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Review

Official multiresidue methods of pesticide analysis in vegetables, fruits and soil

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Abstract

Many different types of pesticides are used extensively on fruits and vegetables. The present contribution represents an overview of the multiresidue methods of analysis of the most widely used pesticides.

Keywords: Vegetables; Reviews; Fruits; Soil; Multiresidue methods; Pesticides

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1. Introduction

The development of multiresidue methods represents a relatively new trend in pesticide residue analysis and this review referred mainly to the official multiresidue methods. During the past few decades, the clean-up procedures and the tools for analysis have been greatly improved. General methods of pesticide residue analysis were recently reviewed by some authors [1,2].

The use of solid-phase extraction columns or disks and the application of gel permeation chromatography significantly simplify the clean-up procedures.

Because of the environmental concerns, analytical procedures which do not require the use of organochlorine solvents such as dichloromethane have been introduced.

The purpose of this contribution is to present a review on the multiresidual methods using gas

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chromatography (GC), thin-layer chromatography (TLC), and high-performance liquid chromatography (HPLC).

The multiresidual methods applied to a single matrix, such as wine [3,4], potable water [5–8], rice [9,10], etc. are not included in this review.

A few methods for resolution of optical isomers using standard reagents have been reported. However, they are beyond the scope of this review [11,12].

2. Analytical procedures

2.1. Extraction

The sequence of steps in the analysis are the extraction, clean-up, and determination. Although the extraction procedures are generally performed by using a solvent, the supercritical fluid extraction (SFE) methods have been noticed and examined for the multiresidue method of pesticides [13,14]. The SFE was expected to be a useful technique for the analysis of pesticide residues in food and environmental samples. Consequently, the SFE methods have been applied to the determination of the pesticide residues in foods, such as SFE of chlorpyrifos methyl in wheat [15], a polar drug in animal foods [16], 2,4-dichlorophenol in food crop tissues [17], three carbamate pesticides (bendiocarb, methiocarb and carbaryl) in chicken muscle [18], fluazifop-P-butyl and its major metabolite, fluazifop-P in onion [19], analysis of organophosphrus pesticides in rice by an atomic emission detector [20], organochlorine, organophosphorus and organonitrogen pesticides in grains [21], heptachlor, dieldrin and endrin in poultry tissues [22].

More references on SFE are presented as follows: the direct coupling method of SFE and supercritical fluid chromatography (SFC) [23], translation and optimization of SFE methods to commercial instrumentation [24], SFE and GC/ion trap mass spectrometry of seven pentachloronitrobenzene pesticides in vegetables [25].

Recently, a supercritical fluid extraction (SFE) method in environmental samples was reviewed by Janda et al. [26]

For the initial multiresidual analysis, acetonitrile was used as the extraction solvent [27].

Luke et al. used acetone instead of acetonitrile as the extraction solvent in the multiresidual method and it has become a major extraction solvent. Acetone (b.p. 56.5 °C) is more volatile than acetonitrile (b.p. 81.6 °C), and easier to concentrate and remove than acetonitrile [28].

Acetone–water (2:1) was also used as the extraction solvent [29].

Acetone has been used in a Swedish study monitoring pesticide residues since 1981 [30]. However, recent tests with ethyl acetate as the solvent gave promising results.

Ethyl acetate and hexane–acetone (8:2) were investigated as the extraction solvents to eliminate the liquid–liquid partition procedure. While ethyl acetate gave lower recoveries for some pesticides, hexane–acetone (8:2) is a possible alternative solvent to acetone [31].

Acetonitrile has two significant advantages over other solvents in trace pesticide residue analysis. One advantage is that acetonitrile exhibits a very strong dissolving ability and is readily miscible with water. The other advantage of acetonitrile as the initial extraction solvent is that acetonitrile solution of pesticides can be separated from water by a simple salting out procedure. A two-phase azeotrope of acetonitrile and hexane can easily be concentrated and has a boiling point of 52 °C [32].

Thus, the sample concentration is relatively simpler in this case than with an aqueous alcohol or aqueous acetone solution.

2.2. Clean-up

In the early 1970s, methamidophos, a new highly polar pesticide, was introduced and found not to be detected by the recommended analytical method [33].

Rapid multiresidue procedure for 31 pesticides utilizing the minimal clean-up necessary for GC was presented. The samples were extracted with acetone and partitioned with light petroleum–dichloromethane to remove water. The organophosphorus and organonitrogen compounds were quantitated by GC using a KCl thermionic detector. A Florisil clean-up of the extract was performed for the determination of

organochlorine compounds by GC using electron-capture detection (ECD) [13].

The extraction procedures for the multiresidue method are presented in Table 1.

Almost the same clean-up in the multiresidue procedure was also applied to the separation of 79 pesticides. The procedure was simple and shorter compared with the former method due to the elimination of the Florisil clean-up procedure. The extract was analyzed by GC using conductivity detection [electrolytic (ELCD) or Hall electrolytic (HECD)] for organohalogen, organonitrogen and organosulfur pesticides or flame-photometric detection (FPD) for organophosphorus pesticides [34].

Although the specificity of ELCD is generally superior to ECD for the determination of organohalogen pesticides, the sensitivity of ELCD is inferior to ECD. The clean-up procedure is closely related to the method of measurement [35].

Another modified multiresidue procedure was used for low moisture and nonfatty products [36].

The pesticides in the ground sample were extracted with water–acetone (35:65), and the subsequent work-up was according to Luke et al. [34].

The levels and incidences of pesticide residues in foods and animal feeds in 19 851 samples were determined by the multiresidue analysis during a 5 year period from 1982 to 1986 [37].

One hundred and ten pesticides were detected by a rapid multiresidue screening method. Samples were extracted, analyzed and evaluated within 6.5 h after they had been received. The pesticides in the sample were extracted with acetonitrile, filtered, and the filtrate was shaken with brine. The acetonitrile layer was separated, and the samples of the acetonitrile extract were concentrated to near dryness under a stream of nitrogen, and dissolved, in benzene, acetone and methanol–water (1:3), respectively. The solutions were used to analyze for organochlorine by GC–ECD, for organophosphate by GC–FPD, and for carbamate by HPLC, respectively [38].

A coupled GC–mass spectrometric (MS) multiresidue screening method was used to determine 143 pesticides. Samples were extracted with acetonitrile and filtered. Then the filtrate was separated into two phases, the acetonitrile layer and the aqueous layer, by addition of brine. A volume of the acetonitrile extract was analyzed by GC–MS [39].

More than 150 pesticides in fresh fruits and vegetables for screening were determined by a multiresidue chromatographic technique. Samples were homogenized with acetonitrile, the resulting aqueous acetonitrile extract was filtered and cleaned up via a reversed-phase solid-phase extraction apparatus. The pH of the filtrate was adjusted to neutral by a buffer solution and partitioned. The acetonitrile layer was dried, concentrated, and then dissolved in acetone. A part of the effluent was used to analyze for organochlorine and organophosphorus pesticides by GC, and the remaining effluent was further cleaned up with aminopropyl-bonded silica phase extraction cartridge, and analyzed by HPLC for carbamate pesticides [32].

A new multiresidue screening method was also described. Samples were extracted with acetone and filtered. The filtrate was passed through a Sep-Pak C_{18} cartridge, and the cartridge was washed with water–acetone (30:70). Acetone and dichloromethane were added to the combined eluates and partitioned. The organic layer was dried and dissolved in acetone and petroleum ether. The solution was filtered through the connected ion-exchange solid-phase extraction cartridges (Accell Plus QMA and Sep-Pak NH_2 in tandem). The effluent was analyzed by GC–MS (ion trap, chemical ionization) [40].

The first use of gel permeation chromatography (GPC) for pesticides was introduced by Stalling et al. [41].

A clean-up procedure was used to determine different pesticides in foods and fruits using a multiresidue method, with a combination of Luke's method and GPC. Pesticides were extracted with acetone–water from samples with a different water content (acetone–water ratio depended on the water content in the sample). The filtrate was partitioned with dichloromethane after the addition of brine. The organic phase was dried, concentrated, and then dissolved in ethyl acetate–cyclohexane. The solution was cleaned up by gel permeation chromatography on Bio-Beads SX-3 (polystyrene gel beads) with cyclohexane–ethyl acetate (1:1). Organophosphate and carbamate pesticides were determined by GC using nitrogen–phosphorus specific detection (NPD). For the determination of organochlorine pesticides, the solution was further cleaned up by mini silica gel column chromatography, and analyzed by GC with

Table 1
Extraction procedures

Analyte	Sample	Extraction solvent	Clean-up procedure	Determination	Ref.
Organochlorines, organophosphates, organonitrogens	Fruits, vegetables	Acetone	The filtrate was partitioned with light petroleum–CH_2Cl_2. NaCl was added to the aq. phase and partitioned with CH_2Cl_2. The organic phases were combined and dried with anhyd. Na_2SO_4. Organophosphates and organonitrogens: Determined by GC. Organochlorines: Cleaned up with Florisil CC and determined by GC.	GC–KCl thermionic detection GC–ECD	[28]
Organochlorines, organophosphates, other pesticides (organonitrogens etc.)	Foods, feed, fat	Acetone–water (2:1) (The amount of water depended on the water content in the sample)	NaCl was added to the filtrate and partitioned with CH_2Cl_2. The organic phase was dried with anhyd. Na_2SO_4, concentrated and dissolved in cyclohexane–ethyl acetate (1:1). The solution was cleaned up by GPC with cyclohexane–ethyl acetate (1:1). Fats were dissolved in the mobile phase and cleaned up by GPC directly. The fraction was taken, concentrated and dissolved in ethyl acetate. Organophosphates, organonitrogens and sulfur-containing pesticides: Determined by GC. Organohalogens: Further cleaned up by mini silica gel chromatography, and determined by GC. Eluates: (1) hexane–toluene (65:35), (2) toluene, (3) toluene–acetone (95:5), (4) toluene–acetone (80:20), (5) acetone. Organohalogens and PCB: Instead of clean-up with CC, the organic phase was washed with conc. H_2SO_4. The solvent was replaced with isooctane, and determined by GC.	GC–ECD GC–FPD GC–NPD GC–MS (SIM)	[29,42]
Organohalogens organophosphates, organonitrogens	Fruits, vegetables	Acetone	The filtrate was partitioned with light petroleum–CH_2Cl_2. NaCl was added to the aq. phase and partitioned with CH_2Cl_2. The organic phases were combined and dried with anhyd. Na_2SO_4. Organohalogens and organonitrogens: Determined by GC (ELCD). Organophoshpates: Determined by GC (FPD).	GC–ELCD GC–FPD	[34]
Pesticides	Low moisture (<10% water) nonfatty products	35% water in acetone	The filtrate was partitioned with light petroleum–CH_2Cl_2. NaCl was added to the aq. phase and partitioned with CH_2Cl_2. The organic phases were combined, dried with anhyd. Na_2SO_4, and injected into a GC or further cleaned up by CC with Carbon mixture (carbon–Celite–Magnesium oxide, 1:4:2) or Florisil	GC–ELCD GC–FPD	[36]
Organochlorines, organophosphates, carbamates and others	Fruits, vegetables	Acetone, acetone–water (for cereals)	Water and brine were added to the filtrate and partitioned with CH_2Cl_2 or hexane. The organic phase was dried with anhyd. Na_2SO_4, concentrated and dissolved with cyclohexane–CH_2Cl_2 (85:15). The solution was cleaned up by GPC with the same solution. The fraction was taken, concentrated, dissolved and determined by GC.	GC–ECD GC–NPD	[43]

Organochlorines, organophosphates, carbamates, fungicides	Fruits, vegetables	Acetone	The filtrate was partitioned with CH_2Cl_2–hexane (1:1). The organic phase was dried with anhyd. Na_2SO_4, concentrated and dissolved with cyclohexane–CH_2Cl_2 (1:1). The solution was cleaned up by GPC with the same solution. The fraction was taken, concentrated, dissolved with 10% acetone in cyclohexane, and determined by GC. If more clean-up is needed for some matrices, silver-loaded alumina or Sep-Pak silica fractioning was performed.	GC–ECD GC–FPD GC–NPD GC–FID	[44]
Organochlorines, organophosphates, fungicides	Fruits, vegetables, fats, cereals, liver	Ethyl acetate (anhyd. Na_2SO_4 was added)	The filtrate was concentrated and injected onto GPC Column, and cleaned up by GPC with cyclohexane–ethyl acetate (1:1). The fraction was collected, an internal standard was added and the sample solution was injected into GC without evaporation.	GC–ECD GC–NPD	[45]
Organochlorines,	Vegetables, rice, tea leaves	Acetone	The filtrate was concentrated, 5% NaCl solution was added and partitioned with hexane. The organic layer was concentrated and dissolved with cyclohexane–CH_2Cl_2 (1:1). The solution was cleaned up by GPC with the same solution. The fraction was concentrated, dissolved with hexane and analyzed by GC.	GC–ELCD	[34]
Pesticides	Fatty and nonfatty foods	Supercritical fluid extraction (CO_2)	The sample was mixed with pelletized diatomaceous earth as extraction enhancer in advance, and extracted. Fatty sample extractants were cleaned up by GPC with hexane–CH_2Cl_2 (1:1), and determined by GC.	GC–FPD GC–ELCD	
Organochlorines, organophoshpates, carbamates	Fruits, vegetables	Acetonitrile	NaCl was added to the filtrate and partitioned. The acetonitrile layer was placed in three separate vials, concentrated, and reconstituted with benzene for organochlorine determination with acetone for organophoshpate determination. The third portion was reconstituted with methanol–water (1:3) and used for carbamate analysis.	GC–ECD GC–NPD GC–FPD HPLC GC–MS	[38]
Pesticides	Fruits, vegetables	Acetonitrile	NaCl was added to the filtrate and partitioned. The acetonitrile layer was dried with anhyd. Na_2SO_4, concentrated and dissolved with acetone.	GC–MS	[39]
Organochlorines, organophoshpates, carbamates	Fruits, vegetables	Acetonitrile	The filtrate was filtered through SPE C_8. Buffer/brine was added to the eluate and partitioned. The acetonitrile layer was concentrated and analyzed by GC for the determination of organochlorine and organophosphate pesticides. A part of acetonitrile layer was passed through solid-phase extraction cartridge (aminopropyl bonded silica) and carbamates were analyzed by HPLC.	GC–ELCD GC–FPD HPLC	[32]
Pesticides, organophosphates, halogenated fungicides, pyrethroids, triazines, phenylureas, carbamates	Fruits, vegetables	Acetone	The procedure was performed with the multiresidue procedure DFG S19. Partitioned with CH_2Cl_2 and cleaned up by GPC with cyclohexane–ethyl acetate (1:1). Fractionated with silica gel minicolumn. Eluents: (1) hexane–toluene (65:35), (2) toluene, (3) toluene–acetone (95:5), (4) toluene–acetone (80:20), (5) acetone.	HPTLC	[58]

(Continued on p. 338)

Table 1 (*continued*)

Analyte	Sample	Extraction solvent	Clean-up procedure	Determination	Ref.
Carbamate	Fruits, vegetables	For nonfatty materials (1) CH_2Cl_2–water mixture (2) acetonitrile	Pre-purification using acetonitrile–hexane partitioning was necessary for the extraction with the latter solvent. Cleaned up by CC with Florisil or Extrelut cartridge.	HPLC	[55]
		For fatty materials acetonitrile	The same procedure was described above was performed with the pre-purification and CC with Extrelut cartridege.		
Pesticides	Crops	Ethyl acetate (anhyd. Na_2SO_4 was added)	The filtrate was concentrated and dissolved with cyclohexane–ethyl acetate and cleaned up by GPC with the same solution. The fraction was collected, concentrated and dissolved with cyclohexane–ethyl acetate (1:1) and determined by GC.	GC–ECD GC–FPD GC–NPD	[30]
Pesticides	Agricultural products	Acetone	Brine was added to the filtrate and partitioned with hexane. The organic phase was washed with water, dried with anhyd. Na_2SO_4, concentrated, and dissolved with cyclohexane–acetone (1:1). The solution was cleaned up by GPC with cyclohexane–acetone (1:1). The fraction was concentrated and injected into GC–MS.	GC–MS	[46,47]
Carbamates, triazines, acetamide, dinitroaniline and others	Soil	Methanol–water (2:1)	Extracted by a Soxhlet apparatus. The volume of the extract was reduced on a vacuum rotary evaporator (complete removal of solvent). The aqueous phase was diluted with water, placed in RP C_{18} cartridge and eluted with ethyl acetate.	GC–NPD GC–MS	[53]
Insecticides, fungicides	Fruits, vegetables	Acetone–water (2:1)	The procedure was performed with the multiresidue approach DFG S19. Partitioned with CH_2Cl_2 and cleaned up by GPC with cyclohexane–ethyl acetate (1:1). Fractionated with silica gel minicolumn. (1) CH_2CH_2, (2) hexane–acetone (8:2), (3) ethyl acetate, (4) methanol–water (6:4), (5) methanol–water (7:3), (6) acetonitrile–water (7:3).	HPTLC	[59]
Organochlorines, organophosphates pyrethroids, carbamates, triazines, urea	Fruits, vegetables	–	Ground sample was mixed with Florisil, transferred into a column, and eluted with ethyl acetate or CH_2Cl_2–acetone (9:1)	GC–ECD GC–FPD GC–NPD	[54]

Pesticides	1. high moisture products 2. low moisture products 3. fatty foods	Acetone	1. High moisture products: The sample was homogenized with acetone and filtered. The filtrate was filtered through Sep-Pak C_{18} column. The column was eluted with 30% water in acetone, and the eluates were combined. 2. Low moisture products: The sample was homogenized with water in advance, blended with acetone at high speed and filtered. The filtrate was filtered through Sep-Pak C_{18} column. The column was eluted with 30% water in acetone, and the eluates were combined. 3. Fatty foods: Potassium oxalate and celite were added to the sample, ground with pestle to smooth power, transferred to a pre-partition column attached to Sep-Pak C_{18} column, and eluted with 20% water in acetone. The eluate was partitioned with acetone–CH_2Cl_2 (50:100). The organic layer was dried with anhyd. Na_2SO_4, concentrated, and dissolved with acetone–light petroleum (5:10). The solution was filtered through Accell Plus QMA-Sep-Pak NH_2 column, and filtered through acetone–light petroleum (1:2). The combined eluate was concentrated and dissolved with acetone.	GC–MS (ion trap, CI) HPLC	[40,63]
Pesticides	Fruits, vegetables	1. acetone–water (2:1)	Brine was added to the filtrate and partitioned with the following solutions: 1. ethyl acetate 2. *tert.*-butyl methyl ether 3. diethyl ether 4. light petroleum 5. cyclohexane–ethyl acetate (1:1) 6. cyclohexane The organic phase was dehydrated with anhyd. Na_2SO_4, concentrated and dissolved with cyclohexane–ethyl acetate (1:1). The solution was cleaned up by GPC, with the same solvent. The fraction was taken, concentrated, dissolved with ethyl acetate, and determined by GC.	GC–ECD GC–NPD	[31]
		2. (i) ethyl acetate (ii) hexane–acetone (8:2)	The subsequent procedure was the same as the above procedure.		
Organochlorines, organophosphates, carbamates, pyrethroids and others	Fruits, vegetables	SFE with CO_2	Trapped with Hypersil ODS, and eluted with acetonitrile.	GC–MS (ion-trap)	[14]

ECD. This method of Specht et al. has been widely adopted as an official analytical method for the determination of pesticides (DFG S19) in Germany [29] (Table 2).

Further, a number of different conditions in gel permeation chromatographic methods and mini silica gel column chromatographic methods for the determination of pesticides were investigated by Specht et al. using the above approach [29]. Data for the elution of more than 400 pesticides and their metabolites were presented [42]. The GPC method for the clean-up procedure was shown as a convenient technique [30,31,35,43–47].

Andersson et al. showed that the recovery of thiabendazole with the multiresidue method was 57% [44]. The low recoveries were unacceptable, and the method could not be used for quantitative determination of thiabendazole. The multiresidue method could only indicate the presence of a thiabendazole residue. Therefore, an individual residue method for thiabendazole is necessary [48–50].

The analytical conditions for GPC are presented in Table 2.

Four eluent mixtures to optimize the experimental conditions, such as toluene–ethyl acetate (1:3), cyclohexane–dichloromethane (85:15), cyclohexane–dichloromethane (1:1), and cyclohexane–ethyl acetate (1:1), were evaluated for the recoveries of a wide range of pesticides. Cyclohexane–dichloromethane (1:1), and cyclohexane–ethyl acetate (1:1) were found to be suitable for the purification of fatty and vegetable samples [51].

At present, the use of dichloromethane is being avoided because the solvent is known to be carcinogenic. On the other hand, acetone is a harmless solvent used in the extraction procedure. Thus, acetone is appropriate as the mobile phase solvent for GPC. Two mobile phases, such as cyclohexane–acetone (1:1) and light petroleum–acetone (75:25), were also recommended for GPC [52].

To avoid the use of dichloromethane in the clean-up procedure, other suitable partitioning solvents were investigated. After the extraction with acetone–water (2:1), ethyl acetate, *tert.*-butyl acetate, cyclohexane–ethyl acetate (1:1), and cyclohexane were examined as the solvents instead of dichloromethane in the liquid–liquid partition. Cyclohexane was selected as the best substitute out of the five solvents and was used in the clean-up procedure by GPC [31].

A multiresidue method for pesticides in soil was investigated. A soil sample was extracted with

Table 2
Gel permeation chromatography

Stationary phase	Mobile phase	Flow-rate (ml/min)	Ref.
Bio-Beads SX-3 (32 cm×25 mm)	Cyclohexane–ethyl acetate (1:1)	5	[29]
Bio-Beads SX-3 (30 cm, 60 g)	Cyclohexane–CH_2Cl_2 (85:15)	5	[33]
Bio-Beads SX-3	Cyclohexane–ethyl acetate (1:1)	5	[42]
Bio-Beads SX-3 (50 cm×10 mm, 7.2 g)	Cyclohexane–CH_2Cl_2 (1:1)	1	[44]
Bio-Beads SX-3 (45 cm×10 mm)	Cyclohexane–ethyl acetate (1:1)	1	[45]
(1) Bio-Beads SX-3 (50 g)	Cyclohexane–acetone (75:25)		[52]
(2) Bio-Beads SX-3 (2.8 g)	Light petroleum–acetone (1:1)		
Bio-Beads SX-3 (60 cm×25 mm)	Cyclohexane–CH_2Cl_2 (1:1)	5	[35]
Bio-Beads SX-3 (32 cm×25 mm)	Hexane–CH_2Cl_2 (1:1)	5	[13]
(1) Bio-Beads SX-3 (27 cm×25 mm)	Toluene–ethyl acetate (1:3)	5	[51]
(2) Bio-Beads SX-3 (29 cm×25 mm)	Cyclohexane–CH_2Cl_2 (85:15)	5	
(3) Bio-Beads SX-3 (45 cm×25 mm)	Cyclohexane–CH_2Cl_2 (1:1)	5	
(4) Bio-Beads SX-3 (30 cm×25 mm)	Cyclohexane–ethyl acetate (1:1)	5	
Bio-Beads SX-3	Cyclohexane–ethyl acetate (1:1)		[58]
Bio-Beads SX-3	Cyclohexane–ethyl acetate (1:1)		[30]
Bio-Beads SX-3 (45 cm×10 mm)	Cyclohexane–acetone (1:1)	1	[46]
Bio-Beads SX-3 (45 cm×10 mm)	Cyclohexane–acetone (1:1)	1	[47]
Bio-Beads SX-3	Cyclohexane–ethyl acetate (1:1)	5	[31]

Table 3
Conditions for the gas chromatographic analysis

Stationary phase	Column dimensions	Column temperature (°C)	Injection (°C)	Detector	Ref.
(1) 2% DEGS on Chromosorb W HP	6 feet×4 mm	200		KCl thermionic detection	[28]
(2) 2% DEGS on Chromosorb W HP	6 feet×4 mm	165		KCl thermionic detection	
(3) 3% OV-101 on Chromosorb W HP	6 feet×4 mm	200		ECD, KCl thermionic detection	
(4) 10% OV-101 on Chromosorb W HP	6 feet×4 mm	120		ECD, KCl thermionic detection	
(5) 10% OV-101+15% OV-210 on Chromosorb W HP	6 feet×4 mm	120		FID	
(1) 2% DEGS on Chromosorb W	1.2 m×2 mm	180		FPD (P-mode)	[34]
(2) 2% DEGS+0.5% H_3PO_4 on Chromosorb W	1.2 m×2 mm	180		ELCD (halogen-mode, N-mode)	
(3) 2% DEGS+0.5% H_3PO_4 on Chromosorb W	30.5 cm×2 mm	120		ELCD (S-mode)	
(4) 2% OV-101 on Chromosorb W HP	1.2 m×2 mm	200		HECD (halogen-mode, N-mode)	
(5) 4% SE-30+65% OV-210 on Chromosorb W HP	76.5 cm×2 mm	200		FPD (P-mode)	
(1) 2% DEGS on Chromosorb W	75 cm×2 mm	Conditions were according			[36]
(2) 3% OV-17 on Chromosorb W	1.2 m×2 mm	to Luke et al. [34]			
(1) 1.5% OV-17+1.95% OV-210 on Gas-Chrom Q				ECD	[43]
(2) 3% XE-60 on the Gas-Chrom Q				NPD	
(3) 1% Carbowax 20M on Gas-Chrom Q				NPD	
(4) 10% QF1+7.5% DC-200 on Gas-Chrom Q				NPD	
(5) SE-30	30 m			ECD	
(1) SE-30	25 m×0.32 mm	90–260	250	ECD, NPD	[44]
(2) OV-17	25 m×0.32 mm	90–260	250	FPD	
		100–255	250	FID	
(1) chlorine-containing compounds					
CP SIL-5CB	25 m×0.25 mm	90–250	<200	ECD	[45]
(2) organophosphates					
CP-SIL 19CB	10 m×0.22 mm	90–250	<200	NPD	
(1) DB-1	15 m×0.53 mm	100–280	220	ELCD	[35]
(2) DB-5	15 m×0.53 mm	100–280	220		
(1) DB-1701	30 m×0.32 mm	110–270		ECD	[13]
(2) DB-5	30 m×0.32 mm	110–270		ECD	
(3) DB-17	30 m×0.53 mm	150–230		FPD	

1. Primary analysis					
(1) Organochlorines					
(i) DB-608	30 m×0.53 mm	60–275		ECD	[38]
(ii) DB-5	30 m×0.53 mm	60–275			
(2) Organophosphates					
(i) DB-58	30 m×0.53 mm	60–275		NPD	
(ii) DB-1701	30 m×0.53 mm	60–275		FPD	
2. Conformation analysis					
(1) Organochlorines and organophosphates					
DB-5	30 m×0.25 mm			MS (SIM-mode)	
				MS (ion trap)	
(2) Carbamates					
DB-5	30 m×0.53 mm	40–275		NPD	
				FPD (S-mode)	
HP-1	12 m×0.2 mm	60–265	260	MS	[39]
(1) Organochlorines					
HP-5	30 m×0.53 mm	180–240	220	ELCD	[32]
(2) Organophosphates					
DB-5	15 m×0.53 mm	110–250	220	FPD (P-mode)	
(1) SE-30					
OV-1701				NPD,FPD	[30]
(2) SE-30				ECD	
OV-1701					
CP SIL 5CB	25 m×0.25 mm	70–240	260	MS (ion trap MS gave better results)	[46]
DB-5	30 m×0.25 mm	92–325	60-325	MS (ion trap)	[47]
OV-1	15 m×0.32 mm	65–275	On-column	NPD	[64]
DB-5	60 m×0.25 mm	50–280	250	NPD	[53]
				MS	
(1) DB-5	60 m×0.245 mm	85–300	250	ECD	[54]
(2) DB-1701	30 m×0.25 mm	90–270	250	ECD	
(3) HP-5	30 m×0.53 mm	150–270	250	FPD	
(4) CP SIL 5CB	10 m×0.32 mm	200	230, split (1:10)	ECD	
(5) CP SIL 5CB	10m×0.32 mm	160–220	230	NPD	
DB-5	30 m×0.25 mm	60–270	39–250	MS (ion trap)	[40,63]
(1) DB-5	30 m×0.32 mm	110–280	80–220	ECD	[31]
(2) DB-17	30m×0.25 mm	100–250	320	NPD	
DB-1701 (with phenylmethyl deactivated guard column)	30 m×0.32 mm (5 m×0.32 mm)	130–250	55–250	MS (ion trap)	[14]

Table 4
Conditions for HPLC analysis of pesticides

Analyte	Mode	Column	Mobile phase				Detector	Ref.
Carbamates	Reversed-phase partition	15 cm×4.6 mm Waters carbamates analysis column	Waters post column reaction system with reaction coil at 80 °C.				Modified by means of postcolumn derivatization with *o*-phthalaldehyde and detected with fluorimeter. Ex., λ 338 nm Em., λ 400 nm	[38]
Carbamates	Reversed-phase partition	15 cm×4.6 mm C_{18} Reversed-phase column	Solvent gradient as follows				Modified by means of postcolumn derivatization with *o*-phthalaldehyde and detected with fluorimeter. Ex, λ 340 nm Em., λ 455 nm Ex., λ 340 nm Em., λ 455 nm	[32]
			Time (min)	Water (%)	Methanol (%)	Acetonitrile (%)		
			0	85	0	15		
			5	85	0	15		
			12	50	25	25		
			19	20	40	40		
			20	20	40	40		
			21	85	0	15		
			24	85	0	15		
Carbamates	Reversed-phase partition	15 cm×4.6 mm Zorbax C_8 or 25 cm×4.6 mm Spherisorb RP18	0	80	–	20	detected with fluorimeter. Ex., λ 340 nm Em., λ 455 nm	[55]
			14	20	–	80		
			18	20	–	80		
			20	80	–	20		
Particularly for propoxur, carboforan and bendiocarb		25 cm×4.6 mm Spherisorb RP18	0.0	65	–	35		
			15.0	60	–	40		
			15.1	65	–	35		

methanol–water (2:1) in a Soxhlet extractor, cleaned up by reversed-phase solid-phase extraction cartridge, and determined by GC [53].

A simple multiresidue analysis method for the determination of organochlorines, organophosphates, synthetic pyrethroids and carbamates in fruits and vegetables was investigated. Homogenized sample pulp, prepared from fruits or vegetables with a different water content, with or without additional water, was absorbed on the surface of activated Florisil to obtain a free-flowing powder which was extracted with ethyl acetate or dichloromethane–acetone (9:1) in a glass column. In most cases, no further clean-up was necessary for subsequent GC. This method was used in Hungary by Kadenczki et al. [54].

2.3. Determination

As a rule, the analysis of pesticides is commonly performed by GC. Packed columns were mainly used in the early 1980s. Capillary columns now play a major role in pesticide analysis (Table 3).

An on-column injection with a septum-programmable injector (SPI) significantly minimized the losses of thermally labile pesticides, and the peak shapes of many pesticides were improved by the SPI [14].

So far gas chromatography coupled with element selective detectors has played a great role in the analysis of pesticides, and GC–MS has been used as a secondary confirmation technique in the multiresidue methods. Although the sensitivity of MS is commonly inferior to the element selective detectors, GC–MS methods as a primary screening tool offered simultaneous detection and structure confirmation of pesticides that could be volatilized.

The analytical conditions for GC are presented in Table 3.

HPLC was used for the multiresidue methods for

Table 5
TLC separation of pesticides

Stationary phase	Mobile phase	Comment	Ref.
(1) Silica gel 60	(1) CH_2Cl_2 (2) Hexane–acetone (8:2) (3) Ethyl acetate	Detected with enzyme	[57]
(2) RP-18W	(1) Methanol–water (6:4) (2) Methanol–water (7:3)) (3) Acetonitrile–water (7:3)	Silver nitrate solution sprayed	
(3) Silica gel 60	(1) CH_2Cl_2 (2) Ethyl acetate	*o*-Toluidine solution sprayed	
(4) Nano-Sil C_{18}-100	(1) Methanol–water (7:3) (2) Acetonitrile–water (7:3)	*o*-Toluidine solution sprayed	
(1) Silica gel 60	(1) Hexane–acetone (8:2) for fraction 1,2 (2) CH_2Cl_2 for fraction 3 (3) Ethyl acetate for fraction 4,5	Detected with enzyme	[58]
(2) RP-18W	Methanol–water (7:3) for all fractions	Silver nitrate solution sprayed	
(3) Silica gel 60	(1) CH_2Cl_2 for fraction 1,2,3 (2) Ethyl acetate for fraction 4,5	*o*-Toluidine solution sprayed	
(4) RP-18	(1) Acetonitrile–water (7:3) for fraction 1,2,3,4 (2) Methanol–water (7:3) fraction 5	*o*-Toluidine solution sprayed	
(1) Silica gel 60	(1) CH_2Cl_2 (2) Hexane–acetone (8:2) (3) Ethyl acetate	Detected with enzyme	[59]
(2) RP-18W	(1) Methanol–water (7:3) (2) Acetonitrile–water (7:3)	Silver nitrate solution sprayed	
(3) Silica gel 60	(1) CH_2Cl_2 (2) Ethyl acetate	*o*-Toluidine solution sprayed	
(4) Nano-Sil C_{18}-100	Acetonitrile–water (7:3)	*o*-Toluidine solution sprayed	

pesticides in wine and water. It is not likely to be applied to the pesticide analysis for complicated matrices, such as foods and feeds (Table 4).

HPLC is generally used for the analysis of thermally labile carbamate pesticides [32,38,55]. The HPLC conditions are presented in Table 4. There is a review with 242 references on the analysis of pesticide residues in foods by HPLC [56].

Multiresidue TLC methods have also been used [57–59].

The clean-up procedures before TLC were the same as the DFG S19 method. The TLC conditions are summarized in Table 5. TLC and HPTLC analysis with automated multiple development (AMD) on pesticide were also reviewed by two groups [60,61].

5. Conclusions

The analytical method based on extraction with acetone and partitioning with light petroleum and dichloromethane in the clean-up procedure was adopted as the AOAC official method in the USA [62] and this method was further improved by Cairns et al. [40,63].

In the European countries, Luke's method was combined with the existing GPC method [29].

The clean-up method by solid-phase extraction was also adopted in Specht's procedure. This method was improved to avoid the use of dichloromethane in the clean-up procedure.

In the previously adopted AOAC method in the USA, acetonitrile extraction was used in the extraction procedure and the method was improved for the California Department of Food and Agriculture [32].

At present, the SFE methods are becoming relevant [13,14].

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