

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Overview of Analytical Techniques for Herbicides in Food

Hua Kuang, Libing Wang and Chuanlai Xu
Jiangnan University
China

1. Introduction

It is said that there are more than 5800 kinds of weeds, which significantly do harm to the agricultural production and weed control has always been an important issue in agrochemical practice. Chemical agents, that is herbicides, are used widely in the world in protecting crops from undue competition from weeds.

The main chemical classes of herbicides(Tadeo et al., 2000) include bipiridilium compounds, triazine derivatives containing three heterocyclic nitrogen atoms in the ring structure (atrazine, prometryn, propazin, etc.), chlorophenoxy acid derivatives (2, 4-D, 2, 4, 5-T), substituted chloro-acetanilides (alachlor, propachlor), derivatives of 2, 6-dinitroaniline (benfluralin, trifluralin), substituted phenylcarbamates (carbetamide, chlorbufam), urea derivatives (chlorbromuron, chlorotoluron), substituted sulphonylureas (amidosulfuron, trifusulfuron), etc. The intensive application of herbicides has resulted in the contamination of the atmosphere, soil and waste water, agricultural products (wheat, corn, fruits, vegetables, beans etc.) and, consequently, in the direct or indirect pollution of food and food products and biological system.

More studies have shown that herbicides or its metabolites can enter into the human body along food chain, which creates potential health risks to human. Growing concern has been taken for this issue and some herbicides have been banned to use (see table 1).

The development of a robust analytical method is a complex issue. All steps in the analytical process including sample preparation, extraction, cleanup and instrumental analysis are equally important. There are a vast series of techniques to use in establishing analytical methods, however, some rules should be taken for the differences in polarity of herbicides and the type of sample matrix. The objective of this paper is to summarize the analytical measures developed to detect the different classes of herbicides residues in various foods, and to review future trends.

2. Phenoxy-carboxylic acid herbicides

The herbicidal effect of 2, 4-D was first discovered by Amchem company in 1942 (Kuang et al., 2006b), and more categories were developed by a lot of companies since 1945 based on the structure of 2, 4-D. The general formula of this class herbicides see fig 1 and the chemical structure of some most used phenoxy-carboxylic acid herbicides were summarized in table 2. 2, 4-D is the world's largest broad-leaved weed herbicides. Phenoxy-carboxylic acid

Class of Herbicides	EU	U. S. A	Japan	China
Phenols	Dinoterb 2-Methyl-4, 6-Dinitrophenol (DNOC) Pentachlorophenol	Dinoseb DNOC	Dinoterb Pentachlorophenol	Dinoterb DNOC Pentachlorophenol
Ureas	Monolinuron Chloroxuron Difenoxyuron Noruron Chlorbromuron Cycluron Dimefuron Momuron Neburon Tebuthiuron Thiazafluron Benzthiazuron Ethidimuron Metobromuron Metoxyuron Fenuron	-	Chloroxuron Monolinuron Tebuthiuron Benzthiazuron	-
Amides	Metolachor Butachlor Monalide Diethatyl-Ethyl Mefenacet Tebutam Isocarbamide Diphenamide Chlorthiamid Pentanochlor Flamprop Flupoxam	Metolachor	Metolachor Butachlor Mefenacet Flamprop	
Triazine	Propazine Ametryn Aziprotryne Desmetryne Methoprothryne Trietazine Terbumeton Secbumeton Cyanazine Terbutryn Hexazinone Prometryn	Propazine Ametryn Cyanazine Hexazinone	Propazine Tebutryn	-

Class of Herbicides	EU	U. S. A	Japan	China
Dinitroaniline	Dinitramine Isopropalin Nitralin	Nitralin	-	-
Diphenyl Ethers	Fluoroglycofen Fluorodifen Acifluorfen Fomesafen Chlormethoxyfen	Acifluorfen	Fomesafen	Acifluorfen Fomesafen
Carbomates	Cycloate Vernolate Dimepiperate Dimexano Propham Butylate Chlorbufam Tiocarbazil Karbutilate Di-Allate Barban S-Ethyl-N, N-Dipropylthiocarbamate(EPTC) Orbencarb Pebulate	Propham Cycloate Butylate Pebulate	Cycloate Butylate Pebulate	-
Phenoxy-carboxylic Acids	Fluazifop Quizalofop Fenoxaprop Haloxifop 2, 4, 5-T Dichlorprop Fenoprop 2, 3, 6-Trichlorobenzoic Acid (2, 3, 6-TBA)	Fenoprop	2, 4, 5-T	2, 4, 5-T Fenoprop
Imidazolinones	Chloramben Imazamethabenz Imazapyr	-	Imazamethabenz Imazapyr	-
Cyclohexanediones	Sethoxydim Alloxydim	Sethoxydim	-	-
Others	Chlorfenprop-Methyl Allalacohol Benazolin Benzoylprop Bensulide Bromofenoxim Dalapon	Bensulide MSMA Norflurazon Benfuresate Bromacil	Bensulide Flamprop Pyrazoxyfen TCA Bromacil Naptalam	Bromacil

Class of Herbicides	EU	U. S. A	Japan	China
	Endothal			
	Flamprop			
	Fluridone			
	Flupoxam			
	Methazole			
	Sodium Hydrogen			
	Methylarsenate (MSMA)			
	Norflurazon			
	Perfluidone			
	Pyrazoxyfen			
	Trichloroacetic Acid			
	(TCA)			
	Tridiphane			
	Benfuresate			
	Bromacil			
	Naptalam			

Table 1. List of banned herbicides in various countries

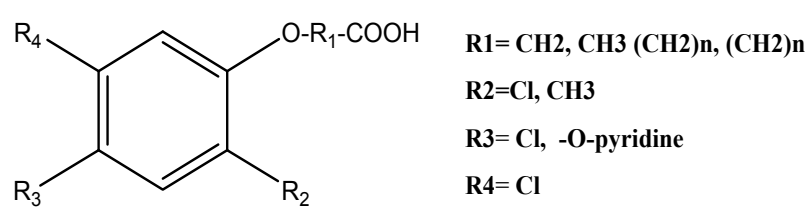


Fig. 1. Parent Chemical Structure of Phenoxy-carboxylic Acid Herbicides

herbicides have been used intensively in the control of the growth of grass and the broad-leaf weeds in many crops such as paddyfield, wheat, soybean, etc. Due to their solubility in water, these herbicides are easy to migrate in agricultural ecosystem causing the pollutions of soil, groundwaters, and air. Phenoxy acid herbicides are medium toxicity themselves, but their metabolic products (especially some halids)are harmful to the human and other creatures. Investigations indicate that they could induce the human parenchyma malignancy tumor and embryotoxicity in animals(Kuang et al., 2006a).

2.1 Sample extraction

Since phenoxy acid herbicides show high polarity and are easily dissolved in the water or aqueous-phase solution, 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. 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(Rimmer et al., 1996). With this aim, acid or base hydrolysis has been used. For acid hydrolysis process, samples have to be acidified with acid solution transferring the analytical objective into the organic phase. It was reported(Baggiani et al., 2001) that the sample should be acidified with acidification water (pH < 2), then extracted with proper organic solvent-water mixture. Solvents, such as

acetonitrile, toluene-ether, dichloromethane and etc., can be used to extract the phenoxy acid herbicides from matrix. For base hydrolysis, alkaline solution (0.1 M NaOH) was used mostly. Many extraction methods including ultrasonic extraction, shaking extraction, microwave-assisted solvent extraction(MASE) and supercritical fluid extraction(SFE) have been reported (table 3).

2.2 Cleanup

Many components in matrix can be co-extracted in sample extraction step and targeted compounds are generally present in very low concentration, they need to be separated from undesirable substances effectively. Some authors have previously summarized the primary cleanup process on these compounds(Cserhádi et al., 2004). Liquid-liquid extraction (LLE) has frequently been used to remove co-extracts from sample constituents. The efficacy of the method is generally high but requires highly purified and expensive solvents. However, serious emulsifying phenomenon sometimes is present during the shaking process. Gel permeation chromatography (GPC) mainly used to remove lipids or colors from extracts based on the differences of molecule size between targeted compounds and interferences. Kuang et al., 2006 successfully purified 14 phenoxy acid herbicides (M. W. ranging from 180 to 327) from soybean extracts.

However, the most common approach to cleanup in herbicide analysis now is solid-phase extraction (SPE), sorbents such as aminopropyl(NH₂), reversed-phase (C₁₈), strong cation exchange(SCX) and normal-phase sorbents(florisil, alumina) are very useful for cleaning up complicated extracts (see table 3).

2.3 Detection

2.3.1 Gas chromatography (GC)

Phenoxy acid herbicides benefit poor volatility for its low p_{ka} (acid dissociation constant) values (see table 2) and derivatization process is needed when analysis by gas chromatography requires. The most frequently used derivatization reagent is diazomethane;however, due to its toxicity, carcinogenicity and explosiveness, other alternative esterification reagents such as sulphuric acid in 1-propanol or in methanol and boron trifluoride in methanol, n-butanol or 2-chloroethanol have been proposed.

Methylation and PFBBBr (pentafluorobenzyl bromide) esterification are common approaches. Methylating agents such as boron trifluoride-methanol, chloroformate, trimethylsilyldiazomethane have been reported in detection of phenoxy acid herbicides (Table 4). Diazomethane was applied for methylation of 6 herbicides (Wei et al., 2005) and satisfying derivative effects obtained. Trimethylsilyldiazomethane, as a non-toxic non-mutagenic¹ alternative to diazomethane is widely used in methyl derivatization. The summary in table 4 showed that mainly mass spectrometry and electron capture detector (ECD) were used to detect phenoxy acid herbicides. Other detectors including hydrogen flame ionization detector (FID) and nitrogen-phosphorus detector(NPD) were also reported for analysis. Kuang(Kuang et al., 2006a) found that ECD response of methylated product of phenoxy acid herbicides, especially single-chlorine substituted molecules (MCPA, MCPP, MCPB etc.), was much lower than that of PFBBBr ester. A comparison of the response factors between PFBBBr ester and methyl ester of MCPA, 2, 4-D and 2, 4, 5-T had been made (Lee et al., 1991). The response factor of the chlorophenoxy herbicide of PFBBBr ester was almost 600 times than that of methyl ester.

Name	Chemical Strucutre	CAS. No	pKa
Mecoprop (MCP)		7085-19-0	3.78
2-Methyl(4-Chlorophenoxy) Acetic Acid (MCPA)		202-360-6	3.07
2-Methyl(4-Chlorophenoxy) Acbutyric Acid (MCPB)		94-81-5	4.84
2, 4-Dichlorophenoxyacetic Acid(2, 4-D)		94-75-1	2.73
2, 4-Dichlorophenobutyric Acid		94-26-8	4.80
Dicamba		1918-00-9	1.97
Fluazifop		69335-91-7	3.20
4-Chlorophenoxyacetic Acid		122-88-3	--
Dichlorprop		28631-35-8	3.00
2-(4-Chlorophenoxy) Propionic Acid		3307-39-9	--
3, 4-Dichlorophenoxyacetic Acid		588-22-7	--
2, 4, 5-(Trichlorophenoxy) Propionic Acid (2, 4, 5-T)		93-76-5	3.14
Fenoprop		93-72-1	3.10
Phenoxy Butyric Acid		6303-58-8	--

Table 2. Information for 14 phenoxy acid herbicides

Matrix	Herbicide	Extraction	Clean-up	Ref
Oranges	2, 4-D	Methanol-homogeniser	-	(Williams et al., 1997)
Fruits, vegetables	2, 4-D	Diethyl ether-hexane (acidic pH), homogeniser	NH ₂ cartridge	(TING & Kho, 1998)
Wheat	2, 4-D	Ethanol-water, homogeniser	LLE-Florisil column	(Cessna & Holm, 1993)
Onions	Fluazifop-butyl	CO ₂ -SFE	-	(Wigfield & Lanouette, 1993)
Fruits, vegetables	2, 4-D	Methanol-water (basic pH), blender	C ₁₈ cartridge	(Richman et al., 1996)
Oranges, grapefruits	2, 4-D	Acetonitrile-water, homogeniser	LLE	(Rochette et al., 1993)
Citrus fruits	Dichlorprop	Methylene chloride-acetone, shaker	LC-SCX cartridge	(Peruzzi et al., 2000)
Barley, triticale	Mecoprop, 2, 4-D	0.1 M NaOH, blender Ethanol-water, homogeniser	LLE-Florisil column	(Cessna, 1992) (Sánchez-Brunete et al., 1994)
Wheat, barley	Phenoxyacids	Methanol, homogeniser	LLE-Florisil column	(Su, 1975)
Mushrooms	2, 4-D	Diethyl ether (acidic pH), homogeniser	Alumina column	(Siltanen, 1978)
Wheat	2, 4-D	0.1 M NaOH-diethyl ether-hexane (pH 1), blender	LLE-Florisil column	(Smith, 1984)
Potatoes, soybeans	Fluazipop-butyl	0.1 M NaOH, shaker	LLE-Florisil column	(Clegg, 1987)
Wheat	2, 4-D,	0.1 M NaOH, blender	LLE-Florisil column	(Cessna, 1980)
Soybean	Phenoxyacids	acetonitrile-50mM HCl (v/v 7:3)	LLE- anion exchange column GPC- anion exchange column	(Kuang et al., 2006a; Kuang et al., 2006b)

Table 3. Extraction and cleanup of phenoxy acid herbicides

Reagents	Matrix	Detection system	Ref
Diazomethane	Rice, Soil, water	GC-MS	(Wei et al., 2005); (Hodgeson et al., 1994)
CH ₃ I	Vegetables, water	GC-ECD	(Rompa, 2005)
Dimethyl sulfate	water	GC-MS	(Catalina et al., 2000)
Trimethylsulfonium hydroxide(TMSH)	water	GC-MS	(Neitzel et al., 1998)
Tetramethylammonium hydroxide (TMAH)	Standards	GC-MS	(Brondz & Olsen, 1992)
tetrabutyl ammonium salt · TBA	water	GC-MS	(Ding et al., 2000)
2-cyanoethylmethyldieth N, O-bis(trimethylsilyl) trifluoroacetamide, BSTFA	Standards	GC-NPD	(Bertrand et al., 1987)
	Standards	GC-MS	(Lou et al., 1999)
PFBBBr	Water, Soil, rice, air	GC-MS, GC-ECD	(Cserháti & Forgács, 1998); (Tadeo et al., 2000)
Benzyl bromide	water	GC-MS, GC-FID	(Nilsson et al., 1998)
Chloromate	water	GC-MS, GC-ECD	(Butz & Stan, 1993)
Concentrated sulfuric acid	water	GC-MS	EPA Method 8151A
HCl- Acetic Anhydride	water	GC-MS	(Xing et al., 2002)
BF ₃	Soil, Meat, Rice	GC-MS, GC-ECD	(Sánchez-Brunete et al., 1994)

Table 4. Derivatization method of phenoxy acid herbicides

The requirement of the maximum residue limits (MRLs) of phenoxy acid herbicides was critical, especially in Japan where 2, 4, 5-T can not be detected in foods. Most derivatization products can be separated on weakly polarity [stationary phase of column, (5%-Phenyl)-methylpolysiloxane and medium polarity [(14%-Cyanopropyl-phenyl)-methylpolysiloxane] capillary columns. Because of the similarity of these herbicides between their structures and polarities, slow temperature program-up was needed to acquire an effective separation. A typical programmed temperature is set as follows:
The oven initial temperature 60 °C holding 1 min and was programmed at 25 °C / min to 180 °C, (1min hold), then programmed at 2 °C / min to 205 °C, (3 min hold), finally programmed to 260 °C at 10 °C / min (5 min hold).

2.3.2 High performance liquid chromatogeaphy (HPLC)

Considering weak volatility of phenoxy acid herbicides, liquid chromatographic separation seems more suitable than gas chromatography. Derivatization, not only is time consuming, but also affects the reproducibility and stability of the method.
Most phenoxy acid herbicides showed maximal UV absorption ranged from 200-220nm, where mighty interference existed and stable baseline often can't be gotten. Thus, some

analysts carried out derivatization process in analysis of these class compounds aimed to change their chromatographic behavior not to improve the detection sensitivity.

Phenoxy acid herbicides showed high polarity with pKa distributed in 2 to 5(Kuang et al., 2006a), the analysts need to adjust the pH of the mobile phase. Organic acids such as acetic acid, trifluoroacetic acid or inorganic acid can be used to adjust the acidity.

The great advantage of HPLC tandem mass spectrometry (HPLC-MS/MS) is its highly selectivity, which greatly reduce the false positive results in detection. Kim (Kim et al., 1991) applied HPLC-MS to detect 2, 4, 5-T, 2, 4-D and fenoprop residues in water, which was the first application of HPLC-MS techniques in phenoxy acid herbicide detection. Ultra Performance Liquid Chromatography (UPLC) employs 1.7 μm particles, resulting in a very flat VanDeemter plot and a linear velocity faster than usual one with 5 μm packings; consequently, improves resolution, speed and sensitivity for many HPLC methods. Chu, 2008(Chu et al., 2008) realized simultaneous determination of more than 100 herbicides in soybeans within 11 min by UPLC-MS/MS.

2.3.3 Other analytical methods

Capillary zone electrophoresis(CZE) and micellar electrokinetic chromatography(MEKC) (Farran & Ruiz, 2004) have been used by some researchers to separate phenoxy acid herbicides. Trace level analysis by electrophoresis meets some difficulties in detectors. UV-Vis(Nemoto & Lehotay, 1998) or fluorescence detector is common in the application. Besides, the process in separation with electrophoresis is greatly depending on the mobile phase (ionic strength, pH) and peak shift sometimes is very serious, thus, quantitative analysis may be inaccurate.

Compared with instrumental separation methods, immunochemical determination technology exhibits remarkable specificity, sensitivity, rapidness and high throughput in detection. Moreover, immunochemical methods cost less and can be used in the field. I. A. Lyubavina, (Lyubavina et al., 2004) used monoclonal antibodies labeled with colloidal gold to detect 2, 4-D residues in aqueous samples.

3. Dinitroaniline herbicides

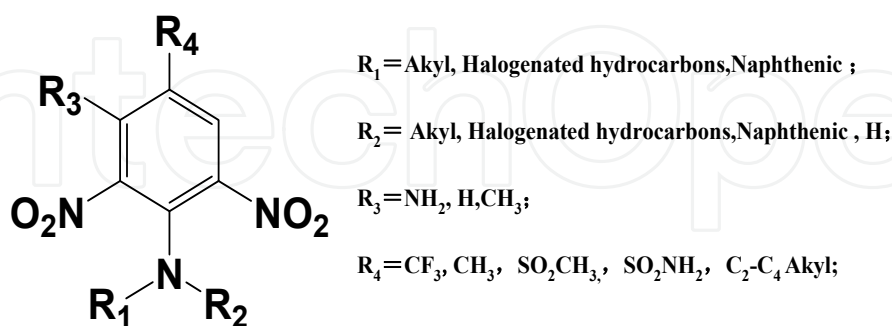


Fig. 2. Chemical structure for dinitroaniline herbicides

Dinitroaniline herbicides are used to control some broad-leaved weeds and the major annual grasses(García-Valcárcel et al., 1996). There are two classes of dinitroaniline herbicides depending on different substituents at R^4 site (Fig 2). The R_4 is alkyl or halogenated hydrocarbon for class I dinitroaniline herbicides, that is methyl aniline herbicide. Trifluralin, pendimethalin and ethalfluralin are typical methyl aniline herbicides.

For class II, the R4 group contains sulfone structure and nitralin belongs to this class. Some toxicological experiments showed that dinitroaniline herbicides exhibits carcinogenicity and impaired the normal function of organs. MRLs of some dinitroaniline herbicides in agricultural products were listed in table 5.

3.1 Sample preparation

Because of the strong polarity of dinitroaniline herbicides, some slightly polarity organic solvents such as acetonitrile, methanol and acetic ether are most applied to extract these herbicides from various matrix by a single or mixed manner. Few reports were found using single non-polar solvents (e. g. n-hexane). For extraction procedure, MASE, SFE, sonication and pressurized liquid extraction (PLE) are reported (table 6). Some analysts applied solid phase microextraction (SPME), which is intensively used in headspace analysis, to analyze dinitroaniline herbicides, but recoveries were poor.

In nitrobenzene herbicide pre-treatment methods, SPE technique was used more often. Commonly used stationary phase was based on florisil and C₁₈ sorbents depending on different nature of the targeted compounds and matrix. Florisil maily was used for removing lipophilic interferences in purification (Huo et al., 2006) procedure and usually florisil (25g, previously activated with 3% H₂O) can adsorbed 1g fat), so particularly suitable for oily substances Florisil. Some reports have showed that good purification effects (the average recovery rate was 74% or more) using florisil in cleanup step in food analysis. Another material - C₁₈ sorbent is also widely used in purification step. Darcy D. Shackelford (Shackelford et al., 2000) successfully applied C₁₈ sorbent to remove co-extracts in analysis (recovery> 80%)

3.2 Detection

In the residue analysis of dinitroaniline herbicides, chromatography detection was dominant, especially GC with high sensitivity and good separation effects based on the summary of recent 20 year literature. Detectors such as ECD, FID, NPD and MS were used widely (see table 7)

Herbicide	Agricultural product	USA	Japan	China	Canada	New Zealand	South Korea
Trifluralin	Grains, fruits, vegetables and vegetable oil	0.05	0.15	0.05-0.15	0.5	0.03	0.05
pendimethalin	Drinking water, fruits, nuts, vegetables	0.1	0.2	0.2	-	0.02	-
Benfluralin	Peanuts, lettuce	0.05	-	-	-	-	-
ethalfluralin	Soybean, peanuts, Sunflower seeds	0.05	-	-	-	-	-
Oryzalin	Apples, kiwi fruits, Pan pomegranate and drinking water	0.05	0.05-0.2	-	-	0.4	-

Table 5. MRLs of some dinitroaniline herbicides (mg/kg)

Matrix	Solvents for extraction	Cleanup	Recovery %
Carrots and fruit	Hexane + acetic ether (1:1)	SPE (Florisil)	—
Fruits, nuts, vegetables	Methanol, methanol-water, 2 - propionaldehyde and n-hexane	GPC& SPE (florisil)	72-126
Industrial wastewater and urban domestic water	Dichloromethane	—	73-99
Soil	Acetonitrile-water	SPE(Florisil)	90-120
Soil, plants and air	Methanol, acetic ether	SPE(Florisil)	75
Blood, urea and water	SPME	—	35-64
Peanuts	Methanol, Dichloromethane	SPE(Florisil)	75.6-80.4
Banana, cucumber, apple, lettuce and oranges	Acetonitrile	SPE(C ₁₈)	70-120
River water	-	SPE	>80
Canola seed, crude powder and Refined oil	Acetonitrile	SPE(C ₁₈)	89-96
Fruits and Vegetables	Acetonitrile	SPE	85-101
Soil	Acetone - water - acetic acid	—	96.6
Soil, water	Ether	SPE (C ₁₈)	89-104
water	-	SPE	50-77
Soil	Acetonitrile	—	—
Juice	Methanol	SPE (C18)	93.8~99.5
Buckwheat	n-hexane	SPE(Florisil)	>74

Table 6. Extraction and cleanup of initroaniline Herbicides

Targeted compounds	Analytical measure	Limit of Detection (LOD)	Ref
Benfluralin, Trifluralin	GC/FID	—	(Boyd-Boland & Pawliszyn, 1995)
Trifluralin, Benfluralin, ethalfluralin, isopropalin, Benfluralin, ethalfluralin, isopropalin, profluralin, pendimethalin, fluchlorlin	GC/ECD	0.01mg/kg	(West et al., 1988)
	GC/ECD	0.1 ng/ mL (water, urea) 1 mg/ mL(blood)	(Guan et al., 1998)
pendimethalin	GC/NPD	0.01 ppm (soil) 0.1 ppb(water)	(Sanchez-Brunete et al., 1994)
Trifluralin, ethalfluralin, profluralin,	GC/ECD	-	(Hsu et al., 1991)
Trifluralin	GC/ECD	2.5 pg/ uL	(D'Amato, 1993)
pendimethalin	GC/ECD	0.022-0.045 mg /kg	(Engebretson et al., 2001)
pendimethalin	GC/NPD	0.1-4.4 µg/kg	(Fenoll José et al., 2007)
Trifluralin	GC/ECD	-	(Cessna & Kerr, 1993)
Trifluralin	Electrochemical analysis	2×10 ⁻⁹ mol/L	(Wen et al., 2008)
Benfluralin, pendimethalin,	GC/MS	0.05 -0.1mg /kg	(Tanabe et al., 1996)
Trifluralin			
Ethalfluralin, Trifluralin	GC/MS	0.1-4.6 ug/L	(Albero et al., 2005)
ethalfluralin, Benfluralin	GC/MS		
dinitramine	GC/NPD	0.001-0.02 ug/ g	(Sánchez-Brunete et al., 1998)
Trifluralin, ethalfluralin, pendimethalin, isopropalin	HPLC/UV	0.5µg/kg-0.02mg/kg	(Cabras et al., 1991)
Trifluralin, ethalfluralin, pendimethalin	HPLC/ UV	0.09-0.14ug/L	(Vitali et al., 1994)
nitralin	HPLC- UV	6.9 ng	(Ruiz de Erenchun et al., 1997)
Trifluralin	HPLC/ UV	1µg/kg	(Topuz et al., 2005)
Trifluralin	HPLC/ UV	0.025mg/kg	(Huang et al., 2004)
Trifluralin	ELISA	0.1-100ng/mL	(Gyöngyvér et al., 2000)
Trifluralin	Immunosensor	2×10 ⁻¹⁷ -3×10 ⁻⁵ ng/mL	(Szendr et al., 2003)

Table 7. Summary of analytical methods for dinitroaniline herbicides

4. Sulfonylurea herbicides

Sulfonylurea herbicides are one of the largest families of herbicides in the world. DuPont company first reported the herbicidal activity of sulfonylurea compounds and the first sulfonylurea herbicide- chlorsulfuron was marketed in 1976, which opened the era of super-efficient herbicide application (Mughari et al., 2007). Now the number of the patents related to sulfonylurea herbicides is more than 400. The information of some common sulfonylurea herbicides was shown in table 8.

These herbicides, which have low toxicity to mammals, are highly toxic to plants and, consequently, are used at low application rates (3-40 g ha⁻¹). The general structure of the sulfonylurea herbicides (R-SO₂NH-CONH-R, fig) consists of two R groups attached to either side of the sulfonylurea linkage (fig 3). The R group attached to the sulfur atom of the sulfonyl moiety can be an aliphatic, aromatic, or heterocyclic group, whereas that attached to the terminal nitrogen atom of the urea moiety can be a substituted triazine or pyrimidine ring.

In recent years, sulfonylurea herbicides have become very popular worldwide because of their low application rates, low toxicity to mammals, and unprecedented herbicidal activity. These herbicides are non-volatile, and their water solubilities are pH dependent being greater in alkaline than in acidic solution

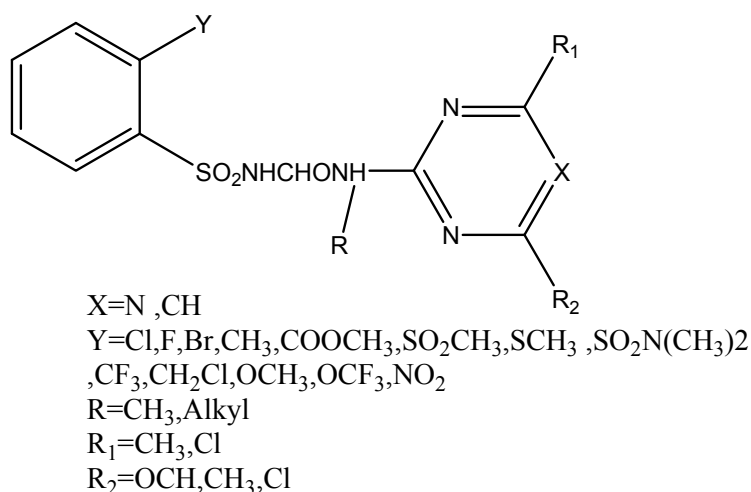


Fig. 3. Parent chemical structure of Sulfonylurea herbicides

4.1 Sample preparation

As weak acids, sulfonylurea herbicides show a more rapid degradation in environment. Therefore, the concentration of this class herbicides usually found in environmental and food samples is about 100-1000-fold lower as compared to other herbicides. Generally, the trace analysis of complex environmental and food samples needs pretreatment steps in order to reduce matrix interferences and enrich trace level analytes.

Traditional liquid-liquid extraction (LLE) or more rapid and economic solid phase extraction (SPE) or dispersive solid phase extraction (DSPE) have been reported in sulfonylurea herbicide detection. Materials such as RP-C₁₈, ion exchangers, mixed mode phases, graphitized carbon, and polystyrene divinylbenzene supports have been shown to be valuable sorbents for sample enrichment of various sulfonylurea herbicides in different matrix. Acidified organic solvents such as acetonitrile, dichloromethane, ethyl acetate (pH=2) were often used to extract sulfonylurea herbicides from various matrix (table 9).

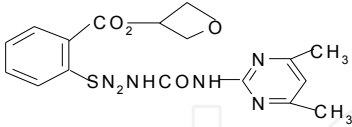
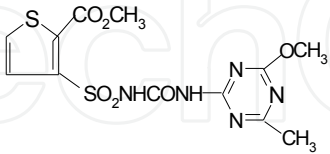
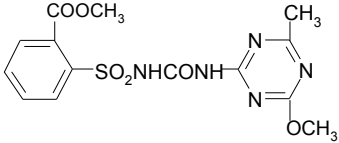
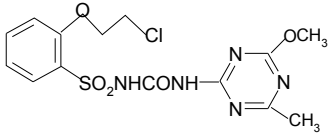
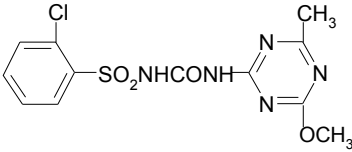
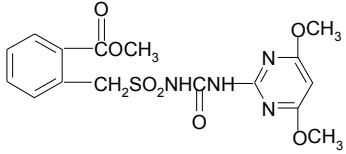
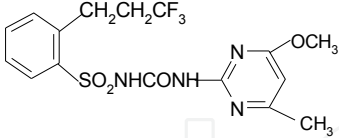
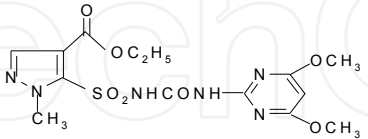
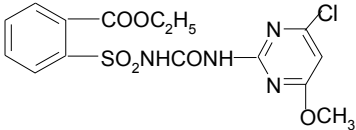
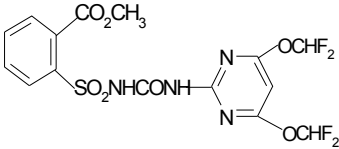
sulfonylureas herbicides	Structures	molecular formula	MW	pKa
oxasulfuron		$C_{17}H_{18}N_4O_6S$	406.4	5.1
thifensulfuron-methyl		$C_{12}H_{13}N_5O_6S_2$	387.4	4.0
metsulfuron-methyl		$C_{14}H_{15}N_5O_6S$	381.4	3.3
triasulfuron		$C_{14}H_{16}ClN_5O_5S$	401.8	4.6
chlorsulfuron		$C_{12}H_{12}ClN_5O_4S$	357.8	3.6
bensulfuron-methyl		$C_{16}H_{18}N_4O_7S$	410.4	5.2
prosulfuron		$C_{15}H_{16}F_3N_5O_4S$	419.4	3.8
pyrazosulfuron-methyl		$C_{14}H_{18}N_6O_7S$	414.4	3.7
chlorimuron-ethyl		$C_{15}H_{15}N_4O_6S$	414.8	4.2
primisulfuron-methyl		$C_{15}H_{12}F_4N_4O_7S$	468.3	5.1

Table 8. Infomation for some Sulfonylurea herbicides

Matrix	Herbicide	Extraction	Clean-up	Ref.
Carrots	Linuron	Hexane-diethyl ether, homogeniser	Florisil cartridge	(D'Amato, 1993)
Potatoes	Linuron	Acetone, homogeniser	LLE-Silica cartridge	(Miliadis & Vasilikiotis, 1990)
Cereals	Metsulfuron	Methanol, homogeniser	Liquid chromatography	(Zhou et al., 1994)
Rice	Bensulfuron	Methylene chloride, homogeniser	Silica cartridge	(Zhou et al., 1996)
Carrots	Linuron	Water (acidic pH), shaking	-	(Sojo et al., 1997)
Garlic	Linuron	Methanol, homogeniser	Alumina column	(Cessna, 1991a)
Asparagus	Linuron	Methanol, homogeniser	LLE-Florisil column	(Cessna, 1990)
Cereals	Chlortoluron	Ethanol-water, homogeniser	Silica column	(Pérez et al., 1993)
Potatoes	Isoproturon	Methanol, homogeniser	-	(Yaduraju, 1993)
Grains	Sulfonylureas	Acetonitrile, homogeniser	Cation-exchange cartridge	(Krynitsky & Swineford, 1995)
Potatoes	Linuron	Acetone, homogeniser	LLE-Florisil column	(Mattern, 1989)
Grains, cereals	Chlorsulfuron	Ethyl acetate, blender	LLE-GPC	(Slates, 1983)

Table 9. Extraction and clean-up for sulfonylurea herbicides

In order to determine the multiresidue of oxasulfuron, thifensulfuron-methyl, metsulfuron-methyl, triasulfuron, chlorsulfuron, bensulfuron-methyl, prosulfuron, pyrazosulfuron-methyl, chlorimuron-ethyl and primisufuron-methyl in soybeans, Qi tried various solvent system including acetone, acetonitrile, dichloromethane, ethyl acetate to optimize the extraction procedure. It showed that the serious emulsification occurred when using dichloromethane and more interferences were extracted by acetone and ethyl acetate. Finally, they used acetonitrile to extract these compounds from soybean. For clean-up step, Qi tested the purification effects of SPE packed with different materials (C₁₈ 500mg, Florisil 1000mg & 3000mg, Al₂O₃-Neutral 500mg & 1000mg) and satisfied results were obtained when using SPE columns packed with Florisil (3000mg).

4.2 Detection

Various methods for sulfonylurea herbicide determination have been published up to now. These compounds are not directly amenable to GC, because of their low volatility and thermal instability. Few is reported by GC analysis after derivatization. Most of the applications known are based on HPLC using reversed phase columns followed either by ultraviolet (UV) or mass spectrometric (MS) detection. The typical conditions for HPLC separation were set as follows (table 10):

Column: C₁₈ (250*4.6mm i.d., 5.0μm), temperature 45 °C; UV wavelength: 230nm
Mobile -phase: acetonitrile-water (pH=2.5, adjusted with 85% phosphoric acid); flow rate: 1.0mL/min
The gradient elution program of HPLC separate condition (table). Qi (Qi et al., 2004)applied this procedure to analyze the sulfonylurea herbicide residues in soybean samples.

Time (min)	Water acidfied with Phosphoric acid (pH=2.5) %	acetonitrile (%)
0.00	80	20
1.75	65	35
10.00	60	40
13.00	50	50
15.00	40	60
22.00	40	60
22.01	10	90
27.00	10	90

Table 10. Gradient elution program for HPLC

5. Triazine herbicides

Triazine herbicides are a class of herbicides used for protecting crops from weeds before emergence or during early stage after emergence. The history of their use can be traced back to1952 when J. R. Geogy synthesized and screened the first triazine derivatives. A great triazine herbicides are derived from s-triazine (fig 4) For R1 position, this is most often - Cl(the commercial names ending with ~azine), -SCH3(-tryn) and -OCH3(-ton). The substitunts at R2 or R3 are usually amino groups. (See table 1)
Triazines and their degradation products are toxic and persistent in water, soil and organisms(Vitali et al., 1994). Moreover, atrazine is a member of the triazine family and has been classified as human carcinogen(Dean et al., 1996). From the view of their ecological and health hazards in use, some triazine herbicides have been banned in certain countries (e. g. atrazine banned to use in 1991, Germany). In the EU, the maximum allowed limit for each individual herbicide has been set at 0.1 ugL⁻¹, but the EPA of USA has set the maximum allowable level of atrazine at 3ug/L⁻¹.

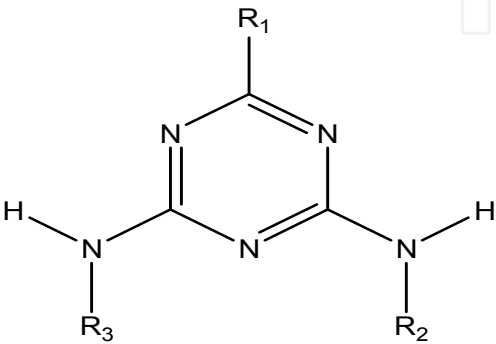


Fig. 4. Chemical structure for triazines

Compound	Substituents			Partition coefficient between octanol and water lg $P_{OC/w}$
	R ₁	R ₂	R ₃	
Simazine	Cl	NHC ₂ H ₅	NHC ₂ H ₅	2.3
Atrazine	Cl	NHC ₂ H ₅	NHCH(CH ₃) ₂	2.7
Propazine	Cl	NHCH(CH ₃) ₂	NHCH(CH ₃) ₂	2.91
Terbutylazine	Cl	NHC ₂ H ₅	NHC(CH ₃) ₃	3.06
Trietazine	Cl	NHC ₂ H ₅	N(C ₂ H ₅) ₂	3.07
Ipazine	Cl	N(C ₂ H ₅) ₂	NHCH(CH ₃) ₂	-
Deethylatrazine	Cl	NH ₂	NHCH(CH ₃) ₂	1.6
Deisopropylatrazine	Cl	NHC ₂ H ₅	NH ₂	1.2
Deethyldeisopropylatrazine	Cl	NH ₂	NH ₂	0
Hydroxysimazine	OH	NHC ₂ H ₅	NHC ₂ H ₅	-
Hydroxyatrazine	OH	NHC ₂ H ₅	NHCH(CH ₃) ₂	1.4
Hydroxypropazine	OH	NHCH(CH ₃) ₂	NHCH(CH ₃) ₂	-
Hydroxydeethylatrazine	OH	NH ₂	NHCH(CH ₃) ₂	0.2
Hydroxydeisopropylatrazine	OH	NHC ₂ H ₅	NH ₂	-0.1
Simeton	OCH	NHC ₂ H ₅	NHC ₂ H ₅	-
Atrazon	OCH	NHC ₂ H ₅	NHCH(CH ₃) ₂	2.69
Desmetryn	SCH ₃	NHCH ₃	NHCH(CH ₃) ₂	-
Simetryn	SCH ₃	NHC ₂ H ₅	NHC ₂ H ₅	2.8
Ametryn	SCH ₃	NHC ₂ H ₅	NHCH(CH ₃) ₂	3.07
Prometryn	SCH ₃	NHCH(CH ₃) ₂	NHCH(CH ₃) ₂	3.34
Terbutryn	SCH ₃	NHC ₂ H ₅	NHC(CH ₃) ₃	3.74

Table 11. Information for some triazine herbicides

5.1 Sample preparation

Numerous methods have also been published that examine a large variety of the triazines in many different matrices. Usually, the targeted compounds are extracted from foods by mechanical shaking or homogenisation with organic solvents, then clean-up of the extracts is carried out on SPE columns(Florisol, silica, alumina, cation-exchange cartridge). Triazine compounds are organic bases and very easy to be absorbed by cation exchange resin. For the great differences in physical and chemical properties of different triazine herbicides, a wide array of solvents (acetone, ethanol, ether, chloroform, methanol, water et. c) have been used in analytical method development. (see table 12)

5.2 Detection

Different analytical methods, such as GC, HPLC and capillary electrophoresis, have been developed for the separation and quantification of triazine herbicides (table 13). Gas chromatography mainly with ECD, NPD and MS detection has been extensively employed for the measurement of triazine herbicide residues. DB-5 capillary column (5 % polydiphenyl- and 95 % polydimethylsiloxane; 30 m x 0.25 mm, film thickness 0.25 µm) or its analogue is suitable for triazine analysis.

Matrix	Herbicide	Extraction	Clean-up	Ref.
Vegetables, rye	Triazines	Dichloromethane maceration, shaker	Silica column	(Roseboom & Herbold, 1980)
Cereals, apples, celery	Triazines	Methanol, blender	LLE-Cation-exchange cartridge	(Pardue, 1995)
Vegetables	Triazines	Acetonitrile-water, homogeniser	Carbopack cartridge SCX column	(Battista et al., 1989)
Corn, vegetables, sugar beet	Simazine	Water, homogeniser Chloroform, shaker	Alumina column	(Pringle et al., 1978)
Cereals, vegetables	Metribuzine	Acetonitrile-water, reflux	LLE-Florisil column	(Thornton & Stanley, 1977)
Potatoes	Metribuzine	Water, steam distillation	LLE-Silica column	(Ohms, 1976)
Fruits, vegetables	Atrazine	Ethyl acetate, shaker	C18 column	(Wittmann & Hock, 1993)
Grape juice	Simazine	Diethyl ether (acidic pH), shaker	-	(Ortiz-Gomez et al., 1995)
Oil	Simazine	Acetonitrile, blender	-	(Montiel & Sánchez, 1996)
Olives	Simazine	Ethyl acetate, blender	-	(Cessna & Benoit, 1992)
Onions	Cyanazine	Ethanol-water, homogeniser	LLE-Florisil column	(Bailey et al., 1978)
Vegetables	Triazines	Acetone, blender	LLE-Florisil column	(Lawrence & Laver, 1974)
Cereals, fruits, vegetables	Triazines	Methanol, blender	Alumina column	(Mortimer et al., 1994)

Table 12. Extraction and clean-up for triazine herbicides

Tomkins and Ilgner (Tomkins & Ilgner, 2002) developed a GC-MS method for the detection of triazine herbicides (atrazine, cyanazine, simazine) and their decomposition products (deethylatrazine, deisopropylatrazine) in environmental waters. Balduini (Balduini et al., 2003) measured the triazine herbicides in breast milk. Five triazines were adsorbed on a graphitized carbon black SPE cartridge, desorbed and analysed by GC/MS. Detection and quantification limits were 0.3 and 1 ppb from 1 mL of breast milk. Some triazine herbicides and their degradation products have been separated by reversed phase HPLC, and their atmospheric pressure chemical ionization (APCI) or electrospray mass spectra were measured. The APCI technique gives primarily [M+H]⁺ ions, but fragment ions are observed with electrospray and conditions that favor CID The LC/MS techniques are

Matrix	Herbicide	Analytical measure	LOD	Ref
Corn	Atrazine	GC-ECD	0.002 ppm	(Pylypiw et al., 1993)
Onion	Cyanazine	GC-NPD HP-1 Column	10 mg/kg	(Cessna, 1992)
Cereals, vegetables	Metribuzin	GC-ECD OV-225 Column	0.01 mg/g	(Ohms, 1976; Thornton & Stanley, 1977)
Vegetables, corn, sugar beet Oil, olives	Simazine	GC-NPD OV-101 Column HP-1 Column	mg/kg 0.01 ppm	(Pringle et al., 1978; Montiel & Sánchez, 1996)
Rye, vegetables Cereals, celery, apples	Triazines	GC-NPD Carbowax 20 M; OV-225 DB-17	0.01–0.02 mg/kg 0.02–1.0 ppm	(Roseboom & Herbold, 1980)
Breast milk	Triazines	GC-MS BPX-5 SGE	0.3-1 ppb	(Pardue, 1995)
Tap water, rice, maize and onion	Triazines	GC/MS CP-Sil 5 CB GC-FID CP-Sil 8 CB,	- 14-74 ngmL ⁻¹	(Bailey et al., 1978)
Oranges, corn	Atrazine	HPLC Reversed-phase C18 Methanol–water UV 230 nm	0.015–0.300 ppm	(Wittmann & Hock, 1993)
Blueberries	Simazine	HPLC Reversed-phase C18 Acetonitrile–water UV	0.08–0.17 ppm	(Ely et al., 1993)
Grape juice	Simazine	HPLC Reversed-phase C18 Methanol–acetate buffer pH 5.0 UV 230 nm	20 mg/ L	(Ortiz-Gomez et al., 1995)
Vegetables	Triazines	HPLC Reversed-phase C18 Acetonitrile–phosphate buffer pH 6.7 UV 220 nm	10 ng/g	(Battista et al., 1989)
Oysters	Triazines	HPLC-MS/MS	-	(Wittmann & Hock, 1993)
Sediments and water	Triazines	HPLC-APCI-MS/MS	-	(Takats et al., 2001)
-	Triazines	ELISA	<1 ppb.	(Wittmann & Hock, 1993)
Surface water	Simazine	SPFIA	1.3±0.9 ngmL ⁻¹	(Bruun et al., 2001)

Table 13. Extracton and cleanup for triazine herbicides

appropriate for triazine metabolites and their degradation products that are not amenable to GC/MS, but they may not provide advantages over GC/MS for most triazine herbicides and their dealkylated degradation products that are amenable to GC/MS. Hammock 's lab (Wortberg et al., 1995) developed immunoassay to detect four triazines in 1995 and the LOD of the ELISA was lower than 1ppb. Herranz (Herranz et al., 2008) developed solid-phase fluorescence immunoassay (SPFIA) and applied it in simazine detection of surface water with higher sensitivity (LOD 1.3 ± 0.9 ng/mL).

6. Amide herbicides

Amides, especially of chloroacetic acid and substituted anilines, have been and are popular herbicides since the first amide herbicide-allidochlor was found 60 years ago. Acetochlor, alachlor, butachlor, dimethenamide, metolachlor, and propachlor are amides of chloroacetic acid, and especially acetochlor, is used widely in the world for its high efficiency as the treatment agents before emergence. They are also in the list of chemical pollutants that need to be more heavily monitored due to their toxicity and accumulation in environment and their effects on the environment and human health. Acetochlor was listed as B-2 carcinogen by EPA (USA). Other acids used to form the amides include propanoic acid and several substituted benzoic acids (Nartova et al., 2008). An alkyl or alkyloxyalkyl group is usually substituted for the other hydrogen of the amide nitrogen. Some representative amide herbicides are shown in table 14.

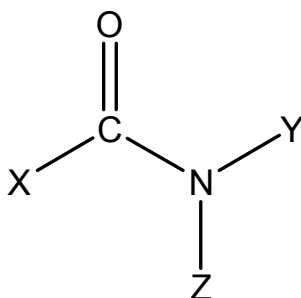


Fig. 5. Parent structure for amide herbicides

6.1 Sample pretreatment

For extraction of amide herbicides from food or agricultural products, solvents such as acetone, acetone-water, petroleum ether or acetonitrile were used widely (table 15). A typical sample treatment procedure was as follows: sample was extracted by acetone, then sulfate solution was added to the extracts, and finally LLE procedure was carried out with petroleum ether. But, the LLE isn't suitable for purification of some polar compounds (e. g. alachlor). For complex samples, further clean-up process is needed, usually based on SPE (florisil, alumina, silica or carbopack cartridge). C_{18} sorbents mainly used for the clean up of water samples before analysis solid-phase microextraction (SPME) considered as solventless analytical techniques, has been reported to detect the acetochlor, alachlor, and metolachlor residues in water samples.

6.2 Detection

GC was the most common method to detect the amide herbicides, usually equipped with selective detectors such as ECD, NPD or MS (Li et al., 2006). Acetochlor often can't be

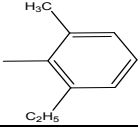
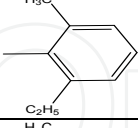
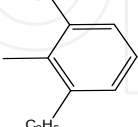
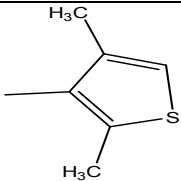
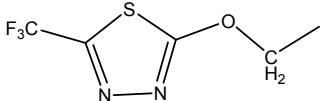
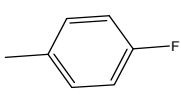
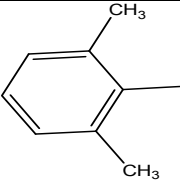
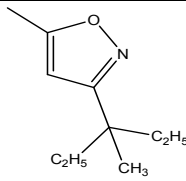
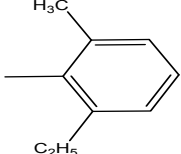
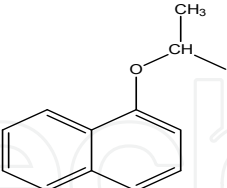
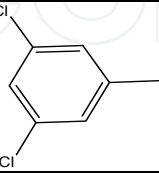
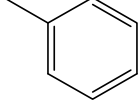
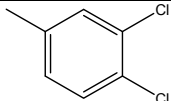
Name	X	Y	Z
Acetochlor	-CH ₂ Cl		-CH ₂ OCH ₂ CH ₃
Alachlor	-CH ₂ Cl		-CH ₂ OCH ₃
Butachlor	-CH ₂ Cl		-CH ₂ O(CH ₂) ₃ CH ₃
Dimethachlor	-CH ₂ Cl		-CH(CH ₃)CH ₂ OCH ₃
Flufenacet			- CH(CH ₃) ₂
Isoxaben			-H
Metolachlor	-CH ₂ Cl		-CH(CH ₃)CH ₂ OCH ₃
Napropamide		-C ₂ H ₅	-C ₂ H ₅
Pronamide		-C(CH ₃) ₂ C≡CH	-H
Propachlor	-CH ₂ Cl		- CH(CH ₃) ₂
Propanil	-C ₂ H ₅		-H

Table 14. Information for some amide herbicides

separated with atrazine on the capillary column and thus, some analysts used NPD connected with ECD to realize the simutanious detection of the two compounds. What’s more, the heated decomposition temperature of some amide herbicides is low (metolachlor, 105 °C), which makes difficulties in detection of these compounds by GC. The HPLC method, based on reversed phase C₁₈ or C₈ column, came into being. The mobile phase often was methanol-water or acetonitrile-water (pH 3, adjusted with acetic acid). MS-MS techiques further improved the analytical selectivity. Steen, (Ling et al., 2006)used GC-MS/MS to detect the pesticide redidues in marine system with LOD ranging from 0.2 to 0.5 ng/L. Striley(Striley et al., 1999) developed ELISA to measure the putative major human metabolite of metolachlor, metolachlor mercapturate (MM) in human urea. Tessier, (Tessier & Marshall, 1998) developed immunoassay to detect alachlor in aqueous samples. Yakovleva, (Szendr et al., 2003) established ELISA and applied to analyze butachlor residues in mineral, ground and surface water. Other application of detection method was listed in table 16.

Matrix	Herbicide	Extraction	Clean-up	Ref
Tamotoes	metolachlor	Water(acidic pH), homogeniser	LLE	(Gaynor et al., 1993)
Carrots	metolachlor	Water(acidic pH), shaker	-	(Sojo et al., 1997)
Potatoes	metolachlor	Acetone-hexane, blender	LLE	(Singh, 1997)
Cereals	Chloroacetamides	Acetonitrile, homogeniser	LLE-florisil column	(Balinova, 1988)
Vegetables	metolachlor	Methanol, blender	LLE-silica cartridge	(Gaynor et al., 1992)
Tea leaves	Amide herbicides	ethyl acetate, shaker	An active carbon SPE column connected to a Florisil column	(Shen et al., 2007)
Soybean	Amide herbicides	Acetone, shaker	Florisil cartridge	(Li et al., 2006)
Onion	Amide herbicides	Acetonitrile microwave-assisted extraction(MAE)	Florisil cartridge	(Hans-Jürgen & Manfred, 1993)
Water	Amide herbicides	SPME	-	(Sauret-Szczepanski et al., 2006)
Water	Amide herbicides	water-acetonitrile MAE		(Fuentes et al., 2006)

Table 15. Extraction and clean-up for amide herbicides

Matrix	Herbicide	Analytical Method	LOD	Ref
Peanut, cereals	Alachlor	NPD, UC-W98	0.02–0.05 ug/g	(Conkin et al., 1978)
Corn	Alachlor, metolachlor	ECD	0.002 ppm	(Pylypiw et al., 1993)
Tomatoes	Metolachlor	Hydrolysis MS Supelcowax	10- 50 ppb	(Ely et al., 1993)
Potatoes	Metolachlor	ECD, OV-1	0.15 ng	(Gaynor et al., 1992)
Potatoes, tomatoes, maize	Chloroacetamides	ECD QF-11DC-200, Apiezon L	0.02–0.05 ng	(Singh, 1997)
Tea leaves	Amide herbicies	GC-NCI-MS GC-EI-MS	<2 ug/kg	(Balinova, 1988)
Soybean	Amide herbicies	HPLC-UV, C ₁₈ 210 nm	1-7.2 ppb	(Li et al., 2006)
Carrots	metolachlor	HPLC-UV 220nm	--	(Sojo et al., 1997)

Table 16. analytical methods for some amide hericides

7. Glyphosate

Glyphosate is the common name for *N*-(phosphonomethyl)-glycine, a total-kill herbicide (first found its herbicidal activity in 1971, introduced in 1974 by theMonsanto Company under the trade name “Roundup” and rapidly became one of leading herbicides in the world.), having the environmental advantages of low mammalian toxicity and rapid breakdown in the soil leaving no harmful residues. Having pKa values of 0.78, 2.29, 5.96 and 10.98, glyphosate is a very polar and amphoteric compound(fig 6).

Glyphosate is used to control grasses, herbaceous plants including deep rooted perennial weeds, brush, some broadleaf trees and shrubs, and some conifers(Tsui et al., 2005). Glyphosate does not control all broadleaf woody plants. Glyphosate applied to foliage is absorbed by leaves and rapidly moves through the plant. It acts by preventing the plant from producing an essential amino acid. This reduces the production of protein in the plant, and inhibits plant growth. Glyphosate is metabolized or broken down by some plants, while other plants do not break it down. Glyphosate dissolves easily in water. Aminomethylphosphonic acid (AMPA) is the main break-down product of glyphosate in plants (Zhao et al., 2009).

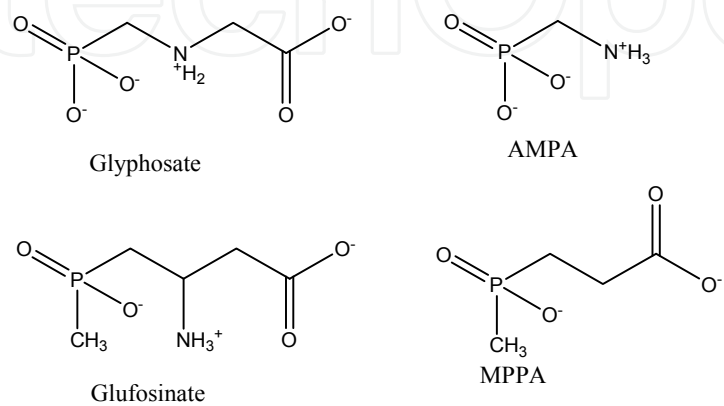


Fig. 6. Chemical structure for glyphosate, glufosinate and their main metabolites

Glufosinate [DL-homoalanine-4-yl(methyl)phosphinic acid], is another highly polar amino acid herbicides. A major breakdown product of glufosinate found in both plants and animals that have been exposed to glufosinate is 3-methylphosphinopropionic acid (MPPA) (Moye et al., 1983).

Based on the results of animal studies, glyphosate does not cause genetic damage or birth defects, and has little or no effect on fertility, reproduction, or development of offspring. There is not enough information available at this time to determine whether glyphosate causes cancer. There have been no reported cases of long term health effects in humans due to glyphosate exposure (Tsui et al., 2005). The Food and Agriculture Organization (FAO) of the United Nations has set a maximum residue limit (MRL) of glyphosate in wheat at 5 mg/kg. The world health organism evaluated glyphosate on its acceptable daily intake value and the data allocated for glyphosate was 0.3 mg/kg body mass.

7.1 Sample preparation

The main problem in glyphosate and its metabolite analysis is their recovery from biological or field samples. Glyphosate is a highly polar herbicide, very soluble in water and insoluble in most organic solvents, which does not allow extraction with organic solvents and makes the extraction difficult and the preconcentration step quite lengthy.

Due to the amphoteric character of glyphosate and AMPA, both anionic and cationic resins have been used for preconcentration and clean-up purposes. Another important aspect to be considered is the binding of glyphosate to organic matter. Some reports showed that humic substances adsorb glyphosate strongly because the hydrogen bonding interactions between the hydrogen acidic and the oxygen group of both substances. Glyphosate extraction is usually carried out with water or water with chloroform, sometimes at acidic pH (table 17). 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. More often used in this purification step is LLE or column chromatography on ion exchange columns.

7.2 Detection

Due to their very polar, and in most cases ionic character, Analytical methods for the analysis of glyphosate and its major metabolite, AMPA, include thin-layer chromatography, capillary electrophoresis (CE), gas (GC) and liquid chromatography (LC) after derivatisation.

The availability of derivatisation techniques compatible with an aqueous extract or sample and the chromatographic separation makes LC an attractive technique. However, for LC with conventional detection systems, such as UV-Vis or fluorescence detectors, glyphosate and AMPA need to be derivatised because of the lack of chromophore or fluorophore. Three different procedures are generally used for the determination of glyphosate with LC: (i) post-column ninhydrin derivatisation and UV detection; (ii) post-column fluorogenic labeling with o-phthalaldehyde and mercaptoethanol after oxidation of glyphosate to glycine; (iii) pre-column derivatization using 9-fluorenylmethyl chloroformate (FMOC-Cl) with fluorescence detection (FLD).

Post-column derivatisation was used in most of the previous studies for glyphosate analysis in water and has also been recommended by the US Environmental Protection Agency (EPA). Moyne and Boning were the first to use the FMOC-Cl reaction for derivatising glyphosate. A disadvantage of this reaction, however, is its reactivity with water, which

Matrix	Extraction	Clean-up	Ref.
Corn, fruits, soybeans	Water, blender	LLE-Cation-exchange column	(Alferness & Iwata, 1994)
Blueberries	Water, homogeniser	LLE-GPC-Cation-exchange column	(Guinivan, 1982)
Legumes, cereals	Water-chloroform, shaker	LLE-Cation-exchange column-Anion-exchange column	(Wigfield & Lanouette, 1991; Wigfield & Lanouette, 1991)
Fruits, field pea, barley and flax seed	0.1 M HCl-chloroform, blender	LLE-Ligand-exchange column-Anion-exchange column	(Cowell et al., 1986) (Cessna, 2002)
Berries	Water-chloroform, blender	LLE-Charcoal-Cation-exchange column	(Konar & Roy, 1990)
Kiwi fruit, asparagus	Water-chloroform, blender	LLE-Anion-exchange column-GPC	(Benfenati et al., 2006)
fruit juices	-	-	(Cláudia et al., 2007)
Fruits, vegetables	Water-chloroform, blender	LLE-Cation-exchange column	(Moye et al., 1983)
Cereals	Water, overnight standing extraction	100 mg C ₁₈ SPE	(Hogendoorn et al., 1999)
Rice, soybean sprouts	Water, acetone homogeniser	anion-exchange column Florisil Cartridge Cleanup.	(Tseng et al., 2004)

Table 17. Extraction and clean-up for glyphosate

leads to the formation of a FMOC-OH product (reaction of the acyl chloride with water) in the reaction mixture. To obtain quantitative yield in derivatisation, excess reagent has to be used. Different concentrations of FMOC-Cl have been reported in the literature for the derivatisation of glyphosate, still, there is little or no general agreement concerning the optimal molar ratio of glyphosate to FMOC-Cl to be used.

The common HPLC conditions for the separation of glyphosate and AMPA were using a single polymeric amino column and mobile phase at pH 10 which contained 55% (v/v) acetonitrile and 50mM phosphate buffer.

FMOC-OH by product make it difficult in separation by chromatography, which is represented by the large peak in front of the glyphosate chromatogram. The FMOC-OH product completely overlaps the glyphosate peak and creates difficulties in its detection (Tadeo et al., 2000). The removal of this FMOC product and separation of the glyphosate peak by column-switching technique using coupled C18 and amino columns was previously

reported. However, these silica-based columns usually degrade under high alkaline conditions. Sancho (Sancho et al., 1994). reported that a gradual decrease in efficiency of the silica-based amino column after two months' use. Ion chromatography (IC) provides a useful tool in detecting ionic substance. Zhu used ion chromatography system equipped with anion exchange column and suppressed conductivity detector to determine the glyphosate in environmental samples with LOD 0.042 ug/mL. Patsias (Patsias et al., 2001) developed an automated method based on the on-line coupling of anion-exchange solid-phase extraction (SPE) and cation-exchange liquid chromatography followed by post-column derivatization and fluorescence detection for the trace level determination of glyphosate and its primary conversion product aminomethyl phosphonic acid (AMPA) in water.

These ionic compounds were also determined in water by liquid chromatography with mass spectrometry (LC-MS) after derivatization with FMOC, achieving quite low detection limits. The coupling of ion chromatography (IC) with electrospray mass spectrometry (ES-MS) opens new ways for the determination of polar organic micropollutants in water samples. The technique of conductivity suppress ion has been found to reduce the background signal in the range of about two-orders of magnitude leading to a significant increase in sensitivity. In addition, the formation of salt adducts has been avoided. Bauer (Bauer et al., 1999) separated glyphosate and AMPA in water on an anion-exchange column without any derivatization and detected the signal by IC-ES-MS.

The GC method can be developed to analyze glyphosate through the preparation of N-heptafluorobutyrylchloroethyl ester, N-trifluoroacetyltrifluoroalkyl ester, N-trifluoroacetylheptafluorobutyl ester and tert-butyldimethylsilyl derivatives. However, it is a time-consuming procedure to prepare the derivatives under anhydrous conditions. The usual detector equipped with GC for glyphosate analysis can be flame photometric, mass-selective detectors or the extreme sensitive electro-capture detector.

Capillary electrophoresis (Corbera et al., 2005), as an important separation technique due to its high resolving power and speed, was also reported for glyphosate analysis. Some (Khrolenko & Wieczorek, 2005) used p-toluenesulfonyl chloride for derivatization prior to CE separation, others (Cikalo et al., 1996) incorporate ribonucleotides into the background electrolyte to realize the indirect photometric detection. Chang (Chang & Liao, 2002) employed fluorescein as the buffer fluorophore and an argon-ion laser to induce the fluorescence background for detection of the glyphosate, AMPA, glufosinate and MPPA.

Mass spectrometry (MS) has the potential to be a rigorous direct detection method for these compounds, particularly in their ionic states. Utilising a simple microelectrospray interface, Goodwin (Goodwin et al., 2003) analyzed glyphosate, glufosinate and their metabolites on capillary electrophoresis-mass spectrometry (CE-MS) using a combination of electrical and pressure drive for interface. The observed concentration limit of detection for glyphosate in water is 1 mM and for a water-acetone extract of wheat is 2.5 mM, allowing the underivatized herbicide to be detected at 10% of the maximum residue limit in wheat.

8. Other herbicides

In addition to the above described types of herbicides, imidazolinone (imazethapyr, imazamox, imazapyr), imazapic, carbamate (isoprocab, oxamyl, propoxur) and diphenyl ether herbicides (acifluorfen, chlornitrofen, acetonifene, bifenox and oxyfluorfen) are also popular in agricultural production.

8.1 Imidazolinone herbicides

This class of herbicide is used to protect beans, peanuts, corn and other crops from weeds. These herbicides are used in a small amount for their long-acting effects and trace residues in soil may cause phytotoxicity on succeeding crop (Lewis et al., 2009). In 2005, Canada set MRL for imazethapyr residue in soybean, 0.1 mg/kg. USA regulated the MRL of imazethapyr residue in rice, 0.3 mg/kg (G/SPS/N/USA/1229). Japan set the MRLs ranging from 0.01 to 0.5 mg/kg of imazethapyr residue in foods depending on the food types.

There are carboxyl group and imino group in the chemical structure of imidazolinone herbicide, which make imidazolinone herbicides show strong polarity, and thus the control of pH in sample extraction is critical.

Many analytical methods such as HPLC, GC-MS, LC/MS have been reported for imidazolinone herbicide detection. A typical HPLC method is as follows: the targeted molecules can be extracted from the matrix with mixed solution of ammonium bicarbonate (0.1 M, pH=5)-methanol (7:3, v/v). The extracts can be partitioned with dichloromethane and the organic layer was collected and condensed for further clean-up on cation exchange column. Separation of imidazolinone herbicides can be carried out by C₁₈ column with acetonitrile-1% acetic acid as mobile phase. The detection UV length can be set 252-258 nm.

With the sensitivity and specificity of HPLC-MS (Chu et al., 2008), some analyzed the imidazolinone herbicides in various matrix. Under positive mode, [M+H]⁺ can be monitored for each compound (m/z 262 for imazapyr, m/z 275 for imazamethabenz acid, m/z 306 for imazamox, m/z 276 for imazapic, m/z 290 for imazethapyr and m/z 312 for imazaquin).

These compounds should be esterized before analysis by GC. Anisuzzaman (Anisuzzaman et al., 2000) detected the imidazolinone herbicides in soil, water and soybean by GC-NPD and GC-MS after synthesis of dimethyl derivatives.

8.2 Carbamate herbicides

Three classes of carbamate pesticides are known. The carbamate ester derivatives, used as insecticides (and nematocides), are generally stable and have a low vapour pressure and low water solubility. Carbamate fungicides contain a benzimidazole group. It is well known that carbamate pesticides are esters of carbamic acid, having the general structure R₁NHC(O)OR₂, in which R₁ and R₂ are aromatic and/or aliphatic moieties.

Carbamate herbicides (Vasilescu et al., 2005) are known to repress cell division as a consequence of their disturbing nucleic acid metabolism and protein synthesis. Clorpropham, sulfallate and phenmedipham are the representatives of this family herbicides. Some examples about extraction and clean-up of carbamates and thiocarbamates are shown in table.

The well-known thermal instability of carbamates has led to the use of HPLC, but its most usual detectors have a limited sensitivity. In the 1980s, some used post-column hydrolysis and derivatization with fluorescence detection to overcome these disadvantages. The carbamates were degraded into methylamine and then derivatized to a fluorescent isoindole product, which was widely used in carbamate residue analysis in fruits and vegetables. In addition, many references investigation showed that both ESI and/or APCI with HPLC/MS were used to analyze the carbamates and APCI can help to reduce matrix effects.

Although careful control of experimental conditions may allow direct determination of carbamates by GC, large number of experimental factors such as injector temperature, residence time in the injector, solvent nature and injection mode, are known to affect the results. Derivatization reactions are therefore required prior to GC analysis.

Matrix	Herbicide	Extraction	Clean-up	Ref.
Rice	Thiobencarb	Methanol or acetone, blender	-	(Au & Fung, 1988)
Potatoes	Chlorpropham	Tetrahydrofuran-water-acetonitrile-acetic acid, homogeniser	-	(Camire et al., 1995)
Fruits, vegetables	Chlorpropham	Methanol, blender	Alumina column	(Wilson et al., 1981)
Potatoes	Chlorpropham	Acetone, homogeniser	LLE	(Tsumura-Hasegawa et al., 1992)
Garlic	Triallate	Methanol, homogeniser	LLE-Florisil cartridges Alumina column	(Cessna, 1991b)
Potatoes	Chlorpropham	Dichloromethane (water), blender	-	(Mondy et al., 1992)
Lentils	Triallate	Acetonitrile, shaker	Alumina column	(Cessna, 1980)
Potatoes	Chlorpropham, propham	Dichloromethane (water), blender	Silica-TLC	(Corti et al., 1991)
Fruits, vegetables	Chlorpropham, propham, triallate	Ethyl acetate, homogeniser	LLE-Florisil column	(Blaicher et al., 1980)
Potatoes	Chlorpropham	Water suspension,	solid-phase microextraction	(Volante et al., 1998)
fruit and vegetables	carbamate herbicides	acetonitrile (MeCN) containing 1% acetic acid (HAc)	dispersive-SPE cleanup step (primary secondary amine+ C ₁₈)	(Martínez Vidal et al., 2006)

Table 18. Extraction and clean-up for some carbamate herbicides

The main derivatization reactions applied to the family of herbicides involve the N-protection for carbamates. Among them, silylation, acylation and alkylation, together with reactions of transformation into aniline have been used. An N-protection reaction for derivatization of compounds containing an NH-reactive group, based on the use of sodium hydride/dimethyl sulphoxide/methyl iodide (NaH/DMSO/CH₃I) has been frequently used.

8.3 Diphenyl ether herbicides

Among the herbicides being used, diphenylether compounds of herbicide are mainly introduced at pre- or post-emergence in controlling annual broad-leaved weeds and some types of grasses in numerous crops like rice, cereals, maize, etc(Murakami et al., 1988). This class of herbicides has proved to be an inhibitor of protoporphyrinogen oxidase, that leads to the accumulation of protoporphrin and therefore blocks the formation of chlorophyll. Molecules that inhibit protoporphyrinogen oxidase (Protox) have been among the most

frequently patented class of herbicides over the past decade. Commercial Protox inhibitors can be classified in a major chemical group, the *p*-nitrodiphenyl-ethers, commercially known as the diphenyl-ethers (DPhE).

This class of herbicides is mainly composed of esters but few compounds are acids or have an acidic behavior, with pKa comprised between 2.7 and 3.8. There are two main metabolites that arise from the degradation of the DPhE herbicides studied, bifenox acid from the hydrolysis of bifenox and acifluorfen from the degradation of lactofen and fluoroglycofen. Bifenox and oxyfluorfen are reported to be carcinogenic or suspected to be carcinogenic compounds (Sabino et al., 2004).

The herbicides in this category have a 2-chlorodiphenyl ether nucleus in common, and most also have nitro and trifluoromethyl substituents. As this class of compounds is usually nonvolatile and thermally unstable, most of the direct methods have been performed by using LC. Acifluorfen and fomesafen can be separated on a C-18 column, with a slightly acidic mobile phase, followed by electrospray to give $[M-H]^-$ ions. Lactofen and oxyfluorfen were also separated on a C-18 column, but without acid in the mobile phase.

Oxyfluorfen is amenable to GC separation (Wong et al., 2003), and nitrofen, with a similar structure, should have favorable properties for GC. Shen (Shen et al., 2008) extracted DPhE from vegetables sample with acetonitrile, then the extract was cleaned up by Envi-Carb SPE column connected to Alumina Neutral SPE column, determined by gas chromatography-negative chemical ionization mass spectrometry. The lactofen esters may be amenable to GC separation, but the acid acifluorfen and the sulfonamide fomesafen require derivatization for GC.

DPhE showed good solubility in acetone and acetonitrile and both organic solvents can be miscible with water. However, acetone can extract more interferences from matrix, especially from samples containing high fat and thus, acetonitrile is used a lot in DPhE extracting from agricultural products. Considering the polarity of DPhE, sorbents such as florisil or alumina are suitable for clean-up steps.

9. Conclusion

Food analysis entails important difficulties owing to the complexity of the sample matrix. Most methods for the analysis of pesticide residues described in the literature use a combination of some form of extraction with an organic solvent, with one or several clean-up and purification steps to remove coextractants before the sample is subjected to a further separation/detection technique.

One of the current trends of modern analytical chemistry is the miniaturization of the various tools daily used by a large number of researchers. Ultrafast separations, consumption of small amounts of both samples and reagents as well as a high sensitivity and automation are some of the most important goals desired to be achieved.

9.1 Sample treatment

Sample treatment has been recognized as the main bottleneck of the analytical process, especially when trace analysis is the purpose. For many years a large number of research laboratories and analytical instrument manufacturing companies have been investing their efforts in this field, which includes miniaturized extraction materials, sample pre-treatment procedures and separation techniques.

Solid-phase microextraction (SPME) is a relatively new technique introduced by Pawliszyn and coworkers in the early 1990s (Janusz, 1997). The feature of this technique is that it enables sample preparation and enrichment in one step. SPME is based on the partitioning of analytes between a coated fibre and a sample. The coated fibre consists of a small fused-silica rod coated with a thin layer of a sorbing material. Upon exposure to the vapour phase above a solution or upon direct immersion in the solution, a mass-transfer process begins, driven by the second law of thermodynamics, according to which the chemical potential of each compound should be equal throughout the system. If the analyte is in the gas phase and the extractant is liquid, dissolution of the gas in the liquid is the main process, and that is governed by Henry's law and Raoult's law. As solubility is the main concept, partition of the analyte between the gas and the liquid phases will take place and all variables affecting it will influence the extraction (Volante et al., 1998).

PLE (pressurized liquid extraction) is another extraction technique recently attracted considerable attention. PLE is a sample preparation technique that combines elevated temperature and pressure with liquid solvents to achieve fast and efficient extraction of the analytes from solid matrices (Marchese et al., 2009). In PLE, the variables that affect extraction efficiency are the nature of the solvent or mixture of solvents, the solvent volume/sample mass ratio, extraction pressure and temperature, the number of extraction cycles and the duration of each cycle. However, the temperature and type of solvent seem to be the two variables with the greatest bearing on the extraction process. The solvents commonly used in pesticide extraction from vegetables and fruit are acetone, n-hexane, ethyl acetate, dichloromethane and water, while those least used are acetonitrile, ethanol and 1-propanol (Nemoto & Lehotay, 1998).

Molecularly imprinted polymers (MIPs) with better specificities than those of traditional SPE adsorbents have recently been introduced as novel matrices for the extraction and clean-up of target compounds (Hu et al., 2010). To date, many papers describing the use of MIPs as SPE materials to clean-up and preconcentrate trace compounds from various matrices have been published (She et al., 2010; Baggiani et al., 2001; Sambe et al., 2007; Mhaka et al., 2009). She et al, 2010 prepared class-specific molecularly imprinted polymers for the selective extraction and determination of sulfonylurea herbicides in maize samples by high-performance liquid chromatography–tandem mass spectrometry.

9.2 Separation system

Among the separation techniques, capillary electromigration methods (which also include capillary electrochromatography, CEC), microchip and nano-LC/capillary LC have received especial attention. Besides their well known advantages over other separation tools, the role of these miniaturized techniques in food analysis is still probably in an early stage. In fact, applications in this field carried out by CEC, microchip, nano-LC and capillary LC are only a few when compared with other more established procedures such as conventional GC or HPLC (Myint et al., 2009).

In the last few years biosensors have shown great potential as analytical tools for the development of rather automatic, fast and direct analysis methods that in many cases avoid sample pretreatment or require minimal sample preparation, allowing on-site field monitoring (Salmain et al., 2008). For example, an optical fiber based biosensor was developed for atrazine and endrine monitoring in water using *Scenedesmus subspicatus* cells, immobilized on filter paper and covered with a thin alginate layer hardened with calcium chloride (Védrine et al., 2003).

10. References

- Albero, B.S., Nchez-brunete, C. & Tadeo, J.L. (2005). Multiresidue determination of pesticides in juice by solid-phase extraction and gas chromatography-mass spectrometry. *Talanta* 66(4), 917-924.
- Alferness, P.L. & Iwata, Y. (1994). Determination of glyphosate and (aminomethyl)phosphonic acid in soil, plant and animal matrixes, and water by capillary gas chromatography with mass-selective detection. *Journal of Agricultural and Food Chemistry* 42(12), 2751-2759.
- Anisuzzaman, A.K., Amin, M., Ogg, N., Hoq, F., Kanithi, M.R. & Jenkins, R.E. (2000). Synthesis of dimethyl derivatives of imidazolinone herbicides: their use in efficient gas chromatographic methods for the determination of these herbicides. *Journal of Agricultural and Food Chemistry* 48(12), 5893-5902.
- Au, A.M. & Fung, W.D. (1988). Rapid technique for thiobencarb residue determination in rice samples. *Bulletin of Environmental Contamination and Toxicology* 40(5), 655-659.
- Baggiani, C., Giovannoli, C., Anfossi, L. & Tozzi, C. (2001). Molecularly imprinted solid-phase extraction sorbent for the clean-up of chlorinated phenoxyacids from aqueous samples. *Journal of Chromatography A* 938(1-2), 35-44.
- Bailey, R., Lebel, G. & Lawrence, J.F. (1978). Gas-liquid chromatography of triazine herbicides as heptafluorobutyryl derivatives and some applications to analysis in foods. *Journal of Chromatography A* 161, 251-257.
- Balduini, L., Matoga, M., Cavalli, E., Seilles, E., Riethmuller, D., Thomassin, M. & Guillaume, Y.C. (2003). Triazinic herbicide determination by gas chromatography-mass spectrometry in breast milk. *Journal of Chromatography B* 794(2), 389-395.
- Balinova, A. (1988). Gas chromatographic determination of chloroacetamide herbicides in plants and soil. *Journal of Chromatography A* 455, 391-395.
- Battista, M., Di corcia, A. & Marchetti, M. (1989). Extraction and isolation of triazine herbicides from water and vegetables by a double trap tandem system. *Analytical Chemistry* 61(9), 935-939.
- Bauer, K.H., Knepper, T.P., Maes, A., Schatz, V. & Voihsel, M. (1999). Analysis of polar organic micropollutants in water with ion chromatography-electrospray mass spectrometry. *Journal of Chromatography A* 837(1-2), 117-128.
- Benfenati, E., Natangelo, M. & Tavazzi, S. (2006). *Gas Chromatography/Mass Spectrometry Methods in Pesticide Analysis*. John Wiley & Sons, Ltd.
- Bertrand, M.J., Ahmed, A.H., Sarrasin, B. & Mallet, V.N. (1987). Gas chromatographic and mass spectrometric determination of chlorophenoxy acids and related herbicides as their (cyanoethyl)dimethylsilyl derivatives. *Analytical Chemistry* 59(9), 1302-1306.
- Blaicher, G., Pfannhauser, W. & Woidich, H. (1980). Problems encountered with the routine application of HPLC to the analysis of carbamate pesticides. *Chromatographia* 13(7), 438-446.
- Boyd-boland, A.A. & Pawliszyn, J.B. (1995). Solid-phase microextraction of nitrogen-containing herbicides. *Journal of Chromatography A* 704(1), 163-172.
- Brondz, I. & Olsen, I. (1992). Intra-injector formation of methyl esters from phenoxy acid pesticides. *Journal of Chromatography A* 598(2), 309-312.

- Bruun, L., Koch, C., Jakobsen, M.H., Pedersen, B., Christiansen, M. & Aamand, J. (2001). Characterization of monoclonal antibodies raised against different structures belonging to the s-triazine group of herbicides. *Analytica Chimica Acta* 436(1), 87-101.
- Butz, S. & Stan, H.J. (1993). Determination of chlorophenoxy and other acidic herbicide residues in ground water by capillary gas chromatography of their alkyl esters formed by rapid derivatization using various chloroformates. *Journal of Chromatography A* 643(1-2), 227-238.
- Cabras, P.M., Spanedda, M.L., & Tuberoso, C. (1991). High-performance liquid chromatographic determination of dinitroaniline herbicides in soil and water. *Journal of Chromatography A* 585(1), 164-167.
- Camire, M.E., Bushway, R.J., Zhao, J., Perkins, B. & Paradis, L.R. (1995). Fate of thiabendazole and chlorpropham residues in extruded potato peels. *Journal of Agricultural and Food Chemistry* 43(2), 495-497.
- Catalina, M.I., Dall ge, J., Vreuls, R.J.J. & Brinkman, U.A.T. (2000). Determination of chlorophenoxy acid herbicides in water by in situ esterification followed by in-vial liquid-liquid extraction combined with large-volume on-column injection and gas chromatography-mass spectrometry. *Journal of Chromatography A* 877(1-2), 153-166.
- Cessna, A., Benoit, D.L. (1992). Weed control and herbicide residues in onion following use of chlorpropham and cyanazine. *Pesticide Science* 35(4), 355-362.
- Cessna, A. (1991a). Residue analysis of garlic (*Allium sarivum* L.) cloves following a postemergence application of linuron. *Canadian J Plant Sci* 71, 951-955.
- Cessna, A.J. (1991b). Residues of triallate in garlic (*Allium sativum* L.) cloves following preplant incorporation. *Canadian Journal of Plant Science* 71(4), 1257-1261.
- Cessna, A.J. (1980). Simultaneous extraction and detection of residues of (2, 4-dichlorophenoxy)acetic acid and bromoxynil from wheat. *Journal of Agricultural and Food Chemistry* 28(6), 1229-1232.
- Cessna, A.J. (1990). HPLC determination of linuron residues in asparagus following pre- and early postemergence applications. *Canadian Journal of Plant Science* 70, 591-597.
- Cessna, A.J. (1992). Comparison of extraction/hydrolysis procedures for the determination of acidic herbicides in plants: residues of mecoprop in barley following postemergence application. *Journal of Agricultural and Food Chemistry* 40(7), 1154-1157.
- Cessna, A.J., Darwent, A.L., Townley-smith, L., Harker, K.N. & Kirkland, K.J. (2002). Residues of glyphosate and its metabolite AMPA in field pea, barley and flax seed following preharvest applications. *Canadian Journal of Plant Science* 82, 485-489.
- Cessna, A.J., Holm, F. A. (1993). Residues of 2, 4-d in wheat following application after heading. *Canadian Journal of Plant Science* 74(1), 199-203.
- Cessna, A.J., Holt, N.W. & Drew, B.N. (1980). Tolerance and residue studies of triallate in lentils. *Canadian Journal of Plant Science* 60(4), 1283-1288.
- Cessna, A.J. & Kerr, L.A. (1993). Use of an automated thermal desorption system for gas chromatographic analysis of the herbicides trifluralin and triallate in air samples. *Journal of Chromatography A* 642(1-2), 417-423.

- Chang, S.Y. & Liao, C.H. (2002). Analysis of glyphosate, glufosinate and aminomethylphosphonic acid by capillary electrophoresis with indirect fluorescence detection. *Journal of Chromatography A* 959(1-2), 309-315.
- Chu, X.G., Yong, W., Ling, Y., Qiu, W.L., Yao, H.Y. (2008). Herbicides in soybean by ultra performance liquid chromatography tandem mass spectrometry. *Chinese Journal of Analytical Chemistry* 36(3), 325-329.
- Cikalo, M.G., Goodall, D.M. & Matthews, W. (1996). Analysis of glyphosate using capillary electrophoresis with indirect detection. *Journal of Chromatography A* 745(1-2), 189-200.
- Claudia, F.B.C., Coutinho, L.F.M., Luiz, H.M., Suzana, L.N., Carlos, A.P.C., Fernando, M.L. (2007). Direct determination of glyphosate using hydrophilic interaction chromatography with coulometric detection at copper microelectrode. *Analytica Chimica Acta* 592(1), 30-35.
- Clegg, B.S. (1987). Gas chromatographic analysis of fluazifop-butyl (Fusilade) in potatoes, soybeans, and soil. *Journal of Agricultural and Food Chemistry* 35(2), 269-273.
- Conkin, R.A., In Zweig, G., Sherma, J. (EDS.), (1978). *Analytical Methods for Pesticides and Plant Growth Regulators*. New York, Academic Press.
- Corbera, M., Hidalgo, M., Salvad, V. & Wiecezorek, P.P. (2005). Determination of glyphosate and aminomethylphosphonic acid in natural water using the capillary electrophoresis combined with enrichment step. *Analytica Chimica Acta* 540(1), 3-7.
- Corti, P., Dreassi, E., Politi, N. & Aprea, C. (1991). Comparison of an HPTLC and an HPLC procedure for the determination of chlorpropham, propham and thiabendazole residues in potatoes. *Food Additives and Contaminants* 8(5), 607 - 615.
- Cowell, J.E., Kunstman, J.L., Nord, P.J., Steinmetz, J.R. & Wilson, G.R. (1986). Validation of an analytical residue method for analysis of glyphosphate and metabolite: an interlaboratory study. *Journal of Agricultural and Food Chemistry* 34(6), 955-960.
- Cserhati, T. & Forgacs, E. (1998). Phenoxyacetic acids: separation and quantitative determination. *Journal of Chromatography B: Biomedical Sciences and Applications* 717(1-2), 157-178.
- Cserhati, T., Forgacs, E., Deyl, Z., Miksik, I. & Eckhardt, A. (2004). Chromatographic determination of herbicide residues in various matrices. pp. 350-359. John Wiley & Sons, Ltd.
- Damato, A., Semeraro, I., Bicchi, C. (1993). Simultaneous determination of linuron and trifluralin residues in carrots and their pulp by liquid chromatography and gas chromatography. *Journal of AOAC International* 76(3), 657-662.
- Dean, J.R., Wade, G. & Barnabas, I.J. (1996). Determination of triazine herbicides in environmental samples. *Journal of Chromatography A* 733(1-2), 295-335.
- Ding, W.H., Liu, C.H. & Yeh, S.P. (2000). Analysis of chlorophenoxy acid herbicides in water by large-volume on-line derivatization and gas chromatography-mass spectrometry. *Journal of Chromatography A* 896(1-2), 111-116.
- Ely, C.B., Frans, R.E., Lavy, T.L., Talbert, R.E., Mattice, J.D. (1993). Determining diuron, simazine, and methiocarb residues in highbush blueberries (*Vaccinium corymbosum*). *HortScience* 28(1), 33-35.

- Engelbreton, J., Hall, G., Hengel, M. & Shibamoto, T. (2001). Analysis of pendimethalin residues in fruit, nuts, vegetables, grass, and mint by gas chromatography. *Journal of Agricultural and Food Chemistry* 49(5), 2198-2206.
- Farran, A. & Ruiz, S. (2004). Application of solid-phase extraction and micellar electrokinetic capillary chromatography to the study of hydrolytic and photolytic degradation of phenoxy acid and phenylurea herbicides. *Journal of Chromatography A* 1024(1-2), 267-274.
- Fuentes, E., Baez, M.E., Reyes, D. (2006). Microwave-assisted extraction through an aqueous medium and simultaneous cleanup by partition on hexane for determining pesticides in agricultural soils by gas chromatography: A critical study. *Analytica Chimica Acta* 578(2), 122-130.
- Garcia-valcarcel, A.I., Sanchez-brunete, C., Martinez, L. & Tadeo, J.L. (1996). Determination of dinitroaniline herbicides in environmental samples by gas chromatography. *Journal of Chromatography A* 719(1), 113-119.
- Gaynor, J.D., Hamill, A.S., Mactavish, D.C. (1993). Efficacy, fruit residues, and soil dissipation of the herbicide metolachlor in processing tomato. *J. Am. Soc. Hort. Sci.* 118, 68-72.
- Gaynor, J.D., Mactavish, D.C. & Hamill, A.S. (1992). A GC/MSD method for the analysis of metolachlor in cabbage, broccoli, and tomato. *Communications in Soil Science and Plant Analysis* 23(13), 1549 - 1558.
- Goodwin, L., Startin, J.R., Keely, B.J. & Goodall, D.M. (2003). Analysis of glyphosate and glufosinate by capillary electrophoresis-mass spectrometry utilising a sheathless microelectrospray interface. *Journal of Chromatography A* 1004(1-2), 107-119.
- Guan, F., Watanabe, K., Ishii, A., Seno, H., Takeshi, K., Hattori, H. & Suzuki, O. (1998). Headspace solid-phase microextraction and gas chromatographic determination of dinitroaniline herbicides in human blood, urine and environmental water. *Journal of Chromatography B: Biomedical Sciences and Applications* 714(2), 205-213.
- Guinivan, R.A., Thompson, N.P., Wheeler, W.B. (1982). Derivatization and Cleanup Improvements in Determination of Residues of Glyphosate and Aminomethylphosphonic Acid in Blueberries. *J. Assoc. Off. Anal. Chem.* 65, 35-39.
- Gyongyver, H., Ivan, B., Andras, S. (2000). Development of an enzyme-linked immunosorbent assay (ELISA) for the herbicide trifluralin. *Analytica Chimica Acta* 421(2), 121-133.
- Jose, F., Pilar, H., Martinez, C.M., Miguel, M. & Flores, P. (2007). Multiresidue method for analysis of pesticides in pepper and tomato by gas chromatography with nitrogen-phosphorus detection. *Food Chemistry* 105(2), 711-719.
- Hans-jurgen, S., Manfred, L. (1993). Capillary gas chromatography – atomic emission detection: A useful instrumental method in pesticide residue analysis of plant foodstuffs. *Journal of High Resolution Chromatography* 16(9), 539-548.
- Herranz, S., Ramon-azcon, J., Benito-pena, E., Marazuela, M., Marco, M. & Moreno-bondi, M. (2008). Preparation of antibodies and development of a sensitive immunoassay with fluorescence detection for triazine herbicides. *Analytical and Bioanalytical Chemistry* 391(5), 1801-1812.

- Hodgeson, J., Collins, J. & Bashe, W. (1994). Determination of acid herbicides in aqueous samples by liquid--solid disk extraction and capillary gas chromatography. *Journal of Chromatography A* 659(2), 395-401.
- Hogendoorn, E.A., Ossendrijver, F.M., Dijkman, E. & Baumann, R.A. (1999). Rapid determination of glyphosate in cereal samples by means of pre-column derivatisation with 9-fluorenylmethyl chloroformate and coupled-column liquid chromatography with fluorescence detection. *Journal of Chromatography A* 833(1), 67-73.
- Hsu, R.C., Biggs, I. & Saini, N.K. (1991). Solid-phase extraction cleanup of halogenated organic pesticides. *Journal of Agricultural and Food Chemistry* 39(9), 1658-1666.
- Hu, X., Dai, G., Huang, J., Ye, T., Fan, H., Youwen, T., Yu, Y. & Liang, Y. (2010). Molecularly imprinted polymer coated on stainless steel fiber for solid-phase microextraction of chloroacetanilide herbicides in soybean and corn. *Journal of Chromatography A* In Press, Accepted Manuscript.
- Huang, L.Z., Dai, H., Li, Y.J., Gao, X.L. (2004). Determination of Trifluralin Residues in Garlic by HPLC. *Chinese Food Science* 25(7), 151-153.
- Huo, J.L., LI, J., Ge, Y.Q., Chu, X.G. (2006). Determination of dinitroaniline multi-residues in soybean by gas chromatography-mass spectrometry. *Chinese Journal of Analytical Chemistry* 34, S63-S67.
- Janusz, P. (1997). *Solid Phase Microextraction Theory and Practice*. NewYork, NyWiley-VCH. Inc.
- Khrolenko, M.V. & Wieczorek, P.P. (2005). Determination of glyphosate and its metabolite aminomethylphosphonic acid in fruit juices using supported-liquid membrane preconcentration method with high-performance liquid chromatography and UV detection after derivatization with p-toluenesulphonyl chloride. *Journal of Chromatography A* 1093(1-2), 111-117.
- Kim, I.S., Sasinos, F.I., Stephens, R.D., Wang, J. & Brown, M.A. (1991). Determination of chlorinated phenoxy acid and ester herbicides in soil and water by liquid chromatography particle beam mass spectrometry and ultraviolet absorption spectrophotometry. *Analytical Chemistry* 63(8), 819-823.
- Konar, S.K. & Roy, D.N. (1990). Method for the determination of residues of the herbicide glyphosate and its principal metabolite, aminomethylphosphonic acid, in plant materials by nitrogen-selective gas chromatography. *Analytica Chimica Acta* 229, 277-280.
- Krynitsky, A.J., Swineford, D.M. (1995). Determination of sulfonylurea herbicides in grains by capillary electrophoresis. *Journal of AOAC International* 78(4), 1091-1096.
- Kuang, H., Chu, X.G., Hou, Y.X., Xu, C.L. (2006a). Simultaneous Determination of 13 Phenoxy Acid Herbicide Residues in Soybean by GC-ECD *Analytical Letters* 39, 2617-2627.
- Kuang, H., Hou, Y.X., Chu, X.G., Xu, C.L. (2006b). Simultaneous Determination of Phenoxyacid Herbicides in Soybean by Gas Chromatography-Mass Spectrometry. *Chinese Journal of Analytical Chemistry* 34(12), 1733-1736.
- Lawrence, J.F. & laver, G.W. (1974). Analysis of triazine herbicides by combined thin-layer chromatography and fluorimetry. *Journal of Chromatography A* 100(1), 175-179.

- Lee, H.B., Te, P., John, M. (1991). Chemical derivation analysis of pesticides residues. Part . an improved method for the determination and confirmation of acidic herbicides in water. *J. Assoc Off. Anal. Chem* 74(3), 835-842.
- Lewis, S.E., Brodie, J.E., Bainbridge, Z.T., Rohde, K.W., Davis, A.M., Masters, B.L., Maughan, M., Devlin, M.J., Mueller, J.F. & Schaffelke, B. (2009). Herbicides: a new threat to the great barrier reef. *Environmental Pollution* 157(8-9), 2470-2484.
- Li, J.Z., Chu, X., Cai, H.X., An, J., Yang, Q. (2006). Simultaneous determination of residues of 12 amide herbicides in soybeans by high performance liquid chromatography. *Chinese Jour nal of Chromatography* 24(6), 585-588.
- Li, J.Z., CuI, X., Cai, H.X., An, J., Yang, Q. (2006). Simultaneous determination of residues of 12 amide herbicides in soybeans by high performance liquid chromatography. *Chinese Jour nal of Chromatogr a phy* 24(6), 585-588.
- Lou, X., Miller, D.J. & Hawthorne, S.B. (1999). Static subcritical water extraction combined with anion exchange disk sorption for determining chlorinated acid herbicides in soil. *Analytical Chemistry* 72(3), 481-488.
- Lyubavina, I.A., Zinchenko, A.A., Salomatina, I.S., Zherdev, A.V. & Dzantiev, B.B. (2004). An immunochromatographic assay of 2, 4-dichlorophenoxyacetic acid and simazine using monoclonal antibodies labeled with colloidal gold. *Russian Journal of Bioorganic Chemistry* 30(2), 178-183.
- Marchese, S., Perret, D., Bafile, E., Gentili, A., Caretti, F. & Berardino, M. (2009). Pressurized liquid extraction coupled with LC-ESI-MS-MS for the determination of herbicides chlormequat and mepiquat in flours. *Chromatographia* 70(5), 761-767.
- Martinez Vidal, J.L., Frenich, A.G. & Lehotay, S.J. (2006). Quick, easy, cheap, effective, rugged, and safe approach for determining pesticide residues. In *Pesticide Protocols* (Ed J. M. Walker), pp. 239-261. Humana Press.
- Mattern, G.C., Singer, G.M., Louis, J, Robson, M., Rosen, J.D. (1989). Determination of linuron in potatoes using capillary column gas chromatography/mass spectrometry. *Journal of the Association of Official Analytical Chemists* 72(6), 970-974.
- Mhaka, B., Cukrowska, E., Tsesumbui, B., Ramstr, M.O., Haupt, K., Tutu, H. & Chimuka, L. (2009). Selective extraction of triazine herbicides from food samples based on a combination of a liquid membrane and molecularly imprinted polymers. *Journal of Chromatography A* 1216(40), 6796-6801.
- Miliadis Ge, S.P., Vasilikiotis, G.S. (1990). Simplified cleanup and liquid chromatographic ultraviolet determination of linuron and three metabolites in potatoes. *J Assoc Off Anal Chem.* 73(3), 435-437.
- Mondy, N.I., Sharada, D., Munshi, C.B. & Wurm, C.M. (1992). Effect of storage time, temperature, and cooking on isopropyl N-(3-chlorophenyl)carbamate levels in potatoes. *Journal of Agricultural and Food Chemistry* 40(2), 197-199.
- Montiel, A.Y., Sánchez, I. (1996). Study of the presences of Simazine residues in fruit and oil obtanined from olives collected from the ground. . *Bol. San. Veg. Plagas*, 22(3), 571-575.
- Mortimer, R.D., Black, D.B. & Dawson, B.A. (1994). Pesticide residue analysis in foods by NMR. 3. comparison of 19F NMR and GC-ECD for analyzing trifluralin residues in field-grown carrots. *Journal of Agricultural and Food Chemistry* 42(8), 1713-1716.

- Moye, H.A., Miles, C.J. & Scherer, S.J. (1983). A simplified high-performance liquid chromatographic residue procedure for the determination of glyphosate herbicide and (aminomethyl)phosphonic acid in fruits and vegetables employing postcolumn fluorogenic labeling. *Journal of Agricultural and Food Chemistry* 31(1), 69-72.
- Mughari, A.R., Vazquez, P.P. & Galera, M.M. (2007). Analysis of phenylurea and propanil herbicides by solid-phase microextraction and liquid chromatography combined with post-column photochemically induced fluorimetry derivatization and fluorescence detection. *Analytica Chimica Acta* 593(2), 157-163.
- Murakami, Y., Matsumoto, H., Kuwabara, K., Nishimune, T. & Tanaka, R. (1988). Survey of diphenyl ether herbicides in dietary foods by the total diet study in Osaka, Japan. *Bulletin of Environmental Contamination and Toxicology* 40(1), 69-73.
- Myint, K.T., Uehara, T., Aoshima, K. & Oda, Y. (2009). Polar Anionic Metabolome Analysis by Nano-LC/MS with a Metal Chelating Agent. *Analytical Chemistry* 81(18), 7766-7772.
- Nartova, Y., Ermolaeva, T., Fleisher, M., Abuknesha, R. & Eremin, S. (2008). Determination of Alachlor in food products by a fluorescence polarization immunoassay. *Journal of Analytical Chemistry* 63(5), 499-505.
- National foodsafety resource database. beijing www.fsr.org.cn
- Neitzel, P.L., Walther, W. & Nestler, W. (1998). In-situ methylation of strongly polar organic acids in natural waters supported by ion-pairing agents for headspace GC-MSD analysis. *Fresenius' Journal of Analytical Chemistry* 361(3), 318-323.
- Nemoto, S. & Lehotay, S.J. (1998). Analysis of multiple herbicides in soybeans using pressurized liquid extraction and capillary electrophoresis. *Journal of Agricultural and Food Chemistry* 46(6), 2190-2199.
- Nilsson, T., Baglio, D., Galdo-migue, Z., Madsen, J. & Facchetti, S. (1998). Derivatisation/solid-phase microextraction followed by gas chromatography-mass spectrometry for the analysis of phenoxy acid herbicides in aqueous samples. *Journal of Chromatography A* 826(2), 211-216.
- Ohms, R.E. (1976). Minutes Potato Pathology Section PAA Chicago, Ill. Feb. 18, 1976. *American Journal of Potato Research* 53(12), 463-470.
- Ortiz-gomez, M.T., Perez-arribas, L.V., Leon-gonzalez, M.E. & Polo-diez, L.M. (1995). Liquid Chromatography Determination of Simazine and Antimycin A in Must. *Journal of Agricultural and Food Chemistry* 43(11), 2883-2886.
- Pardue, J. (1995). Multiresidue method for the chromatographic determination of triazine herbicides and their metabolites in raw agricultural products. *J AOAC Int.* 78(3), 856-862.
- Patsias, J., Papadopoulou, A. & Papadopoulou-mourkidou, E. (2001). Automated trace level determination of glyphosate and aminomethyl phosphonic acid in water by on-line anion-exchange solid-phase extraction followed by cation-exchange liquid chromatography and post-column derivatization. *Journal of Chromatography A* 932(1-2), 83-90.
- Peruzzi, M., Bartolucci, G. & Cioni, F. (2000). Determination of phenoxyalkanoic acids and other herbicides at the ng/ml level in water by solid-phase extraction with poly(divinylbenzene-co-N-vinylpyrrolidone) sorbent and high-performance liquid

- chromatography-diode-array detection. *Journal of Chromatography A* 867(1-2), 169-175.
- Prez, S., Matienzo, M. & Tadeo, J. (1993). GC-ITD analysis of chlortoluron and its metabolites in cereals. *Chromatographia* 36(1), 195-200.
- Pringle, J.C., Anderson, L.W.J. & Raines, R.W. (1978). Residues in crops irrigated with water containing simazine. *Journal of Agricultural and Food Chemistry* 26(5), 1143-1147.
- Pylypiw, H.M., Bugbee, G.J. & Frink, C.R. (1993). Uptake of pre-emergent herbicides by corn: Distribution in plants and soil. *Bulletin of Environmental Contamination and Toxicology* 50(3), 474-478.
- Qi, Y., Li, S., Zhan, C.R., Peng, T. (2004). Simultaneous determination of sulfonylurea herbicides residues in soybeans by high performance liquid chromatography-mass spectrometry. *Chinese Journal of Analytical Chemistry* 32(11), 1436-1440.
- Richman, S.J., Karthikeyan, S., Bennett, D.A., Chung, A.C. & Lee, S.M. (1996). Low-level immunoassay screen for 2, 4-dichlorophenoxyacetic acid in apples, grapes, potatoes, and oranges: circumventing matrix effects. *Journal of Agricultural and Food Chemistry* 44(9), 2924-2929.
- Rimmer, D.A., Johnson, P.D. & Brown, R.H. (1996). Determination of phenoxy acid herbicides in vegetation, utilising high-resolution gel permeation chromatographic clean-up and methylation with trimethylsilyldiazomethane prior to gas chromatographic analysis with mass-selective detection. *Journal of Chromatography A* 755(2), 245-250.
- Rochette, E.A., Harsh, J.B. & Hillijr, H.H. (1993). Supercritical fluid extraction of 2, 4-D from soils using derivatization and ionic modifiers. *Talanta* 40(2), 147-155.
- Rompa, M.K.E., Zygmunt, B. (2005). Screening of alkanocarboxylic and phenolicherbicides in water samples by means of derivatization-based gas chromatography. *Polish Journal of Environmental Studies* 14(1), 81-86.
- Roseboom, H. & Herbold, H.A. (1980). Determination of triazine herbicides in various crops by capillary gas chromatography with thermionic detection. *Journal of Chromatography A* 202(3), 431-438.
- Ruiz De, E.N., Goicolea, M.A., Gomez de balugera, Z., Portela, M.J. & Barrio, R.J. (1997). Determination of herbicides by reductive amperometric detection in liquid chromatography. *Journal of Chromatography A* 763(1-2), 227-235.
- Sabino, A., Bufo, M.D.A., Laura, S., Roberto, T. (2004). Determination of herbicide residues by laser microprobe mass analysis (Lamma). *International Journal of Environmental Analytical Chemistry* 84(1), 39 - 45.
- Salmain, M., Fischer-durand, N. & Pradier, C.M. (2008). Infrared optical immunosensor: Application to the measurement of the herbicide atrazine. *Analytical Biochemistry* 373(1), 61-70.
- Sambe, H., Hoshina, K. & Haginaka, J. (2007). Molecularly imprinted polymers for triazine herbicides prepared by multi-step swelling and polymerization method: Their application to the determination of methylthiotriazine herbicides in river water. *Journal of Chromatography A* 1152(1-2), 130-137.

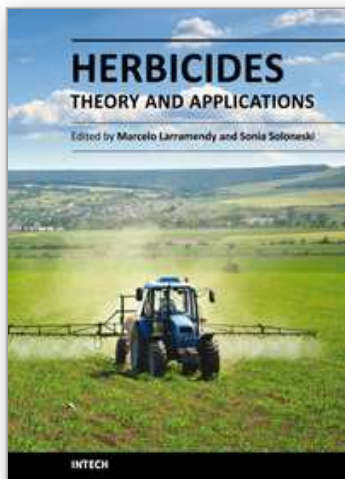
- Sanchez-brunete, C., Garcia-valcircel, A.I. & Tadeo, J.L. (1994). Determination of residues of phenoxy acid herbicides in soil and cereals by gas chromatography-ion trap detection. *Journal of Chromatography A* 675(1-2), 213-218.
- Sanchez-brunete, C. Martinez, L. & Tadeo, J. L. (1994). Determination of corn herbicides by GC-MS and GC-NPD in environmental samples. *Journal of Agricultural and Food Chemistry* 42(10), 2210-2214.
- Sanchez-brunete, C., Pirez, R.A., Miguel, E. & Tadeo, J.L. (1998). Multiresidue herbicide analysis in soil samples by means of extraction in small columns and gas chromatography with nitrogen-phosphorus and mass spectrometric detection. *Journal of Chromatography A* 823(1-2), 17-24.
- Sancho, J.V. F. J., López, F., Hernández, F., Hogendoorn, E.A. & Van zoonen, P. (1994). Rapid determination of glufosinate in environmental water samples using 9-fluorenylmethoxycarbonyl precolumn derivatization, large-volume injection and coupled-column liquid chromatography. *Journal of Chromatography A* 678(1), 59-67.
- Sauret-szczepanski, N., Mirabel, P. & Wortham, H. (2006). Development of an SPME-GC-MS/MS method for the determination of pesticides in rainwater: Laboratory and field experiments. *Environmental Pollution* 139(1), 133-142.
- Shackelford, D.D., Ma, R., West, S.D., Turner, L.G. (2000). Determination of ethalfluralin in canola seed, meal, and refined oil by capillary gas chromatography with mass selective detection. *J Agric Food Chem.* 48(9), 4422-4427.
- She, Y.X., Cao, W.Q., Shi, X.M., Lv, X.L., Liu, J.J., Wang, R.Y., Jin, F., Wang, J. & Xiao, H. (2010). Class-specific molecularly imprinted polymers for the selective extraction and determination of sulfonylurea herbicides in maize samples by high-performance liquid chromatography-tandem mass spectrometry. *Journal of Chromatography B* 878(23), 2047-2053.
- Shen, W.J., Xu, J., Yang, W.Q., Shen, C.Y. (2007). Determination of acetanilide herbicide residues in tea by gas chromatograph- Mass Spectrometry with two different ionization techniques *Chinese Journal of Chromatography* 25(5), 753-757.
- Shen, W.J., Xu, J.Z., Zhao, Z.Y., Ding, T., Jiang, Y., Chu, X.G., Shen, C.Y. (2008). Determination of 11 kinds of ether herbicide residues in vegetables by gas chromatography-negative chemical ionization mass spectrometry. *Chinese Journal of Analytical Chemistry* 36(5), 663-667.
- Siltanen, H.R.C. (1978). Analysis of 2, 4-D and 2, 4, 5-T in lingonberries, wild mushrooms, birch and aspen foliage. *Bull Environ Contam Toxicol.* 19(2), 177-182.
- Singh, S.B., Yaduraju, N.T., Kulshrestha, G. (1997). Residues of metolachlor herbicide in soil and potato tubers under Indian tropical conditions. *Bulletin of Environmental Contamination and Toxicology* 59(2), 216-221.
- Slates, R.V. (1983). Determination of chlorsulfuron residues in grain, straw, and green plants of cereals by high-performance liquid chromatography. *Journal of Agricultural and Food Chemistry* 31(1), 113-117.
- Smith, E. (1984). Gas chromatographic method for analysis of 2, 4-D in wheat: interlaboratory study. *J Assoc Off Anal Chem* 67(4), 794-798.

- Sojo, L.E., Gamble, D.S. & Gutzman, D.W. (1997). Sorption and Bound Residue Formation of Linuron, Methylparathion, and Metolachlor by Carrot Tissues: Kinetics by On-Line HPLC Microextraction. *Journal of Agricultural and Food Chemistry* 45(9), 3634-3641.
- Striley, C.A.F., Biagini, R.E., Mastin, J.P., Mackenzie, B.A. & Robertson, S.K. (1999). Development and validation of an ELISA for metolachlor mercapturate in urine. *Analytica Chimica Acta* 399(1-2), 109-114.
- Su, K. (1975). Electron capture gas-liquid chromatographic method for the simultaneous analysis of 2, 4-D, dicamba, and mecoprop residues in soil, wheat, and barley. *J Assoc Off Anal Chem.* 58(5), 1027-1031.
- Szendr, S.A.A., Trummer, N.A., Danyi, N., Varadi, M. & Szendro, I. (2003). Development of a non-labeled immunosensor for the herbicide trifluralin via optical waveguide lightmode spectroscopic detection. *Analytica Chimica Acta* 487(1), 31-42.
- Tadeo, J.L., Sanchez-brunete, C., Perez, R.A., Fernandez, M.D. (2000). Analysis of herbicide residues in cereals, fruits and vegetables *Journal of Chromatography A* 882, 175-191.
- Takats, Z., Vargha, M., Vekey, K. (2001). Investigation of atrazine metabolism in river sediment by high performance liquid chromatography/mass spectrometry. *Rapid Communications in Mass Spectrometry* 15, 1735-1742.
- Tanabe, A., Mitobe, H., Kawata, K. & Sakai, M. (1996). Monitoring of herbicides in river water by gas chromatography-mass spectrometry and solid-phase extraction. *Journal of Chromatography A* 754(1-2), 159-168.
- Tessier, D.M. & Marshall Clark, J. (1998). An enzyme immunoassay for mutagenic metabolites of the herbicide alachlor. *Analytica Chimica Acta* 376(1), 103-112.
- Ting, K.C., Kho, P.K. (1998). *Determination of trace 2, 4-dichlorophenoxyacetic acid in fresh produce by gas chromatography with boron trichloride/2-chloroethanol derivatization.* Gaithersburg, MD, ETATS-UNIS: AOAC International.
- Tomkins, B.A. & Ilgner, R.H. (2002). Determination of atrazine and four organophosphorus pesticides in ground water using solid phase microextraction (SPME) followed by gas chromatography with selected-ion monitoring. *Journal of Chromatography A* 972(2), 183-194.
- Tong, L., Ma, X.D. & Li, C.J. (2006). Application of gas chromatography-tandem mass spectrometry (GC-MS-MS) with pulsed splitless injection for the determination of multiclass pesticides in vegetables. *Analytical Letters* 39(5), 985 - 996.
- Topuz, S., Ozhan, G. & Alpertunga, B. (2005). Simultaneous determination of various pesticides in fruit juices by HPLC-DAD. *Food Control* 16(1), 87-92.
- Thornton, J.S. & Stanley, C.W. (1977). Gas chromatographic determination of Sencor and metabolites in crops and soil. *Journal of Agricultural and Food Chemistry* 25(2), 380-386.
- Tseng, S.H., LO, Y.W., Chang, P.C., Chou, S.S. & Chang, H.M. (2004). Simultaneous Quantification of Glyphosate, Glufosinate, and Their Major Metabolites in Rice and Soybean Sprouts by Gas Chromatography with Pulsed Flame Photometric Detector. *Journal of Agricultural and Food Chemistry* 52(13), 4057-4063.
- Tsui, M. T. K. Wang, W. -X. & Chu, L. M. (2005). Influence of glyphosate and its formulation (Roundup? on the toxicity and bioavailability of metals to *Ceriodaphnia dubia*. *Environmental Pollution* 138(1), 59-68.

- Tsumura-hasegawa, Y., Tonogai, Y., Nakamura, Y. & Ito, Y. (1992). Residue levels of dichlorvos, chlorpropham, and pyrethrins in postharvest-treated potatoes during storage or processing into starch. *Journal of Agricultural and Food Chemistry* 40(7), 1240-1244.
- Vadrine, C., Leclerc, J.C., Durrieu, C. & Tran-minh, C. (2003). Optical whole-cell biosensor using *Chlorella vulgaris* designed for monitoring herbicides. *Biosensors and Bioelectronics* 18(4), 457-463.
- Vasilescu, M.N., Medvedovici, A.V., Paul, W., Alan, T. & Colin, P. (2005). Herbicides. In *Encyclopedia of Analytical Science* pp. 243-260. Oxford: Elsevier.
- Vitali, P., Venturini, E., Bonora, C., Calori, R. & Raffaelli, R. (1994). Determination of triazines and dinitroanilines in waters by high-performance liquid chromatography after solid-phase extraction. *Journal of Chromatography A* 660(1-2), 219-222.
- Volante, M., Cattaneo, M., Bianchi, M. & Zoccola, G. (1998). Some applications of solid phase micro extraction (SPME) in the analysis of pesticide residues in food. *Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes* 33(3), 279 - 292.
- Wei, F., Li, D.Z., Yu, L. (2005). Simultaneous determination of phenoxy acid herbicides in rice. *Chinese Journal of Instrumental Analysis* 24, 304-308.
- Wen, X., Fei, J., Chen, X., Yi, L., Ge, F. & Huang, M. (2008). Electrochemical analysis of trifluralin using a nanostructuring electrode with multi-walled carbon nanotubes. *Environmental Pollution* 156(3), 1015-1020.
- West, S.D., Weston, J.H., Day, E.W.Jr. (1988). Gas chromatographic determination of residue levels of the herbicides trifluralin, benefin, ethalfluralin, and isopropalin in soil with confirmation by mass selective detection. *J Assoc Off Anal Chem.* 71(6), 1082-1085.
- Wigfield, Y.Y. & Lanouette, M. (1991). A modified clean-up for the determination of glyphosate and its metabolite residues in lentils using high pressure liquid chromatography and post-column fluorogenic labelling. pp. 491-498. John Wiley & Sons, Ltd.
- Wigfield, Y.Y. & Lanouette, M. (1993). Supercritical fluid extraction of the fortified residues of fluazifop-P-butyl (Fusilade II) and its major metabolite, fluazifop-P, in onions. *Journal of Agricultural and Food Chemistry* 41(1), 84-88.
- Wigfield, L.M. (1991). Residue analysis of glyphosate and its principal metabolite in certain cereals, oilseeds, and pulses by liquid chromatography and postcolumn fluorescence detection. *J Assoc Off Anal Chem.* 74(5), 842-847.
- Williams, K.J., James, C.R., Thorpe, S.A. & Reynolds, S.L. (1997). Two analytical methods for the measurement of 2, 4-d in oranges: an ELISA screening procedure and a GC-MS confirmatory procedure. pp. 135-140. John Wiley & Sons, Ltd.
- Wilson, A.M., Bushway, A.A. & Bushway, R.J. (1981). Residue analysis of isopropyl N-(3-chlorophenyl)carbamate in fruits and vegetables using high-performance liquid chromatography. *Journal of Agricultural and Food Chemistry* 29(4), 746-749.
- Wittmann, C. & Hock, B. (1993). Analysis of atrazine residues in food by an enzyme immunoassay. *Journal of Agricultural and Food Chemistry* 41(9), 1421-1425.

- Wong, J.W., Webster, M.G., Halverson, C.A., Hengel, M.J., Ngim, K.K. & Ebeler, S.E. (2003). Multiresidue pesticide analysis in wines by solid-phase extraction and capillary gas chromatography-mass spectrometric detection with selective ion monitoring. *Journal of Agricultural and Food Chemistry* 51(5), 1148-1161.
- Wortberg, M., Kreissig, S.B., Jones, G., Rocke, D.M. & Hammock, B.D. (1995). An immunoarray for the simultaneous determination of multiple triazine herbicides. *Analytica Chimica Acta* 304(3), 339-352.
- Xing, Q., Xi, R., Zhou, Z. (2002). *Basic organic chemistry*. Beijing: Higher Education Press.
- Yaduraju, N.T.K.G., Sharma, R.P., Ahuja, K.N. (1993). Isoproturon for weed control in potato (*Solanum tuberosum*) and its residue in soil and tubers. *Indian Journal of Agricultural Sciences* 63(11), 731-773.
- Zhao, B., Zhang, J., Gong, J., Zhang, H. & Zhang, C. (2009). Glyphosate mobility in soils by phosphate application: Laboratory column experiments. *Geoderma* 149(3-4), 290-297.
- Zhou, M., Bramble, Q.F., Devine, J.T. & Norwood, I.G. (1996). *Determination of bensulfuron methyl in rice and crayfish by liquid chromatography with a column- and eluant-switching system and UV detection*. Gaithersburg, MD, ETATS-UNIS: AOAC International.
- Zhou, M., Li, G.Y. & Whalen, A.S. (1994). *Determination of metsulfuron methyl and its two metabolites in crops by liquid chromatography with ultraviolet detection*. Gaithersburg, MD, ETATS-UNIS: AOAC International.

IntechOpen



Herbicides, Theory and Applications

Edited by Prof. Marcelo Larramendy

ISBN 978-953-307-975-2

Hard cover, 610 pages

Publisher InTech

Published online 08, January, 2011

Published in print edition January, 2011

The content selected in Herbicides, Theory and Applications is intended to provide researchers, producers and consumers of herbicides an overview of the latest scientific achievements. Although we are dealing with many diverse and different topics, we have tried to compile this "raw material" into three major sections in search of clarity and order - Weed Control and Crop Management, Analytical Techniques of Herbicide Detection and Herbicide Toxicity and Further Applications. The editors hope that this book will continue to meet the expectations and needs of all interested in the methodology of use of herbicides, weed control as well as problems related to its use, abuse and misuse.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Hua Kuang, Libing Wang and Chuanlai Xu (2011). Overview of Analytical Techniques for Herbicides in Foods, Herbicides, Theory and Applications, Prof. Marcelo Larramendy (Ed.), ISBN: 978-953-307-975-2, InTech, Available from: <http://www.intechopen.com/books/herbicides-theory-and-applications/overview-of-analytical-techniques-for-herbicides-in-foods>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen