

Chromatographic determination of herbicide residues in various matrices

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ABSTRACT: The newest results in the use of various extraction techniques and chromatographic methods such as gas–liquid and high-performance liquid chromatography used for the assessment of herbicide residues in various matrices have been compiled and critically evaluated. Practical employments in water and soil research, environmental protection, clinical and food chemistry are presented. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: herbicide residues; extraction methods; water; food; soil; gas–liquid and high performance liquid chromatography

INTRODUCTION

The increasing world population demands a continually growing supply of food and food products. Because of the relative lack of new areas suitable for agriculture, the performance of the existing agricultural areas has to be substantially enhanced. Pesticides such as insecticides, molluscicides, nematicides, rodenticides, avicides, piscicides, herbicides, plant growth regulators, defoliants, fungicides, algicides, etc. have been extensively used in agrochemical practice (Tomlin, 1994). Herbicides are chemicals with the capacity to kill selectively or non-selectively plants, representing more than the half of all pesticides employed. They show a wide range of beneficial effects, improving plant health, maintaining agro-ecosystems, food supply, economical advantages, etc. Although the employment of herbicides has been questioned many times, it has been proven that the rational application of herbicides results in a steady and sufficient flow of food products of high quality, and that herbicides improve and do not deteriorate food quality, therefore the public concerns about herbicide residues in foods are untenable. Herbicides protect crops from undue competition from weeds and enhance the nutritional quality of foods. Furthermore, the total quantity of herbicides used is small and they are generally used pre-emergence or post-emergence, leaving time for the decomposition of the majority of

herbicides, and the quality of end products is indistinguishable from that produced by excluding the use of synthetic herbicides.

However, the intensive application of herbicides has resulted in the contamination of the atmosphere, ground and waste waters, agricultural products (wheat, corn, fruits, vegetables, etc.) and, consequently, in the direct or indirect pollution of food and food products and biological systems (Johnen, 1999). As herbicide molecules are more or less toxic, they represent not only an environmental risk but also a health hazard (Manahan, 2000).

Because of their excellent separation capacity and versatility, various chromatographic and electrochromatographic techniques have found growing acceptance and application for the separation and quantitative determination of herbicide residues in different, frequently complicated organic and anorganic matrices such as food, biological fluids and soil (Cserhádi and Forgács, 2001).

The main chemical classes of herbicides include bipiridilium compounds (diquat, paraquat, etc.), 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.

Because of the wide variety of molecular structures of herbicides, the development of a considerable number of chromatographic separation methods was necessitated for their successful analysis.

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Abbreviations used: CFLME, continuous-flow liquid membrane extraction; ODS, octadecylsilica; SPME, solid-phase microextraction.

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Many herbicides are semi-volatile, therefore they can be analysed by capillary gas-chromatography (cGC). Non-volatile herbicides can be derivatized with various derivatization agents before cGC analysis. As the volatility of herbicides may differ considerably, multiresidue analyses generally use thermal programming for the separation of the components of a herbicide mixture.

Thermolabile or non-volatile herbicides can be determined only by liquid chromatographic methods such as thin-layer chromatography (TLC) and high-performance liquid chromatography (HPLC). Because of the higher sensitivity of HPLC, this technique has mainly been applied in the measurement of herbicide residues; however, the use of automated multiple development TLC for the analysis of phenylurea herbicides in plants has been reported (Lautie and Stakovic, 1996). As the retention capacity of herbicides may also be markedly different, a gradient elution technique has to be employed for their multiresidue analysis. The special application of hydro-methanolic and micellar HPLC for the successful separation of metoxuron, chloridazon, propazine, simazine and atrazine has also been reported recently (Halko and Hutta, 2002). Other analytical methods such as enzyme immunoassay and various electrophoretic techniques such as capillary electrophoresis (CE), micellar electrokinetic chromatography (MEKC) (Carabias-Martinez *et al.*, 1997) and isotachopheresis have also been used for the determination of herbicides residues. The determination of triazines and their decomposition products in environmental waters by MEKC has also been reported (Turiel *et al.*, 2000). CE methods applied for the analysis of herbicides and plant growth regulators in water, food and soil has been previously reviewed (Eash and Bushway, 2000) and its application for the separation of triazines has been also reported (Lin *et al.*, 2001).

The objectives of this review are the concise enumeration of the chromatographic separation methods used for the determination of herbicide residues in various organic and anorganic matrices, and the compilation and critical evaluation of the most meaningful results.

CHROMATOGRAPHIC DETERMINATION OF HERBICIDE RESIDUES

Sample preparation

As herbicide pollutants are generally present in very low concentrations, they have to be separated from the majority of the components of the accompanying matrix and enriched before analysis. The selection of the most effective extraction and preconcentration procedure is of paramount importance for the reliable measurement of herbicides. Liquid-liquid extraction (LLE)

has frequently been used for the enrichment of selected sample constituents. The efficacy of the method is generally high but requires highly purified and expensive solvents. However, some solvents may endanger the health of laboratory staff and increase environmental pollution when discarded.

A considerable number of alternative extraction techniques has been developed and applied in the measurement of herbicide residues. Solid-phase extraction (SPE) uses a solid sorbent filled in a short column or embedded in a disc. The liquid sample or the liquid extract of the solid sample is passed through. Herbicide residues are retained on the solid adsorbent and selectively eluted with an appropriate solvent or solvent system. The selection of the most effective adsorbent and solvent markedly depends both on the physicochemical character of the herbicide and the components of the accompanying matrix (Pico *et al.*, 2000). The successful use of combined sorbents (Ferrer *et al.*, 1999), polymeric materials (Loos and Niessner, 1999; Rodriguez *et al.*, 2000) has been previously reported. SPE can also be applied for the preconcentration of herbicides from biological fluids such as urine (Mendas *et al.*, 2001; Pozzebon *et al.*, 2003a,b).

Similarly to SPE solid-phase microextraction (SPME) also concentrates the solutes to be separated on a solid adsorbent. However, SPME uses a short solid rod of adsorbent which is immersed directly into the liquid phase or remains in the head-space of the vial containing the sample. After a predetermined adsorption time the adsorbent is withdrawn and inserted into the injector of cGC. Bonded analytes are desorbed by heating the injector and separated on the capillary column. The application of SPME in the pesticide residue analysis has been reviewed many times (Beltran *et al.*, 2000; Krutz *et al.*, 2003). A modification of SPME so-called stir-bar sorptive extraction (Baltussen *et al.*, 1999) has also been used in environmental protection studies (Sandra *et al.*, 2001; Vercauteren *et al.*, 2001).

Supercritical fluid extraction (SFE) uses CO₂ mobile phases in a supercritical state where the viscosity and diffusibility can be regulated both by temperature and pressure. The efficacy of extraction can be further increased by adding organic modifiers to the mobile phase (Tadeo *et al.*, 1996; Pensabene *et al.*, 2000).

Some other extraction methods such as continuous-flow liquid membrane extraction (CFLME) (Liu *et al.*, 2002; Chao *et al.*, 2002), class-selective immunoelectroextraction (Shahtaheri *et al.*, 1998; Dalluge *et al.*, 1999) using various immunosorbents (Rollag *et al.*, 1999; Delaunay *et al.*, 2000; Bou Carrasco *et al.*, 2001), pressurized liquid extraction (David *et al.*, 2000; Ezzelle, 2000), its modification using water and organic modifier instead of pure organic solvent (Curren and King, 2001), microwave-assisted extraction (Xiong *et al.*, 1998) and simultaneous steam distillation extraction (Wittke *et al.*,

2001) have also been found application. However, their use is not widespread and their advantages and disadvantages cannot be exactly assessed.

The good application parameters and efficacy of each individual extraction method have been adequately documented. Unfortunately, the overwhelming majority of studies in this field use one new method and compare it only with the traditional LLE. The exact comparison of the performance of the various new extraction techniques taking into consideration simultaneously rapidity, time and solvent consumption, repeatability and reproducibility, and extraction efficacy is a considerable challenge for the analytical chemists working in this area.

Herbicide residues in atmosphere and soil

Because of the relatively low volatility of the majority of herbicides their spontaneous evaporation does not contribute to their presence in the atmosphere. They enter the atmosphere mainly by drift during spraying operations and/or by wind erosion of soil (Watanabe, 1998). A new GC-mass spectrometric method (GC-MS) has been developed for the screening of insecticide and herbicides (alachlor and atrazine) residues in the atmosphere. Pesticides were preconcentrated by passing through 4.8 L of air on a stainless steel tube (4 i.d. \times 89 mm) containing 125 mg of adsorbents at a flow-rate of 80 mL/min. In order to find the optimal adsorbent, the adsorption efficacy of seven different sorbents has been compared. Pesticides were desorbed by an automatic thermal desorption unit and analysed by cGC-MS. Separation was carried out on a dimethylpolysiloxane DB-1 column (30 m \times 0.249 mm i.d.; film thickness 0.25 μ m) using helium as carrier gas. The temperature programme was initiated at 60°C (held for 1 min) then increased to 200°C at 15°C/min, and further increased to 260°C at 5°C/min (final hold 5 min). It was established that the sorbent Tenax TA demonstrated the best adsorption characteristics. It was further stated that the method is rapid, accurate and sensitive and can be successfully used for the monitoring the rapid concentration changes of atrazine in the atmosphere (Clement *et al.*, 2000).

Because of the possible strong binding of herbicides to the polar or apolar components of soil and sediment, the use of an appropriate extraction and preconcentration method is the prerequisite of a reliable chromatographic analysis. A SPE preconcentration technique followed by cGC-MS was developed for the simultaneous determination of various organic pollutants in soil and sediment. Analysis included polycyclic aromatic hydrocarbons, polychlorinated biphenyls and N-, P- and Cl-containing pesticides (atrazine, propazine, simazine and terbuthylazine herbicides). Pollutants were extracted from the solid matrix with dichloromethane and

after cleaning passed through one or more SPE cartridges. After desorption the samples were analysed by cGC-MS. Separation was performed on a Rtx-5MS capillary column (30 m \times 0.25 mm; film thickness, 0.24 μ m). The temperature programme was started at 50°C (1.5 min hold), and was increased to 180°C at 30°C/min then to 275°C at 30°C/min (final hold 15 min). The results indicated that pollutants cannot be effectively preconcentrated using one type of SPE sorbent. The best result was achieved using the combination of phenyl bonded silica + octadecyl bonded silica + alumina (Dabrowska *et al.*, 2003). Subcritical water extraction has been employed for the preconcentration and prepurification of pesticides (among them the herbicides alachlor, atrazine and simazine) from soil. Extraction was performed at 300°C for 25 and 60 min then the aqueous phase was extracted with dichloromethane and the concentrated organic phase was analysed by cGC/MS. Separation was carried out on a HP-5MS column (30 m \times 0.25 mm i.d.; film thickness, 5 μ m). Oven temperature started at 70°C (2 min hold) increased to 150°C at 25°C/min, to 200°C at 3°C/min and then to 280°C at 8°C/min (final hold 3 min). The recovery of the method for herbicides was between 78.6 and 95.0% and the detection limit varied from 14.3 to 16.0 μ g/kg. It was found that the recovery obtained by the method is similar to the control LLE procedure (Richter *et al.*, 2003).

Herbicide residues determined in water by capillary gas chromatography

Gas chromatography mainly with MS detection has been extensively employed for the measurement of herbicide residues in water (Gonzalez and Alpendurada, 2002; Hauser *et al.*, 2002; Shen and Lee, 2003). Because of its advantageous application parameters, MS detection has been extensively used in the cGC analysis of herbicide residues (Tomkins and Ilgner, 2002). Thus, a cGC-MS method was developed for the detection of triazine herbicides (atrazine, cyanazine, simazine) and their decomposition products (deethylatrazine, deisopropylatrazine) in environmental waters. Water samples were passed through an octadecylsilica SPE cartridge at a flow rate of 10–15 mL/min. After drying the cartridge, analytes were eluted twice with 2 mL of ethyl acetate, concentrated in nitrogen flux and injected to the cGC system. Separation was performed on a DB-5 column (30 m \times 0.25 mm; film thickness, 0.25 μ m). The oven temperature programme started at 90°C (0.5 min hold), and was increased to 160°C at 15°C/min then to 280°C at 25°C/min (final hold 5 min). The relative standard deviation and the detection limit of the technique were 3.2% and 1.7 ppt, respectively. Because of its reproducibility, reliability and sensitivity, the method has been proposed for the analysis of this

type of herbicides in environmental waters (Ma *et al.*, 2003).

SPME combined with cGC-MS was developed and employed for the determination of 10 herbicides (alachlor, atrazine, chlorotoluron, diclofop, diflufenicam, ethofumesata, isoproturon, linuron, terbutryn and trfluralin) in surface and ground water. Microextraction was performed with a polyacrylate fibre, the extraction time was 75 min at 25°C and the sample was continually stirred. After preconcentration analytes were desorbed for 5 min at 270°C. Herbicides were separated on a DB-5 capillary column (5% polydiphenyl- and 95% polydimethylsiloxane; 30 m × 0.25 mm, film thickness 0.25 µm). The oven temperature programme was initiated at 50°C (5 min hold), increased to 180°C at 40°C/min then to 190°C at 5°C/min, and finally to 270°C at 20°C/min (final hold 12 min). It was found that thermally unstable phenylurea herbicides decompose and the resulting anilines can be used for their identification. The recovery of herbicides varied between 94 ± 16 and 107 ± 12 and the detection limit was below 1 µg/L. It was stated that the method is sensitive, reproducible, easy to carry out, does not require expensive instrumentation and can be applied for the quantitative determination of these herbicides in water (Carabias-Martinez *et al.*, 2003a,b).

Immunoaffinity-based solid-phase extraction on-line coupled to cGC has also found application in the measurement of *s*-triazine herbicides in water and orange juice. Monoclonal antibodies were immobilized on beaded cellulose and a cartridge of 10 × 3 mm i.d. was filled with the immunoaffinity sorbent and used for the preconcentration of the herbicides (atrazine, dipropetryn, cyanazine, prometryne, sebuthylazine, simetryn, terbuthylazine and terbutyn). Herbicide desorbed from the immunoaffinity sorbent were adsorbed on a styrene-divinyl benzene copolymer, removed by ethyl acetate and then injected into the HP-5MS capillary column (25 m × 0.25 mm, film thickness, 0.25 µm). Analytes were detected by a flame ionization (FID) and by a nitrogen-phosphorous (NP) detector. It was demonstrated that the immunoaffinity sorbent is highly specific for these types of herbicides. The authors suggested that, because of the high recovery and sensitivity, the method can be used for the screening of herbicides residues and water and orange juice (Dalluge *et al.*, 1999). Stir-bar sorptive extraction technique combined with cGC was applied for the determination of 35 priority semivolatiles in water. Herbicides such as ametryn, atrazine, prometryn, propazine, simazine, terbutryn, terbuthylazine and trietazine were also included in the experiments. The optimal conditions for the extraction were the use of 100 mL of water sample with 20% NaCl addition, an extraction time of 14 h, a stir bar of 20 mm length and 0.5 mm film thickness of polydimethylsiloxane at 900 rpm. After desorption

analytes were separated and quantitatively determined by cGC using a HP-5MS column (30 m × 0.25 mm; film thickness 5 µm). The column temperature programme was started at 70°C (2 min hold), increased to 200°C at 30°C/min (1 min hold), and then to 280°C at 3°C/min (final hold 2 min). Because of the good repeatability, recovery and simplicity, the authors propose the method for the routine quality control of these pollutant classes in water (Leon *et al.*, 2003). Ion trap MS and cGC has been also applied for the measurement of atrazine, cyanazine, simazine and the decomposition products of atrazine (deethylatrazine and deisopropylatrazine). Water samples were spiked with atrazine-*d*₅ standard at the concentration of 24 ng then flowed through a C₁₈ SPE cartridge. After drying, the cartridge analytes were removed with 2 × 2 mL of ethyl acetate. The combined organic extracts were concentrated and investigated by cGC (DB-5 column of 30 m × 0.25 mm; film thickness 0.25 µm). The temperature programme was initiated at 90°C (0.5 min hold), increased to 160°C at 15°C/min (3.7 min hold) and then to 280°C at 25°C/min (final hold 5 min). The isotope dilution method was used for the quantitation of atrazine. Recoveries were acceptable for triazine herbicides (from 83 to 94%) but relatively low for the decomposition products. The relative standard deviation varied between 3.2 and 16.1% and the detection limit was 0.75–12 ng/L using a sample of 1 L volume. It has been stated that the high sensitivity, accuracy and precision of the method makes it suitable for the measurement of triazine herbicide residues in waters at a low nanogram level (Cai *et al.*, 2004). Another cGC-MS procedure was developed for the screening of 22 pesticides in drinking water. Experiments included the herbicides alachlor, atrazine, cyanazine, dichlobenyl, metazachlor, metolachlor, propazine, simazine, terbuthylazine and terbutryn. Water samples of 500 mL with 5% methanol added were flowed through a cartridge containing 200 mg of styrene divinylbenzene at a flow rate of 5 mL/min. The cartridge was preconditioned with 3 mL of ethylacetate, 3 mL of methanol and 6 mL of water. After extraction the sorbent was dried and eluted with ethyl acetate. The concentrated extract was injected into the DB-5 capillary column (30 m × 0.25 mm i.d.; film thickness, 0.25 µm). The carrier gas was helium. The temperature programme started at 85°C, increased to 150°C at 10°C/min then to 160°C at 1°C/min, and finally to 250°C at 5°C/min (final hold 5 min). The lower detection limit was between 5 and 35 ng/L; the linearity range started at 10–150 ng/L and finished at 500 ng/L; the repeatability (5.1–8.8%), reproducibility (5.5–20.5% and recovery (73–131%) values were high (Quintana *et al.*, 2001). Subsequent detection by FID and MS has been used for the analysis of environmental pollutants (chlorophenols, polynuclear aromatic hydrocarbons, atrazine and simazine) in water. A polypyrrole-based

polymer was synthesized and used as an SPE sorbent. After extraction analytes were removed with methanol, concentrated and measured by cGC. The temperature programme for the HP-5MS column was 140°C (7 min hold), increasing to 260°C at 20°C/min (final hold 5 min). The extraction recoveries for herbicides varied between 72 and 104% depending on both the type of herbicide and the volume of the sample. This new SPE sorbent has been proposed for enrichment of environmental pollutants prior to chromatographic analysis (Bagheri and Mohammadi, 2003).

Herbicide residues determined in water by high-performance liquid chromatography

Various HPLC techniques have also been frequently used for the residue analysis of herbicides (Aspenger *et al.*, 2002). Thus, SPE combined with HPLC and photochemical reaction has also been used for the measurement of herbicides in water (Lee *et al.*, 1999). HPLC followed by diode array (DAD) and atmospheric pressure chemical ionization detection was employed for the measurement of rice herbicides (Santos *et al.*, 2000) and HPLC-DAD was used for the control of herbicide residues in surface and ground waters (Carabias-Martinez *et al.*, 2000a,b). HPLC-DAD has also been applied for the screening of 17 herbicides in river water. Herbicides were preconcentrated on a HLB polymeric cartridge then desorbed with 10 mL of ethyl acetate. Separation was performed on an octadecylsilica (ODS) column (250 × 4.0 mm i.d.; particle size, 5 µm). Gradient elution started with 5% acetonitrile (ACN)–0.005 M phosphate buffer (pH = 7.2) and the ACN ratio was increased to 90% in 60 min. The column was thermostated at 25°C. Spectra were measured between 190 and 400 nm. Detection limit for herbicides varied from 4 to 80 ng/L. The method has been successfully used for the measurement of these herbicides in water (Carabias-Martinez *et al.*, 2003a,b).

On-line continuous flow liquid membrane extraction followed by reversed-phase HPLC (RP-HPLC) was employed for the trace analysis of sulphonylurea herbicides (metsulphuron methyl, bensulphuron methyl, tribenuron methyl, sulphometuron methyl and ethan-metsulphuron) in water. After extraction the preconcentrated samples were injected on an ODS column (16 × 4 mm i.d.; particle size, 5 µm). Isocratic separation was performed with methanol–67 mmol/L KH₂PO₄–Na₂HPO₄ (pH = 5.9) buffer (55:45, v/v) at a flow-rate of 0.4 mL/min. Analysis time was 40 min, solutes were detected at 240 nm. The extraction efficacy was between 85 ± 4 and 108 ± 7%, the lowest detection limit was 10–50 ng/L when enriching 120 mL of sample. The simple and efficacy technique was proposed for the determination of phenylurea herbicides in water (Liu *et al.*, 2003). The advantages of class-selective immunoadsorption

has also been exploited in the HPLC analysis of triazine herbicides. The performance of three immunosorbents has been compared for the preconcentration efficacy using nine herbicides and eight decomposition products as model compounds. The preconcentrated solutes were separated by RP-HPLC on an ODS column (250 × 4.6 mm i.d.; particle size, 5 µm). Gradient elution began with ACN–0.005 M phosphate buffer (pH = 7) (5:95, v/v) for 2 min then to 25% ACN from 2 to 6 min, 25–30% from 6 to 20 min, and 40% at 50 min. It has been established that the performance of anti-dichloroatrazine, anti-atrazine and anti-ametryn immunosorbents showed considerable differences with anti-ametryn showing the highest binding capacity. It has been supposed that the rational design of immunosorbents may facilitate the selective or class-selective preconcentration of herbicides (Delaunay-Bertoncini *et al.*, 2003). SPE followed by RP-HPLC was used for the determination of three herbicides (atrazine, chlorotoluron and terbutryne) and their seven decomposition products in surface and ground water. The adsorption performance of ODS and polymeric sorbents has been compared. An aliquot of 250 mL of the sample was flowed through the cartridges conditioned with 5 mL of ethyl acetate and 5 mL of water. Solute were desorbed with 5 mL of methanol and 5 mL of ethyl acetate and separated on an ODS column (250 × 4 mm i.d.; particle size, 5 µm). Gradient elution was carried out with mixture of ACN and 0.005 M phosphate buffer (pH = 7.2) using linear gradient of ACN from 2 to 90% in 60 min. The column was thermostated at 25°C, the flow rate was 1 mL/min. DAD was employed in the range 190–400 nm. The results demonstrated that the highest recovery can be obtained by using styrene–divinylbenzene copolymer sorbent. The detection limit was 1 or 2 µg/L. The method has been applied for the determination of these solutes in surface and ground waters (Carabias-Martinez *et al.*, 2002). Molecularly imprinted polymers (MIP) have also been used for the preconcentration of triazines (Ferrer *et al.*, 2000; Koeber *et al.*, 2001). A new MIP has been developed with terbutylazine as template molecule and was employed for the class-selective extraction of triazines from water. After the extraction step solutes were desorbed from MIP with methanol, concentrated and injected on an ODS column (20 × 2.1 mm i.d.; particle size, 5 µm). Elution was performed with ACN–0.005 M phosphate buffer (pH = 7) at a flow-rate of 1 mL/min. Analytes were detected by DAD (triazines at 220 nm and phenylureas at 244 nm). It was established that phenylureas were not retained by MIP while the extraction efficacy was high for triazines. The method was successfully applied for the measurement of triazine derivatives in industrial effluent and surface water (Chapuis *et al.*, 2003). SPME followed by HPLC has also been

employed for the analysis of nine phenylurea herbicides in water.

The extraction efficacy of four fibers has been determined and compared (Carbowax templated resin, polydimethylsiloxane, polyacrylate and polydimethylsiloxane-divinylbenzene). Samples were stirred during the extraction period (40 min at 25°C). After extraction solutes were desorbed from the fibre with the mobile phase both in static and dynamical modes. Separation was performed on an ODS column (15 cm × 3.9 mm i.d.; particle size, 4 µm). The mobile phase was ACN–water (40:60, v/v). Solute were detected at 243 nm. The experiments indicated that carbowax templated resin and polydimethylsiloxane–divinylbenzene copolymer are equally suitable for the extraction of the herbicide residues from water. The precision of the method varied from 1.0 to 5.9% and the detection limits were between 0.5 and 5.1 ng/mL (Lin *et al.*, 2003).

Herbicide residues determined in water by other chromatographic techniques

Besides cGC and HPLC, other chromatographic techniques also found application in the analysis of herbicides in water. Thus, a TLC method for the rapid screening of triazines in water developed. The six triazines under investigation were extracted from 1 L of water on an ODS cartridge, desorbed with methanol. The herbicides were derivatized with dansyl chloride and the methanolic extract was concentrated and spotted to the silica, ODS and Diol TLC plates. After development the plates were evaluated by a TLS scanner. It was established that the lower detection limit was about 100 ng/L, therefore this sensitive, rapid and inexpensive method can be used for the measurement of triazines in water (Hamada and Wintersteiger, 2002). Electrochromatographic methods such as CE and MEKC have also been employed for herbicide residue analysis in water. Thus, CE has been applied for the trace analysis of multiresidue pesticides in water and carrot extracts. Pesticides (ametryn, atrazine, diuron, linuron, propazine, simazine, etc.) were preconcentrated on ODS cartridge, desorbed with methanol, dried and redissolved in 1 mL of appropriate solution. Separation was performed on a fused-silica capillary (58.3 × 75 µm i.d.; effective length 50.0 cm) at 25°C. Samples were injected hydrodynamically, the voltage was –25 kV and solutes were detected at 220 nm. Electrolyte contained 0.020 M/L phosphate buffer (pH = 2.5), 0.025 M/L SDS and 10% methanol. The lower detection limit (2.5 µg/L) indicated that the method can be used for the screening of herbicides in drinking water (Silva *et al.*, 2003). The use of MEKC for the analysis of 11 triazines in groundwater has also been reported (Frias *et al.*, 2004). Because of the various separation capacities of the individual chromatographic

techniques, the advantages of combined methods have also been exploited in the analysis of herbicide residues in water. Thus, atrazines and their decomposition products were extracted from water with a styrene–divinylbenzene SPE cartridge, and the eluate was analysed by cGC/MS (atrazine and terbutylazine), CE and MKC (decomposition products). It was demonstrated that the combined method is suitable for the measurements of atrazines and decomposition products in water at the low µg/L range (Loos and Niessner, 1999). The advantages of a combined cGC/MS–HPLC/MS procedure were exploited in the analysis of priority pesticides (among them alachlor, atrazine, simazine and terbutylazine) and other organic pollutants in river water. After SPE the samples were analysed by cGC/MS and HPLC/MS. It was stated that the detection limit for herbicides was 0.01–0.5 µg/L (Azevedo *et al.*, 2000).

Herbicide residues in food and food products

Because of their paramount importance in human and animal nutrition, much effort has been devoted to the development and application of adequate analytical techniques for the study of the effect of herbicides on the quality of agricultural products and for the separation and quantitative determination of herbicides in crops. Herbicides present in soil and water can pollute crops and pasture and hence can enter the food chain. Fruit and vegetables can be directly polluted by herbicides or they can be polluted by taking up the herbicides from contaminated soil or surface and groundwaters. It has to be borne in mind that theoretically each food or food product can be contaminated by herbicides, therefore sensitive and selective methods have to be developed for the measurement of herbicide residues in any food and food product. Without these control techniques accurate risk assessment is impossible. The use of various chromatographic techniques for the determination of herbicide residues in crops and food (Tekel and Kovacicova, 1993) and in cereals, fruit and vegetables has been previously reviewed (Tadeo *et al.*, 2000).

Herbicide residues determined in food and food products by capillary gas chromatography

A combined method using SFE followed by cGC has been developed for the determination of 10 herbicides in eggs. Extraction, liquid–liquid partition and enrichment on a silica column has been employed as control method. SFE working conditions were: oven, 50°C; micrometering valve, 120°C; extraction pressure, 10,000 psi (680 atm); flow rate of expanded gas, 3.0 L/min; total flow, 120 L. Separation of herbicides was achieved on a DB-17 column (30 m × 0.25 mm i.d.; film thickness,

0.25 μm). Oven temperature was 35°C (2 min hold) increased to 100°C at 25°C/min then to 250°C at 5°C/min (final hold 6 min). The mean recovery values and the relative standard deviations for the individual herbicides were: ametryn (81.6 7.8); atrazine (90.4 3.3); cyanazine (79.1 3.4); prometon (75.5 3.0); prometryne (89.2 3.5); propazine (78.0 6.5); secbumeton (75.1 4.0); simazine (73.4 7.2); simetryn (85.7 6.4); and terbuthylazine (87.9 5.6). The method was superior to the traditional extraction method, used a smaller quantity of organic solvent and was rapid. It was proposed for the measurement of the residues of triazine herbicides in eggs (Pensabene *et al.*, 2000).

Atrazine and other pesticides were determined in baby foods too. Both SFE and accelerated solvent extraction were used for the preconcentration of pesticides, the analyses were performed with cGC/MS and the ELISA test. It was found that the efficacy of SFE is lower than that of the accelerated solvent extraction (Chuang *et al.*, 2001). A multiresidue method was developed for the determination of 90 pesticides (partially herbicides) in apples, green beans, oranges, cereals, spinach and carrot. Pesticides were extracted by SPE using polystyrene–divinylbenzene sorbent and were separated and quantitatively determined by cGC/MS. In the majority of cases the recovery was higher than 80% and the limit of quantitation 0.01 mg/kg (Stajnbaher and Zupancic-Kralj, 2003). A similar method was developed for the analysis of seven phenylurea herbicides in wet plant materials. After SPE extraction the herbicides were separated by cGC/MS. The detection limit was between 0.5 and 5.0 ng/mL and the precision (RSD) about 7.0% (Pena *et al.*, 2002).

Triazine herbicides were also measured in breast milk. The five triazines were adsorbed on a graphitized carbon black SPE cartridge, desorbed and analysed by cGC/MS. Detection and quantification limits were 0.3 and 1 ppb from 1 mL of breast milk (Balduini *et al.*, 2003).

Chlorophenoxy acid herbicides (mecoprop, MCPA, 2,4-DP, 2,4-D, 2,4,5-T and 2,4-DB) have been determined in wheat and flour. The samples were extracted with acetone–water mixture. Subsequent alkaline hydrolysis made possible the simultaneous isolation of both free and conjugated residues. Free acids have been methylated and they were separated and quantitated by GC/ECD (electron capture detection) and GC/MS (mass spectrometry). The method showed good recovery (over 80%) and reproducibility (lower than 10%). Derivatization with trichloroethanol has also been employed for the measurement of phenoxy acid herbicides (2,4-D, 2,4,5-T, MCPA, β -naphthoxyacetic acid, dichlorprop, fenoprop, mecoprop, 2,4-DB and MCPB) in crops. Separation and quantitation were performed by cGC using ECD and MS detection. Recoveries varied between 70 and 90% and the

determination limits were 0.02–0.1 mg/kg depending on the number of chlorine atoms in the molecule (Anastassiades and Scherbaum, 1996).

The herbicides trifluralin and terbuthylazine and another 12 pesticides have been analysed in 10 white and 11 red wines using SPME followed by cGC/MS. It has been stated that limit of detection was 0.10–6.0 $\mu\text{g/L}$, the relative standard deviation being between 9.7 and 18%. Because of the short sampling time, solvent-free extraction, rapidity, simplicity and low cost, the SPME method can be employed for the determination of different pesticide residues in wines (Vitali *et al.*, 1998).

An accelerated solvent extraction method coupled with cGC has been developed for the determination of four herbicides (atrazin, linuron, tri-allate, trifluralin), and some other pesticides in wheat grain, and the results have been compared with those obtained by the traditional shake extraction. Extraction conditions were: temperature, 100°C; pressure, 10 MPa (1500 psi); heat-up time, 5 min; static time, 5 min; flush volume 60%; purge time 100 s; total extraction time per sample 14–18 min; and total acetonitrile used, 15–45 mL. The recovery values were very high (atrazin, 92.8%; linuron, 83.6%; triallate, 87.8%; trifluralin, 99.6%) and comparable with the recoveries of shaken extraction. Because of the short extraction time and low solvent consumption, ASE has been proposed for routine applications in pesticide residue analysis laboratories (Ezzelle, 2000).

Herbicide residues determined in food and food products by high-performance liquid chromatography

The residues of glyphosate and its main metabolite AMPA (aminome–thylphosphonic acid) have been measured in the seed of canola (*Brassica rapa* L.). Samples were milled, extracted with aqueous HCl solution and cleaned up on an anion exchange resin. The purified extract was analysed by HPLC using fluorescence detection following post-column o-phthalaldehyde derivatization (Cessna *et al.*, 2000).

The high separation power and detection sensitivity of capillary HPLC has been exploited in the measurement of some chlorophenoxy acid herbicides (2,4-D, MCPA, 2,4-DP, 2,4-DB, MCPB and fenoprop) and dicamba residues in green bean samples. Herbicides have been separated on a capillary C_{18} column (150 \times 0.3 mm i.d., particle size, 3 μm) using both isocratic and gradient elution. Samples of green bean have been hydrolysed and purified on an ion exchange column. Recoveries varied between 41 and 119%, the relative standard deviation (RSD) being 5–33% (Lucas-Delfa *et al.*, 2000).

Five selected sulphonylurea, diphenylether and sulphonamide herbicides were determined in maize.

Herbicides were extracted with methanol, the methanolic solution further purified with SPE (carbon black and ODS sorbents) and analysed with HPLC/MS. Because of the good validation parameters (recovery 81–92%; precision 7–13%; sensitivity 0.354–4 ng/g) the method was proposed for the determination of this class of herbicide residues in other food products too (Lagana *et al.*, 2000).

Membrane separation coupled to HLPC has been developed and applied for the determination of pesticide residues in egg. After the extraction step pesticides were separated on an ODS column using isocratic elution. The mobile phase consisted of ACN–water in 0.01 M acetic acid–acetate buffer. The flow-rate was 1 mL/min, and solutes were detected at 220 nm. The recoveries were 60–98%, and the detection limit of atrazine was 0.002 mg/kg (Carabias-Martinez *et al.*, 2000a,b).

FUTURE TRENDS

Preconcentration and prepurification of herbicide residues are decisive steps in the determination of this class of pollutants. The efficacy of the extraction determines the reliability of the subsequent chromatographic separation and quantitation. The development of sorbents with higher adsorption capacity and enhanced selectivity is needed to increase the overall performance of the whole analytical system. Until now the majority of extraction steps have been time-consuming and not on-line coupled to the chromatographic instrument. The output of laboratories can be considerably enhanced by the development and application of more rapid on-line extraction procedures.

HPLC and cGC equally require more selective and/or more general detectors besides MS. The widespread use of new detector types such as atomic emission detector and the simultaneous application of two or more detectors with different selectivity may considerably enhance the performance of the separation system without increasing the theoretical plate number.

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