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Review

Analysis of herbicide residues in cereals, fruits and vegetables

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Abstract

The determination of herbicide residues in cereals, fruits and vegetables by chromatographic methods is reviewed. The principal chemical groups of herbicides, like phenoxyacids, benzonitriles, ureas, triazines, dinitroanilines, chloroacetamides, carbamates, uracils, glyphosate and bipyridylium compounds, are considered. This review briefly provides some basic information on food sample extraction, clean-up, derivatization and determination of herbicide residues.

Keywords: Reviews; Fruits; Cereals; Vegetables; Food analysis; Sample preparation; Derivatization, GC; Derivatization, LC; Pesticides

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1. Introduction

Modern agricultural production depends considerably on the use of herbicides to control weeds in crops. There are many compounds registered as herbicides, which can be classified into several chemical classes in accordance with their chemical structures [1]. The herbicides reviewed in this work are summarised in Table 1 and the chemical structures of the major herbicide classes are depicted in Fig. 1. Some important physicochemical properties of these herbicides, together with the crops where they can be applied, are shown in Table 2.

A large number of these compounds are soil-applied herbicides and, in general, the toxicity of herbicides for mammals is low. Therefore, the risk of

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Table 1
The herbicidal compounds reviewed

Herbicide	Structural group	R_1	R_2	R_3	R_4
2,4-D	Phenoxyacids	–Cl	–Cl	–H	–H
Dichlorprop	Phenoxyacids	–Cl	–Cl	–H	$-CH_3$
4-Chloro-2-methylphenoxyacetic acid (MCPA)	Phenoxyacids	$-CH_3$	–Cl	–H	–H
Mecoprop	Phenoxyacids	$-CH_3$	–Cl	–H	$-CH_3$
Diclofop	Aryloxyphenoxyacids	$C_6H_3Cl_2$			
Fluazifop	Aryloxyphenoxyacids	$C_6H_3F_3N$			
Bromoxynil	Benzonitriles	–Br	–Br		
Ioxynil	Benzonitriles	–I	–I		
Chlorotoluron	Phenylureas	$-CH_3$	–Cl	$-CH_3$	
Isoproturon	Phenylureas	$(CH_3)_2CH-$	–H	$-CH_3$	
Linuron	Phenylureas	–Cl	–Cl	$-OCH_3$	
Metobromuron	Phenylureas	–Br	–H	$-OCH_3$	
Metoxuron	Phenylureas	$-OCH_3$	–Cl	$-CH_3$	
Neburon	Phenylureas	–Cl	–Cl	$-(CH_2)_3CH_3$	
Bensulfuron	Sulfonylureas	$-CH_2-C_6H_4-COOH$	–C–		
Metsulfuron	Sulfonylureas	–COOH	–H		
Ametryn	Triazines	$-CH_2CH_3$	$-CH(CH_3)_2$	$-SCH_3$	
Atrazine	Triazines	$-CH_2CH_3$	$-CH(CH_3)_2$	–Cl	
Cyanazine	Triazines	$-CH_2CH_3$	$-CCN(CH_3)_2$	–Cl	
Prometryn	Triazines	$-CH(CH_3)_2$	$-CH(CH_3)_2$	$-SCH_3$	
Propazine	Triazines	$-CH(CH_3)_2$	$-CH(CH_3)_2$	–Cl	
Simazine	Triazines	$-CH_2CH_3$	$-CH_2CH_3$	–Cl	
Terbutryn	Triazines	$-CH_2CH_3$	$-C(CH_3)_2$	$-SCH_3$	
Metribuzin	Triazinone	$-C(CH_3)_3$	$-SCH_3$		
Butralin	Dinitroanilines	–H	$-C(CH_3)_3$	–H	$-CH(CH_3)CH_2CH_3$
Ethalfluralin	Dinitroanilines	–H	$-CF_3$	$-CH_2CH_3$	$-CH_2C(CH_3)=CH_2$
Pendimethalin	Dinitroanilines	$-CH_3$	$-CH_3$	–H	$-CH(CH_2CH_3)_2$
Trifluralin	Dinitroanilines	–H	$-CF_3$	$-(CH_2)_2CH_3$	$-(CH_2)_2CH_3$
Alachlor	Amides	$-CH_2CH_3$	$-CH_2OCH_3$		
Metolachlor	Amides	$-CH_3$	$-CH(CH_3)CH_2OCH_3$		
S-ethyl dipropylthiocarbamate (EPTC)	Thiocarbamates	$-CH_2CH_3$	$-(CH_2)_2CH_3$	$-(CH_2)_2CH_3$	
Thiobencarb	Thiocarbamates	$-CH_2-C_6H_4Cl$	$-CH_2CH_3$	$-CH_2CH_3$	
Triallate	Thiocarbamates	$-CH_2CCl=CCl_2$	$-CH(CH_3)_2$	$-CH(CH_3)_2$	
Propham	Carbamates	$-CH(CH_3)_2$	$-C_6H_5$		
Chlorpropham	Carbamates	$-CH(CH_3)_2$	$-C_6H_4Cl$		
Terbacil	Uracils	$-C(CH_3)_3$	–Cl	$-CH_3$	
Bromacil	Uracils	$-CH(CH_3)CH_2CH_3$	–Br	$-CH_3$	
Lenacil	Uracils	$-C_6H_{11}$	$-CH_2CH_2CH_2-(R_2,R_3)$		
Diquat	Bipyridylium				
Paraquat	Bipyridylium				
Glyphosate					

ingesting toxic herbicide levels in foods would be rather low. However, the widespread use of these compounds in agriculture has increased the public concern on the presence of their residues in foods. Many countries monitor residue levels of these compounds in foods and the outcome of this control shows that the accepted maximum residue levels are seldom exceeded [2].

Analysis of herbicide residues involves different steps, like extraction, clean-up or interference removal, determination of herbicide residues and confirmation of their identity, and these analyses are performed by using various techniques [3]. The determination of herbicides was initially carried out by colorimetric and spectrophotometric methods, but these methods do not generally achieve the sensitivi-

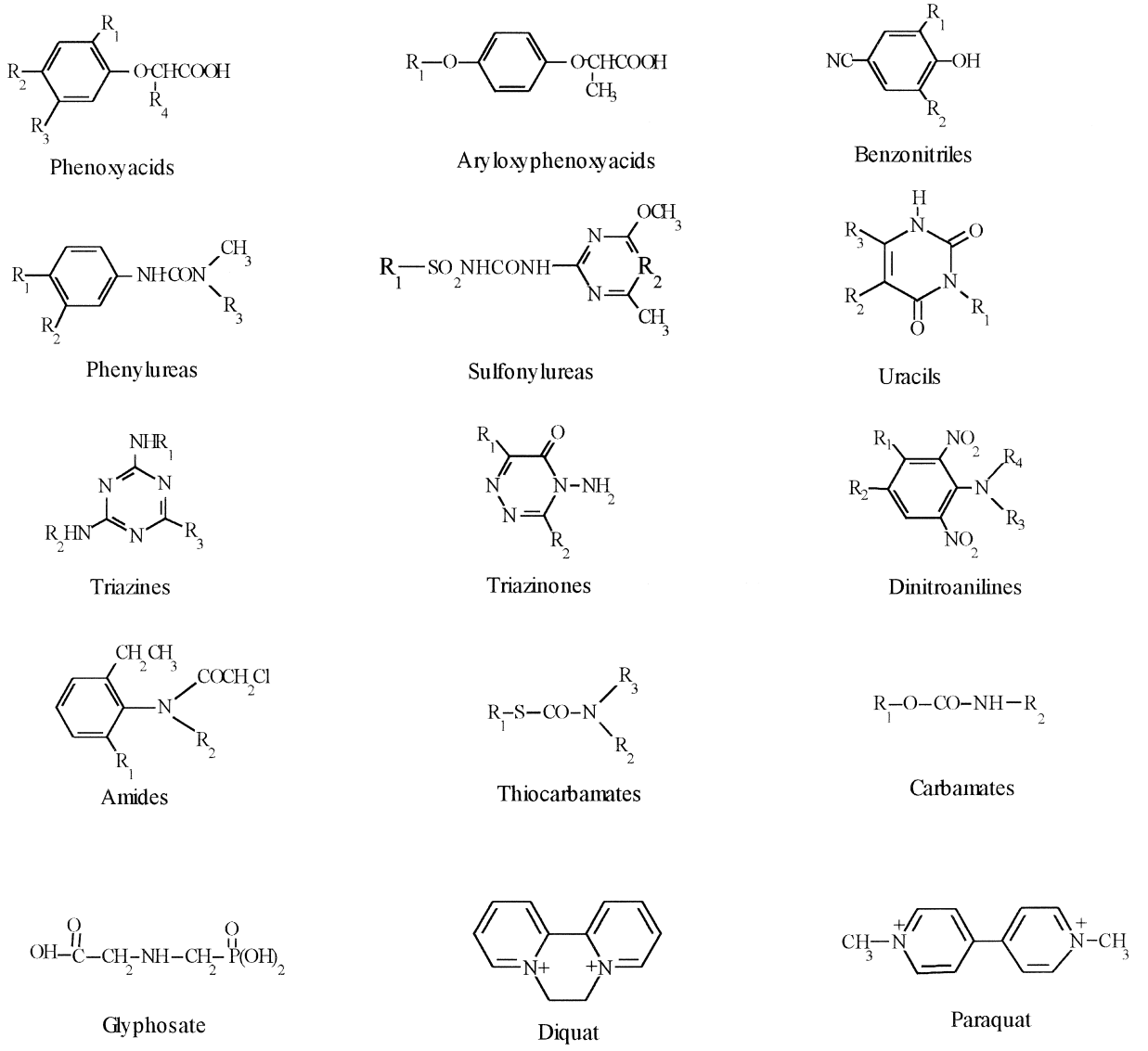

Fig. 1. Structures of the herbicides reviewed.

ty of modern chromatographic methods and, in some cases, they are not able to distinguish between the parent compounds and their metabolites or hydrolysis products.

Gas chromatography (GC) is, at present, the most versatile and sensitive method for residue analysis, due to the high sensitivity obtained with electron-capture (ECD), nitrogen–phosphorus (NPD) and flame photometric (FPD) detection. In addition, mass spectrometry (MS) is the most valuable detection technique, because it provides information on the compound molecular structure and it is also highly sensitive and selective when used in the single ion monitoring (SIM) mode. High-performance liquid chromatography (HPLC) is normally used when the volatility of a compound is low or when it is

Table 2
Physicochemical properties and use of herbicides included in this review[a]

Herbicide	Molecular formula	Crop	Water solubility (mg/l, pH 7)	log K_{ow} (pH 7)[b]
2,4-D	$C_8H_6Cl_2O_3$	Cereals, vegetables	311 (pH 1, 25°C)	2.6–2.8 (pH 1)
Dichlorprop	$C_9H_8Cl_2O_3$	Cereals	350 (20°C)	1.77
MCPA	$C_9H_9ClO_3$	Cereals, fruits, vegetables	734 (25°C)	0.46 (pH 5)
Mecoprop	$C_{10}H_{11}ClO_3$	Cereals, fruits	734 (25°C)	0.10
Diclofop-methyl	$C_{16}H_{14}Cl_2O_4$	Cereals, vegetables	0.8 (pH 5.7, 20°C)	4.58
Fluazifop-butyl	$C_{19}H_{20}F_3NO_4$	Fruits, vegetables	1 (pH 6.5)	4.5
Bromoxynil	$C_7H_3Br_2NO$	Cereals, vegetables	130 (25°C)	
Ioxynil	$C_7H_3I_2NO$	Cereals, vegetables	50 (25°C)	
Chlorotoluron	$C_{10}H_{13}ClN_2O$	Cereals	74 (25°C)	2.5
Isoproturon	$C_{12}H_{18}N_2O$	Cereals	65 (22°C)	2.5
Linuron	$C_9H_{10}Cl_2N_2O_2$	Cereals, vegetables	81 (25°C)	3.00
Metobromuron	$C_9H_{11}BrN_2O_2$	Cereals, vegetables	330 (20°C)	2.41
Metoxuron	$C_{10}H_{13}ClN_2O_2$	Cereals, vegetables	678 (24°C)	1.60
Neburon	$C_{12}H_{16}Cl_2N_2O$	Cereals, vegetables	5 (25°C)	
Bensulfuron–methyl	$C_{16}H_{18}N_4O_7S$	Rice	120 (25°C)	0.62
Metsulfuron–methyl	$C_{14}H_{15}N_5O_6S$	Cereals	2790 (25°C)	−1.74
Ametryn	$C_9H_{17}N_5S$	Cereals, fruits	200 (25°C)	2.63
Atrazine	$C_8H_{14}ClN_5$	Cereals, fruits, vegetables	33 (20°C)	2.5
Cyanazine	$C_9H_{13}ClN_6$	Cereals, vegetables	171 (25°C)	2.1
Prometryn	$C_{10}H_{19}N_5S$	Vegetables	33 (25°C)	3.1
Propazine	$C_9H_{16}ClN_5$	Vegetables	5.0 (20°C)	
Simazine	$C_7H_{12}ClN_5$	Cereals, fruits, vegetables	6.2 (20°C)	2.1
Terbutryn	$C_{10}H_{19}N_5S$	Cereals, fruits, vegetables	22 (20°C)	3.65
Metribuzin	$C_8H_{14}N_4OS$	Cereals, vegetables	1050 (20°C)	1.57 (pH 5.6)
Butralin	$C_{14}H_{21}N_3O_4$	Cereals, fruits, vegetables	1.0 (24°C)	
Ethalfluralin	$C_{13}H_{14}F_3N_3O_4$	Cereals, vegetables	0.3 (20°C)	5.11
Pendimethalin	$C_{13}H_{19}N_3O_4$	Cereals, fruits, vegetables	0.3 (20°C)	5.18
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	Cereals, fruits, vegetables	0.221 (25°C)	5.27 (pH 7.7–8.9)
Alachlor	$C_{14}H_{20}ClNO_2$	Cereals, vegetables	242 (25°C)	
Metolachlor	$C_{15}H_{22}ClNO_2$	Cereals, vegetables	488 (25°C)	2.9
EPTC	$C_9H_{19}NOS$	Cereals, fruits, vegetables	375 (25°C)	3.2
Thiobencarb	$C_{12}H_{16}ClNOS$	Rice	30 (20°C)	3.42
Triallate	$C_{10}H_{16}Cl_3NOS$	Cereals, vegetables	4 (25°C)	
Propham	$C_{10}H_{13}NO_2$	Vegetables	250 (20°C)	
Chlorpropham	$C_{10}H_{12}ClNO_2$	Vegetables	89 (25°C)	
Terbacil	$C_9H_{13}ClN_2O_2$	Fruits, vegetables	710 (25°C)	1.91
Bromacil	$C_9H_{13}BrN_2O_2$	Fruits	700 (25°C)	1.87
Lenacil	$C_{13}H_{18}N_2O_2$	Vegetables	6 (25°C)	2.31
Clopyralid	$C_6H_3Cl_2NO_2$	Cereals, vegetables	143 000 (20°C)	−2.63
Diquat dibromide	$C_{12}H_{12}Br_2N_2$	Cereals, fruits, vegetables	700 000 (20°C)	−4.60
Paraquat dichloride	$C_{12}H_{14}Cl_2N_2$	Fruits, vegetables	700 000 (20°C)	
Glyphosate	$C_3H_8NO_5P$	Cereals, fruits, vegetables	12 000 (25°C)	

[a] From Ref. [129].
[b] K_{ow}, octanol–water partition coefficient.

thermally unstable rendering it unsuitable for GC determination. HPLC has, in general, lower sensitivity for trace analysis, particularly with ultraviolet (UV) detection.

The analysis of herbicide residues in foods has been previously reviewed by several authors [4–6]. In this paper we will review the residue analysis in cereals, fruits and vegetables of the herbicidal compounds shown in Table 1, considering the different steps in their determination by GC or by HPLC.

2. Extraction and clean-up

Extraction of residues from foods depends on the polarity of the herbicide as well as on the type of sample matrix. The extraction procedure generally involves sample homogenisation with an organic solvent, alone or mixed with water or pH-adjusted water, using a homogeniser, blender or sonicator. Acetone, acetonitrile, methanol and ethyl acetate are the most usual organic solvents employed in the extraction of herbicide residues from foods.

Recently, supercritical fluid extraction (SFE) has been used for the extraction of herbicide residues [3–6]. This technique offers a number of advantages, like saving organic solvents and sample preparation time, decreasing the exposure of analysts to toxic organic solvents and reducing the need for space and glassware. One additional advantage of SFE is that various solid-phase sorbents, like alumina and octadecylsilyl-bonded silica, can be incorporated at the extraction procedure for purification purposes.

A clean-up procedure is usually carried out to remove co-extracted compounds that may interfere in the chromatographic determination or be detrimental to the analytical instrumentation. This commonly involves one or more steps utilising liquid–liquid extraction (LLE), gel permeation chromatography (GPC), chromatography on columns packed with different adsorbents or solid-phase extraction (SPE). The requirement for clean-up will strongly depend on the selectivity and sensitivity of the detection technique employed in the determination of herbicide residues.

Matrix solid-phase dispersion (MSPD) is a new extraction and clean-up technique developed for pesticide multiresidue analysis [6]. This technique allows the extraction of pesticides from homogeneously dispersed food samples in a solid support, such as Florisil or silica. The homogenised mixture is placed in a column and pesticides are selectively eluted with organic solvents. Thus, sample extraction and clean-up are carried out in the same step with good recovery and reproducibility, reducing the analysis time and the amount of solvent employed.

The extraction and clean-up procedures used in the residue analysis of the different herbicide classes are considered below in more detail.

Phenoxyacids and benzonitriles are widely applied as salts or esters, but they are decomposed rapidly by hydrolysis, in the treated plants, to their respective phenols or acids. Extraction of these herbicides can be carried out with high polarity organic solvents, like methanol or ethanol in mixtures with water. However, residues of these acidic herbicides are best extracted from foods when a hydrolytic step is included to release the free acidic herbicide from the conjugated products formed with plant components. In general, acid or base hydrolysis have been used

Table 3
Extraction and clean-up of phenoxyacids and benzonitriles

Matrix	Herbicide	Extraction	Clean-up	Ref.
Oranges	2,4-D	Methanol–homogeniser	–	[7]
Fruits, vegetables	2,4-D	Diethyl ether–hexane (acidic pH), homogeniser	NH_2 cartridge	[8]
Wheat	2,4-D	Ethanol–water, homogeniser	LLE–Florisil column	[9]
Onions	Fluazifop-butyl	CO_2–SFE	–	[10]
Fruits, vegetables	2,4-D	Methanol–water (basic pH), blender	C_{18} cartridge	[11]
Oranges, grapefruits	2,4-D	Acetonitrile–water, homogeniser	LLE	[12]
Citrus fruits	Dichlorprop	Methylene chloride–acetone, shaker	LC-SCX cartridge	[13]
Barley, triticale	Mecoprop, 2,4-D	0.1 *M* NaOH, blender	LLE–Florisil column	[14]
		Ethanol–water, homogeniser		[15]
Wheat, barley	Phenoxyacids	Methanol, homogeniser	LLE–Florisil column	[16]
Mushrooms	2,4-D	Diethyl ether (acidic pH), homogeniser	Alumina column	[17]
Wheat	2,4-D	0.1 *M* NaOH–diethyl ether–hexane (pH 1), blender	LLE–Florisil column	[18]
Potatoes, soybeans	Fluazipop-butyl	0.1 *M* NaOH, shaker	LLE–Florisil column	[19]
Wheat	Bromoxynil	Methanol, blender	LLE–Florisil column	[20]
Onions, wheat	Bromoxynil	0.1 *M* NaOH, homogeniser	LLE–Florisil column	[21,22]
Wheat	2,4-D, Bromoxynil	0.1 *M* NaOH, blender	LLE–Florisil column	[23]
Cereals	Bromoxynil, Ioxynil	0.1 *M* NaOH, homogeniser	LLE	[24]

Table 4
Extraction and clean-up of urea herbicides

Matrix	Herbicide	Extraction	Clean-up	Ref.
Carrots	Linuron	Hexane–diethyl ether, homogeniser	Florisil cartridge	[25]
Potatoes	Linuron	Acetone, homogeniser	LLE–Silica cartridge	[26]
Vegetables	Phenylureas	Acetone, homogeniser	LLE–GPC Florisil cartridge	[27]
Cereals	Metsulfuron	Methanol, homogeniser	Liquid chromatography	[28]
Rice	Bensulfuron	Methylene chloride, homogeniser	Silica cartridge	[29]
Carrots	Linuron	Water (acidic pH), shaking	–	[30]
Garlic	Linuron	Methanol, homogeniser	Alumina column	[31]
Asparagus	Linuron	Methanol, homogeniser	LLE–Florisil column	[32]
Cereals	Chlortoluron	Ethanol–water, homogeniser	Silica column	[33]
Potatoes	Isoproturon	Methanol, homogeniser	–	[34]
Vegetables	Phenylureas	Ethanol, homogeniser	LLE	[35]
Vegetables	Phenylureas	Methanol, homogeniser	LLE–Florisil column	[36]
Wheat	Phenylureas	Methanol, shaking	–	[37]
Grains	Sulfonylureas	Acetonitrile, homogeniser	Cation–exchange cartridge	[38]
Potatoes	Linuron	Acetone, homogeniser	LLE–Florisil column	[39]
Grains, cereals	Chlorsulfuron	Ethyl acetate, blender	LLE–GPC	[40]

with this aim following two different strategies. In one approach, samples are subjected to hydrolysis followed by the extraction of the free acidic herbicide with organic solvents. In the other approach, the parent herbicide and its conjugates are extracted by organic solvents and subsequently hydrolysed. Table 3 summarises some of the extraction and clean-up procedures followed in the analysis of these compounds.

A large number of herbicides belonging to different groups, such as phenylureas, triazines, dinitroanilines, chloroacetamides, carbamates and uracils, are extracted from foods by mechanical shaking or homogenisation with organic solvents, like methanol, acetonitrile, often in mixture with water, dichloromethane or ethyl acetate, sometimes at acidic pH. Clean-up of extracts is required in some cases and it is carried out by column chromatography on Florisil, silica or alumina. SPE purification of extracts by cation-exchange columns is sometimes used. The extraction and clean-up procedures used in the determination of these compounds are presented in Tables 4–9.

Glyphosate is a highly polar herbicide, very

Table 5
Extraction and clean-up of triazines

Matrix	Herbicide	Extraction	Clean-up	Ref.
Vegetables, rye	Triazines	Dichloromethane, maceration, shaker	Silica column	[41]
Cereals, apples, celery	Triazines	Methanol, blender	LLE–Cation-exchange cartridge	[42]
Vegetables	Triazines	Acetonitrile–water, homogeniser	Carbopack cartridge SCX column	[43]
Corn, vegetables, sugar beet	Simazine	Water, homogeniser Chloroform, shaker	Alumina column	[44]
Cereals, vegetables	Metribuzine	Acetonitrile–water, reflux	LLE–Florisil column	[45]
Potatoes	Metribuzine	Water, steam distillation	LLE–Silica column	[46]
Fruits, vegetables	Atrazine	Ethyl acetate, shaker	C_{18} column	[47]
Grape juice	Simazine	Diethyl ether (acidic pH), shaker	–	[48]
Oil	Simazine	Acetonitrile, blender	–	[49]
Olives	Simazine	Ethyl acetate, blender	–	[49]
Onions	Cyanazine	Ethanol–water, homogeniser	LLE–Florisil column	[50]
Vegetables	Triazines	Acetone, blender	LLE–Florisil column	[51]
Cereals, fruits, vegetables	Triazines	Methanol, blender	Alumina column	[52]

Table 6
Extraction and clean-up of dinitroanilines

Matrix	Herbicide	Extraction	Clean-up	Ref.
Carrots	Trifluralin	Acetone, homogeniser	LLE	[53]
Onions	Pendimethalin	Toluene–methanol, blender	Alumina column	[54]
Carrots	Trifluralin	Hexane–diethyl ether, homogeniser	Florisil cartridge	[25]
Radishes, turnips	Trifluralin	Methanol, soxhlet	LLE–Silica column	[55]
Onions	Pendimethalin	Methanol–water (acidic pH)	LLE–Silica column	[56]

Table 7
Extraction and clean-up of chloroacetamides

Matrix	Herbicide	Extraction	Clean-up	Ref.
Tomatoes	Metolachlor	Water (acidic pH), homogeniser	LLE	[57]
Carrots	Metolachlor	Water (acidic pH), shaker	–	[30]
Potatoes	Metolachlor	Acetone–hexane, blender	LLE	[58]
Cereals	Chloroacetamides	Acetonitrile, homogeniser	LLE–Florisil column	[59]
Vegetables	Metolachlor	Methanol, blender	LLE–Silica cartridge	[60]

Table 8
Extraction and clean-up of carbamates and thiocarbamates

Matrix	Herbicide	Extraction	Clean-up	Ref.
Rice	Thiobencarb	Methanol or acetone, blender	–	[61]
Potatoes	Chlorpropham	Tetrahydrofuran–water–acetonitrile –acetic acid, homogeniser	–	[62]
Fruits, vegetables	Chlorpropham	Methanol, blender	Alumina column	[63]
Potatoes	Chlorpropham	Acetone, homogeniser	LLE	[64]
Garlic	Triallate	Methanol, homogeniser	LLE–Florisil cartridges Alumina column	[65]
Potatoes	Chlorpropham	Dichloromethane (water), blender	–	[66]
Lentils	Triallate	Acetonitrile, shaker	Alumina column	[67]
Potatoes	Chlorpropham, propham	Dichloromethane (water), blender	Silica-TLC	[68]
Fruits, vegetables	Chlorpropham, propham, triallate	Ethyl acetate, homogeniser	LLE–Florisil column	[69]
Potatoes	Chlorpropham	Water suspension, solid-phase microextraction	–	[70]
Apples	Propham	Toluene–hexane, homogeniser	Florisil column	[71]

Table 9
Extraction and clean-up of uracils

Matrix	Herbicide	Extraction	Clean-up	Ref.
Oranges	Bromacil	Water (basic pH), shaker	LLE	[72]
		Ethyl acetate–water, shaker	–	
		Ethyl acetate–water, shaker	LLE–Florisil column	
Citrus, pineapples	Bromacil	Ethyl acetate, blender	–	[73]
Strawberries	Lenacil	Methanol–water (basic pH), homogeniser	LLE–Alumina column	[74]
Spinach	Lenacil	Methanol–water, shaker	LLE–HPLC	[75]
Spinach	Lenacil	Acetonitrile–water	LLE–HPLC	[76]
Blueberries, fruits	Terbacil	1% NaOH, blender	LLE–Florisil column	[77,78]
Asparagus	Terbacil	Methanol, homogeniser	LLE–Florisil column	[79]

Table 10
Extraction and clean-up of glyphosate

Matrix	Extraction	Clean-up	Ref.
Corn, fruits, soybeans	Water, blender	LLE–Cation-exchange column	[80]
Blueberries	Water, homogeniser	LLE–GPC–Cation-exchange column	[81]
Legumes, cereals	Water–chloroform, shaker	LLE–Cation-exchange column–Anion-exchange column	[82,83]
Fruits, vegetables	0.1 *M* HCl–chloroform, blender	LLE–Ligand-exchange column–Anion-exchange column	[84,85]
Berries	Water–chloroform, blender	LLE–Charcoal–Cation-exchange column	[86,87]
Kiwi fruit, asparagus	Water–chloroform, blender	LLE–Anion-exchange column–GPC	[88]
Cereals, lentils, beans	Water or dilute sulfuric acid, homogeniser	LLE–Anion-exchange column	[89]
Fruits, vegetables	Water–chloroform, blender	LLE–Cation-exchange column	[90]

soluble in water and insoluble in most organic solvents. For this reason, the extraction of glyphosate from foods cannot be accomplished with organic solvents. Glyphosate extraction is usually carried out with water or water with chloroform, sometimes at acidic pH. In this procedure, other water soluble components of foods, like amino acids, amino sugars, etc. are also extracted. These compounds interfere in the glyphosate determination making necessary the clean-up of extracts. The procedures more often used in this purification step are liquid-liquid partition and column chromatography on ion-exchange columns. Table 10 shows some of the extraction and clean-up procedures followed in the determination of glyphosate residues.

The bipyridylium herbicides, diquat and paraquat, are quaternary ammonium compounds that show matrix sorption interactions. Their extraction from samples have been usually achieved by refluxing or heating with strong sulphuric or hydrochloric acid solutions to free herbicides from their adsorbed or bound state. The clean-up of extracts is commonly achieved by column chromatography on silica or alumina and, in some cases, extracts are purified by SPE. Table 11 summarises some of the extraction and clean-up procedures employed in their determination.

Multiresidue and single residue methods generally consist of the same basic steps, but multiresidue methods allow the determination of a large number of pesticides in a single analysis, reducing thus time and cost of analysis. Therefore, multiresidue methods are the best practical approach in a monitoring program to maximise the number of pesticides to be determined with given resources. The herbicides amenable to be analysed by a multiresidue method are all the compounds that can be extracted, clean-up, separated and detected in the conditions used in the analytical procedure. In multiresidue methods, extraction from foods is usually carried out by homogenising or blending samples with organic solvents, like acetone, acetonitrile, methylene chloride or methanol. The addition of water may improve, in some cases, desorption of herbicides from the matrix. SFE, using usually CO_2, has also been used for the extraction of herbicides and MSPD has been recently proposed as an alternative technique. Table 12 shows some of the extraction and clean-up procedures used in the multiresidue determination of herbicides.

Table 11
Extraction and clean-up of bipyridylium herbicides

Matrix	Herbicide	Extraction	Clean-up	Ref.
Potatoes	Bipyridylium	2 *M* HCl, reflux	Silica cartridge	[91,92]
Potatoes	Bipyridylium	0.2 *M* HCl ($NiCl_2$+$NaBH_4$)–toluene	LLE	[93]
Potatoes	Diquat	EtOH–water ($NaBH_4$), shaker	LLE	[94]
Cereals, fruits, vegetables	Bipyridylium	6 *M* HCl, heat	Amberlite column	[95]
Cereals, vegetables	Bipyridylium	6 *M* HCl, homogeniser-reflux	Silica cartridge	[96]
Dry beans	Bipyridylium	6 *M* HCl, reflux	Silica column	[97]
Lettuce, carrots, onions	Paraquat	2.5 *M* H_2SO_4, reflux	Alumina column	[98]

Table 12
Extraction and clean-up of multiresidue herbicides

Matrix	Herbicide	Extraction	Clean-up	Ref.
Vegetables	Triazines, methylcarbamates	Acetone, homogeniser	LLE	[99]
Blueberries	Simazine, methiocarb	Acetonitrile, blender	LLE–Alumina column	[100]
Carrots, broccoli, celery, oranges	Benzonitriles, amides, dinitroanilines	Acetonitrile, homogeniser	Florisil cartridges C_{18} cartridges	[101]
Fruits, vegetables	Phenylureas	Acetone, homogeniser	LLE	[102]
Fruits, vegetables	Atrazine, trifluraline, chlorpropham	CO_2-SFE	–	[103]
Fruits, vegetables	Triazines, carbamates, dinitroanilines	Acetonitrile, homogeniser	Charcoal, celite column	[104]
Fruits, vegetables	Triazines, amides, dinitroanilines	Methylene chloride, homogeniser	–	[105]
Fruits, vegetables	Triazines, carbamates, ureas	MSPD	–	[106]
Blueberries	Phenylureas, triazines	Acetone–water, blender	C_{18} cartridges	[107]
Fruits, vegetables	Phenylureas, amides, dinitroanilines	Dichloromethane, homogeniser	Florisil column	[108]
Potatoes	Triazines, chlorpropham	CO_2-SFE	–	[109,110]
Onions, red radishes	Propachlor, diclofop-methyl	Acetone, homogeniser	GPC Silica column	[111]
Maize	Alachlor, metholaclor, atrazine	Methanol, blender	Alumina column Florisil column	[112]
Vegetables	Phenylureas, amides, uracils	Acetone, blender	LLE–Florisil column	[113]
Vegetables	Triazines, carbamates, uracils, amides, dinitroanilines	Acetone, maceration	GPC	[114]

3. Derivatization

3.1. Gas chromatography

Derivatization is often used in GC to increase the volatility of an analyte, to improve its thermal stability and to enhance the sensitivity or selectivity of the detection. In general, herbicides requiring derivatization prior GC determination are those possessing a hydroxyl, carboxylic or amino group.

Derivatization of the carboxylic group of phenoxy-acids and aryloxyphenoxy acids is accomplished by obtaining the corresponding ester. These compounds are derivatized to their methyl esters with diazomethane [10,11,13,17,19,116]. Alternative methods for methylation, avoiding the use of the hazardous diazomethane reagent include methanol–BF_3 [7,9,12,15,18], Trimethylsilyl-diazomethane–methanol [117–119] and tetrabutyl–ammonium hydroxide (TBAH) with methyl iodide [115]. Additional bromination of the methyl ester of mecoprop [16] allows the increase in the ECD response for this phenoxy-acid, which cannot be detected at low levels of concentration. BCl_3 and 2-chloroethanol [8] are used to produce a different derivative, the 2-chloroethyl ester, which gives a better response in GC–ECD.

The phenol group of benzonitriles may be derivatized to increase their volatility and improve GC analysis. Derivatization usually involves alkylation with diazomethane to form an ether [21–23] or perfluoroacylation with heptafluorobutyric anhydride (HFBA) to form a butyryl derivative [24], which increases the sensitivity of ECD detection.

Conventional GC methods for the determination of phenylureas generally involve derivatization with different reagents to overcome their thermal instability. Thus, methylation with sodium hydride and methyl iodide [35] allows obtaining thermally stable products, which can be analysed by gas chromatography through a wide range of conditions. This method can also be used in carbamate analysis by GC.

However, ureas may be determined directly without derivatization by using persilanized thin film capillary columns in connection with cold on-column injection to avoid thermal decomposition [25]. Another possibility is their determination as isocyanates, products of thermal decomposition of phenylureas that may be obtained quantitatively under closely controlled conditions [33,120].

Glyphosate may be considered as a special case, due to its polar nature and high water solubility, which limits the possibility of using the standard derivatization techniques often employed in GC analysis. Glyphosate analysis by GC requires extensive derivatization of the analyte. Derivatization

involves the use of trifluoroacetic anhydride (TFAA) and trifluoroethanol [86,87], TFAA and diazomethane [88] or HFBA and 2-chloroethanol [81]. The use of mixtures of fluorinated anhydrides and perfluorinated alcohols, such as TFAA and heptafluorobutanol, allows obtaining derivatives of glyphosate that can be detected by GC–MS with high sensitivity and selectivity [80].

HFBA has also been used in the GC analysis of several triazine herbicides, in order to obtain electron capture sensitive derivatives [51].

3.2. High-performance liquid chromatography

Derivatization is usually employed in HPLC analysis to improve the sensibility of the analyte detection, but not its chromatographic behaviour.

HPLC methods with selective postcolumn reaction followed by fluorescence detection avoid matrix interference well enough to determine herbicides at low levels. Thus, postcolumn photodegradation, chemical derivatization with ortho–phthalaldehyde and spectrofluorometry is used in the analysis of phenylurea herbicides [36].

The lack of a chromophore or fluorophore makes necessary the derivatization of glyphosate for its determination by HPLC. Methods for glyphosate analysis in cereals, fruits and vegetables by HPLC include postcolumn derivatization with *ortho*-phthalaldehyde [84,85] or *ortho*-phthalaldehyde and 2-mercaptoethanol [82,83,90], after oxidation of glyphosate to a primary amine, and fluorescence detection. These methods also allow the determination of its major metabolite, aminomethylphosphonic acid (AMPA).

A novel way to determine glyphosate has been reported [89]. This method nitrosates this herbicide to the N-nitrosoglyphosate derivative and then determines this derivative using a thermal energy analyser (TEA), a detector that is highly sensitive and specific to N-nitroso compounds.

4. Chromatographic determination

4.1. Gas chromatography

GC determination of herbicide residues in foods has been performed on packed columns during many years. Methyl silicones (SE-30, DC-200, OV-1), methyl phenyl silicones (OV-17) and fluoropropylsilicones (QF-1) have been some of the stationary phases more used in these analysis, Table 13. In the last decade, fused capillary columns of low polarity have been widely used in herbicide residue analysis. These capillary columns are open tubular columns with cross-linked stationary phases, like HP-1, DB-1, HP-5 or DB-5 (Table 13), a length of 12–30 m and an internal diameter of 0.2–0.5 mm. The increase in sensitivity and resolution achieved with these columns has made packed columns to be replaced by capillary columns.

Gas chromatography is widely used in the analysis of herbicide residues, due to the high selectivity and sensitivity of the detectors that can be interfaced with this technique.

One detection method very often used in the analysis of nitrogen containing herbicides is a modification of flame ionisation detection (FID) by the addition of a bead covered by an alkaline salt. This detection method, known as nitrogen–phosphorus detection (NPD), alkali-flame ionisation detection (AFID) or thermionic detection, is employed in the determination of ureas [33,34,120], triazines [41,42, 44,49,50], chloroacetamides [124], carbamates [50,69], uracils [73,79], glyphosate [86,88], bipyridylium herbicides [93,94] and in multiresidue analysis [112].

Another detection method commonly used in the determination of herbicide residues is ECD. This detection method has high sensitivity for halogenated compounds, although its linear range is narrow. It has been frequently used in the analysis of some halogenated phenoxyacids [9,11,12,17,18,23,115, 116], benzonitriles [20–23], dinitroanilines [25,53,54,56,122], chloroacetamides [58,59,121], thiocarbamates [61,67], uracils [72,77], glyphosate [81] and in multiresidue analysis [101,106]. ECD can also be used in the detection of non halogenated compounds, after obtaining halogenated derivatives [81]. Derivatization with halogenated reagents can also be used to increase the response of some halogenated herbicides [8,16]. In these cases, the excess of reagent must be completely removed to avoid interference in the determination procedure.

MS, coupled to GC, is rapidly becoming the choice for the analysis and identification of herbicide residues, particularly in multiresidue analysis

Table 13
GC methods used to determine the different herbicides in food samples[a]

Herbicide class	Derivatizations	Chromatographic methods		D.L.[b]	Matrix	Ref.
Phenoxyacids						
2,4-D	BF_3–MeOH	ECD	HP-1	0.05 mg/kg[c]	Wheat	[9]
			DC-200	0.01 μg/g	Grapes, oranges	[12]
			Ultrabond 20M	0.20 ppm	Wheat	[18]
		HECD	Ultrabond	0.1 mg/kg[c]	Triticale	[15]
		MS	DB-1701	0.2 mg/kg[c]	Oranges	[7]
	BCl_3-2-chloroethanol	ECD	DB-17	0.1 ppm[c]	Fruits, vegetables	[8]
	Diazomethane	ECD	DB-5	10 ppb[c]	Fruits, potatoes	[11]
			XE-60, SE-30, FFAP	0.05, 0.02 ppm	Berries, mushrooms	[17]
			Ultrabond	0.05 ppm	Wheat	[23]
2,4-D, mecoprop	Diazomethane and bromine–iodine	ECD	OV-17+QF-1	0.05, 0.5 ppm	Wheat, barley	[16]
Mecoprop	BF_3–MeOH	HECD	Dexil 300	0.05 mg/kg[c]	Barley	[14]
Phenoxyacids	TBAH–CH_3I	ECD, HECD	OV-101		Vegetables, oranges, corn	[115]
Chlorophenoxyacids	Diazomethane	ECD	OV-17, OV-225, Apiezon L	0.02 mg/kg	Barley	[116]
Aryloxyphenoxyacids						
Fluazifop, fluazifop-butyl, fluazifop-methyl	Diazomethane	NPD, MS	SE-54	0.01 μg/g	Potatoes, soybean	[19]
Fluazifop, fluazifop-butyl	Diazomethane	MS	DB-1701	0.02 ppm	Onions	[10]
Benzonitriles						
Bromoxynil	HFBA	MS	BP-1	0.001 μg/g	Cereals	[24]
	Diazomethane	ECD	HP-1	10 μg/kg	Onions	[21]
			Ultrabond	0.01 ppm	Wheat	[23]
Bromoxynil n-butyrate, bromoxynil octanoate, bromoxynil	Diazomethane	ECD	HP-1	0.003 mg/kg	Wheat	[22]
Bromoxynil octanoate		ECD	OV-210+SE-30, OV-1	0.005 ppm	Wheat	[20]
Phenylureas						
Linuron		ECD	OV-1	1.6 ppb	Carrots	[25]
		MS	DB-1	0.1 ppm	Potatoes	[39]
Chlorotoluron		NPD	OV-17	0.01 μg/g	Cereals	[33,120]
Isoproturon		NPD		0.042 μg/g[c]	Potatoes	[34]
Phenylureas	MeI–NaH	Coulson	OV-1	0.005–0.01 ppm	Cereals, fruits, vegetables	[35]
Triazines						
Atrazine		ECD		0.002 ppm	Corn	[121]
Cyanazine		NPD	HP-1	10 μg/kg	Onion	[50]
Metribuzin		ECD	OV-225	0.01 μg/g	Cereals, vegetables	[45,46]
Simazine		NPD	OV-101	0.1 μg/kg	Vegetables, corn, sugar beet	[44]
			HP-1	0.01 ppm	Oil, olives	[49]
Triazines		NPD	Carbowax 20 M; OV-225	0.01–0.02 mg/kg	Rye, vegetables	[41]
			DB-17	0.02–1.0 ppm	Cereals, celery, apples	[42]
	HFBA	ECD, HECD	OV-101	0.13–0.86 ppm[c]	Potatoes, peas, tomatoes	[51]
Dinitroanilines						
Trifluralin		ECD	OV-1	0.4 ppb	Carrots	[25]
			DB-5	0.002 ppm	Carrots	[53]
			HP-5	0.01 mg/kg	Onions	[54,56]
			Carbowax 20M	10 ppb[c]	Crucifers	[122]
Dinitroanilines		MS	BP-1	0.05 μg/g	Cereals	[123]
Chloroacetamides						
Alachlor		NPD	UC-W98	0.02–0.05 μg/g	Peanut, cereals	[124]
Alachlor, metolachlor		ECD		0.002 ppm	Corn	[121]
Metolachlor	Hydrolysis	MS	Supelcowax 10	50 ppb	Tomatoes	[57]
		ECD	OV-1	0.15 ng	Potatoes	[58]
Chloroacetamides		ECD	QF-1+DC-200, Apiezon L	0.02–0.05 ng	Potatoes, tomatoes, maize	[59]

Table 13. Continued

Herbicide class	Derivatizations	Chromatographic methods		D.L.[b]	Matrix	Ref.
Carbamates						
Chlorpropham		MS	CBP-1	0.001 ppm	Potatoes	[64]
			DB-1	0.01 mg/kg	Potatoes	[70]
		NPD	DB-5	50 μg/kg	Onions	[50]
Carbamates		NPD	5% OV-17	0.01 mg/kg	Fruits, vegetables	[69]
	MeI–NaH	Coulson	3% OV-1	0.005–0.01 ppm	Cereals, fruits, vegetables	[35]
Thiocarbamates						
Triallate		NPD	Dexsil 300	0.02 mg/kg	Garlic	[65]
			OV-1	20 ppb	Wheat, barley	[125]
		ECD	OV-1	20 ppb	Lentils	[67]
		MS	BP-1	0.01 mg/kg	Cereals	[126]
		Coulson	OV-1	0.1 μg/g	Lettuce, peas, corn	[127]
Thiobencarb		ECD, NPD	OV-17+OV-210	4 μg/g[c]	Rice	[61]
Uracils						
Bromacil		ECD	XE-60	0.08 ppm[c]	Oranges	[72]
		NPD	OV-17+QF-1	0.04 ppm[c]	Citrus, pineapple	[73]
Lenacil	DMFA–BSTFA	MS	OV-1		Spinach	[75]
			DB-5	0.0003 ppm	Spinach	[76]
Terbacil		ECD	QF+DC-200	1 ppb	Blueberries	[77]
		Microcoulometric	XE-60+Epon resin 1001	0.04 ppm	Fruits	[78]
		NPD	DB-17	1 μg/kg	Asparagus	[79]
Glyphosate						
	TFAA–HFB	MS	Durabond 5.625	0.01 mg/kg	Corn, soya, fruits	[80]
	TFAA–TFE	NPD	Ultrabond 20SE	0.03 mg/kg	Berries	[86,87]
	TFAA–Diazomethane	NPD	SP-2250, SP-2401	0.05 ppm	Kiwi, asparagus	[88]
	HFBA/BCl_3-2-chloroethanol	ECD	DC-200	0.05 ppm	Blueberries	[81]
Bipyridylium						
Paraquat	H_2-PtO_2	FID	Carbowax (KOH)	0.05 ppm	Lettuce, carrots, onions	[98]
Diquat	$NaBH_4$	NPD	OV-17, OV-101, Carbowax (KOH)	0.01 ppm	Potatoes	[94]
Paraquat, Diquat	$NaBH_4$ –$NiCl_2$	NPD, MS	Apiezon L (KOH)	0.005 mg/kg	Potatoes	[93]
Multiresidues						
		MS	DB-1	0.05–0.25 ppm	Fruits, vegetables, corn	[108]
			DB-5	0.6–6 ng/g	Fruits, potatoes, beans	[103,127]
			DB-1701	0.004–0.20 ppm	Fruits, vegetables	[104,109,110]
			CP SIL 5CB		Apple, wheat, vegetables	[114]
		MS–MS	Rtx-5	1–4 ppb	Fruits, vegetables	[105]
		ECD	Phenyl–methyl silicone	0.2 ppm	Vegetables, oranges	[101]
			DB-5; DB-1701	0.003–0.08 mg/kg	Apples, vegetables	[106]
		AED	HP-1	0.01 ppm	Onions, red radishes	[111]
		NPD	HI-EFF 8BP; OV-17	0.005–0.01 mg/kg	Maize	[112]
		Coulson, ECD	OV-1	0.2 ppm[c]	Cereals, vegetables	[113]

[a] Abbreviations: HFB, heptafluorobutanol; TFAA, trifluoroacetic anhydride; TFE, trifluoroethanol; HFBA, heptafluorobutiric anhydride; DMFA, dimethylformamide; BSTFA, bis(trimethylsilyl)trifluoroacetamide; TBAH, tetrabutylammonium hydroxide; HECD, electrolytic conductivity detection; AED, atomic emission detector.

[b] DL, detection limit.

[c] Lowest concentration determined.

[103,104,108–110,114,127]. This technique can be employed as a universal detector when used in the cyclic scanning mode or as a very sensitive and selective detector when used in the SIM mode.

A technique introduced recently is the atomic emission detection. This detector, formed by a microwave-induced helium plasma and an atomic emission spectrometer, allows monitoring charac-

Table 14
HPLC methods used to determine the different herbicides in food samples[a]

Herbicide class	Derivatization	Mode	Column	Mobile phase	Detector	D.L.[b]	Matrix	Refs.
Phenoxyacids								
Dichlorprop		Reversed-phase	C_{18}	Methanol–acetic acid–water	UV 280 nm	2 ppb	Citrus	[13]
Aryloxyphenoxyacids								
Fluazifop, fluazifop-butyl		Reversed-phase	C_{18}	Methanol–phosphate buffer pH 2.3	UV 270 nm	0.2 ppm	Onions	[10]
Benzonitriles								
Bromoxynil–octanoate		Reversed-phase	C_{18}	Methanol–water	UV 228 nm	0.05 ppm	Wheat	[20]
Phenylureas								
Diuron		Reversed-phase	C_{18}	Acetonitrile–water	UV	0.08–0.17 ppm	Blueberries	[100]
Linuron		Normal phase	NH_2	Isopropanol–isooctane	UV 248 nm	0.015 μg/g	Potatoes	[26]
		Reversed-phase	C_{18}	Acetonitrile–water	UV 220 nm		Carrots	[30]
				Methanol–water	UV 245 nm	0.016 ppm	Carrots	[25]
					UV 249 nm	0.02 mg/kg	Garlic	[31]
					UV 248 nm	10 μg/kg	Asparagus	[32]
Phenylureas		Reversed-phase	C_{18}	Methanol–acetonitrile–water	UV 242 nm	0.01 mg/kg	Vegetables	[27]
				Methanol–water	UV 240 nm	0.02 μg/g	Wheat	[37]
				Acetonitrile–ammonium acetate–water	MS	0.25–0.50 ppm	Fruits, vegetables	[102]
	Photolysis OPA-MERC	Reversed-phase	C_{18}	Methanol–water	FL 340, 455 nm	0.001–0.006 ppm	Fruits, vegetables, corn	[36]
Sulphonylureas								
Metsulfuron-methyl		Reversed-phase	C_8	Methanol–phosphate buffer pH 7.0	UV 254 nm	0.005 μg/g	Cereals, sugarcane	[28]
Bensulfuron-methyl		Reversed-phase	Phenyl and C_8	Acetonitrile–phosphate buffer pH 7.6 and pH 3.2	UV 254 nm	0.008, 0.020 ppm	Rice	[29]
Triazines								
Atrazine		Reversed-phase	C_{18}	Methanol–water	UV 230 nm	0.015–0.300 ppm[c]	Oranges, corn	[47]
Simazine		Reversed-phase	C_{18}	Acetonitrile–water	UV	0.08–0.17 ppm	Blueberries	[100]
				Methanol–acetate buffer pH 5.0	UV 230 nm	20 μg/l	Grape juice	[48]
Triazines		Reversed-phase	C_{18}	Acetonitrile–phosphate buffer pH 6.7	UV 220 nm	10 ng/g	Vegetables	[43]
Chloroacetamides								
Metolachlor		Reversed-phase	C_{18}	Acetonitrile–water	UV 220 nm		Carrots	[30]

Carbamates								
Chlorpropham		Reversed-phase	C_{18}	Methanol–acetonitrile–water	UV 236 nm	0.12 ppm	Vegetables	[62,63]
		Normal-phase	CN	Dichloromethane–hexane	UV 238 nm	0.06 ppm	Potatoes	[66,128]
Chlorpropham, propham		Reversed-phase	C_{18}	Methanol–phosphate buffer pH 6.6	UV 248 nm	0.002 μg/g	Potatoes	[68]
Carbamates		Normal-phase	Silica	Isooctane–dioxane	UV 254 nm	0.1–1 μg	Fruits, vegetables	[69]
Uracils								
Lenacil		Reversed-phase	C_{18}	Methanol–water	UV 270 nm	0.02 mg/kg	Strawberries	[74]
Glyphosate								
	Calcium hypochlorite OPA	Anion-exchange	Aminex A-9	Methanol–phosphate buffer pH 1.9	FL 340, 455 nm	0.01–0.05 ppm	Fruits, vegetables	[84,85]
	Calcium hypochlorite OPA-MERC	Anion-exchange	Aminex A-9	Methanol–phosphate buffer pH 1.9	FL 230, 418 nm	0.07–0.14 μg/g	Lentils, cereals, vegetables	[82,83]
			Aminex A-27	Phosphoric acid–sulphuric acid–water	FL 360, 455 nm	0.05 ppm	Fruits, vegetables	[90]
	$NaNO_2$	Anion-exchange	Dionex AS4A	Phosphoric acid–water	TEA	0.005–1 μg/g	Cereals, lentils, beans	[89]
	IK-sulfamic acid–acetic acid–H_2SO_4							
Bipyridylium								
Diquat, Paraquat		Reversed-phase	C_{18}	Acetonitrile–chlorhydric buffer pH 2.2	UV 257, 310 nm	0.01 ppm	Vegetables, corn	[96,97]
			NH_2	Acetonitrile–methanol–phosphate buffer pH 3	UV 257, 310 nm	0.02 μg/g	Cereals, fruits, vegetables.	[95]
		Reversed-phase (ion-pair)	PRP-1	Water–orthophosporic acid–diethylamine	UV 254, 313 nm	0.01 ppm	Potatoes	[91,92]
Multiresidues								
		Normal-phase	Silica	Isopropanol–isooctane	UV 254 nm	0.2 ppm[c]	Cereals, vegetables	[113]
		Reversed-phase	C_{18}	Acetonitrile–ammonium acetate–water	MS	0.25–0.50 ppm	Vegetables, apples	[102,108]
	Photolysis	Reversed-phase	C_{18}	Methanol–water	MS	5 ng	Blueberries, lettuce	[107]

[a] Abbreviations: OPA, *o*-phthalaldehyde; MERC, 2-mercaptoethanol; TEA, thermal energy analyser.
[b] D.L., detection limit.
[c] Lowest concentration determined.

teristic emission lines for phosphorus, nitrogen and sulphur. This detector has been used in multiresidue analysis of herbicides [111].

4.2. High-performance liquid chromatography

In general, detection limits obtained by HPLC are higher than those achieved by GC (Table 14). For example, GC was about 10-fold more sensitive than HPLC when they were applied to the analysis of fluazifop [10] or bromoxynil [20]. However, HPLC is more attractive than CG when derivatization is necessary prior GC analysis, since derivatization decreases the method reproducibility by adding one more sample-handling step.

HPLC analysis of herbicides is most often performed on reversed-phase columns, mainly on C_{18} columns. However, normal-phase columns have sometimes been used in the analysis of carbamates [66,69,128] and ureas [26]. Glyphosate analysis is usually performed on anion-exchange columns [82–85,89,90], due to the high polarity of this herbicide. In some cases, two different columns are used in the determination, and column switching is performed to minimise background interference and increase sensitivity. This technique has been applied to the analysis of residues in complex matrices. Some substituted ureas, like bensulfuron–methyl [29] and linuron [31,32] have been determined using this technique.

UV detection, with fixed or variable wavelength, is the detection technique most frequently used in the determination of herbicide residues (Table 14). Another detector occasionally used is the fluorescence detector. This usually requires postcolumn derivatization with ortho–phthalaldehyde, to increase the sensibility and selectivity of the method. Postcolumn derivatization followed by fluorescence detection has been used in the analysis of phenylureas [36] and glyphosate [82–85,90].

Detection by UV absorption is not selective and sensitive enough to determine some herbicide residues in complex food samples, and fluorescence detection cannot be applied to non-fluorescent herbicides or herbicide derivatives. Therefore, herbicide residues of different chemical classes are not always amenable to be determined by these techniques in multiresidue analysis. MS can perform the determination of herbicide residues in complex samples [102,108] and provides structural information that allows their identification. There are different possibilities for coupling mass spectrometers to HPLC, like electrospray, thermospray, particle beam or nebulization into an atmospheric pressure chemical ionisation source. Nevertheless, these systems are more expensive than those used in GC–MS, and hence they are less widely employed in routine residue analysis.

5. Conclusions

A wide number of herbicides are routinely monitored in foods by analytical laboratories in many countries. These compounds are generally determined by using multiresidue methods.

Herbicides are commonly extracted by homogenisation with organic solvents, although other techniques, like SFE and MSPD are recently used in the extraction of these compounds. Clean-up of extracts is necessary after sample extraction, and LLE and column chromatography on various adsorbents are widely employed in the clean-up procedure.

In the large body of literature concerning these analyses, GC, equipped with capillary columns, is the technique most widely used for the determination of herbicide residues. NPD and ECD, together with MS for confirmation purposes, are the detection methods usually employed in their determination.

However, HPLC analysis is performed in some cases, particularly when herbicides are not volatile or if they are thermally unstable. These analyses are commonly performed on reversed-phase columns with ultraviolet detection of residues. In the future, HPLC–MS may become the method of choice for multiresidue analysis and in the confirmation of the identity of residues.

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