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Reviews

Determination of cereal herbicide residues in environmental samples by gas chromatography

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Abstract

Gas chromatographic analysis of cereal herbicide residues in water, soil, plant and air is reviewed. Herbicides widely used in spring and winter cereals, i.e., phenoxyacids, benzonitriles, ureas, triazines, dinitroanilines, chloroacetamides and thiocarbamates, are considered. The main procedures used in the residue analysis, extraction, clean-up, derivatization and gas chromatographic determination are summarized and discussed.

Keywords: Reviews; Environmental analysis; Sample preparation; Derivatization, GC; Pesticides

Contents

1. Introduction

Cereals are one of the most important crops cultivated all over the world since the beginning of agriculture. In these crops, herbicides are widely used at present, particularly in the more developed countries. This widespread use contributes to their presence in the environment and thus herbicides are often found in surface and ground water [1] and in other environmental matrices [2].

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The herbicides reviewed in this paper are summarized in Table 1 and their molecular structure shown in Fig. 1. The crop where they are normally applied and some important physical-chemical properties of these herbicides are also presented in Table 2 [3].

Residue analysis of these compounds was initially carried out by colorimetric methods [4,5] or by thin-layer chromatography [6,7]. At present, gas chromatography (GC) is the technique more commonly used in the residue analysis of these herbicides in environmental samples, due to the high sensitivity obtained with nitrogen–phosphorous (NPD) and electron-capture (ECD) detection and to the selectivity and identification of residues achieved by coupling GC with mass spectrometry (MS). An alternative technique with growing use in the determination of pesticide residues, particularly in water samples, is high-performance liquid chromatography (HPLC) [8,9].

Various reviews have been published on pesticide residue analysis [9–12]. In this review we will focus on residue analysis of cereal herbicides in environmental samples, water, soil, plant and air, by gas chromatography and will consider all aspects of

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	$-CH_3$
Diclofop	Phenoxyacids	-H	$C_6H_3Cl_2O$-	-H	$-CH_3$
Fenoxaprop	Phenoxyacids	-H	CH_3ClNO	-H	$-CH_3$
MCPA	Phenoxyacids	$-CH_3$	-Cl	-H	-H
MCPP	Phenoxyacids	$-CH_3$	-Cl	-H	$-CH_3$
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	$-(CH_2)_3CH_3$	
Methabenzthiazuron	Substituted ureas	C_7H_4SN	$-CH_3$	$-CH_3$	-H
Chlorsulfuron	Sulphonylureas	-Cl	-H		
Metsulfuron	Sulphonylureas	-COOH	-H		
Triasulfuron	Sulphonylureas	$-OCH_2CH_2Cl$	-H		
Tribenuron	Sulphonylureas	-COOH	$-CH_3$		
Ametryn	Triazines	$-CH_2CH_3$	$-CH(CH_3)_2$	$-SCH_3$	
Atrazine	Triazines	$-CH_2CH_3$	$-CH(ClH_3)_2$	-Cl	
Cyanazine	Triazines	$-CH_2CH_3$	$-CCN(CH_3)_2$	-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	$-CH_3$	$-CH(CH_3)CH_2OCH_3$		
EPTC	Thiocarbamates	$-CH_2CH_3$	$-(CH_2)_2CH_3$	$-(CH_2)_2CH_3$	
Triallate	Thiocarbamates	$-CH_2CCl=CCl_2$	$-CH(CH_3)_2$	$-CH(CH_3)_2$	

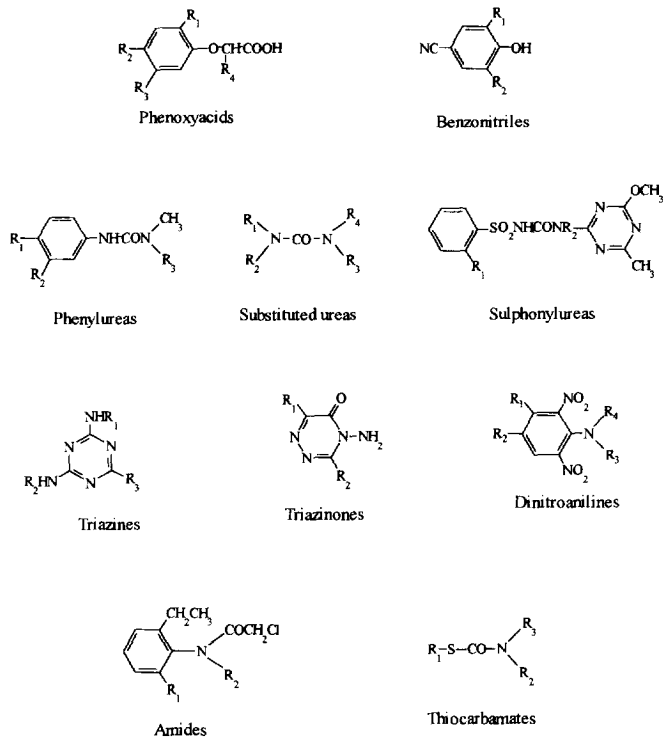

Fig. 1. Structures of the herbicides reviewed.

determination, including extraction and clean-up (Tables 3–8),) derivatization and chromatographic determination (Table 9).

2. Extraction and clean-up

2.1. Phenoxyacids and benzonitriles

Phenoxyacids have been, besides triazines and substituted ureas, one of the most used herbicides since their introduction in agriculture after the second world war, and, although the demand for these compounds is lately declining, their use will probably continue due to the low production costs [13]. The group of herbicides known as phenoxyacids or phenoxyalkanoic acids consists of phenoxyacetic, phenoxybutyric and phenoxypropionic acids. These compounds are frequently applied in combination with the benzonitriles bromoxynil or ioxynil to broaden the range of weeds controlled. Table 3 summarizes the extraction and clean-up procedures followed in the analysis of these compounds.

These herbicides are generally extracted from water at acidic pH with medium polarity solvents such as diethyl ether [14–16], methylene chloride [17] or ethyl acetate [18]. An alternative method used more recently is solid-phase extraction [19–24]. Clean-up of sample extracts is not usually required, although sometimes a Florisil column clean-up is done before their determination by GC with ECD [15,18].

Although these herbicides are applied as salts or esters, they are hydrolysed to their parent compounds and found in acidic form in the soil. Their extraction from soil is mainly carried out at acidic pH with different organic solvents like acetone [25], diethyl ether [14,26,27], methylene chloride [28], acetoni-

Table 2
Physical-chemical properties and use of cereal herbicides included in this review

Herbicide	Molecular formula	Crop	Water solubility (mg/l, pH=7)	log K_{ow} (pH=7)
2,4-D	$C_8H_6Cl_2O_3$	cereals	311 (pH=1, 25°C)	2.6–2.8
Diclorprop	$C_9H_8Cl_2O_3$	cereals	350 (20°C)	1.77
Diclofop	$C_{15}H_{12}C_2O_4$	wheat, barley	0.8 (pH=5.7, 20°C)	4.58
Fenoxaprop	$C_{16}H_{12}ClNO_5$	wheat,triticale	0.9 (25°C)	
MCPA	$C_9H_9ClO_3$	cereals	734 (25°C)	0.46 (pH=5)
MCPP	$C_{10}H_{11}ClO_3$	cereals	734 (25°C)	0.10
Bromoxynil	$C_7H_3Br_2NO$	cereals	130 (25°C)	
Ioxynil	$C_7H_3I_2NO$	cereals	50 (25°C)	
Chlorotoluron	$C_{10}H_{13}ClN_2O$	wheat, barley	74 (25°C)	2.5
Isoproturon	$C_{12}H_{18}N_2O$	wheat, barley, triticale	65 (22°C)	2.5
Linuron	$C_9H_{10}Cl_2N_2O_2$	winter wheat, maize	81 (25°C)	3.00
Metobromuron	$C_9H_{11}BrN_2O_2$	maize	330 (20°C)	2.41
Metoxuron	$C_{10}H_{13}ClN_2O_2$	winter wheat, barley	678 (24°C)	1.60
Neburon	$C_{12}H_{16}Cl_2N_2O$	cereals	5 (25°C)	
Methabenzthiazuron	$C_{10}H_{11}N_3OS$	cereals	59 (20°C)	2.64
Chlorsulfuron	$C_{12}H_{12}ClN_5O_4S$	winter cereals	27 900 (pH=7, 25°C)	−1
Metsulfuron	$C_{13}H_{13}N_5O_6S$	wheat, barley	2790 (25°C)	−1.74
Triasulfuron	$C_{14}H_{16}ClN_5O_5S$	cereals	815 (25°C)	−0.59
Tribenuron	$C_{14}H_{15}N_5O_6S$	cereals	280 000 (pH=6, 25°C)	−0.44
Ametryn	$C_9H_{17}N_5S$	maize	200 (25°C)	2.63
Atrazine	$C_8H_{14}ClN_5$	maize	33 (20°C)	2.5
Cyanazine	$C_9H_{13}ClN_6$	cereals	171 (25°C)	2.1
Simazine	$C_7H_{12}ClN_5$	maize	6.2 (20°C)	2.1
Terbutryn	$C_{10}H_{19}N_5S$	winter cereals, maize	22 (20°C)	3.65
Metribuzin	$C_8H_{14}N_4OS$	winter cereals	1050 (20°C)	1.57 (pH=5.6)
Butralin	$C_{14}H_{21}N_3O_4$	rice, barley	1.0 (24°C)	
Ethalfluralin	$C_{13}H_{14}F_3N_3O_4$	maize, sorghum	0.3 (20°C)	5.11
Pendimethalin	$C_{13}H_{19}N_3O_4$	cereals	0.3 (25°C)	5.18
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	winter cereals	0.221 (25°C)	5.27 (pH=7.7–8.9)
Alachlor	$C_{14}H_{20}ClNO_2$	maize	242 (25°C)	
Metolachlor	$C_{15}H_{22}ClNO_2$	maize, sorghum	488 (25°C)	2.9
EPTC	$C_9H_{19}NOS$	maize	375 (25°C)	3.2
Triallate	$C_{10}H_{16}Cl_3NOS$	wheat, barley	4 (25°C)	

trile [17,29,30] or with mixtures of solvents [31–34]. Soil extraction at basic pH is seldom accomplished [14,35,36]. Recently, extraction by supercritical fluids has also been proposed [37]. Clean-up of soil extracts is usually required and it is performed in some cases by liquid–liquid partition (LLP) at basic pH [26,28] or, in other cases, a more complete clean-up is required and LLP is followed by column chromatography of the derivatized residues on Florisil [14,25] or silica gel [31,33,35] using low polarity solvents as eluent.

Extraction of these compounds from plants is commonly carried out with aqueous solutions at basic pH [28,34,38–42]. These acidic herbicides are best released from plant materials at basic pH and a hydrolytic step is usually included in the extraction procedure [38]. The extraction with organic solvents followed by hydrolysis at basic pH is also used [42,43]. Clean-up of plant extracts is normally required, being LLP [28,34], usually followed by column chromatography on Florisil [38–40, 42–45], the procedures employed.

Extraction of these herbicides from air is accomplished by using different trapping phases, polyurethane foam plugs, (PUF) [46–48], XAD-resins [49,50] or ethylene glycol [51]. These compounds are recovered from the trapping phase in hexane and usually determined without a further clean-up.

Table 3
Extraction and clean-up of acidic herbicides, phenoxyacids and benzonitriles

Matrix	Herbicide	Extraction	Clean-up	Refs.
Water	Acidic herbicides	Et_2O–Shaking	-	[14,16]
	Acidic herbicides	Et_2O–Shaking, pH=1	Florisil column	[15]
	Diclofop	CH_2Cl_2, pH=1	Florisil column	[17]
	Phenoxyacids	EtOAc–Shaking, pH=1	LLP–Florisil column	[18]
	Phenoxyacids	Supported liquid membrane	-	[19]
	Phenoxyacids	SPE (C_8 pH=2.2, C_{18} pH=1–2.5)	-	[20–23]
	Phenoxyacids	XAD 2-resin	-	[24]
Soil	Acidic herbicides	$Ca(OH)_2$ solution–Shaker	LLP–XAD 2 resin	[36]
	2,4-D	Et_2O–Shaker, pH=1	LLP–Florisil column	[14,26]
	2,4-D	NaOH 0.2 *N*–Shaker	LLP–Florisil column	[14]
	Diclofop	MeOH:H_2O:EtOAc–Shaker, acidic pH	-	[32]
	MCPP	Et_2O–Shaker, pH=1	-	[27]
	Fenoxaprop	CH_3CN:H_20(8:2)–Shaker	LLP–Silica column	[31]
	Phenoxyacids	CH_3CN (acidic pH)	LLP	[17,29]
	Phenoxyacids	Acetone:Hexane–Stirring, pH=1	LLP–Silica column	[33]
	Phenoxyacids	$Ca(OH)_2$ solution–Sonication	Silica column	[35]
	Phenoxyacids	CH_2Cl_2–Shaker, pH=1	LLP	[28]
	Phenoxyacids	Acetone–Shaker, pH=1.6	LLP–Florisil column	[25]
	Phenoxyacids	Supercritical fluid extraction	-	[37]
	Benzonitriles	CH_2Cl_2:H_2O–Shaker, pH=1	-	[34]
	Bromoxynil	CH_3CN–Shaker, acidic pH	-	[30]
Plant	Acidic herbicides	NaOH 0.1 *M*–Homogenizer	LLP–Florisil column	[38–40,42]
	Acidic herbicides	NaOH 0.1 *M*–Homogenizer	LLP	[28,34]
	Acidic herbicides	EtOH:H_2O (80:20)–Homogenizer	LLP–Florisil column	[39,42,43]
	Acidic herbicides	MeOH–Homogenizer	LLP–Florisil column	[25,44]
	2,4-D	Acetone: $CHCl_3$–Reflux, pH=1.5	LLP–Florisil column	[45]
	Phenoxyacids	Aqueous basic buffer–Homogenizer	-	[41]
	Bromoxynil	NaOH 0.1 *M*–Homogenizer	LLP–Florisil column	[40]
Air	2,4-D	Polyurethane foam (PUF)	-	[46,47]
	2,4-D	Ethylene glycol	-	[51]
	2,4-D	XAD-resin	-	[49]
	Bromoxynil	Silica gel–XAD 4	-	[50]
	Bromoxynil	Polyurethane foam (PUF)	-	[48]

2.2. Ureas

Substituted ureas are also one of the oldest herbicide groups used in agriculture, phenylureas being one important class of these substituted ureas employed since early fifties and sulphonylureas another main class developed more recently with a high herbicidal activity [13]. Their extraction from environmental samples and clean-up procedures are presented in Table 4.

These compounds are mainly extracted from water with dichloromethane [16,52–55] or, in some cases, with chloroform [56]. Another important procedure is solid-phase extraction (SPE), C_{18} being the phase normally employed [57,58]. In addition, automatic on line procedures followed by HPLC analysis have been developed [59]. Extract clean-up of water samples is seldom required [55].

Methanol is the solvent most often used in the extraction of substituted ureas from soil samples with mechanical shaking [52,53,57,60–65]. The use of other solvents like dichloromethane [54], acetone with Soxhlet extraction [66] or in combination with other solvents [67], or extraction by supercritical fluids [68] has also been proposed. Clean-up of extracts is sometimes carried out by column chromatography [54,57,63].

The extraction of substituted ureas from plants has been usually accomplished with water miscible solvents like methanol [69–71], ethanol [72], acetone

Table 4
Extraction and clean-up of urea herbicides

Matrix	Herbicide	Extraction	Clean-up	Refs.
Water	Chlorsulfuron	CH_2Cl_2 acidic pH–Shaking	Florisil column	[55]
	Neburon	$CHCl_3$–Shaking	-	[56]
	Phenylureas	CH_2Cl_2–Shaking	-	[16,52–54]
	Phenylureas	SPE (Pt, C_{18}), on line	-	[59]
	Sulphonylureas	SPE (C_{18})	-	[57,58]
Soil	Linuron	MeOH–Shaker	Florisil column	[63]
	Methabenzthiazuron	Acetone:EtOAc:$CHCl_3$–Shaker	LLP	[67]
	Metobromuron	Acetone–Soxhlet	-	[66]
	Metoxuron	CH_2Cl_2–Homogenizer	Silica column	[54]
	Phenylureas	MeOH–Shaker	-	[52,53,60–62,64,65]
	Phenylureas	Supercritical fluid extraction	-	[68]
	Sulphonylureas	MeOH+HOAC–Shaker	C_{18} column	[57]
Plant	Chlorotoluron	MeOH:H_2O (80:20)–Homogenizer	Silica column	[69,70]
	Linuron	Acetone–Homogenizer	Florisil column	[73]
	Metoxuron	Acetone (basic pH)	LLP–silica column	[54]
	Phenylureas	MeOH–Homogenizer	LLP–Florisil column	[71]
	Phenylureas	EtOH–Homogenizer	LLP	[72]
	Phenylureas	CH_3CN–Homogenizer	Florisil:MgO:cellulose column	[6]
	Sulphonylureas	EtOAc–Homogenizer	C_{18} column	[57]
	Sulphonylureas	Supercritical fluid extraction	-	[74]

[54,73] or acetonitrile [6]. The use of supercritical fluid extraction has been proposed in recent years [74]. The determination of urea herbicides in plants normally needs the clean-up of extracts. Column clean-up, alone or in combination with LLP are the methods more employed. Florisil [6,71,73], silica gel [54,69,70] and C_{18} [57] are the most used columns.

Substituted ureas are rarely detected in air due to their low vapour pressure [75].

2.3. Triazines

Triazines are a numerous and important group of herbicides employed for several decades to control many grass and broad-leaf weeds in non-cropped land and in a variety of crops, especially in maize where atrazine is most often used [13]. Table 5 shows the extraction and clean-up procedures followed in their determination.

LLP has commonly been used for the extraction of triazines from water, dichloromethane being the organic solvent most widely used [17,76–81] and acetonitrile [82] and ethyl acetate [83] sometimes employed. SPE has a growing use in herbicide extraction from water and C_{18} [84–87], cyclohexyl [88] or XAD-resins [85,89] are normally used.

Extraction of these compounds from soil is generally accomplished by mechanical shaking or Soxhlet with an organic solvent, alone or in mixture with water [76,79,90–96], sometimes at acidic pH [97]. Clean-up of extracts is required in some cases, according to the soil organic matter content or the detection level needed. This clean-up is commonly achieved by LLP, column chromatography or both. Supercritical fluid extraction is a novel technique which has also been used [98].

Triazines are extracted from plants by homogenizing with polar organic solvents, like methanol [79,99–101] or acetonitrile [102], often in mixture with water [92,93,103] or with methylene chloride [104] or chloroform [105]. Clean-up of extracts is usually needed and carried out by LLP with ethyl acetate or diethyl ether, followed by column chromatography on alumina, silica gel or Florisil.

These compounds have been determined in air by trapping them in PUF [47,106], although triazine volatilization losses to the atmosphere are not important.

Table 5
Extraction and clean-up of triazines

Matrix	Herbicide	Extraction	Clean-up	Refs.
Water	Atrazine	SPE (cyclohexyl)	-	[88]
	Atrazine	CH_2Cl_2–Stirring	Florisil column	[17]
	Metribuzin	CH_3CN:CH_2Cl_2 (1.75:1)–Shaking	-	[82]
	Triazines	CH_2Cl_2–Shaking	Florisil column	[80,81]
	Triazines	CH_2Cl_2–Shaking	-	[76–79]
	Triazines	XAD 2-resin	-	[85,89]
	Triazines	EtOAc–Stirring	-	[83]
	Triazines	SPE (C_{18})	-	[84–87]
Soil	Atrazine	CH_3CN:H_2O (9:1)–Shaker	LLP–Alumina column	[90,91]
	Atrazine	H_2O–0.35 *M* HCl–microwave oven	Cyclohexyl cartridge	[88]
	Atrazine	Acetone:hexane 50:50	-	[77]
	Atrazine	AcOEt–Shaker	-	[76]
	Cyanazine	MeOH:H_2O (1:1)–Shaker	LLP–Alumina column	[93]
	Metribuzin	CH_3CN:H_2O (5:1)–Reflux	LLP–Florisil column	[92]
	Metribuzin	MeOH:H_2O (2:8)–Soxhlet	LLP	[94]
	Simazine	Acetone:buffer (pH=2) (9:1)–Shaker	LLP–Silica column	[97]
	Triazines	MeOH–Soxhlet	Florisil column	[95,96]
	Triazines	MeOH–Shaker	LLP	[79]
	Triazines	Supercritical fluid extraction	-	[98]
Plant	Atrazine	MeOH–Homogenizer	Acidic Aluminum oxide	[99]
	Cyanazine	MeOH:H_2O (4:1)–Homogenizer	LLP–Alumina column	[93]
	Metribuzin	Acetone:water (3:1)	LLP–Silica column	[103]
	Metribuzin	CH_3CN:H_2O (4:1)–Reflux	LLP–Florisil column	[92]
	Simazine	CH_3CN–Homogenizer	LLP–Alumina column	[102]
	Simazine	H_2O, $CHCl_3$–Homogenizer, shaker	Alumina column	[105]
	Triazines	CH_2Cl_2–Maceration	Silica column	[104]
	Triazines	MeOH–Blender	LLP–Alumina column	[79,100]
	Triazines	MeOH–Homogenizer	LLP–TLC	[101]
Air	Atrazine, Simazine	Polyurethane foam (PUF)	-	[47,106]

2.4. Dinitroanilines

Dinitroaniline herbicides are usually soil applied in a wide variety of agronomic crops and particularly, in winter and spring cereals. Their high lipophilicity and low water solubility mean that they are scarcely present in surface or underground water. Some dinitroanilines have a noticeable vapour pressure, volatilization being an important way of disappearance from soil. Their extraction from environmental matrices and clean-up procedures are summarized in Table 6.

Extraction of these compounds from water have usually been accomplished by SPE on reversed-phase columns [20,107] or XAD-resins [108] and by dichloromethane partition followed in some cases by a column clean-up [76,81,109].

The extraction of these herbicides from soil has been carried out with various organic solvents [107,110–116] followed by a Florisil column or LLP clean-up in some cases.

Methanol is widely used in the extraction of these compounds from plants [111,117–119] and ethanol is sometimes employed [120]. The clean-up of extracts, generally necessary, is accomplished by LLP along with Florisil column in some cases.

Different phases have been used to trap these compounds from air. The trapping phases employed are organic solvents [121–123] or adsorbents [111,115,118,121,124–129]. After the extraction of these compounds from the trapping phase a clean-up of samples is seldom required.

2.5. Chloroacetamides

These herbicides also termed anilides are, in

Table 6
Extraction and clean-up of dinitroanilines

Matrix	Herbicide	Extraction	Clean-up	Refs.
Water	Dinitroanilines	SPE (C_{18})	-	[107]
	Pendimethalin	CH_2Cl_2–Shaking	-	[76]
	Pendimethalin	XAD 2-XAD 7 resins	-	[108]
	Pendimethalin	SPE (C_8), pH=2.2	-	[20]
	Trifluralin	CH_2Cl_2–Shaking	Florisil column	[81]
	Trifluralin	CH_2Cl_2–Shaking	Silica microcolumn	[109]
Soil	Dinitroanilines	MeOH:H_2O (25:3)–Shaker	LLP	[110]
	Dinitroanilines	Et_2O–Shaker	-	[107]
	Dinitroanilines	EtOAc–Shaker	-	[76,111]
	Dinitroanilines	CH_3CN:H_2O (99:1)–Shaker	Florisil cartridge	[112]
	Trifluralin	MeOH–Shaker	-	[113]
	Trifluralin	Acetone–Shaker	-	[114]
	Trifluralin	Hexane:propanol (1:1)–Shaker	-	[115]
	Trifluralin	Hexane:benzene (4:1)–Shaker	-	[116]
Plant	Dinitroanilines	MeOH–Homogenizer	LLP–Florisil column	[111,117]
	Dinitroanilines	MeOH–Homogenizer	LLP	[118]
	Trifluralin	MeOH–Homogenizer	Florisil column	[119]
	Trifluralin	EtOH 95%–Homogenizer	-	[120]
Air	Dinitroanilines	Florisil	-	[111,128,129]
	Pendimethalin	Different trapping phases	-	[121]
	Pendimethalin	XAD 4-resin	-	[118]
	Pendimethalin	XAD 4-resin	C_{18} column	[124]
	Trifluralin	Polyurethane foam (PUF)	-	[115]
	Trifluralin	Xylene	-	[122]
	Trifluralin	Hexane–Ethylene glycol	-	[123]
	Trifluralin	Polyurethane foam (PUF)	-	[125,126]
	Trifluralin	Activated charcoal–$CaSO_4$	-	[127]

Table 7
Extraction and clean-up of chloroacetamides

Matrix	Herbicide	Extraction	Clean-up	Refs.
Water	Chloroacetamides	CH_2Cl_2–Stirring	-	[81]
	Chloroacetamides	CH_2Cl_2–Stirring	Florisil column	[76,130,131]
	Chloroacetamides	CH_3CN–Stirring	Florisil column	[135]
	Chloroacetamides	CH_2Cl_2–Stirring	Silica microcolumn	[109]
	Chloroacetamides	Micro LLP (acetone:CH_2Cl_2)	-	[132–134]
	Chloroacetamides	SPE C_{18} cartridge	-	[136–139]
	Chloroacetamides	SPE C_{18} silica membrane	-	[131]
Soil	Alachlor	MeOH:H_2O (4:1)–Shaker	-	[140]
	Alachlor	CH_3CN:H_2O (4:1)–Shaker	-	[142]
	Alachlor	XAD 2-resin	-	[130]
	Chloroacetamides	CH_3CN–Shaker	-	[141]
	Chloroacetamides	AcOEt–Shaker	-	[76]
	Chloroacetamides	MeOH–Shaker	Acidic alumina	[99]
	Chloroacetamides	Acetone–Shaker	-	[143]
Plant	Alachlor	CH_3CN:H_2O (4:1)–Shaker	Florisil column	[142]
	Chloroacetamides	MeOH–Shaker	Acidic alumina+Florisil column	[99]
	Chloroacetamides	CH_3CN–Homogenizer	LLP	[144]
Air	Alachlor	Polyurethane foam (PUF)	-	[106]
	Chloroacetamides	Different trapping phases	-	[121]
	Metolachlor	Ethylene glycol	-	[145]

Table 8
Extraction and clean-up of thiocarbamates

Matrix	Herbicide	Extraction	Clean-up	Refs.
Water	EPTC	Hexane–Shaking	-	[146]
	Triallate	Hexane, pH=12–Shaking	Florisil column	[15]
	Triallate	CH_2Cl_2–Shaking	-	[16]
	Triallate	CH_2Cl_2, pH=1–Shaking	Florisil column	[17]
Soil	EPTC	Steam distillation	LLP	[152]
	EPTC	Hexane:Acetone–Shaker	-	[146]
	Triallate	Acetone–Sonication	LLP–Florisil column	[151]
	Triallate	MeOH–Shaker	C_{18} column	[147]
	Triallate	MeOH–Shaker	-	[148]
	Triallate	CH_3CN:H_2O (9:1)	-	[149]
	Triallate	CH_3CN:H_2O–Shaker	LLP	[150]
Plant	EPTC	Steam distillation	Silica column	[152]
	Triallate	CH_3CN–Homogenizer, shaker	Alumina column	[148,153,155,156]
	Triallate	Hexane:CH_3CN–Blender	Alumina column	[154]
	Triallate	Steam distillation	Florisil column	[157]
Air	EPTC	Polyurethane foam (PUF)	-	[146]
	Triallate	Polyurethane foam (PUF)	-	[125,159]
	Triallate	Polyurethane foam (PUF)	Florisil column	[158]

general, used pre-emergence for the control of annual grass and certain broad-leaf weeds. Among these compounds, alachlor and metolachor are herbicides commonly applied in mixtures with atrazine in maize. Table 7 presents the extraction and clean-up procedures used in their determination.

Extraction of these compounds from water has been done by LLP with dichloromethane, alone or in mixture with acetone [76,81,109,130–134], or acetonitrile [135] followed by a Florisil column clean-up in some cases, or by SPE, usually with C_{18} cartridges [136–139], without further clean-up.

These herbicides have been extracted from soil by using different organic solvents [76,99,140–143], clean-up of extracts being scarcely required [99].

Extraction of these compounds from plants has been achieved by homogenizing with polar organic solvents. Clean-up of extracts is necessary, LLP and column chromatography being the procedures used [99,142,144].

Although volatilization of these compounds is low, they have been analyzed in air by trapping them in various adsorbents [106,121] or in ethylene glycol [121,145].

2.6. Thiocarbamates

Thiocarbamates have been used as herbicides in maize and wheat, frequently in combination with antidotes [13], for several decades. Their extraction from environmental samples and clean-up of extracts are summarized in Table 8.

The extraction of these compounds from water has been carried out at different pHs with good recoveries using dichloromethane [16,17] or hexane [15,146], and a Florisil column clean-up has often been required [15,17].

Water miscible solvents, like methanol [147,148], acetonitrile [149,150] and acetone [151] are generally used for the extraction from soil of these compounds. A clean-up of extracts is usually done by column chromatography on Florisil [151] or C_{18} [147] or by LLP [150–152].

Acetonitrile is widely used for the extraction from plant tissues of these compounds [148,153–156]. Steam distillation has also been employed by some authors, obtaining good recoveries [152,157]. Clean-up of plant extracts is necessary and it is mainly accomplished by using column chromatography on alumina, Florisil or silica gel.

PUF has been used as trapping phase in the analysis of these herbicides in air by different authors [125,146,158,159], with occasional clean-up.

2.7. Multiresidue

Herbicide residue analysis in environmental samples, where usually little is known about the nature

Table 9
GC methods used to determine the different herbicides in environmental samples

Herbicide class	Derivatization	Chromatographic methods		D.L.[a]	Matrix	Refs.
Phenoxyacids	BCl_3 or BF_3–MeOH	ECD	OV-210	0.1 μg/l	water	[18]
			OV-17	0.01 μg/g	soil	[32]
			Ultrabond 20 M (U-20M)	ng	plant	[38]
			OV-17	>0.05 μg/g	plant	[45]
		MS	BP-1	0.005–0.04 μg/g	soil, plant	[28]
		CCD	Dexil 300	0.05 μg/g	plant	[42]
			Ultrabond	0.1 ng	plant	[39]
	BCl_3–buthylalcohol	ECD	OV-17, Carbowax	ng	water, soil	[14]
	BCl_3–2 chloroethanol	ECD	OV-17, DC-200	0.01 μg/g	soil	[26]
	Diazomethane	CCD	U-20 M	<0.5 ppb	water	[15]
		MS	DB-1	0.02 μg/l	water	[16]
		ECD	U-20 M	<0.5 ppb	water	[15]
			DB-5	0.1 μg/l	water	[169]
			OV-17, QF-1	0.08–0.4 ng	soil, plant	[25]
			Ultrabond, OV-225	0.05–0.01 μg/g	plant	[40,168]
	TMS–Diazomethane	MS	BP-1	0.01 μg/g	soil	[143]
	H_2SO_4–2,2,2-trifluorethanol	ECD	BP-5	0.4–4 nmol/l	water	[171]
		MS	SE-54			
	Pentafluorobenzylbromide (PFBBr)	ECD	U-20 M, OV-17, OV-210	10–25 μg/g	soil	[33]
			XE-60+Epon resin	0.05 mg/kg	soil	[172]
		MS	HP-5	<1 ng/l	water	[21]
			U-20 M, OV-1, OV-17	0.5–1 μg/g	soil	[35]
			DB-5	0.8–1.8 ng/l	air	[46]
	Iodoethane–TBHS	ECD	SE-30	0.01 μg/g	soil	[36]
	H_2SO_4–2,2,2-trifluorethanol	ECD	Rtx-1	2 pg	soil	[27]
		MS	HP-5			
Benzonitriles	Diazomethane	ECD	U-20 M	0.04–0.4 ng	water	[15]
			Apiezon L	0.05 μg/g	soil	[170]
			HP-1	ppb	plant	[43]
		MS	DB-1	0.03 μg/l	water	[16]
		CCD	Ultrabond	0.01 μg/g	plant	[40]
	TMS–diazomethane	MS	BP-1	0.001 μg/g	soil	[143]
	HFBA	MS	BP-1	0.001 μg/g	soil	[34]
				0.002 μg/g	plant	

Phenylureas	NaH–EtI in DMSO	NPD	OV-210	50 ppb	soil	[175]
		ECD	SE-30			
		NPD	OV-17	0.01 μg/g	soil	[65]
		MS	BP-5			
	NaH–MeI in DMSO	CCD	SE-30, QF-1	0.1 ppm	plant	[72,176]
	HFBA	ECD	OV-210, FFAP, CP-sil 5	0.1–1 ppb	water, plant	[177–181]
	Br_2	ECD	glass column	0.02–1 ppm	soil, plant	[184,185]
	FDNB	ECD	GE-XE 60	0.01 ppm	water, soil, plant	[186]
	-	NPD	OV-17	0.01 μg/g	plant	[69,70]
		MS	BP-5			
	-	NPD	SE-54	0.5–1 ng	water	[174]
Sulphonylureas	Diazomethane	ECD		25 ng/l	water	[55]
	PFBBr	ECD	E 301, BP 10	0.1 pg	water, soil	[57]
Triazines	-	ECD	CHDMS, OV-225	0.01 μg/g	soil	[92,93]
			Silar 5CP	0.01 ng	soil	[94]
	-	NPD	Ultrabond, OV-1, DB-1, DX-4	0.025 μg/l	water	[80]
			Carbowax	200 ng	water	[79]
			PS 255+OV-1701	0.001 μg/l	water	[89]
			Carbowax+CHDMS+Silar 5CP	0.01 μg/l	water	[83]
			BP-5, SPB-20	0.05–0.1 μg/l	water	[76,84]
			OV-1, SP-2100	0.1–0.08 μg/l	water	[17,85]
			DB-225	0.1 ng/l	water	[81]
			BP-5, Supelcowax 10	0.01–0.005 μg/g	soil	[76,97]
			HI-EFF8BP or OV-17	0.005 mg/kg	soil, plant	[99]
			OV-101	0.1 μg/kg	plant	[105]
			OV-17	ng	plant	[84]
			OV-225, Carbowax 20 M	<0.01 mg/kg	plant	[104]
			OV-101	0.1 $\mu g/m^3$	air	[47]
			SPB-5	-	air	[106]
	-	MS	BP-1, SE-54	0.1–0.3 μg/l	water	[76,85]
			DB-225, DB-1	0.1 ng, 1 ng	water	[81,187]
			DB-5	0.1 ppb, 1 ppb	water, soil	[77]
			DB-225	24 pg	soil	[96]
	-	CCD	Carbowax	200 ng	water	[79]
			OV-17	0.001 ppm	water	[78]
			Silar 5CP	1 ng	soil	[94]
			SE-30	<0.02 μg/g	plant	[100]
	-	FPD	Carbowax	200 ng	water	[79]
	-	FID	SE-30 Reoplex 40+SE-30	4 ng	soil	[91]

(*Continued on p. 358*)

Table 9 (*continued*)

Herbicide class	Derivatization	Chromatographic methods		D.L.[a]	Matrix	Refs.
Dinitroanilines	-	ECD	DC-200, Carbowax 20 M, OV-17	0.01–0.03 μg/g	soil	[110,112,113,116]
			OV-1	<0.03 μg/g	soil	[114]
			XE-60	0.01 μg/g	plant	[117]
			SE-30	-	air	[127]
	-	MS	DB-5, BP-5	0.1–0.05 μg/l	water	[76,108]
			BP-1, BP-5, OV-101	0.01, 0.05 μg/g	soil, plant	[76,111,112]
			BP-1	1 ng	air	[111]
		NPD	BP-5	0.1 μg/l	water	[76]
			HP-1, BP-5	0.01, 0.05 μg/g	soil, plant	[76,111]
			HP-1	1 ng/l	air	[111]
Chloroacetamides	-	NPD	DB-225	0.1 ng/l	water	[81]
			BP-5, DB-17	0.1–0.2 μg/l	water	[76,132]
			DB-5, DB-1701	5 μg/kg	soil	[130]
			BP-5	0.01 μg/g	soil	[76]
			UC-W98	0.02–0.05 μg/g	soil, plant	[142]
	-	MS	DB-225	0.1 ng/l	water	[81]
			DB-5, BP-1	0.1–0.2 μg/l	water	[76,132]
			BP-1, OV-17	0.01 μg/g	soil	[76,99]
			EFF8BP	0.01 μg/g	plant	[99]
			BP-1	0.5 ng/l	air	[121]
	-	ECD	QF-1+DC-200, Apiezon L	0.02–0.05 ng	plant	[144]
			NPGS	-	air	[145]
Thiocarbamates	-	ECD	OV-1, OV-225, OV-17	10 ng/l	water	[17]
			OV-1, OV-225, OV-17	10–1 ng/g	soil	[149–151]
			SE-30, OV-1	0.05 ng, 20 ppb	plant	[154,155]
			SP-2401, OV-101	0.1 μg/g	plant	[157]
			U-20 M, DB-5	0.5 ng/m^3	air	[125,158,159]
	-	CCD	OV-1	0.1 μg/g	plant	[157]
		NPD	OV-1, OV-17	0.01–0.02 μg/g	plant	[153,156]
			OV-1	0.5 ng/m^3	air	[158]
	-	ITD	DB-1	0.02 μg/dm^3	water	[16]
			BP-1	0.01 mg/kg	plant, soil	[148]
			OV-1	0.5 ng/m^3	air	[158]
	-	FPD	OV-17	0.02 ppm	plant, soil	[152]
			OV-101	-	air	[146]

[a] D.L. = Detection limit.

of possible contaminants, requires methods as universal and reliable as possible. Multiresidue methods allowing the determination of residues of different chemical classes in the same extract and in a single run have been developed with that aim.

Herbicide residues in air samples are generally trapped on adsorbents like PUF and XAD-resins [47,121], residues are then extracted with organic solvents and GC determined without further clean-up.

Multiresidue extraction from soil and plant samples is usually carried out with organic solvents, acetone, methanol, ethyl acetate or acetonitrile being the most used extractants [12,143,151,160]. The addition of water may improve, in some cases, desorption of herbicides from the matrix. Plants are commonly extracted by homogenizing and soils by means of a wrist action or orbital shaker. The organic extract is generally reduced in volume and a clean-up procedure is accomplished before GC determination. In plant extracts, this procedure usually consists of a LLP between organic and aqueous phases, followed by a column chromatography on silica gel, Florisil [151] or alumina [161]. Clean-up of soil extracts is similar, but not as intensive as for plants. Supercritical fluid extraction has recently been employed for extraction of herbicides, mainly from soil samples, by using supercritical CO_2 with polar modifiers in some cases, and acceptable recoveries were obtained in the analysis of several herbicide groups [37,68,98].

Extraction of herbicide residues from water has been accomplished by partitioning into an organic solvent, usually dichloromethane [81,162], or by SPE [20,48,50,163–165]. LLP is a laborious process which usually requires large amounts of solvents, often toxic for the environment, although micro liquid–liquid extraction has been proposed in order to avoid these problems [166]. SPE does not have these disadvantages; it only requires small amounts of solvents, but the presence of sediments may reduce flow-rate or even cause column plugging in some cases. Extraction discs, containing solid-phases similar to those used in prepacked columns have been used with the aim of increasing water flow-rate and therefore analysis productivity [164]. An alternative technique, solid-phase microextraction, has been recently proposed [167]. This technique performs direct extraction by using a syringe assembly containing a small diameter optical fiber coated with a polymeric stationary phase, where the compounds are sorbed, being directly injected in the gas chromatograph.

3. Derivatization

Various groups of the reviewed herbicides, i.e., phenoxyacids, benzonitriles and substituted ureas, cannot be directly analyzed by GC and suitable derivatives have to be obtained prior GC determination, Table 9.

Derivatization of phenoxyacids is necessary to render them volatile and different derivatives, alkyl, chloroalkyl, silyl or pentafluorobenzyl, are obtained with that aim.

The sensitivity generally achieved with the silyl derivatives is not high enough for their determination at trace level. Among the other derivatives, methyl esters have been widely used for residue analysis. The reagents most commonly employed have been diazomethane [15,16,25,40,43,168–170] and boron trifluoride or boron trichloride methanol [18,28,32,38,39,42,45]. In addition, trimethylsilyl diazomethane [143], a reagent less dangerous than diazomethane, has also been used and good results were obtained. Methyl esters of common phenoxyacids have low retention times and interferences from sample co-extractives and poor separation on many GC columns often occur.

Alkyl derivatives containing fluorine or chlorine atoms such as 2,2,2-trifluoroethyl (TFE) [27,171] or 2-chloroethyl [26] are used with the aim of increasing their response in ECD. Nevertheless, the excess reagent and related byproducts must be carefully removed before ECD determination when using halogenated reagents.

Pentafluorobenzyl esters (PFB) are other commonly employed derivatives [21,33,35,46,172], obtained after reaction with pentafluorobenzylbromide (PFBBr). PFB esters give a higher response in ECD than the corresponding 2-chloroethyl esters [26] and similar response to that of TFE esters of some phenoxy acids. These PFB derivatives have longer retention times and higher response compared with methyl esters [173], but they have the disadvantage,

as in the case of the other halogenated reagents, of producing a large amount of interfering substances in the extract when it has to be determined by ECD [21].

Benzonitriles are easily converted in the environment to the free phenolic compounds. GC determination of these phenols may be accomplished by direct injection, although a limited sensitivity and poor reproducibility is obtained [34]. Thus, determination of benzonitriles at residue level have been commonly accomplished by derivatization with diazomethane [5,16,40,43,170] or recently with trimethylsilyl diazomethane [143] followed by GC analysis. Another reagent employed is heptafluorobutyric anhydride (HFBA) [34] which produces stable derivatives with good chromatographic response, the excess reagent being easy to remove.

Although some phenylureas can be determined directly by GC [69,70,174] various derivatization reactions have been used to make the molecule more thermostable and to obtain compounds less polar and more volatile. Alkylation of phenylureas have been carried out commonly with alkyl iodide and parent compounds can be distinguished from N-dimethyl metabolites if ethyl iodide [65,175] instead of methyl iodide [72,176] is used. Another reaction usually employed is acylation, HFBA being a reagent widely used [177–181]. The fluoroacyl groups introduced improve the stability of the molecule and make it more volatile and with higher ECD response. The fluoroacyl derivatives of the parent compounds are less stable and produce smaller peaks that the derivatives obtained from their corresponding anilines, and some authors carry out a previous hydrolysis of phenylureas followed by the derivatization of the obtained anilines.

Direct GC determination of intact sulphonylurea herbicides has not been achieved due to their thermal instability, although their decomposition products have been determined in some cases [182]. Alkylation of sulphonylureas has been studied to overcome thermal instability and improve chromatography, but a mixture of two derivatives was obtained in some cases [55]. Diazomethane has been used in the methylation of these compounds with good results. This reaction can be oriented to obtain the monomethyl derivative, which has been used to determine chlorsulfuron in water at trace level [55], or to produce the dimethyl derivatives of chlorsulfuron and metsulfuronmethyl which show good chromatographic properties and can be determined at ppb level [183]. These sulphonylurea herbicides have also been determined after derivatization with PFBBr, which form the bis PFB derivative of the hydrolysis product, 2-chlorobenzenesulfonamide, and application of this method to water and soil samples produced good results [57].

Other, less often used, derivatization reactions of substituted ureas are also indicated in Table 9 [184–186].

4. GC determination

4.1. Columns

Separation of herbicides was initially performed on packed columns containing supports coated with stationary phases of different polarity, Table 9. Nonpolar methyl silicones like DC-200, SE-30, OV-1 and OV-101 were often used [26,72,110,112,114,127,176] together with the more polar silicones OV-17, OV-210 and OV-225 and Ultrabond [14,25,26,32,69,70,112,151,175].

Capillary columns have been growing in use and replacing packed columns in most cases, due to the increase in resolution and sensitivity and to the reduction in analysis time. These columns are wall-coated open tubular (WCOT) columns of I.D. ca. 0.2 mm and 12–25 m long with bonded stationary phases. Herbicide residues are commonly analyzed on capillary columns coated with low polarity phases, like BP-1, HP-1. DB-1, BP-5, HP-5 or DB-5 [34,46,65,76,108,111,121,132,143].

4.2. Detectors

Flame ionization detection (FID) was often used, at the beginning, for analysis of herbicide residues, but an extensive sample clean-up is needed and at present it is only used if a more specific detector is not available. A modification of this detector by the addition of a bead covered with an alkaline salt makes it more sensitive for the detection of nitrogen or phosphorous compounds. This NPD method is routinely employed in the determination of her-

bicides containing nitrogen [188], particularly triazines, substituted ureas, dinitroanilines, chloroacetamides and thiocarbamates, Table 9. Residues of these herbicides can be determined in environmental samples with this detector at the ppm–ppb range, triazines being the compounds normally giving the best response, according to the highest N:C ratio of their molecules.

ECD is widely used for the analysis of halogenated compounds or derivatives, Table 9. ECD has been used extensively in the determination of cereal herbicides in environmental samples in the range of ppm–ppb. The best response is obtained with polyhalogenated herbicides, like some dinitroanilines and thiocarbamates, and it is also very often used in the analysis of phenoxyacids, benzonitriles and substituted ureas, frequently after derivatization with reagents which introduce several halogen atoms in their molecules. ECD is very sensitive for the detection of halogenated compounds but has several disadvantages like not being very selective, having a narrow linearity range and requiring a good removal of excess reagent and by-products after derivatization with halogenated reagents. An alternative for the detection of halogenated herbicides is the Coulson electrolytic conductivity detector (CCD), but this also requires avoidance of contaminants and good maintenance.

Flame photometric detection (FPD) has occasionally been used for the residue analysis of some triazines and thiocarbamates containing sulphur in their molecules [79,91,146,152].

MS is a technique with growing use in the residue analysis of herbicides, especially with the development of simpler spectrometers that, although more complex and sophisticated, can almost be used as other GC detectors. Two classes of bench-top MS detectors are often used, one is a quadrupole MS detector and the other an ion-trap detector. These detectors differ in the ion formation and mass filtration processes, but both produce good results when used in residue analysis.

When MS is operated in the cyclic scanning mode, it is an universal detector, but with a moderate sensitivity. Single-ion monitoring increases sensitivity and selectivity of MS, allowing the determination of herbicides at trace levels. This technique has been widely used in the residue analysis of cereal herbicides in environmental samples, Table 9. Quantitative determinations have been achieved at the ppm–ppb range and confirmation of the identity of residues can be done at those levels by monitoring their characteristics ions.

A novel atomic emission detection method has recently been introduced for the analysis of pesticides. This detector consists of a microwave-induced helium plasma and an atomic emission spectrometer, and detection limits of most common elements found in herbicides are in the range of pg/s. In addition, the quantitative analysis of each element makes feasible calculation of the approximate empirical formulas of the analyzed herbicides [189].

5. Conclusions

There is a large body of literature concerning the residue analysis of cereal herbicides in environmental samples. GC is the technique most employed at present, although the use of HPLC is growing, especially in water analysis. Multiresidue methods have been and continue to be developed for herbicide determination in environmental matrices. WCOT capillary columns coated with low polarity phases have replaced packed columns in most GC determinations. NPD and ECD are routinely employed in residue analysis with increasing use of MS, particularly for confirmation of the identity or in research studies. Additional developments in different steps of the analytical procedure, particularly in sensitivity and selectivity of the detection systems and in automation of the analysis would increase the reliability and productivity of herbicide residue determination.

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