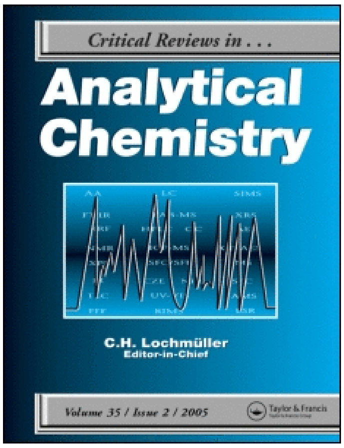

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Determination of Urea Pesticide Residues in Vegetable, Soil, and Water Samples

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ABSTRACT: The main physico-chemical, toxicological, and environmental properties of urea pesticides are summarized. General characteristics of analytical methods for residues of phenylurea herbicides (PUHs), sulfonylurea herbicides (SUHs), and Benzoylurea insecticides (BUIs) in crops, soil, and water samples, employed in the last 5 years are reviewed. Provided it is information about liquid-liquid and solid-phase extraction of the samples and clean-up steps. The applications of gas chromatography (GC), liquid chromatography (LC), and capillary electrophoresis (CE) techniques in the analysis of these compounds are exposed in tabular form and commented on. Sensitivity and instrument conditions of liquid and gas chromatographic techniques coupled to mass spectrometric detectors are outlined. The advantages and drawbacks of the analytical methods developed recently are discussed.

KEY WORDS: phenylurea herbicides, sulfonylurea herbicides, benzoylurea insecticides, liquid chromatography, gas chromatography, capillary electrophoresis, foods, water.

I. INTRODUCTION

Substituted ureas are an important group of pesticides that are used as herbicides (phenylureas and sulfonylureas) and insecticides (benzoylureas). Phenylurea herbicides (PUHs) are largely used in field applications for pre- and post-emergence weed control in a variety of crops. The main groups of phenylurea herbicides are the *N*-phenyl-*N*',*N*'-dialkylureas, *N*-phenyl-*N*'-methoxyureas, and compounds containing a heterocyclic group. More recently a group of sulfonylurea herbicides (SUHs) has been developed. SUHs are very specific to the target organisms, and thus the applied amounts in the field are much smaller than with conventional pesticides. The mechanism of action of all ureas is common, consisting in act inhibiting the photosynthesis producing herbicidal activity, impeding the chlorophyll's function due to the inhibition light reaction at the level of Hill reaction. Sulfonylureas act inhibiting acetolactate synthasa. This enzyme intervenes in the biosynthesis of branched chain amino acids conducting the photosynthesis inhibition. Benzoylurea compounds are promising insecticides (BUIs) and used because their ability to act as insect growth regulators that inhibit the synthesis of cuticle chitin in target pests. Figure 1 shows some examples of structures of the main groups of urea pesticides, and Tables 1 and 2 outline the physicochemical and toxicological properties of these compounds.

For the determination of urea pesticides several techniques can be used.[1,2] Gas chromatography (GC) is used because of its high sensitivity and selectivity for the detection of these compounds, but the thermal instability of some urea pesticides makes it necessary to first prepare stable derivatives, indirectly determine them in the form of their derivatives, or to use other techniques such as liquid chromatographic (LC) or capillary electrophoresis (CE). Although in recent years the preference for LC methods has increased in the applications for urea compounds, CG methods, when applicable, still have the advantages of great separation efficiency, high speed of analysis, and the availability of a wide range of highly

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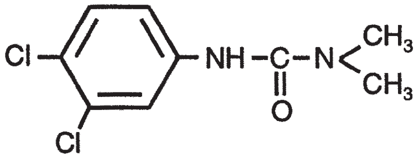
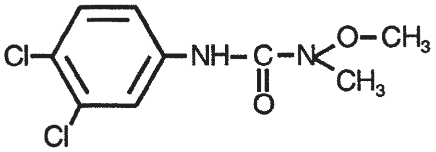
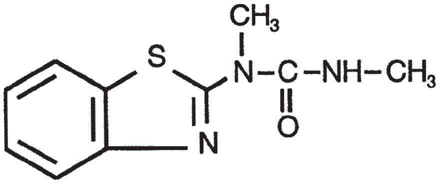
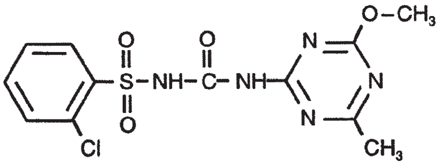
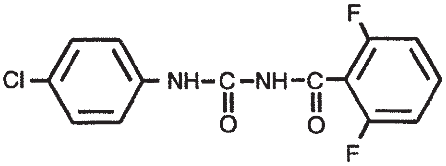
Urea pesticide group		Chemical structure of typical examples
Phenylurea (PUH)	N-phenyl -N', N'-dialkylurea	 Diuron
	N-phenyl-N'-alkyl-N'-methoxyurea	 Linuron
	Substituted urea with an heterocyclic group	 Metabenzthiazuron
Sulfonylurea (SUH)		 Chlorsulfuron
Benzoylurea (BUI)		 Diflubenzuron

FIGURE 1. Examples of the chemical structures of the main groups of substituted urea pesticides

TABLE 1
Characteristic Physico-Chemical Properties of Urea Pesticides

Common name	IUPAC name, Molecular Formula	Molecular weight	Melting Point (°C)	Vapour pressure μPa (Temp°C)	Log P_{ow} (Temp°C)	Solubility g/L (Temp °C)			
						Water	Methanol	Dichloromethane	Acetone
Diuron	3-(3,4-Dichlorophenyl)-1,1-dimethylurea $C_9H_{10}Cl_2N_2O$	233.1	180-189*	0.230	2.8-2.9 (25)	$42\ 10^{-3}$ (25)	-	1-2 (25)	53 (27)
Fluometuron	1,1-Dimethyl-3-(α, α, α -trifluoro-m-tolyl)urea $C_{10}H_{11}F_3N_2O$	232.2	163	67 (20)	2.23	$105\ 10^{-3}$ (20)	110-140 (20)	23 (20)	105-150 (20)
Linuron	3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea $C_9H_{10}Cl_2N_2O_2$	249.1	180-190*	1470 (24)	3 (22)	$81\ 10^{-3}$ (25)	-	-	500 (25)
Metobromuron	3-(4-Bromophenyl)-1-methoxy-1-methylurea $C_9H_{11}BrN_2O_2$	259.11	95.5-96	400 (20)	2.41	0.33 (20)	240 (20)	550 (20)	500 (20)
Methabenzthiazuron	1-(Benzothiazol-2-yl)-1,3-dimethylurea	221.29	119-121	5.9 (20)	2.64	$59\ 10^{-3}$ (20)	65.9 (20)	>200 (20)	115.9 (20)

TABLE 1 (continued)

Chlorsulfuron	1-(2-Chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea $C_{12}H_{12}ClN_5O_4S$	357.8	192*	613 (25)	-	0.125 (25)	14 (22)	102 (22)	57 (25)
Triasulfuron	3-(6-Methoxy-4-methyl-1,3,5-triazin-2-yl)-1-(2-(2-chloroethoxy) phenylsulfonyl) urea $C_{14}H_{16}ClN_5O_5S$	401.83	186	$0.1\ 10^{-3}$ (20)	-0.96	1.5 (20)	3.4 (25)	15 (20)	16 (25)
Chlorfluazuron	1-(3,5-Dichloro-4-(3-chloro-5-trifluoro-methyl-2-pyridiloxy) phenyl)3-(2,6-difluorobenzoyl) urea $C_{20}H_9\,Cl_3F_5N_3O_3$	540.66	228*	$<13.3\ 10^{-3}$ (20)	5.8	$16\ 10^{-6}$ (25)	2.2	22 (25)	52.1 (25)
Diflubenzuron	1-(4-Chlorophenyl)-3-(2,6-difluorobenzoyl) urea $C_{14}H_9ClF_2N_2O_2$	310.69	230-232*	<1000 (20)	3.89 (22) pH 3	$0.14\ 10^{-3}$ (20)	1	<10 (20)	6.5 (20)

* decomposition beginnings

TABLE 2
Characteristic Toxicological and Environmental Properties of Urea Pesticides

Common name	Oral toxicity (rats, mg/ kg)	ADI (mg/ kg)	MRL (mg/kg)		Hydrolysis per day (Temp, pH)	Photolysis per day (Temp, pH)	Field Dissipation half life in days (pH- % OM)	Half life in soil in days	Application (kg /ha)
			Cereals	Fruit and vegetables					
Diuron	3400	0.002	0.2	0.5	<0.0014 (25, 5-9)	0.016 (25,7)	90	372	8 - 25
Fluometuron	6416-8900	0.005	0.05	0.05	Stable (25, 5-9)	Stable (25, 5-9)	95	189	1.25 - 2
Linuron	1500-4000	0.00625	0.2	0.5	0.00086 (25, 5) 0.00051 (25,9)	0.014 (25, 5)	60 (6.4 - 2.7) 30 (5.5 - 1.3)	81	0.5 - 3
Metobromuron	2000	0.03	0.02	0.02	-	-	90	-	1 - 2.5
Methabenzthiazuron	>2500	0.075	0.05	0.05	-	-	60 - 180	-	2 - 3
Chlorsulfuron	3053-5545	0.05	0.05	0.05	0.0289 (25, 5) 0.0005 (25, 7) 0.0010 (25, 9)	0.0034 (25, 5) Stable (25, 7.9)	39 (6.9 - 1.0) 185 (5.6 - 3.8)	20 - 46	15 - 20 10^{-3}
Triasulfuron	>5000	0.005	0.05	0.05	0.023 (20, 5) Stable (20, 7-9)	0.0080 (25, 9)	10 - 87	114 -161	10 - 20 10^{-3}
Chlorfluazuron	>8500	0.025	0.05	0.05	-	-	-	-	10 - 100 10^{-3}
Diflubenzuron	>4640	0.011	0.05	0.05	0.0046 (22, 5.7)	0.1	8 (2 - 35)	4	20 - 125 10^{-3}

ADI: Admissible Dairy Intake
MRL: Maximum Residue Level
OM: Organic Matter

sensitive detectors.[3] Capillary electrophoresis (CE) is a promising analytical tool that provides improved resolution over LC with similar sensitivity at trace levels of urea pesticides in a variety of matrices with several different sets of CE conditions.[4]

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, thus reducing time and cost of analysis. The Maximum Admissible Concentration (MAC) of pesticides in drinking water, defined by European Community Directive as 0.1 μg L^{-1} for individual pesticides and 0.5 μg L^{-1} for the sum of pesticides. posed certain demands of the analytical methods for pesticide residue determination. This subject has been reviewed by several authors.[5-7] Analytical methods have also been reviewed to screen, quantify, and confirm pesticide residues in agricultural products under Maximum Residue Limits (MRLs) established by regulations.[8-10]

The aim of this review is to summarize and discuss the extraction methods developed to isolate and preconcentrate urea pesticides, and the methods used to determine these compounds the last 5 years in water and food samples.

II. EXTRACTION AND CLEAN-UP

Several of the substituted urea pesticides are highly persistent in the environment and can contaminate surface waters damaging crops if the contaminated water is used for irrigation or increasing residues in drinking water. Extraction and clean-up procedures play an important role in the determination of urea pesticides in food and water samples. An important advantage of reversed-phase column LC in conjunction with aqueous samples is that the low eluotropic strength of water samples allows the injection of large sample volume.[11] Phenylureas can be determined using a GC method by large volume injection.[12] Aqueous samples can be analyzed directly by CE.[13] Although the traditional liquid–liquid extraction (LLE) requires the handling of a large volume of solvents, some methods are proposed for the analysis of waters with dichloromethane,[14-17] ethyl acetate,[18,19] or acetonitrile,[20] for vegetables with ethyl acetate,[21,22] acetone,[23,24] dichloromethane,[12,16,25-27] or acetonitrile.[28-30] The extracts from vegetal samples are cleaned up by gel permeation chromatography[21,23,24,27] or solid-phase extraction (SPE) to clean up with silica,[19,22,25] aminopropyl cartridges,[28] or cation exchange SPE.[13]

SPE is a very useful preconcentration technique that allows both extraction and concentration of pesticide residues. Water samples can be extracted using SPE bulk C18 sorbent,[31] disks,[32,33] columns,[34-36] or cartridges.[37-45] After SPE extraction, extracts can be cleaned up with alumina cartridges.[36] Considerable reduction of solvent consumption can be achieved by miniaturizing the scale of sample extraction. Adoption techniques such as matrix solid-phase dispersion (MSPD) can help to reduce considerably the size of sample and the solvent consumption. C8 bonded silica is used to extract BUIs from citrus fruits.[46,47] Solid-phase microextraction (SPME), a solvent-free, easy sample preparation method, is used to extract urea pesticides from water.[48,49]

Automatic devices that couple on-line the sample pretreatment by SPE-LC in one analytical run are nowadays commercially available. This method is well suited for multiresidue analysis of water samples.[50-53] Both parent and breakdown products of sulfonylureas were extracted on-line from large water samples by supercritical fluid chromatography SFC.[54] The combination of an on-line concentration and extraction and microbore LC is capable of providing good recoveries in the determination of herbicides in environmental water samples.[55]

Tables 3 and 4 summarize the main liquid-liquid and solid-phase extraction procedures found in the literature and the cleaning-up steps used before determination. In general, analytical procedures based on GC detectors do not need extracts of great purity, and cleaning-up can usually be avoided. Dichloromethane is the most frequently used solvent for extraction and clean-up purposes in methods based on liquid-liquid partition, whereas octadecylsilica is largely preferred over other supports in SPE methods.

III. DETERMINATION SYSTEMS

A variety of analytical methods have been used for the analysis of pesticides. Most analyti-

TABLE 3
Liquid-Liquid Extraction and Clean Up Procedures of Urea Pesticides

Type of compound	Matrix (Volume)	Extracting solvent	Clean up sequence	Method of determination	Ref.
Phenylurea	Water (500mL)	3x 50mL dichloromethane	–	GC	[18]
Phenylurea	Water (500mL)	3x50mL dichloromethane	–	GC	[12]
Phenylurea	Crops (100g)	200mL acetone	Solvent exchange 2 x 100mL dichloromethane Gel permeation chromatography Ethyl acetate-cyclohexane (1:1)	GC	[24]
Benzoylurea	Apples (25g)	125mL dichloromethane	–	GC	[26]
Phenylurea and benzoylurea	Water	3x100mL dichloromethane	–	LC	[14]
Phenylurea	Water (300mL)	30mL dichloromethane	–	LC	[15]
Phenylurea and sulphonylurea	Water (1L)	3x60mL dichloromethane	–	LC	[16]
Benzoylurea	Grapes (50mL)	100mL ethyl acetate	Silica cartridges Dichloromethane-isopropanol (9:1)	LC	[19]
Benzoylurea	Plant material (50g)	100mL ethyl acetate	Gel permeation chromatography Ethyl acetate-cyclohexane (1:1)	LC	[21]
Benzoylurea	Apples and pears (50g)	100mL ethyl acetate	Silica cartridge Dichloromethane-2-propanol (9:1)	LC	[22]
Phenylurea	Carrot and potato (20g)	40mL acetone 20mL Ethyl acetate-cyclohexane (1:1)	Gel permeation chromatography Ethyl acetate-cyclohexane (1:1) Florisil cartridge Ethyl acetate-n-hexane Acetone-n-hexane	LC	[23]
Sulfonylurea	Rice and crayfish (5g)	100mL dichloromethane	Hexane Silica cartridges Isopropyl alcohol-hexane (1:9)	LC	[25]
Benzoylurea	Apples (50g)	100mL acetone	Solvent exchange 50mL dichloromethane Gel permeation chromatography Cyclohexane-chloroform (3:2)	LC	[27]

TABLE 3 (continued)

Sulfonylurea	Soil (50g)	Methanol-0.1M NaOH (1:1)	Dichloromethane washing (pH 11) Solvent exchange dichloromethane (pH 3-4)	LC	[35]
Sulfonylurea	Cottonseed and cotton gin trash (5g)	50mL acetonitrile-0.1M ammonium carbonate (8:2)	_	LC	[45]
Sulfonylurea	Water (1L)	pH 6.0 3x 60mL dichloromethane	_	CE	[17]
	Soil (20g)	2 x 100mL Methanol-0.1M Potassium phosphate (1:1)	Solvent exchange 3 x 30mL dichloromethane		
Sulfonylurea	Grains (10g)	2 x 50mL acetonitrile	2 x 20mL Hexane washing Isolute SCX cartridge 0.1M ammonium acetate Solvent exchange 2 x 20 mL acetonitrile-dichlorometane (5:95)	CE	[30]

TABLE 4
Solid phase Extraction and Clean Up Procedures of Urea Pesticides

Type of compound	Matrix (Volume)	Extracting phase (Eluting solvent)	Clean up sequence	Method of determination	Ref.
Phenylurea	Water (1 L)	C_{18} cartridges (30 mL Ethyl acetate)	-	GC	[38]
Phenylurea	Water (1 L)	C_{18} column (Hexane-2-propanol (3:1))	-	GC	[39]
Phenylurea	Water (1 L)	C_{18} column (2 x 10 mL ethyl acetate)	-	GC	[31]
Phenylurea Sulfonylurea	Water (2 mL)	85 µm Polyacrylate (SPME) 14,3% NaCl pH 4, 60 min	-	GC	[48]
Benzoylurea	Wines (3 mL)	100 µm Polydimethylsiloxane (SPME) 12.5% Ethanol Tª 45°C, 30 min	-	GC	[49]
Phenylurea	Water (1 L)	47 mm Empore disks 2 x 5 mL Ethyl acetate	-	LC	[32]
Phenylurea	Water (100 mL)	25 mm C_{18} Empore disk 1.5 mL Acetonitrile-methanol (1:1)	-	LC	[33]
Phenylurea	Water (1 L)	C_{18} Bond Elut column 3 x 7 mL Ethyl acetate	-	LC	[34]
Sulfonylurea	Water (100 mL)	C_{18} Bakerbond column 5 mL Methanol	-	LC	[35]
	Soil (50 g)	2 x 100 mL 0.1M Sodium hydrogen carbonate C_{18} Bakerbond column (pH 2.5) 5 mL Methanol		LC	
Sulfonylurea	Water (200 mL)	2 x C_{18} column 10 mL 0.1% Acetic acid in ethyl acetate	Silica cartridges 0.1% acetic acid in ethyl acetate	LC	[41]
	Soil (50 g)	100 mL 0.1M Ammonium carbonate-acetone (8:2) C_{18} column 10 mL 0.1% Acetic acid in ethyl acetate			
Sulfonylurea	Water (1 L)	SAX-RP 102 tandem cartridges (pH3) 3 x 4 mL 1% Acetic acid in acetone	-	LC	[42]

TABLE 4 (continued)

Phenylurea	Water (1 L)	Carbograph 4 SPE cartridges 1.5 mL Methanol 6 mL Dichloromethane	-	LC	[37]
Phenylurea	Water (1 L)	SPE column Hexane-2propanol (3:1)	-	LC	[40]
Benzoylurea	Wine (10 mL)	Isolute C_{18} 2 mL Methanol	-	LC	[19]
Benzoylurea	Citrus fruits (0.5 g)	0.5 g C_8 (MSPD) 10mL Dichloromethane	-	LC	[46,47]
Phenylurea	Water (25-50 mL)	On line SPE 30 x 4.6 Silica-based immunosorbent Gradient acetonitrile with phosphate buffer (pH7)		LC	[51]
Sulfonylurea	Water (100 mL)	On line SPE 10 x 2 mm C_{18} (pH3) Gradient methanol-100 mM acetic acid	-	LC	[52]
Phenylurea	Water (100 mL)	On line SPE 10 x 2 mm C_{18} 10 x 2 mm PLRP Gradient acetonitrile-water	-	LC	[53]
Sulfonylurea	Water (100 mL)	On line SPE C_{18} column	-	SFC	[54]
Sulfonylurea	Water (500 mL)	RP-102 Column 10 mL Methanol	SAX-Alumina Bakerbond cartridges 17mL 0.5% acetic acid-dichloromethane	CE and LC	[36,44]

SPME: Solid phase micro-extraction
MSPD: Matrix solid-phase dispersion

cal schemes are currently based on GC, LC, and CE techniques.

A. Gas Chromatography

The behavior of the analytes in the GC or LC columns is the main criterion for the selection of the separation method. Most of the phenylurea herbicides are non-GC-amenable compounds, due to thermal instability, but in some cases despite their degradation under GC conditions the precision of analysis is not significantly affected. Some compounds can be determined unchanged by GC with electron capture detector (ECD)[24,26,31,49,54] and nitrogen phosphorus detector (NPD).[31,54] In other cases, a degradation product is quantified,[48,56] or the pesticide is derivatized before GC determination.[31] GC coupled with a quadrupole MSD[24,26,39,48,56] or an ion trap (IT) MSD operating in electronic impact mode[12,38] sometimes performs confirmation of identity of pesticide residues. Table 5 summarizes the use of GC methods in the determination of urea pesticides.

B. Liquid Chromatography

LC is the most commonly adapted technique for analyzing urea pesticides. A summary of methods based on LC is given in Table 6. Many of these applications employ UV or diode array detection (DAD). PUHs[11,32,33,51] and SUHs[41,44,54] are determined currently in water with UV detection. PUHs,[23] SUHs,[25] and BUIs[21,22,46] can also been determined in fruits and vegetables with UV detection thanks to the previous processes of concentration and purification. LC with DAD performed satisfactorily for determining PUHs, SUHs, and BUIs in water samples,[14,15,18,34,35,40] fruits,[27] and wine.[19]

The LC-MS technique is now widely applied to determine urea pesticides in food and water analysis.[57] Due to completely different ionization techniques such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), in contrast to electron impact ionization (EI), as well as different fragmentation mechanisms, new mass spectral libraries have been constructed.[58] In the last few years, interfaces based on atmospheric pressure ionization (API) increased in the number of applications.[59] The most abundant ions in the MS spectra of PUHs and sulfonylureas are produced in positive-ion mode [M+H]+. ESI is an effective interface for assessing trace levels of PUHs and their major related degradation products[37,55] and sulfonylureas[42,43,52] in water and in cottonseed and cotton gin trash.[29] SUHs can also been determined in water using ESI in negative ion mode.[16] PUHs are best ionized as positive ions with APCI[16,60] and determined in water samples. APCI spectra of BUIs typically provided intense molecular ions in negative-ion mode, allowing the acquisition of primarily molecular weight information rather than promoting fragmentation. An LC/APCI-MS method was applied to determine these compounds in mushrooms,[61] plums, strawberries, and blackcurrant-based fruit drinks,[62] and in citrus fruits.[47]

C. Sensitivity of Mass Spectrometric Techniques

Routinely, GC-MS is used for monitoring pesticides in aqueous samples. Several methods have been reported for the determination of either the intact ureas[38,63] or their breakdown products.[56,64] The mass spectra of the urea derivatives obtained with electronic impact mode (-70 eV) show few fragments and an intense molecular ion [M+], for this an adequate selection of few *m/z* ions (two or three) to perform a SIM provides both good sensitivity and the correct identification of such derivatives.

Polar pesticides are the most likely to leach to ground water, which is the way analytical methods based on LC are often preferred and, in particular, methods using LC-MS. Different interfaces such as particle beam (PB),[65] thermospray, and atmospheric pressure ionization (API) have been used for urea pesticides. However, during the last few years, API techniques, high flow pneumatically assisted electrospray ionization (ES),[36,66-69] or ionspray (ISP)[70] and atmospheric pressure chemical ionization (APCI),[65,71] both of these soft ionization modes, have become the most popular interfacing techniques. Table 7 details

TABLE 5
Gas Chromatographic Methods for Determining Urea Pesticides

Urea pesticide	Matrix	Derivative conditions (Solvent of injection)	Injector Temp (°C)	Column	Detector	LOD	Determined compound	Ref
Chlorsulfuron Triasulfuron	Soil (50g)	Diazomethane/Ethyl acetate (Ethyl acetate)	250	25m x 0.2mm 0.33µm HP-5	NPD	0.1 ppb 0.2 ppb	Methyl derivative	[77]
Metabenzthiazuron	Water (0.5L)	(Cyclohexane-acetone)	250	20m x 0.32mm 0.25µm CP-sil 19CB	NPD	-	-	[31]
Diuron				20m x 0.32mm 0.25µm CP-sil 5CB	ECD			
Chlorsulfuron	Water (2mL)	(Solvent free)	300	30m x 0.25mm 0.25µm BP10.	NPD ECD	0.05 ppb	Amine triazine	[48]
Fluometuron Isoproturon Linuron Metobromuron Monuron							Anilines	
Diflubenzuron	Apple (25g)	Toluene/HFBA/Pyridine Room Temp/1.5-2h (Toluene)	225 240	25m x 0.32mm 0.52µm NB-1701. 25m x 0.32mm 0.52µm HP-5.	ECD	0.03 ppb	Heptafluorobutyryl derivative	[26]
Linuron Metobromuron	Crop samples (100g)	(Acetone-hexane)	250	30m x 0.25mm 0.25µm SPB-608	ECD	0.01 ppb	-	[24]
Flufenoxuron	Wine (3mL)	(Solvent free)	250	25m x 0.32mm 0.25µm HP-PAS 1701	ECD	13 ppb	-	[49]
Diuron	Sugar cane Orange (1kg)	(Acetone)	250	30m x 0.25mm 0.35µm 5% phenylmethylpolysiloxane	ECD		-	[78]
Chlortoluron Diuron Fluometuron Isoproturon Linuron Metobromuron Monuron	Standard and Water (100mL)	(Methanol)	300	30m x 0.25mm 0.25µm BP-10	NPD ECD MS (SIM)	0.1 pg	Carbamic acid methyl esters	[64,76]
Metabenzthiazuron							Benzothiazolamine	

Diuron Linuron Monuron	Water (1L)	(n-Hexane)	220	30 m x 0.32mm DB-1	FTD	0.08 ppb 0.002 ppb 0.02 ppb	-	[63]
Linuron Monuron	Water (1 L)		240	25m x 0.25mm HP-5	MS (SIM)	0.01 ppb 0.005 ppb		
Fenuron Monuron Isoproturon Linuron	Standards	(Dichloromethane)	280	30m x 0.25mm 0.25μm DB5	MS	20.0 ppb	Phenyl isocyanates	[56]
Linuron Tebuthiuron	Water (1L)	(Hexane-2-propanol)			MS	0.02 ppb	-	[39]
Fluometuron Linuron Metobromuron Monolinuron	Water (1L)	(Ethyl acetate)	230	30m x 0.25mm 0.25μm DB-5ms	MS-ITD	0.005 ppb 0.05 ppb 0.005 ppb 0.005 ppb	Phenyl isocyanates	[38]
Diuron Isoproturon Chlortoluron Linuron	Water (500mL)	Dichloromethane/HFBA 37°C/ 1h (Dichloromethane)	Programmed 35°C (0.7min), 12°C/s -300°C	30m x 0.25mm 0.25μm DB-5ms	MS-ITD	0.09 ppb 0.09 ppb 0.08 ppb 0.15 ppb	Heptafluorobutyryl derivative	[12]
Linuron Diuron Neburon Isoproturon	Water (500mL)	HFBA/Pyridine 37°C/ 1h (Acetonitrile)		30m x 0.25mm 0.25μm DB-5	MS-ITD	0.1ppb	Heptafluorobutyryl derivative	[18]
Tebuthiuron	Milk (1L)	MBTFA/Toluene 90°C/2h (Toluene)	250	30m x 0.25mm 0.25μm DB-5	MS (SIM)	0.01 ppb	Trifluoroacetyl derivative	[79]
Tebuthiuron	Water (100mL)	Acetic anhydride/Toluene 270°C/2h (Acetone)	240	30m x 0.25mm 0.25μm DB5	MS (SIM)	0.02 ppb	Acetyl derivative	[80]

HFBA: Heptafluorobutyric anhydride
MBTFA: N-Methylbis-(trifluoroacetamide)

TABLE 6
Liquid Chromatographic Methods for Determining Urea Pesticides

Type of compound	Matrix	Stationary phase	Mobile phase	Detection	LOD	Ref.
Phenylureas	Water	Whatman C_{18} Partisphere	Methanol/water/buffer pH 7	UV (225, 254nm)	0.4 ppb	[32]
Phenylureas	Water	4.6 x 150 mm Supelcosil LC-18-DB	Gradient acetonitrile/water	UV (252nm)	1.6 ppb	[33]
Phenylureas	Water	4.6 x 30 mm, 5 μm Supelcosil LC-18DB	Gradient acetonitrile/phosphate buffer pH 7	UV (244nm)	0.05-0.5 ppb	[51]
Phenylurea	Water	4.6 x 30 mm, 5 μm Spherisorb ODS-2 4.6 x 100 mm, 3 μm Microsphere C_{18}	Gradient methanol/water	UV (250, 277 nm)	0.1 ppb	[11]
Sulfonylureas	Soil and water	4.6 x 250 mm, 5 μm Zorbax SB-Phenyl,	Water/acetonitrile	UV (245nm)	0.1 ppb	[41]
Sulfonylureas	Water	4.6 x 250 mm, 5 μm Zorbax SB-Phenyl	Phosphoric acid-potassium phosphate pH 2.7	UV (245nm)	0.1 ppb	[44]
Benzoylureas	Plants	4.6 x 250 mm, 5 μm LiChrosorb RP-18	Methanol/water	UV (245nm)	1 ppm	[21]
Benzoylureas	Citrus	4.6 x 250 mm, 5 μm Kromasil C_{18}	Gradient acetonitrile/water	UV (200 nm)	0.2 ppm	[46]
Phenylureas	Vegetables	4.6 x 250 mm, 5μm LiChrospher R18	Gradient methanol-acetonitrile/water	UV (242 nm)	0.01 ppm	[23]
Sulfonylureas	Rice and crayfish	4.6 x 150 mm, 5 μm Zorbax SB-Phenyl 4.6 x 250 mm, 5 μm Zorbax RX-C_8	Potassium phosphate pH 7.6 Potassium phosphate pH 3.2 Acetonitrile	UV (254 nm)	8 ppb	[25]
Benzoylureas	Apples and pears	2.1 x 250 mm, 5 μm ODS Hypersil C_{18}	Gradient methanol/water	UV (260 nm)	0.02 ppm	[22]
Phenylureas Benzoylureas	Water	4.6 x 250 mm, 5 μm Zorbax SB-C_{18}	Gradient acetonitrile/water	DAD (240nm)	0.5 ppm	[14]
Phenylureas	Water	250 mm TSK ODS 80TM C_{18}	Gradient acetonitrile/water	DAD (220nm)	0.1 ppm	[18]
Phenylureas	Water	4.6 x 250 mm, 5 μm LiChrosorb RP-18	Gradient methanol/water	DAD (250nm)	20 ppb	[34]
Sulfonylureas	Soil and water	4.6 x 120 mm, 5 μm Viospher C_6 4.6 x 250 mm, 5 μm Beckman C_{18}	Gradient 0.01% $HClO_4$ in water-methanol	DAD (224-234nm)	1ppb	[35]
Phenylureas	Soil and water	4.6 x 250 mm, 5 μm Toso Haas 80 TM C_{18}	Gradient acetonitrile/water	DAD (249nm)	0.3 ppb	[15]
Phenylureas	Water	46 x 250 mm, 5 μm Baker C_{18}	Methanol/water	DAD (249nm)	0.1 ppb	[40]
Benzoylureas	Apples	3 x 150 mm, 5 μm Separon SGX C_8	Methanol-water	DAD (260nm)	0.1 ppm	[27]

Benzoylureas	Grapes and wines	2.1 x 250 mm, 5 µm ODS Hypersil C_{18}	Gradient methanol-water	DAD (260nm)	0.01ppm	[19]
Phenylureas	Water	4.6 x 250 mm, 5 µm Alltima C_{18}	Gradient acetonitrile/water	ESI-MS	0.08 ppb	[37]
Phenylureas	Water	2.1 x 150 mm, Zorbax RX-C_{18}	Gradient acetonitrile/water	ESI-MS	0.04 ppb	[55]
Sulfonylureas	Water	3 x 125 mm, 5 µm LiChrospher 60 RP select B	Gradient methanol/water	ESI-MS	0.05 ppb	[52]
Sulfonylureas	Water	2 x 150 mm, 3 µm Metasil basic	Gradient acetonitrile/ammonium formate-formic acid buffer pH 3.7	ESI-MS	0.01ppb	[42,43]
Phenylureas	Water	4.6 x 250 mm, 5 µm Hypersil ODS	Gradient acetonitrile/water	APCI-MS	0.02 ppb	[16]
Phenylureas	Water	4.6 x 250 mm, 5 µm Alltima C_{18}	Methanol/water	APCI-MS	0.5 ppb	[60]
Benzoylurea	Mushrooms	4.6 x 250 mm, S5ODS2	Gradient methanol/water	APCI-MS	17 ppb	[61]
Benzoylurea	Citrus	4.6 x 30 mm, 5 µm Kromasil C_{18}	Gradient methanol/water	APCI-MS	2 ppb	[47]

TABLE 7
Instrument Sensitivity of Liquid and Gas Chromatographic Techniques Coupled to Mass Spectrometric Detectors

Technique	Matrix	Injected herbicide	Selected *m/z* ions	IDL (ng injected) *	Ref.
GC-IT-MS	Water	Fluometuron	72	≈ 0.084	[38]
		Linuron	61	1	
		Metobromuron	61	≈ 0.200	
		Monolinuron	61	0.010	
GC-MS	Water	Linuron	248, 250	0.0075	[63]
		Monuron	198, 200	0.015	
GC-MS	Water	Isoproturon	Scan (29-350)	0.25	[56]
		Fenuron		0.3	
		Monuron		0.35	
		Linuron		0.15	
GC-MS	Water	Chlorsulfuron	191, 128, 111	0.0001	[64]
		Chlortoluron	199, 167, 154	0.0006	
		Diuron	219, 187	0.001	
		Fluometuron	219, 187, 174	0.0009	
		Isoproturon	193, 178, 146	0.0004	
		Linuron	219, 187, 174	0.001	
		Metabenzthiazuron	164, 136	0.0004	
		Metobromuron	229, 197, 184	0.0004	
		Monuron	185, 153, 140	0.0005	
LC-APCI-MS	Water	Isoproturon	207	0.4	[65]
LC-PB(EI)-MS			72	10	
LC-PB(PChI)-MS			205	4	
LC-ES-MS	Water	Bensulfuron-methyl	411	1.875	[36]
		Chlorsulfuron	358	9.375	
		Chlorimuron-ethyl	415	5.625	
		Halosulfuron-methyl	435	7.5	
		Metsulfuron-methyl	382	5.625	
		Nicosulfuron	411	22.5	
		Primisulfuron-methyl	469	9.375	
		Prosulfuron	420	3.75	
		Sulfometuron-methyl	365	3.75	
		Thifensulfuron-methyl	388	7.5	
		Triasulfuron	402	7.5	
		Triflusulfuron-methyl	493	3.75	
LC/ES/MS	Water	Chlortoluron	213	0.288	[66]
		Isoproturon	207	0.065	
		Diuron	233	0.317	
		Linuron	249	0.561	
		Methabenzthiazuron	165	0.211	
		Neburon	276	0.252	

LC-ES-MS	Water	Bensulfuron-methyl	182, 213, 411	1.08	[67]
		Chlorsulfuron	141, 167, 358	1.89	
		Metsulfuron-methyl	167, 199, 382	2.16	
		Rimsulfuron	182, 325, 432	4.05	
		Thifensulfuron-methyl	141, 167, 388	1.89	
		Triasulfuron	141, 167, 402	1.62	
		Tribenuron-nethyl	155, 181, 396	2.97	
LC-ESNI-MS	Soil and water	Chlorsulfuron	356	≈ 0.040	[68]
		Metsulfuron-methyl	380	≈ 0.040	
		Thifensulfuron-methyl	386	≈ 0.040	
		Tribenuron-methyl	394	≈ 0.040	
LC-ES-MS-MS	Water	Chlorsulfuron	356 (primary), 139 (secondary)	0.350	[69]
		Metsulfuron-methyl	380 (primary), 139 (secondary)	0.300	
		Thifensulfuron-methyl	386 (primary), 139 (secondary)	0.300	
		Triasulfuron	400 (primary), 139 (secondary)	0.15	
LC-ISP-MS	Water	Linuron	249, 161	0.0215	[70]
		Monolinuron	215, 127	0.0134	
LC-APCI-MS	Citrus	Diflubenzuron	309, 289	0.01	[47]
		Flufenoxuron	487, 467	0.01	
		Hexaflumuron	459, 439	0.01	
LC-APCI-MS-MS	Water	Chlorbromuron	292.9 (primary) 182.2 (secondary)	0.030-0.200 (QqQ)	[71]
		Chlortoluron	213.0 (primary) 72.0 (secondary)		
		Diuron	233.0 (primary) 72.0 (secondary)	1-2 (Ion Trap)	
		Linuron	249.0 (primary) 282.2 (secondary)		
		Metoxuron	229.1 (primary) 72.0 (secondary)		
		Monuron	199.1 (primary) 72.1 (secondary)		
		Neburon	275.3 (primary) 88.1 (secondary)		
LC-ES-MS	Soil	Chlorsulfuron	141, 167, 358	0.3125	[81]
		Metsulfuron methyl	141,167, 264, 388		
		Thifensulfuron	141, 167, 264, 382		
		Triasulfuron	141, 167, 402		

* Calculated from data reported by authors

** Determined as phenylisocyanate

IDL Instrument detection limit

the instrument sensitivity of several GC-MS and LC-MS methods using different interfaces employed to analyze urea pesticides in several matrices as well as the searched *m*/*z* ions. The sensitivity of GC-MS is very good, instrumental conditions are completely reproducible, and the high separation power of capillary columns can be used. On the other hand, LC-MS techniques become more and more sensitive and allow the determination of intact urea pesticides.

D. Capillary Electrophoresis

Capillary electrophoresis (CE) is rapidly becoming an important tool for the separation of a wide variety of compounds (Table 8). To apply CE for monitoring studies of pesticides, particular attention has to be devoted to the optimization of the separation in order to obtain the best selectivity in a complex matrix as vegetables, where many potential compounds may interfere. There are several separation modes. In micellar electrokinetic chromatography (MEKC), the potential applied across a fused-silica capillary is the driving for migration, as in capillary zone electrophoresis (CZE), but MEKC involves the addition of an anionic micellar additive as sodium dodecyl sulfate (SDS) to the working electrolyte. This allows the separation of nonionic compounds.[72] Experimental retention factors of the phenylurea herbicides, measured using MEKC with working electrolytes containing various micellar concentrations of SDS shows a good agreement with the retention data predicted using the polarity and the lipophilicity indices. MEKC can be used for separations using working electrolytes containing SDS at concentration upper than the critical micellar concentration (CMC).[73] Micellar, mixed micellar, and microemulsion electrokinetic chromatography (EKC) were applied to the separation of phenylureas and chlorsulfuron, showing that the separation efficiencies in mixed micellar and microemulsion EKC were higher than in micellar EKC.[74,75] Sulfonylurea herbicides and their degradation products may be detected simultaneously and separated by MEKC, permitting the quantitation of these compounds at the ng g^{-1} in water,[13,17] mushrooms,[61] and grains.[30] CZE offers also a fast and reliable method to determine sulfonylurea herbicides in water.[20,36,44]

IV. DETERMINATION IN REAL SAMPLES

Considerable research activities have been done to increase the sensitivity of the methods and their reability at trace levels to accomplish the exigencies of the laws. At very low concentrations, matrix interference from complexes samples as foods could cause errors in the final results, and consequently a purification step is required. Water is usually a more simple matrix, and cleanup can be avoided if selective extraction and detection techniques are used (see Tables 3 and 4).

A. Water and Soil

The levels of urea herbicides found in real samples are very low (μg L^{-1} order), which is because its own physico-chemical properties (see the octanol/water partition coefficient and the water solubility of PUHs and BUIs in Table 1), its environmental behavior (see the field dissipation half life and half-life in soil in Table 2), and its low application rate (see Table 2).

Real water samples have been analyzed by GC using direct and indirect determination of urea herbicides in surface and ground water.[18,39,48,76] In the indirect analysis of phenylurea pesticides, the solvent used for injection has influence on the determined compound. In this sense, phenylcarbamic acid alkyl ester derivatives are determined when methanol or ethanol is used, phenylisocyanates are determined when acetonitrile or dichloromethane is used,[64] and phenylamines are formed when water is present, as occurs in SPME.[48] For samples analyzed by GC techniques, typical reported levels in waters are as low as 3.5 to 11.4 μg L^{-1} for chlortoluron in irrigation channels for citrus fields,[76] and 0.28 μg L^{-1} for isoproturon and 1.55 μg L^{-1} for diuron in surface waters.[18]

LC was applied to the determination of PUHs,[11,15,32-34,40,41,51] BUIs,[14] and SUHs[35,41-44,52] in surface and ground water samples. Nicosulfuron is one of the most frequently detected herbicide in surface waters from the Midwestern USA,[43] whereas diuron is a commonly detected compound in surface waters from central and southeastern regions of France.[16] A residue of 23.1 μg L^{-1} of diuron was found in Lake Creek stream water.[33] It

TABLE 8
Capillary Electrophoresis Methods for Determining Urea Pesticides

CE method	Matrix	Buffer (pH)	Detection (λ nm)	Injected herbicide	LOD	Ref.
CE-MEKC	Standards	0.1M SDS (8.5)	UV (234)	Fenuron Metoxuron Linuron	-	[73]
CE-MEKC	Standards	12.4 mM Potassium dihydrogen-phosphate 3.8 mM Sodium Borate 250 mM SDS (7.0)	UV (254)	Chlorsulfuron Chlortoluron Diuron Linuron Fenuron Fluometuron Monuron Linuron	-	[74]
CE-MEKC	Water Soil	25 mM Sodium phosphate 50 mM Lithium dodecyl sulfate (6.5)	UV (214)	Primisulfuron Triasulfuron	50 ppb	[17]
CE-MEKC	Soil	30 mM Sodium borate 80 mM SDS (7.0)	UV (239)	Metsulfuron Chlorimuron Chlorsulfuron	10 ppt	[13]
CE-MEKC	Grains	50 mM SDS 25 mM Sodium phosphate (6.15)	UV (234)	Chlorsulfuron Metsulfuron-methyl Rimsulfuron Thifensulfuron Tribenuron-methyl	0.02 ppt 0.02 ppt 0.035 ppt 0.02 ppt 0.035 ppt	[30]
CE-CZE	Water	50 mM Ammonium acetate (4.75)	UV (240)	Bensulfuron-methyl Chlorimuron-ethyl Chlorsulfuron Halosulfuron-methyl Metsulfuron-methyl Prosulfuron Primisulfuron-methyl Sulfometuron-methyl Thifensulfuron-methyl Triasulfuron Triflusulfuron-methyl	0.2 ppt	[36]

TABLE 8 (continued)

CE- CZE	Water	50 mM Ammonium acetate (4.76)	UV (240)	Bensulfuron-methyl Chlorimuron-ethyl Chlorsulfuron Ethametsulfuron Halosulfuron-methyl Metsulfuron-methyl Primisulfuron-methyl Sulfometuron-methyl Thifensulfuron-methyl Triasulfuron Triflusulfuron-methyl	0.1 ppt	[44]
CE-CZE	Water Sediments	25 mM Acetic acid 25 mM sodium acetate (4.7)	UV (239)	Amidosulfuron Bensulfuron-methyl Chlorimuron-ethyl Chlorsulfuron Ethametsulfuron-methyl Metsulfuron-methyl Nicosulfuron Sulfometuron-methyl Thifensulfuron-methyl Triasulfuron	0.1 ppb 0.02 ppb	[20]
CE-CZE	Soil	50 mM Ammonium acetate (4.76)	UV (239)	Amidosulfuron Bensulfuron-methyl Chlorimuron-ethyl Chlorsulfuron Ethametsulfuron-methyl Metsulfuron-methyl Nicosulfuron Primisulfuron-methyl Sulfometuron-methyl Thifensulfuron-methyl Triasulfuron Tribenuron methyl	2 ppb	[82]

is one of the highest concentrations reported for urea herbicides in waters when an analysis is performed following LC techniques.

B. Foods

Urea pesticide residues in food have been researched by GC, particularly diflubenzuron in apples,[26] linuron, metobromuron, and monolinuron in routine crop monitoring,[24] diuron in orange and sugar cane,[78] and flufenoxuron in wines.[49] After a field treatment applied 55 days before sampling, 0.10 mg kg^{-1} of diflubenzuron residue was found in apples.[26] As a result of a controlled application of diuron (6400 g ha^{-1}) following a good agricultural practice in orange and sugar cane fields from Sao Paulo (Brazil) the diuron residues quantified were of 8.9 to 11.3 μg kg^{-1} for orange samples and 5.3 to 6.6 μg kg^{-1} for sugar cane samples.[78] Seven Portuguese red wine and five white wine samples were analyzed for flufenoxuron and other pesticides, and no residue was found.[49]

LC permits the determination of bensulfuron methyl in rice and crayfish[25] and BUIs in citrus fruits[47] grapes and wine.[19] Diflubenzuron, hexaflumuron, and flufenoxuron were found in several citrus fruit samples from Spain, but no sample exceeded the maximum residue levels established in such state.[47] Teflubenzuron and flufenoxuron were determined in grapes from treated Greek fields and produced wines. Their residues were higher in grapes (0.52 mg kg^{-1} for teflubenzuron and 0.20 mg kg^{-1} for flufenoxuron) than in wines (0.012 mg L^{-1} for teflubenzuron and 0.010 μg kg^{-1} for flufenoxuron).[19]

V. CONCLUSIONS

The extraction with organic solvents is still used from the isolation of urea pesticides from food and water samples. The solid phases are now preferred to analyze water samples as well as food samples by using solid-phase extraction and matrix solid-phase dispersion procedures.

GC is preferably used for an analysis of volatile and thermostable pesticides, but the well-established methods with selective detectors allow the determination of some urea pesticides. However, multiresidue analysis including thermally labile compounds over a wide range of polarity is generally performed by LC and CE techniques. The larger number of applications has been performed by LC. Approximately half uses UV and DAD detectors, and the other half MS detector. In the last few years LC-MS methods operating with different interfaces have been proposed showing the suitability of these techniques. The interfaces ESI and APCI are considered to have a promising future.

CE is an emerging technique complementary to GC and LC, with applications in the area of urea pesticides. The advantages of CE for monitoring routine analyses are the simplicity of the instrumentation, the low solvent consumption, and the easy equipment maintenance with respect to chromatographic techniques. The main limitation of CE is the low loadability of the system that allows the achievement of impressive detection limits without preconcentration or sample stacking techniques to enhance sensitivity. In recent years the employ of MSD configured with ESI or APCI interfaces will permit extending the applications of this technique. Nevertheless, the potential of CE has not been fully exploited in many fields of research, including environmental analyses for urea pesticides.

Monitoring of vegetables and water sources will become extremely important and the methods applied will be intended to achieve efficient and rapid separations whatever the technique may be employed.

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REFERENCES

1. Tadeo JL, Residues of Urea Pesticides in Food; in *Handbook of Food Analysis* Nollet LML, Ed., Marcel Dekker: New York, 1996; pp. 1291-1305.
2. Tadeo JL, Sánchez-Brunete C, Pesticide Residues: Carbamate and Urea Pesticides, in *Food analysis by*

HPLC Nollet LML Ed., Marcel Dekker: New York, 2000, pp. 693-715.

3. Liska I, Slobodník J, *J. Chromatogr. A*, **1996**, 733, 235-258.
4. Eash DT, Bushway J, *J. Chromatogr. A,* **2000**, 880, 281-294.
5. Balinova A, *J. Chromatogr. A*, **1996,** 754, 125-135.
6. Hatrík S, Tekel J, *J. Chromatogr. A*, **1996,** 733, 217-233.
7. Di Corcia, Analysis of Urea Herbicides in Water in *Handbook of Water Analysis,* Nollet LML Ed., Marcel Dekker: New York, 2000, pp. 487-515.
8. Motohashi N, Nagashima H, Párkányi C, Subrahmanyam B, Zhang G, *J. Chromatogr. A*, **1996,** 754, 333-346.
9. Torres CM, Picó Y, Mañes J, *J. Chromatogr. A*, **1996,** 754, 301-331.
10. Tadeo JL, Sánchez-Brunete C, Pérez RA, Fernández MD, *J. Chromatogr. A*, **2000,** 882, 175-191.
11. Sancho JV, Hidalgo C, Hernández F, *J. Chromatogr. A*, **1997,** 761, 322-326.
12. Charrêteur C, Colin R, Morin D, Péron JJ, *Analusis*, **1998,** 26, 8-14.
13. Dinelli G, Vicari A, Bonetti A, *J. Chromatogr. A,* **1995,** 700, 195-200.
14. Dommarco R, Santilio A, Fornarelli L, Rubbiani M, *J. Chromatogr. A*, **1998,** 825, 200-204.
15. Lennartz B, Louchart X, Voltz M, Andrieux P, *J. Environ. Qual.*, **1997,** 26, 1493-1502.
16. Jeannot R, Sabik H, Sauvard E, Genin E, *J. Chromatogr. A*, **2000,** 879, 51-71.
17. Penmetsa KV, Leidy RB, Shea D, *J. Chromatogr. A*, **1997,** 766, 225-231.
18. Charrêteur C, Colin R, Morin D, Péron JJ, Madec CL, *Analusis*, **1996,** 24, 203-211.
19. Miliadis GE, Tsiropoulos NG, Aplada-Sarlis PG, *J. Chromatogr. A*, **1999,** 835, 113-120.
20. Berger BM, Wolfe NL, *Fresenius J. Anal. Chem.* **1996**, 356, 508-511.
21. Balinova A, *J. Chromatogr. A*, **1998,** 823, 11-16.
22. Tsiropoulos NG, *J. AOAC Int.,* **1999,** 82, 213-216.
23. Sannino A, *J. AOAC Int.*, **1998,** 81, 1048-1053.
24. Gelsomino A, Petrovicová B, Tiburtini S, Magnani E, Felici M, *J. Chromatogr. A*, **1997,** 782, 105-122.
25. Zhou M, Bramble FQ, Devine TJ, Norwood G, *J. AOAC Int.,* **1996,** 79, 791-796.
26. Mensah JK, Lundanes E, Greibrokk T, Holen B, *J. Chromatogr. A*, **1997,** 765, 85-90.
27. Tomsej T, Hajslová J, *J. Chromatogr. A,* **1995,** 704, 513-517.
28. Rodríguez E, Barrio RJ, Goicolea A, Gómez de Balugera Z, *Anal. Chim. Acta*, **1999,** 384, 63-70.
29. Stry JJ, Amoo SJ, George WS, Hamilton-Johnson T, Stetser E, *J. AOAC Int.,* **2000,** 83, 651-659.
30. Krynitsky AJ, Swineford DM, *J. AOAC Int.,* **1995,** 78, 1091-1096.
31. Bengtsson S, Ramberg A, *J. Chromatogr. Sci.,* **1995,** 33, 554-556.
32. Senseman SA, Lavy TL, Mattice JD, Gbur EE, Skulman BW, *Environ. Sci. Technol.,* **1997,** 31, 395-401.
33. Field JA, Reed RL, Sawyer TE, Martinez M, *J. Agric. Food Chem.*, **1997,** 45, 3897-3902.
34. Gómez de Barreda Jr D, Gamón Vila M, Lorenzo Rueda E, Saez Olmo A, Gómez de Barreda D, Garcia de la Cuadra J, Ten A, Peris C, *J. Chromatogr. A*, **1998,** 795, 125-131.
35. Galletti GC, Bonetti A, Dinelli G, *J. Chromatogr. A*, **1995,** 692, 27-37.
36. Krynitsky AJ, *J. AOAC Int.,* **1997,** 80, 392-400.
37. Di Corcia, Constantino A, Crescenzi C, Samperi R, *J. Chromatogr. A*, **1999,** 852, 465-474.
38. Patsias J, Papadopoulou-Mourkidou E, *J. Chromatogr. A*, **1996**, 740, 83-98.
39. Kolpin DW, Barbash JE, Gillion RJ, *Environ. Sci. Technol.,* **1998,** 32, 558-566.
40. Pichon V, Chen L, Durand N, Le Goffic, Hennion MC, *J. Chromatogr. A*, **1996,** 725, 107-119.
41. Powley CR, de Bernard PA, *J. Agric. Food Chem.,* **1998,** 46, 514-519.
42. Furlong ET, Burkhardt MR, Gates PM, Werner SL, Battaglin WA, *Sci. Total Environ.*, **2000,** 248, 135-146.
43. Battaglin WA, Furlong ET, Burkhardt MR, Peter CJ, *Sci. Total Environ.*, **2000,** 248, 123-133.
44. Hickes H, Watrous M, *J. AOAC Int.,* **1999,** 82, 1523-1533.
45. Lagana A, Fago G, Fasciani L, Marino A, Mosso M, *Anal. Chim. Acta*, **2000,** 414, 71-78.
46. Valenzuela AI, Lorenzini R, Redondo MJ, Font G, *J. Chromatogr. A*, **1999,** 839, 101-107.
47. Valenzuela AI, Picó Y, Font G, *Rapid Commun. Mass Spectrom.,* **2000,** 14, 572-577.
48. Berrada H, Font G, Moltó JC, *J. Chromatogr. A*, **2000,** 890, 303-312.
49. Correia M, Delerue-Matos C, Alves A, *J. Chromatogr. A*, **2000,** 889, 59-67.
50. Hennion MC, *Analusis*, **1998,** 26, M131-M137.
51. Pichon V, Chen L, Hennion MC, *Anal. Chim. Acta*, **1995,** 311, 429-436.
52. Volmer D, Wilkes JG, *Rapid Commun. Mass Spectrom.,* **1995,** 9, 767-771.
53. Ferrer I, Barcelo D, *J. Chromatogr. A*, **1999,** 854, 197-206.
54. Berger TA, *Chromatographia*, **1995,** 41, 133-140.
55. Wang N, Budde WL, *Anal. Chem.,* **2001,** 73, 997-1006.
56. Gennaro MC, Marengo E, Gianotti V, Maurino V, *J. Chromatogr. A*, **2001,** 910, 79-86.
57. Slodobodník J, van Baar BLM, Brinkman UATh, *J. Chromatogr. A*, **1995,** 703, 81-121.
58. Schreiber A, Efer J, Engewald W, *J. Chromatogr. A*, **2000**, 869, 411-425.
59. Ferrer I, Barcelo D, *Analusis*, **1998,** 26, M118-M122.
60. Baglio D, Kotzias D, Larsen BR, *J. Chromatogr. A*, **1999,** 854, 207-220.

61. Barnes KA, Startin JR, Thorpe SA, Reynolds SL, Fussell RJ, *J. Chromatogr. A*, **1995,** 712, 85-93.
62. Barnes KA, Fussell RJ, Startin JR, Thorpe SA, Reynolds SL, *Rapid Commun. Mass Spectrom.*, **1995,** 9, 1441-1445.
63. Albanis TA, Hela DG, *J. Chromatogr. A*, **1995,** 707, 283-292.
64. Berrada H, Font G, Moltó JC, *Chromatographia*, **2001**, 54, 253-262.
65. Aguilar C, Ferrer I, Borrull F, Marcé RM, Barceló D, *J. Chromatogr. A*, **1998,** 794, 147-163.
66. Crescenzi C, Di Corcia A, Guerriero E, Samperi R, *Environ. Sci. Technol*. **1997,** 31, 479-488.
67. D'Ascenzo G, Gentili A, Marchese S, Marino A, Perret D, *Environ. Sci. Technol.,* **1998,** 32, 1340-1347.
68. Bossi R, Koppen B, Splid N H, *J. AOAC Int.,* **1998,** 81, 775-784.
69. Koppen B, Splid N H, *J. Chromatogr. A*, **1998,** 803, 157-168.
70. Giraud D, Ventura A, Camel V, Bermond A, Arpino P, *J. Chromatogr. A*, **1997,** 777, 115-125.
71. Hogenboom AC, Niessen W M A, Brinkman U A Th, *J. Chromatogr. A*, **1998,** 794, 201-210.
72. Dinelli G, Vicari A, Catizone P, *J. Chromatogr. A*, **1996,** 733, 337-347.
73. Jandera P, Fischer J, Effenberger H, *J. Chromatogr. A*, **1998,** 807, 57-70.
74. Song L, Ou Q, Yu W, Li G, *J. Chromatogr. A*, **1995,** 699, 371-382.
75. Rodríguez R, Picó Y, Font G, Mañes J, *Electrophoresis*, **2001,** 22, 2010-2016.
76. Berrada H, Moltó JC, Font G, *Chromatographia*, **2001,** 54, 360-364
77. James TK, Holland PT, Rahman A, Lu YR, *Weed Research*, **1999,** 39, 137-147.
78. Lanças FM, Rissato SR, *J. Microcol. Sep.*, **1998,** 10, 473-478.
79. Rutherford BS, Shackelford DD, Ulmer JJ, *J. Agric. Food Chem.,* **1995,** 43, 2110-2116.
80. Bonato P S, Lanchote V L, De Carvalho Dreossi S A, Gomez M A, Cerdeira A L, De Carvalho D, *J. High Resol. Chromatogr*, **1999,** 22, 239-241.
81. Marek L J, *J. Agric. Food Chem.,* **1996,** 44, 3878-3881.
82. Menne H J, Janowitz K, Berger BM, *J. AOAC Int.,* **1999,** 82, 1534-1541.