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Review

Chromatographic techniques in the analysis of organochlorine pesticide residues

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Abstract

The review briefly covers the chromatographic techniques used in the analysis of organochlorine pesticide residues. The organochlorines ranging from DDT, HCH, the cyclodiene group and the polychloroterpene group have been covered. It endeavours to examine the existing methodologies and techniques including residue extraction, clean-up, chromatographic procedures involved in clean-up and determination and quantification of organochlorine residues by gas liquid chromatography from different substrates like food commodities, crops, soil and water.

Keywords: Reviews; Environmental analysis; Milk; Food analysis; Water analysis; Soil; Sediments; Sample preparation; Organochlorine compounds; Pesticides

Contents

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1. Introduction

The principal sources of pesticides in crops, soil, water and food commodities, are (i) carry-over from insecticide application to soil or to growing crops, (ii) leaching of pesticides (herbicides) or insecticides into ground water, (iii) drift of the pesticides from adjacent field, (iv) translocation of soil applied pesticide into growing crops, (v) disposal of pesticides in streams, rivers and lakes and (vi) effluents of pesticide industry in rivers and streams, and into soil which may be translocated in crops.

The determination of pesticide residues in food of unknown spray history is a formidable task, because it involves the identification and quantification of several hundred possible single compounds or combinations in the presence of complex matrices. The conventional analytical methods commonly used are time consuming, labour-intensive and costly in terms of expensive solvents and absorbents. This is because the pesticides present at parts per million (ppm) levels have to be separated from the food matrix (sample clean-up) so that they can be identified and measured by gas or liquid chromatography.

The present review compiles the extraction, clean-up and the gas chromatographic determination and quantification of organochlorine insecticides. Organochlorines covered in this review are the DDT group, HCH and its isomers, the cyclodiene group—endosulfan, aldrin, chlordane, heptachlor, endrin, dieldrin and mirex, and the polychloroterpene group-Toxaphene. Most of these organochlorine pesticides are metabolised after their application on different substrates, like in crop plants, soil and water, the parent insecticide may transform or degrade to a compound which may or may not be toxic. The quantification of the total pesticide residues involves the estimation of the parent pesticide and its toxic metabolites, like for total DDT, *p,p* and *o,p* isomers of DDT, *p,p* and *o,p* isomers of DDE and *p,p* and *o,p* isomers of TDE. The last two being the metabolites of DDT. Similarly for HCH, α-, β-, γ- and δ-HCH need to be determined. Likewise for endosulfan, α-endosulfan, β-endosulfan and endosulfan sulfate give the total picture. Endosulfan lactone, diol and ether are non toxic and therefore may not be quantified [1].

The basic units of pesticide residue analysis are:

1. Sampling.
2. Extraction of pesticide from the sample.
3. Clean-up/derivatisation of residues from the sample.
4. Identification and quantitative determination of the pesticide residue.

1.1. Validation

A quantitative analytical procedure based on chromatographic technique is valid only if each of the following five conditions is satisfied (i) extraction is complete, (ii) clean-up is effective and the recovery quantitative, (iii) chromatographic resolution is adequate, (iv) detection of the insecticides and measurement of the response of the detector are sensitive, specific and reproducible and (v) comparison of the unknown calibration standards is reproducible. In most of the methods the commodity is spiked with the pesticide prior to extraction and the percentage recoveries tested, such an approach may prove the validity of the clean-up method but it does not evaluate satisfactorily the effectiveness of the extraction procedure. In order to do this it is necessary to ensure that the maximum amount of pesticide can be extracted from grains containing

aged residues [2–4]. This is because pesticides that have been in contact with the commodity for some time may interact with it and as a result be more difficult to extract than pesticides have been applied (or spiked) for necessary studies. Attempts to distinguish the available and total pesticide levels have involved the use of radiolabelled pesticides to determine the solvent extractable material [5] in the commodity and the bound pesticide is subjected to solvent extraction, followed by acid digestion [6].

For good results, each step requires that studies on each type of sample to be analysed be carried out, because procedures involving extraction, clean-up, separation and quantification are different and specific for each substrate, e.g., quantification for maize corn cobs cannot be assumed to be appropriate for maize flour.

1.2. Extraction

Organochlorine residues may be recovered from agricultural or other biological samples by exhaustive extraction with a variety of organic solvents for example, hexane, ether, acetone, alcohols and their combinations.

The methodology varies from simply standing (keeping) the commodity in a solvent overnight [3,7] to a more exhaustive technique such as Soxhlet extraction [8].

Sample material with a low-fat and wax content can be extracted directly, separated and analyzed by gas chromatography. Extracts of many samples may contain large amounts of fats and pigments which will remain after the extract has been evaporated. This will result in low sensitivity, poor response and may even damage the column packing.

1.3. Non fatty foods

A rapid and simple procedure for determining the chlorinated organic pesticides in non-fatty food consists of extraction with acetonitrile and clean-up by column chromatography [9].

The sample, e.g., celery, cabbage, peaches or pears, is chopped and mixed in a blender for 5 min with benzene–isopropanol (2:1).

Isopropanol layer is diluted by the addition of water followed by partitioning into benzene. The benzene concentrate is then subjected to clean-up [10]. As use of benzene is disallowed, hexane–isopropanol mixture is used [11].

1.4. Milk and milk products

The methodology for the extraction of milk involves extraction with hexane [12], chloroform–methanol [13], diethyl ether–petroleum ether [14], acetone–hexane [15,16], gel permeation chromatography [17], or homogenised with hexane–acetonitrile–ethanol (20:5:1) [18] or with ethyl acetate–methanol–acetone (1:2:2) [19]. In most of these samples the pesticides extracted were isomers of HCH, aldrin, oxychlordane, chlordane, transnonachlor, endrin, dieldrin, heptachlor, isomers of DDT, heptachlor and its epoxides and mirex. The solvents used are polar enough to extract most of the organochlorine pesticides present in milk and milk products:

1.5. Vegetables

Vegetable samples containing organochlorines are homogenised with acetone [20,11], acetonitrile [21,22] and aqueous acetone [23]. The samples are also steam distilled [24] for the extraction of multiresidue organochlorine insecticides.

1.6. Cereals, pulses and animal feed

Cereal products, pulses and animal feed are generally ground with acetone–methanol [25,26] or extracted in a Soxhlet with acetone–hexane [27–29], Soxhlet with cold hexane or hexane–methylene chloride in cold or in a Waring blender with acetone [16,30].

1.7. Water

The usual method for extraction from water is partitioning into an organic solvent to extract the

pesticides. Besides the common methods, like liquid–liquid partitioning [31] some procedures involve extraction of acidified water with hexane [32]. Solid-phase extraction [33] and shaking with an organic solvent [34] and use of Sep pak cartridges packed with CN bonded porus silica [35], are some of the other methods used.

Solid-phase extraction (SPE) of organochlorine residues [26,36,37] provides an alternative to the traditional liquid–liquid extraction based methods. SPE cartridge containing octadecyl groups chemically bonded to silica is first conditioned with solvent, then ground water is passed through it, pesticides retained on the extraction medium are later eluted with a small amount of non-polar solvent.

SPE was found to be more economical, it required fewer operational steps while providing acceptable reproducibility and analyte recoveries.

1.8. Soil and sediment

Soxhlet extraction [37], steam distillation with sulphuric acid–potassium dichromate [38] are the different methods employed for the extraction of multi-residue organochlorines from sediment. Other procedures involve shaking with boron trifluoride in methanol followed by acetone–water extraction [39], with acetonitrile–acetic acid mixture [40].

1.9. Animal fresh and tissues

The flesh and tissues of animals require special care during extraction. They are usually homogenised with diethyl ether [41], ground with hexane [40,42–44], homogenised under liquid nitrogen [45], acetone–hexane extraction [44], Soxhlet under cold and warm conditions [30], Soxhlet extraction with pentane–methylene chloride [46] or with acetonitrile [46].

In all the extractions, especially for multi-residue type, the use of high purity reagents and solvents helped to minimize interference problems. The impurity levels of all solvents and reagents used did not exceed an acceptable blank when subjected to the complete procedure without the sample [33].

1.10. Clean-up of organochlorine pesticide residues extracts from various commodities

There are a large number of clean-up methods available for the organochlorine insecticides.

Clean-up is an essential step for accurate determination of pesticide residues, but many conventional methods are costly and time consuming. Clean-up techniques currently include liquid–liquid partitioning [11,33], open column chromatography [47], thin-layer chromatography [1], steam distillation [48] and low temperature precipitation [49–51]. Of the several new approaches successfully used in modern methodologies use of small columns are the most notable [52].

1.11. Liquid–liquid partitioning

Liquid–liquid partitioning is then frequently used to further the clean-up. Hexane extracts may thus be partitioned with acetonitrile in which organochlorine insecticides are more soluble than most co-extracted lipid materials, the lipids remain largely in the hexane phase.

Partitioning of an extract between immiscible solvent is a simple and mild clean-up method is used. The use has been facilitated by the Beroza P values [50].

1.12. Column clean-up

Commonly used methods for clean-up of raw extracts of samples are chromatographic columns filled with adsorbent [51–56] such as Florisil, alumina. Kieselgel, silica gel, mixtures of alumina and silica gel, gel permeation on Bio-Beads SX3, XAD-2 and macroreticular resin, a mixture of MgO and cellulose graphitized carbon black, sweep co-distillation, cleansol and C_{18} cartridge. Some of these methods are expensive as the cost of adsorbent constitutes 50% of the entire cost of analysis.

Considering that several organochlorines are present together, a crude separation into groups may be effected using various types of column chromatography. For example, aldrin is eluted while dieldrin and endrin are retained on a florisil column, when

eluted with a mixture of ether–light petroleum (1:15) [1].

Similarly, dicofol can be separated from a mixture of DDD, *p,p*-DDT, *o,p*-DDT, DDE, methoxychlor, perthane, chlordane, heptachlor, its epoxide and toxaphene, by elution with ether-benzene or a mixture of benzene–acetonitrile (9:1) [1]. Groups of compounds obtained in this manner may further be separated by paper chromatography [57].

1.13. Clean-up by thin-layer chromatography

Sample clean-up by thin-layer chromatography is also used successfully as one stage clean-up in pesticide residue analysis. Thin layers of aluminum oxide (G) or silica gel (G) are used as the stationary phase [58,59].

1.14. Charcoal clean-up

Graphitized charcoal has been used successfully in the clean-up of organochlorine compounds especially endosulfan, without the use of column chromatography [13,16,27,29,60].

There is a clear trend in the realm of clean-up and derivatization, the simplification of the clean-up procedures by utilizing both material and other resources [61].

1.15. Sulphuric acid clean-up

Treatment of extracts with sulfuric acid is another way of clean-up. It is used especially for removing fats. The earliest clean-up method reported in pulses and oilseeds, by sulphuric acid [26] treatment of the hexane extract used, has a wide application. It is used for the determination of HCH from milk, pulses and oil seeds [11,20].

1.16. Bound residues

To release bound pesticides, however, oxidation with chromium trioxide in acetic acid was used earlier [62]. Now sulphuric acid is being used [63].

1.17. Paper chromatography

Organochlorines are highly lipid soluble, reversed-phase systems are used in which a chromatographic paper is impregnated from 1% solution in ether, with refined soybean oil, vaseline or liquid paraffin as stationary phase. The mobile phase being acetone–water (3:1), methanol–water (85:15), pyridine–water (3:2) or other aqueous organic solvents [1]. The partitioning of the insecticides depends on the separation between non-polar stationary phase and the mobile polar phase so that the less polar aldrin run more slowly than more polar dieldrin. The most common visualising methods involve spraying the chromatogram with silver nitrate solution in ethanol and then visualising in the UV-light, giving distinct reddish purple spots on a white background [64].

1.18. Sep-Pak cartridge

Sep-Pak cartridge is very suitable for extraction [34,43] and common clean-up procedures can be performed in a short time, as compared to charcoal clean-up [60] in endosulfan residues. It is commercially available and has been used [43] for the rapid determination of eight chlorinated pesticides commonly found in environmental aqueous samples. Advantages of Sep-Pak clean-up is demonstrated by Bicchi et al. [61] during estimation of various insecticides using a Florisil Cartridge.

1.19. Gel permeation chromatography

Gel permeation chromatography (GPC) is the method of choice for the rapid clean-up [14] of biological extracts especially from high fat samples to determine pesticide residues [65]. Commercially available florisil cartridges [34] are used to clean adipose tissue extract containing aldrin and HCH. Special care is needed for the determination of pesticides from blood samples as the sample size is small. Heparinized blood is brought onto an Extrelut-1 column covered with glass wool. The column is eluted with hexane diluted with a mixture of ethylacetate–cyclohexane concentrated and then taken for gel chromatography over a mini-silica gel column [66].

Most of the samples can be analysed by gas chromatography without additional clean-up. The solvent from GPC pesticide fraction can be collected and evaporated automatically to dryness. A measured volume of diluting solvent in the evaporation chamber mixed with a stream of air or nitrogen and is ready to injection into a gas or liquid chromatograph.

1.20. Automated clean-up

Automated systems are commercially available for the chromatography steps but not for the clean-up steps. A system intended for rapid screening of crop samples has been developed [21]. It consists of two parts, a solvent partitioning module and a column chromatography module. Both of these systems have been evaluated separately [67] for precision and accuracy.

2. Determination by gas–liquid chromatography

Gas–liquid chromatography (GLC) is one of the most important analytical techniques used in pesticide residue analysis. Two advantages are its sensitive and specific detector systems and ability to separate mixture of analytes on the column. Until recently GLC of pesticides was conducted using packed columns containing a variety of liquid phases and supports [68]. The wide range of volatilities and specific responses of pesticides necessitated numerous analytical conditions in order to chromatograph several classes of pesticides in a single sample. Many pesticides are too polar or do not respond on a packed column while others are thermally labile and degrade in the chromatographic determination.

An electron capture is equipped to determine low amounts of residues from small samples of various substrates. Although total reliance should not be placed on the analytical data obtained from GLC for the identification of a pesticide residue, there is need to compare with other methods like GC–MS and GLC using alternate column packings.

Chromatographic columns fabricated from Pyrex tubing have replaced metal columns to a large extent for pesticide residue analysis. Tubing sizes are generally 6 feet (1 foot=0.3048 m) long with 4.5 mm I.D. or 4–5 feet long and 1/8 inch O.D. (3.2 mm) [69]. U-shaped tubes are more common than coiled columns [69].

2.1. Solid supports

Among the solid supports used in GLC, Chromosorb P and W are commonly used in pesticide analysis.

2.2. Stationary liquid phase

There is no universal type of gas chromatographic column for pesticide analysis.

The capillary columns in gas chromatography have been applied to the analysis of environmental samples for high resolution or separation of isomers of many pollutants. These columns are wall coated with a thin film of liquid phase which produces a large number of theoretical plates so that high resolution of analytes is possible, they provide an inert surface, preventing column decomposition or adsorption and allow temperature programming to produce sharp fundamental peaks without excessive baseline desorption and retention times that are not too long.

Table 1 lists the commonly used stationary phases.

The recent advance is the use is of dual-column dual-detector gas chromatographic determination [69] for organochlorines, two dimensional capillary gas chromatography with three detectors in parallel [70]. The carrier gas used is usually nitrogen, helium or argon–methane mixture.

The use of aldrin as a reference peak and a complement of mixed phase column either the 20M, the 2OSE or OV-210 column represents a useful chromatographic tool for dual column analysis of pesticide residue. 78 pesticides and their metabolites were compared on four different types of ultra bond columns [71]. A few other commonly used column packing materials are SE-54+DB-17 [72] and DC-200+QF-1 [73].

2.3. Use of internal standards

Retention times are difficult to reproduce due to the inevitably slight changes in experimental con-

Table 1
Summary of gas chromatographic methods for the determination of organochlorines using electron capture detector

Sample No.	Commodity	Columns stationary phase (mesh)	Column temperature (°C)	Reference
1	Human milk	Glass 1.5% OV-17+1.95% OV-210 on Chromosorb W (100–120) glass 5% QF 1 on Chromosorb Q (80–100)	–	[12]
2	Human milk	1.3% SF-96+5.3% QF-1 on Supelcoport 5% OV-101 on Chromosorb WDMCS AW 3% OV-101 on Chromosorb W HP 1.5% OV-17+1.95% OV-210 on Gas Chrom Q	–	[13]
3	Human milk	Capillary, methylsilicone gum	100–260	[14]
4	Dairy milk Baby milk Food	Glass, 0.5% OV-17+1.95% OV-210 on Chromosorb W (80–100)	175–220	[15,16]
5	Butter fat	Glass 5% OV-101 on Chromosorb Glass 5% OV-101+3% OV-225 on Chromosorb W HP (80–100)	200 150	[17]
6	Cows milk	Capillary column	190–230	[18]
7	Milk	Fused-silica, SE5214	80–250	[19]
8	Potato Carrot	Glass 10% OV-101+15% OV-210 on Chromosorb W HP (80–100)	160–200	[19]
9	Vegetables	Glass 3% OV-25 on Chromosorb W HP (80–100)	220	[11]
10	Tomato	Glass 3% OV-25 on Chromosorb W (80–100)	220	[21]
11	Fruits and vegetables	Column HP-5	–	[22]
12	Pulses	Glass 1.5% OV-17+1.95% on Chromosorb W HP	175–200	[27]
13	Pulses	Glass 1.5% OV-17+1.95% OV-210 on chromosorb W HP	175	[27]
14	Pulses	Glass 1.5% OV-17+1.95% OV-210 on Chromosorb W HP (80–100) Megabore, methyl silicone gum	210	[29]
15	River water	Glass 1.5% SP 2250+1.95% SP 2401 on Supelcoport (100–120)	180–200	[32]
16	Natural water	Glass 1O% OV-101+15%OV-210 on Chromosorb W HP (80–100)	200	[33]
17	Drinking water	Glass 1.5% OV-17+1.95% on Chromosorb W (100–120) Glass 5% OV-17 on Chromosorb W (100–120)	210	[31]
18	Ground water	Capillary	80–290	[37]
19	Sediment	Fused-silica. DB-5	30–250	[39]
20	Sand	Glass 1.5% OV-17+2% OV-202 on Chromosorb Q (100–120)	–	[41]
21	Animal tissues, fat	1.5% SP-2250+1.95% SP on Supelcoport (100–120)	210	[42]
22	Human adipose	Fused-silica capillary	80–280	[42]
23	Human adipose	Glass 2.5%OV-17+1.95 OV-210 on Supelcoport (100–200) Fused-silica capillary	–	[44]
24	Fish oils	Capillary DB-5	–	[46]
25	Vegetables	Glass 5%OV-101 on Chromosorb W HP (80–100)	200	[67]
26	Ground water	Glass 1.5%OV-17+2%QF-1 on Chromosorb W AW DMCS (80–100)	–	[69]
27	Birds Eggs	Glass OV-210 on Chromosorb W HP(100–120) Glass OV-225 on Chromosorb W HP (100–120)	210 220	[76]
28	Chamois birds	Fused-silica column 5PB-608 Fused-silica column, OV73	150–280 150–280	[77]
29	Cat fish	Glass 1.5% OV-17+1.95% OV-210 on Chromosorb Q (80–100)	200	[78]
30	Bovine adipose tissue	Capillary column	60–310	[44]
31	Human blood	Glass 1.5% OV-17+1.95% OV-210 on Chromosorb Q (80–100)	185	[79]
32	Blood serum	Glass 6% SE-30+4% OV-210 on Supelcoport (100–120) Glass 1.5% SP 2250+1.95% SP 2401	–	[80]
33	Waste water	Glass 1.5% OV-17+1.95 QF-1 on Chromosorb W HP (80–100)	210	[81]
34	Atlantic ocean water	Glass 5% SE-30 on Chromosorb W AW DMCS Glass 5% XE-60	200	[82]
35	Sea water	Glass 8% OV-17 on Chromosorb W HP	–	[83]
36	Water, air	Fused capillary dual column dual detector DB-5 and DB-17	–	[69]
37	Surface water	Fused-silica column DB-5	–	[84]
38	Sediment	Capillary	100–260	[37]
40	Sediment	Fused-silica DB-5	30–250	[38]
41	Soil	Glass 1.5% OV-17+1.95% QF-1 on Chromosorb Q (80–100)	180	[41]
42	Arable soil	Capillary OV-17 Capillary OB-1701 Capillary SE-52	90–274	[85]
43	Soil Glass	1.5% OV-17+1.95% QF-1 on Chromosorb Q (80–100)	180	[41]
44	Sediment, water, fish	Glass 4% SE-30+6% QF-1 on Chromosorb W (80–100)	200	[86]
45	Feed mixture	Glass 1.5% OV-17+1.95% OV-210 on Chromosorb Q (80–100)	185	[87]

Table 2
Retention times of some organochlorines before and after reaction

Pesticides	Hydrobromic-acid–Acetic anhydride		KOH
	Untreated	Hot	
Aldrin	1.0	3.2	1.0
Dieldrin	1.9	4.6	1.9
Endrin	2.4	5.9	2.4
Heptachlor	0.8	1.1	0.8
BHC	0.5	0.5	–
p,p'-DDT	3.3	3.3	1.9

ditions, hence retention times are best expressed as values related to the retention time of a standard reference compound included in the same chromatogram. Aldrin can be used as an internal standard for organochlorines as it has an intermediate retention time and the relative retention time of a compound can be obtained by retention time of unknown divided by that of the standard [74]. The internal standard is still used for minimising error arising from other contaminants [75].

2.4. Confirmation

A substance may be converted by a simple chemical reaction into a derivative with a different retention time. The change in retention time after the conversion, together with the original retention time provides confirmation of the identity of the substance. Dieldrin and DDE when present in a mixture gives one mixed peak but when the mixture is treated with hydrogen bromide at room temperature dieldrin forms a single derivative having a different retention time, (Table 2) well separated from the unchanged DDE [75]. Chemical derivatization serves as a method for the identification and confirmation of pesticides residues. The recent trend is the use of GG–MS for the multi-residue determination. Sufficient literature on organochlorines is not yet available, more data needs to be generated in this area.

3. Conclusion

Future studies of analytical methodology should concentrate on these aspects that are concerned with new application of capillary column–gas liquid chromatography and simplified clean-up procedures for multi-residue methods. Ideally each step of the analytical procedure needs to be assessed on the individual products.

Capillary gas chromatography offers many advantages to the pesticide residue analyst, high resolution, reproducibility of retention time for multi-residue studies. Pesticides are identified as trace solely on the basis of retention times. Hence untreated sample extracts are important as reference materials. Validation of residue methodology is essential for achieving accurate data. Also significant is the confirmation of pesticide residues by conducting the estimation on alternate column packings and the use of GC–MS in multi-residue determination.

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