 22 mm i. d. × 300 mm high, with Quartz wool plugs and Teflon stopcocks.
(b) Chromatographic tank. Suitable for developing 5 plates, 20 × 20 cm, simultaneously; DESAGA.
(c) (1) Gas chromatograph-microcoulometric system. Laboratory built column oven with short glass line to the pyrolysis furnace, S-250; titration cell sensitive to halogen, T-300-S, and C-250-A microcoulometer connected to 2.5 mV strip recorder (Dohrmann Instruments Co.).
(2) Gas chromatograph-thermionic detector. Hy-Fi III, 1200-10, single-column gas chromatograph with a high temperature FID, directly interchangeable with the phosphorus-detector (salt-tip with cesium bromide), connected to 2.5 mV strip recorder (Varian Aerograph).
(d) GLC columns, all glass columns, 5′ long × 0.125″ o. d., packed with
(1) 10% DC-200 on 80/100 Gas-Chrom Q,
(2) 11% QF-1 + OV -17, ratio = 1.30, on Gas-Chrom Q, 80/100.

Extraction and Cleanup
Organochlorine and Organophosphorus Pesticides

Transfer to a Waring blendor 100 g chopped green tobacco or alternatively 25 g ground fermented tobacco soaked for 5 min with 80 ml H_2O; add 200 ml acetonitrile and ca. 5 g Hyflo Super Cel. Blend at low speed 2 min, filter mixture through a Büchner funnel, using coarse filter paper and gentle suction, transfer filtrate to a 250 ml graduated cylinder, and record volume. Then transfer the filtrate to a 1 L separatory funnel; measure 100 ml petroleum ether into the same 250 ml graduated cylinder and add this to the filtrate in the separatory funnel. Shake by vigorous tumbling 1 min; add 10 ml saturated NaCl, plus 600 ml dist. water, shake again 1 min; after layers separate, draw off the bottom (aqueous) layer; re-extract with 50 ml petroleum ether. Rinse combined petroleum ether layers first with 100 ml and then with 50 ml dist. H_2O, draining off aqueous layer after each rinse. Combine aqueous portions, for further determination of water-soluble organothiophosphate pesticides, cool down to + 5° C. Percolate petroleum ether layer through a plug of anhydrous Na_2SO_4.
Evaporate to approximately 10 ml in H_2O bath at 35° C under a stream of clean, dry nitrogen. Calculate as follows:
g Sample equivalent = g sample taken x (ml acetonitrile filtrate)/280 ml, assuming the tobacco contains ca. 85% moisture, without or with added water (factor of 280 allows for 5 ml volume contraction).

Florisil Column Cleanup

(Note: After preparation of the Florisil column, complete the elution without delay, not letting the column become "solvent-free" and guarding against addition of any moisture.)
Pack chromatographic tube (a) with 10 g activated Florisil (g) so it is ca. 40 ± 4 mm high after gentle tapping (do not use tamping rod); top Florisil layer with ca. 20 mm anhydrous Na_2SO_4. Place a receiver under the column, and prewash column with 20–30 ml petroleum ether; after last of the solvent has just sunk into the Na_2SO_4 layer, transfer petroleum ether concentrate to column; let it pass through, adjusting column flow rate to 5–7 ml/min with stopcock. Rinse container and Na_2SO_4 with two ca. 5 ml portions petroleum ether, pour rinsings into column, rinse walls of tube with additional small portions petroleum ether, and after the last rinse has just sunk into the Na_2SO_4 layer, replace receiver containing prewash with a clean 250 ml flask and elute the pesticides with 200 ml eluting mixture (h, 1). Change receiver and elute with 100 ml solvent (h, 2).
Concentrate eluates to ca. 2 ml in a H_2O bath at 35° C under a stream of clean, dry nitrogen, combine and transfer eluates quantitatively to a small tube (a 15 ml glass-stoppered conical centrifuge tube is convenient), evaporate *just* to dryness, and dissolve residue with a known volume of methyl ethyl ketone (usually 0.2–1.0 ml); stopper and swirl to mix. This solution is ready for gas chromatography and contains the chlorinated and petroleum ether-soluble phosphated pesticides.

Water-Soluble Organophosphorus Pesticides and Metabolites

The aqueous tobacco extract set aside after petroleum ether partitioning, cooled to about + 5° C, is extracted four times with 50 ml portions of methylene chloride in a 1 L separator. Evaporate the combined methylene chloride extracts just to dryness in a H_2O bath at 35° C under a stream of clean, dry nitrogen, dissolve the residue in 2 ml acetone, add with swirling 98 ml water, 5 g $Na_2SO_4 \cdot 10\ H_2O$ and 1 g Hyflo Super Cel. Shake on a mechanical shaker for 30 minutes. Filter through a dry fluted filter into a 100 ml graduated cylinder, and record volume, e. g. 98 ml (that means 98% of the calculated sample equivalent). To the filtrate add 40 g $Na_2SO_4 \cdot 10\ H_2O$, heat gently to aid solution of the sodium sulfate and cool to room temperature before transferring to a clean 250 ml separatory funnel. Extract the water phase with 50, 25, 25, 25 ml portions of methylene chloride, shaking for 1 minute each time. Evaporate the combined methylene chloride extracts just to dryness in a H_2O bath at 35° C under a stream of clean, dry nitrogen and then to dryness at room temperature. Dissolve the residue with 0.50 ml methyl ethyl ketone. The solution is ready for gas chromato-

graphy and contains the water-soluble thiophosphates, Metasystox R (78%), dimethoate (89%), Guthion (74%), and water-soluble metabolites of all pesticides.

Carbamate Pesticides

To 100 g chopped green tobacco in a Waring blendor or 25 g fermented tobacco soaked with 75 ml H_2O for 5 min, add 150 ml methylene chloride and 100 g powdered anhydrous sodium sulfate, and blend at low speed 2 min. Decant liquid, filtering with suction into a 500 ml suction flask through a Buchner funnel with rapid filter paper covered with a thin layer of Hyflo Super Cel. Rinse blendor and filter pad with 50 ml methylene chloride. Return most of residue from filter to blendor and repeat extraction. Again wash with 50 ml methylene chloride. Evaporate solvent in a flash evaporator in a H_2O bath at 35° C to ca. 10 ml. Remove flask from bath, swirl until dry and allow to cool. Rinse down sides of flask with 10 ml acetone from pipet and swirl to dissolve residue. While gently swirling flask, add 100 ml coagulating solution (j) and let stand 30 min with occasional swirling. Filter with suction through small filter funnel with medium porosity fritted disc coated with Hyflo Super Cel and receive filtrate in suction flask of 250 ml. Wash precipitate 3 times with 15 ml portions of 10% acetone in coagulating solution, allowing each washing to remain in contact with the precipitate for about 15 seconds before applying suction. Transfer filtrate and washings to 250 ml separator and extract with 50, 25, 15 ml portions of methylene chloride. Combine the extracts and evaporate in a flash evaporator to near dryness. Transfer to a small graduated tube and evaporate solvent with stream of clean, dry nitrogen. Dissolve residue in 0.20 ml acetone, take this solution for TLC.

Figure 1. Temperature-programmed gas chromatogram of eight phosphorus containing insecticides; standard mixture, 6 ng, each.

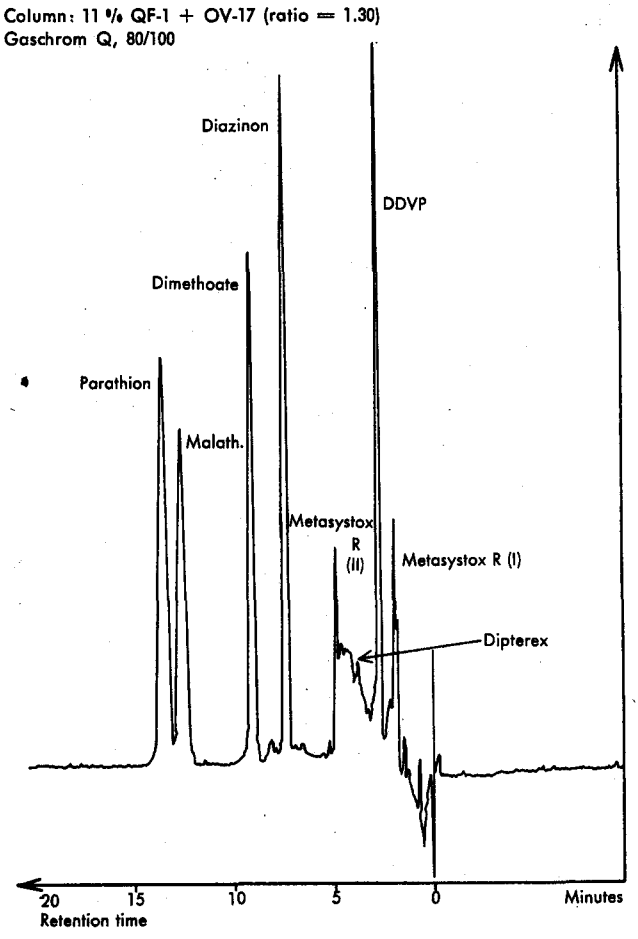


Figure 2. Temperature-programmed gas chromatogram of petroleum ether-soluble fraction of tobacco extract. Field treatment: malathion.

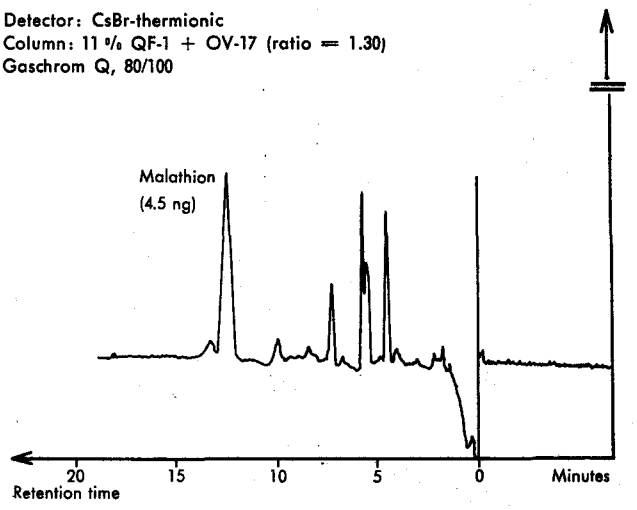


Figure 3. Temperature-programmed gas chromatogram of water-soluble fraction of tobacco extract. Field treatment: malathion.

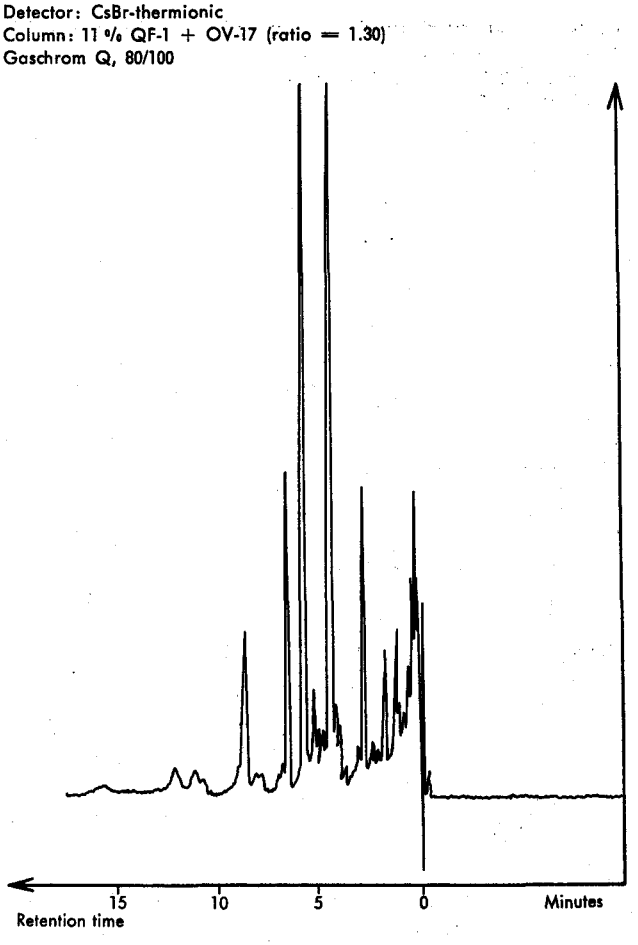


Figure 4. Temperature-programmed gas chromatogram of petroleum ether-soluble fraction of tobacco extract. Field treatment: diazinon.

Detector: CsBr-thermionic
Column: 11 % QF-1 + OV-17 (ratio = 1.30)
Gaschrom Q, 80/100

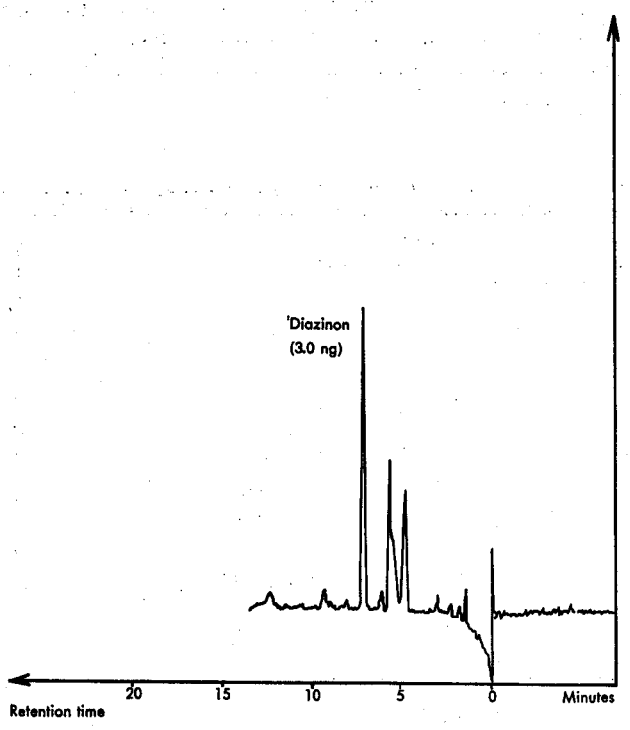


Figure 5. Temperature-programmed gas chromatogram of water-soluble fraction of tobacco extract. Field treatment: diazinon.

Detector: CsBr-thermionic
Column: 11 % QF-1 + OV-17 (ratio = 1.30)
Gaschrom Q, 80/100

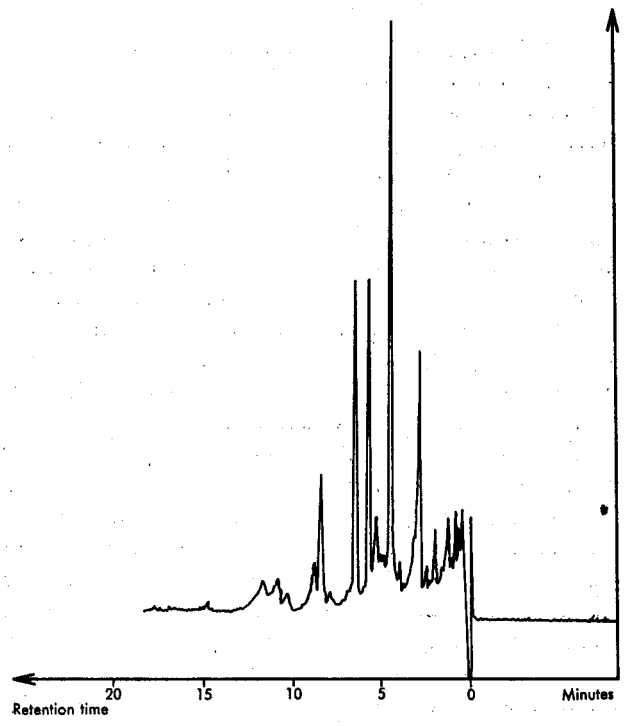


Figure 6. Isothermal gas chromatogram of twelve chlorine-containing insecticides; standard mixture.

Detector: Electron capture
Column: 11 % QF-1 + OV-17 (ratio = 1.30)
Gaschrom Q, 80/100

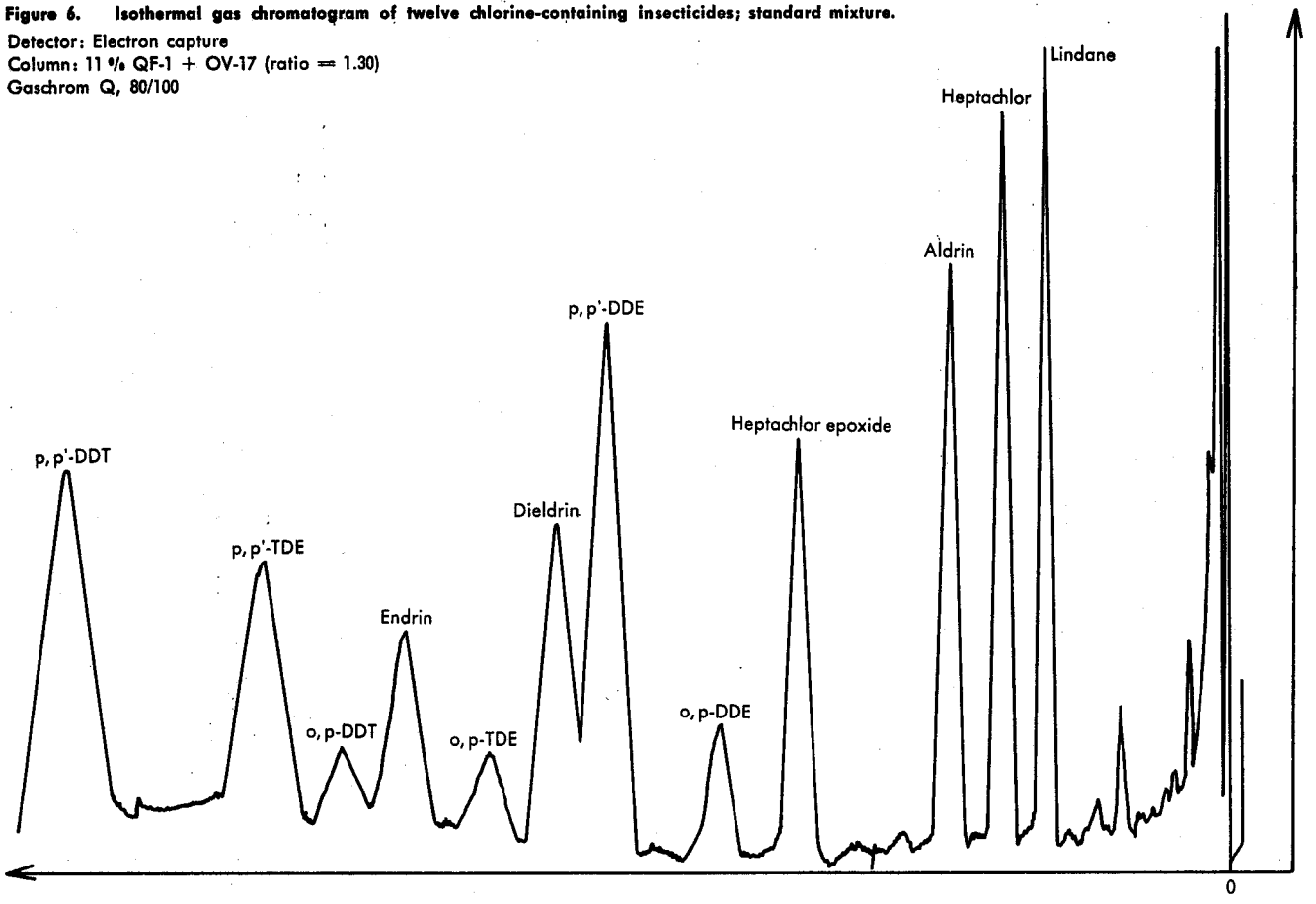


Figure 7. Isothermal gas chromatogram of four chlorine-containing insecticides; standard mixture.

Detector: Microcoulometric system
Column: 10 % DC-200, Gaschrom Q, 80/100

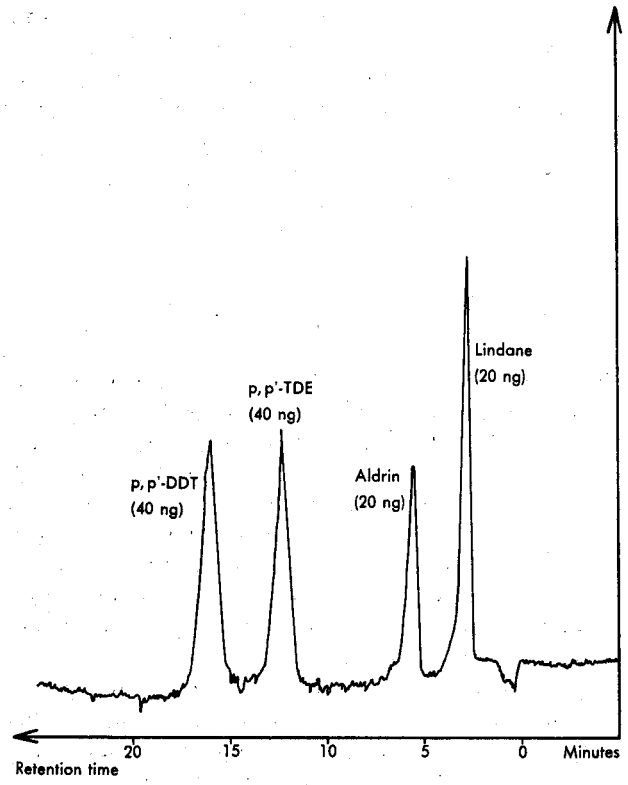
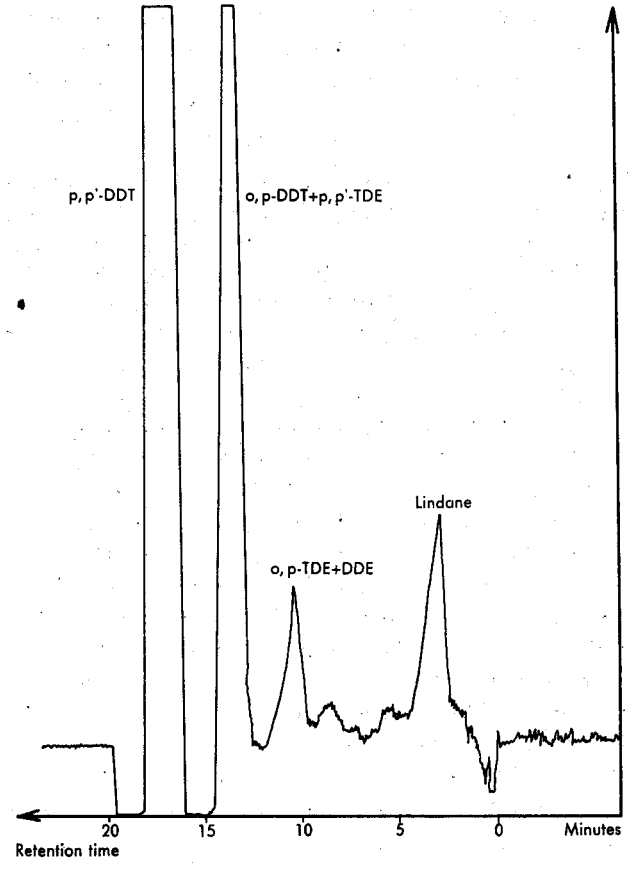


Figure 8. Isothermal gas chromatogram of petroleum ether-soluble fraction of tobacco extract.

Field treatment: DDT + lindane
Detector: Microcoulometric system
Column: 10 % DC-200, Gaschrom Q, 80/100



Residue Detection Methods

GLC Procedure for Phosphated Pesticides

Standardization of equipment. QF-1 + OV-17 column: Condition at 240° C for 48 hours with a nitrogen flow of about 50 ml/min, disconnect the column from the detector; nitrogen, 20 ml/min; injection port, 170° C; detector, 230° C; hydrogen, 18.0 ml/min; synthetic air, 100.0 ml/min.

Standardize system as follows: after equilibrating gas chromatographic oven at 120° C, inject into column (2) 2.0 µl standard mixture (d,2), and immediately program oven temperature upward at 10° C/min to 190° C. For Guthion program up to 240° C. Determine peak area and repeat injections until constant areas result.

Determination. Inject 1 µl of the petroleum ether-soluble fraction, or 3 µl of the water-soluble fraction of the pesticides; starting at 120° C, programming at a rate of 10° C/min to 190° C. For the detection of Guthion work isothermally at 240° C. Calculate the R_P, inject an appropriate amount of standard mixture.

$$R_P = \frac{\text{retention time of sample peak}}{\text{retention time of parathion}} .$$

µg phosphated pesticide in sample aliquot =

$$\frac{\text{area of sample peak}}{\text{area of standard peak}} \cdot \text{µg of standard injected.}$$

Area of sample and standard peaks should be closely matched for quantitative determination.

GLC Procedure for Chlorinated Pesticides

Standardization of equipment. Set microcoulometric system for the following conditions: inlet, 175° C; outlet, 400° C; center, 950—1000° C; bias, 260 mV; range, 150 ohms; gain, low; oxygen flow rate, 60 ml; carrier, 450 ml; recorder chart speed, 0.5 cm/min; GLC conditions; QF-1 + OV-17; column temperature, 195° C; helium flow, 50—70 ml/min; injection port, 220° C.

Standardize system as follows: inject into column (2) 3.0 µl standard mixture (d,1), using 10 µl syringe; determine peak area by suitable means (triangulation, integrator, planimeter). Repeat injections until constant areas result.

Determination. With bypass vent open, inject up to 5 µl sample solution onto the QF-1 + OV-17 column, and mark point of injection on chart paper; after 1—1.5 min, close vent and record the chromatogram. Calculate the R_A (retention time of sample peak/retention time of aldrin), inject an appropriate amount of standard mixture.

µg pesticide in sample aliquot injected =

$$\frac{\text{area of sample peak}}{\text{area of standard peak}} \cdot \text{µg of standard injected.}$$

Area of sample and standard peaks should be closely matched for quantitative determination.

TLC Procedure for Carbamate Pesticides

Using a 10 µl syringe, spot aliquots of sample and standards on a 20×20 cm TLC plate (k), to cover the range expected. Add about 1/2 inch developing solvent (l) to bottom of chromatographic tank lined with blotting paper to saturate atmosphere. Place the plate into the tank and develop until the solvent front just reaches a line drawn 12 cm from the origin. After development, dry the plate for about 10 min in the hood. Develop a second time to the same height; dry again. Spray moderately with alcoholic potassium hydroxide (n), then spray moist plate with chromogenic solutions, (m, 1) and (m, 2), resp. Dry plate with warm air (hair-dryer), to develop maximum intensity of colours. The resulting colours are listed in Table 1.

Table 1. Colours of carbamate pesticides with different chromogenic sprays.

Pesticide	Spray: Fast Blue B	Dichloroquinonechloro-imide
Carbaryl	Reddish-blue	Dark blue
Unden	Light pink	Bright blue

EXPERIMENTAL AND RESULTS

Recoveries of 8 phosphated, 7 chlorinated and 2 carbamate pesticides from tobacco are shown in Table 2. Recovery tests were carried out on samples German field grown flue-cured tobacco, with additions equivalent to 0.5 ppm made before blending with acetonitrile.

Table 2. Recoveries of pesticides added to 25 g tobacco at the 0.5 ppm level.

Pesticide added	Found (ppm)	Recovery (%)	C. V. (%)
Aldrin	0.46	92	9.2
Dieldrin	0.43	86	13.2
Endrin	0.44	88	9.5
Lindane	0.44	88	4.1
p, p'-TDE	0.48	96	
p, p'-DDT	0.505	101	10.9
Thiodan	0.45	90	
Overall average		91	
Diazinon	0.47	94	
Parathion	0.52	104	9.6
Guthion, ethyl	0.37	74	
Malathion	0.485	97	12.0
Dimethoate	0.445	89	
DDVP	0.25	50	
Trichlorofon (Dipterex)	0.275	55	
Metasystox R	0.39	78	
Overall average		80	
Carbaryl	0.41	82	
Unden	0.375	75	
Overall average		78.5	

Metasystox R, Guthion and dimethoate can be satisfactorily recovered from the water-acetonitrile layer by methylene chloride.

Results from the field treatment with 14 different pesticides in Germany 1967 are given in Table 3.

Virginia SCR received two applications of each pesticide at three times the normal dose rate, with an interval of one week between the two applications; harvesting followed one week after the last application. The determinations were made about 6 months later.

DISCUSSION

The recoveries of all pesticides tested are generally good and are considered satisfactory for a rapid "sorting-out" procedure. The cleanup developed was satisfactory for microcoulometric GLC (MCGLC) and detection with the thermionic detector (CsBrTD). This method essentially separates the petroleum ether-soluble compounds from the water-soluble compounds, Metasystox R, Guthion and dimethoate. Many of the thiophosphate metabolites are water-soluble and are partitioned into the aqueous phase. No recovery studies were done on these metabolites, e. g., oxygen analogs (P = O) of thionophosphates (P = S), which should be in the methylene chloride extract (2). But this extract was "clean" enough for GLC with the CsBrTD, and the chromatograms revealed no indication of such compounds. The TLC procedure for carbamate pesticides (carbaryl, Unden) is rapid, too, and the recoveries are good for a screening test. The limit of sensitivity for reliable quantitative measurements with the "150 ohm range" setting on the Dohrman C-250 microcoulometer is about 2–5 ng for the chlorinated pesticides, depending on the compounds. The detector response is essentially linear from at least these lower limits until the recorder pen goes "off-scale" (Fig. 8).

The limit of sensitivity for reliable quantitative measurements with the phosphorus detector (CsBrTD) is about 0.5–2.5 ng for the organophosphate pesticides, although smaller amounts can be detected. But one must take into consideration, that the CsBrTD, compared with the conventional FID, shows an enhanced response for nitrogen compounds, too (10). Increased response for phosphorus was 12,000 fold, for nitrogen about 150 fold. With an unknown response, phosphorus can be distinguished from nitrogen by comparing the thermionic and conventional flame responses. For example, a compound with 10% phosphorus could not be mistaken for one with even 50% nitrogen. The chromatograms, Fig. 2–5, especially of the water-soluble fractions of tobacco extracts, show a great number of peaks from compounds of unknown composition. All chromatograms show the same characteristic sequence of peaks, like "fingerprints", with only slight differences in peak heights.

The recently developed new silicone mixed phase, QF-1 + OV-17, shows great potential for pesticide analysis (11). This packing separates a wider range of

Table 3. Results for pesticide residues in flue-cured tobacco.

Field treatment, Northern Germany 1967

Application			Analysis		
Formulation Active ingredients	Type[a]	Dosage[b] (g)	Pesticide in tobacco (ppm)[c]	Green leaf	Flue-cured leaf
Aldrin	D., soil	37.5	Aldrin	0.06	0.21
			Dieldrin	0.65	0.52
Aldrin	EC., soil	180	Aldrin		0.07
			Dieldrin		0.43
Diazinon	Sp., EC.	2.3	Diazinon		0.058
Dichlorvos (DDVP)	Sp., EC.	9.0	Dichlorvos		Not detectable[d]
Dimethoate	Sp., EC.	4.8	Dimethoate		Not detectable
Trichlorofon	Sp., EC.	4.5	Trichlorofon		Not detectable
Parathion	D.	9.0	Parathion		Not detectable
Parathion	Sp., EC.	2.3	Parathion		0.01
DDT + lindane	Sp., EC.	9.0	Lindane		0.47
			DDE + o, p-TDE		0.67
			o, p-DDT + p, p'-TDE		2.0
			p, p'-DDT		21.4
DDT + lindane	D.	13.0	Lindane		0.31
			DDE + o, p-TDE		0.36
			o, p-DDT + p, p'-TDE		4.5
			p, p'-DDT		14.0
Guthion, ethyl	Sp., WP.	4.5	Guthion, ethyl		Not detectable
Lindane	Sp., EC.	2.3	Lindane		0.31
Lindane	D.	2.4	Lindane		0.41
Malathion	Sp., EC.	15.0	Malathion		0.06
Metasystox R	Sp., EC.	3.8	Metasystox R		Not detectable
Carbaryl	Sp., WP.	6.8	Carbaryl	86.5	2.6
			Naphthol		Present (+)
Thiodan	D.	3.1	α-Thiodan		0.44
Thiodan	Sp., EC.	9.0	α-Thiodan		0.34
Unden (Aprocarb)	Sp., WP.	9.0	Unden	2.3	Not detectable

a) D = dust, G = granular, Sp = spray, EC = emulsion concentrate, WP = wettable powder
b) 2 applications in 3 x normal dosage in g 100% active material per 100 plants = ca. 3 kg flue-cured tobacco
c) Dry weight basis
d) Less than 0.01 ppm

chlorinated as well as phosphated pesticides than any other packing known (Fig. 1, 6, 7).

The separation of 12 chlorinated pesticides is achieved in one run. That means that the previous separation of chlorinated pesticides on a Florisil column is omitted. There is no interference from dieldrin with p,p'-DDE, o,p'-DDT with p,p'-TDE, and endrin with p,p'-DDE or p,p'-TDE.

The results for the field application of 14 different pesticides on tobacco show that there are nil or negligible residues from 8 organophosphorus and 1 carbamate pesticides (Unden); carbaryl and thiodan are well below the legal tolerances. Only the treatment of tobacco with lindane, DDT and aldrin (soil treatment) results in residues above the limits set (Table 3).

CONCLUSIONS

The results of this study show the following:

(1) The extraction and cleanup method originally developed for the determination of chlorinated pesticides was successfully applied to eight organophosphorus pesticides on tobacco. Cleanup was sufficient for both the microcoulometric and thermionic detection systems.

(2) The average recoveries of pesticides added were for organophosphorus, 80% organochlorine, 91%, and for carbamate pesticides, 78%.

(3) From the results of this study it is recommended that the less persistent phosphate and carbamate pesticides be used instead of chlorinated compounds.

SUMMARY

A method has been developed that permits the qualitative and quantitative determination of a number of chlorinated and phosphate insecticide compounds on tobacco. Extraction with acetonitrile, partitioning into petroleum ether, cleanup on a Florisil column are followed by gas chromatography and determination with the microcoulometric system (halogen) and the thermionic detector (phosphorus). A procedure is presented for the extraction and determination of the

thiophosphates and water-soluble metabolites remaining in the acetonitrile-water layer after petroleum ether partitioning. Carbamate insecticides are extracted with methylene chloride, partitioned into water, separated by thin-layer chromatography, identified and estimated by colorimetry.

Recoveries of the compounds (diazinon, parathion, Guthion, malathion, dimethoate) from tobacco fortified just prior to extraction ranged from 74 to 104%; DDVP, Dipterex, Metasystox R 50 to 78%, aldrin, DDT, lindane, thiodan 88 to 101%, carbaryl, Unden 75 to 82%, at levels of 0.5 ppm.

The results for the field application of these 14 different insecticides on tobacco are presented. They show that there are nil or negligible residues from 8 organophosphorus and 1 carbamate insecticides (Unden); carbaryl and thiodan are well below the legal tolerances. Only the treatment of tobacco with lindane, DDT and aldrin (soil treatment) results in residues above the limit set.

ZUSAMMENFASSUNG

Es wurde eine Methode entwickelt, die eine qualitative und quantitative Bestimmung mehrerer chlor- und phosphorhaltiger Insektizide auf Tabak gestattet. Nach der Extraktion mit Acetonitril erfolgt eine Verteilung in Petroläther und eine Reinigung über Florisil. Der so gereinigte Extrakt wird gaschromatographisch getrennt. Die Insektizide werden mit dem Microcoulometer (Halogen) und dem Thermionic-Detektor (Phosphor) bestimmt. Weiterhin wird ein Verfahren beschrieben zur Extraktion und Bestimmung der Thiophosphate und wasserlöslichen Metaboliten, die nach der Verteilung in Petroläther im Acetonitril-Wasser-Gemisch zurückbleiben. Carbamat-Insektizide werden mit Methylenchlorid extrahiert, in Wasser verteilt und durch Dünnschicht-Chromatographie getrennt. Die Identifizierung und Bestimmung erfolgt kolorimetrisch.

Die Ausbeute der einzelnen Insektizide, bestimmt an Tabak, dem vor der Extraktion 0,5 ppm zugesetzt wurden, beträgt 74 bis 104% für Diazinon, Parathion, Guthion, Malathion, Dimethoat; 50 bis 78% für DDVP, Dipterex, Metasystox R, 88 bis 101% für Aldrin, DDT, Lindan, Thiodan und 75 bis 82% für Carbaryl, Unden.

Es wird über die Ergebnisse eines Feldversuches berichtet, in dem Tabak mit diesen 14 Insektiziden behandelt wurde. Die Ergebnisse zeigen, daß keine (< 0,01 ppm) oder fast keine (< 0,07 ppm) Rückstände von 8 Organophosphor-Insektiziden und einem Carbamat-Insektizid nachzuweisen sind. Carbaryl und Thiodan befinden sich noch unter der Toleranzgrenze. Nur aus der Behandlung des Tabaks mit den Organochlor-Insektiziden Lindan, DDT und Aldrin (Bodenbehandlung) resultieren Rückstände, die weit über den gesetzlichen Toleranzen liegen.

RESUME

On a mis une méthode au point permettant la détermination qualitative et quantitative de l'influence d'insecticides chlorés et phosphatés sur le tabac. Après extraction par acétonitrile on procède à la séparation dans l'éther de pétrole et à une purification sur Florisil. L'extrait purifié est ensuite séparé par chromatographie en phase gazeuse, et on détermine les insecticides par système micro-coulométrique (à halogène) et détecteur thermïonique (au phosphore). On présente un procédé d'extraction et de détermination des thiophosphates et des métabolites hydrosolubles restant dans la couche acétonitrile-eau après partition dans l'éther de pétrole. Les insecticides carbamates sont extraits par chlorure de méthylène, dispersés dans l'eau et séparés par chromatographie sur couche mince. L'identification et la détermination quantitative se font par colorimétrie.

Suit le rapport d'une expérience sur le terrain pendant laquelle le tabac est traité par les 14 insecticides décrits ci-dessus. Les résultats prouvent qu'on ne peut pas (< 0,01 ppm) ou presque pas (< 0,07 ppm) déceler des résidus des 8 insecticides organophosphoriques et d'un insecticide à base de carbamate. Avec le carbaril et le thiodan on se trouve en dessous des limites de tolérance. Seul le traitement du tabac par les insecticides organochlorés, lindane, DDT et aldrine (traitement du sol) donne lieu à des résidus qui dépassent de loin les quantités tolérées par la loi.

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The authors' address:

B·A·T Cigaretten-Fabriken GmbH,
Forschung und Entwicklung,
2 Hamburg 36, Esplanade 39.