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Review

Chromatographic methods in the determination of herbicide residues in crops, food and environmental samples

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ABSTRACT

The state of the art of chromatographic methods used in the determination of herbicide residues in crops, food and environmental samples is reviewed. The main structural groups of herbicides, *i.e.*, triazines, phenyl- and sulphonylureas, carbamates, uracils and phenoxyalkanoic and arylphenoxypropanoic acids, and important degradation products (dealkylated triazines, substituted anilines, chlorophenols) are considered. Advantages and drawbacks of gas (GC), liquid (LC) and thin-layer chromatography in this type of analysis are discussed. The characteristics of a modern chromatographic method for the determination of herbicide residues are summarized and trends in the development and combination of current GC and LC methods discussed.

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1. INTRODUCTION

Modern agricultural production depends considerably on the use of pesticides, especially in the major agricultural countries of North America and Europe. In most of them, herbicides represent more than 50% of all pesticides used; in the USA and Germany the proportion of herbicides is *ca.* 60%. In the USA alone over 10^8 ha are currently being treated with herbicides, which is more than half of the total cropland [1]. It is therefore not surprising that herbicides contribute significantly to the con-

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tamination of the environment, particularly of soil and surface and ground waters.

In drinking and environmental waters, atrazine belongs to the most frequent contaminants [2–4]. Owing to the phytotoxic nature of herbicides and their low mammalian toxicity, their residues in crops generally do not present serious risks, but contamination of some food commodities by carry-over through contaminated water and feed has been observed. In feeding experiments, transfer of herbicide residues to milk has been reported for compounds of the uracil group [5,6], triazines [7] and, to some extent, phenoxyalkanoic acids [8]. Low levels of triazines, primarily atrazine, have been found in dairy milk [9,10] and butter [10] and even in sugar [11]. There are indications that atrazine may occur in the human organism [12]. Even though in general the risk of humans ingesting toxic doses of herbicide residues in food seems low, it is important to monitor their levels in the environment and in food commodities because of their extensive use and documented occurrence both in the environment and in foods.

2. ANALYTICAL METHODS FOR HERBICIDE RESIDUES

The general characteristics of analytical methods for residues of herbicides and their degradation products are the same as those for other pesticide residues. The analysis involves sampling and sample handling, for which the recommended approaches are described in refs. 13 and 14, extraction and clean-up procedures [15–17], the determination and evaluation and interpretation of the results. The individual steps of the analytical procedure are designed according to the chemical structure of the analyte compounds and according to the character of the matrix.

The detection and determination limits required for routine analytical methods for herbicide residues should not be higher than 10–50% of the corresponding maximum residue limit (MRL) as recommended by Frehse [18]. This puts the highest requirements on methods for the determination of residue in drinking water where the maximum permissible levels are sometimes as low as 0.1 $\mu g\ l^{-1}$.

The present trends in the development of residue analysis are towards multi-residue methods with adequate recovery characteristics (over 80% as a rule, but not less than 70%), good reproducibility and low determination limits. These are methods that permit the simultaneous determination of herbicides of different structural types, *e.g.*, triazines and ureas, or the simultaneous determination of parent herbicidal compounds and their degradation products, such as triazines and dealkylated and/or hydroxytriazines, phenylureas and substituted anilines, phenoxyalkanoic acids and chlorophenols.

Chromatographic methods, in particular capillary gas chromatography (cGC) and high-performance liquid chromatography (HPLC), are the methods of choice for this purpose. Thin-layer chromatography (TLC), which was popular in late 1960s and the 1970s has been almost completely superceded by the more precise, faster and more convenient instrumental chromatographic techniques, but in special cases it can be of valuable help.

In this paper we review the development of analytical methods for herbicide residues over the last 5–7 years. The herbicidal compounds considered are listed in Table 1 and their classification according to the chemical structure is given in Table 2. The analytical methods for the individual structural groups are reviewed in the sections 2.1–2.7 and are summarized in Table 3.

2.1. Triazines

Triazines belong to the oldest and most commonly used herbicides. Data from the world pesticide market show that the greatest volume (*ca.* 30%) of all herbicides applied in agriculture can be attributed to *s*-triazines [116]. Consequently, and also because of their relative stability in the environment, they also belong to the herbicides most frequently found in environmental samples. This is reflected in the vast number of published methods for the determination of triazine residues. More recently, the use of triazines, especially atrazine, is being limited and they are gradually being replaced with less environmentally hazardous herbicides.

Symmetrical 1,3,5-triazines are well chromatographed by GC and give good responses with nitrogen–phosphorus detection (NPD), owing to the nitrogen atoms in their molecules. Therefore, GC–NPD, usually on DB-1, OV-1 or polyethylene glycol-based stationary phases, is the method mostly

TABLE 1

ALPHABETIC LIST OF THE HERBICIDAL COMPOUNDS REVIEWED AND REFERENCES RELATING TO THEIR RESIDUE ANALYSIS

Common name	Class (see Table 2)	Refs.
Ametryn	Ia	9, 26, 27, 39
Atrazine	Ia	7, 9, 10, 19, 26, 27, 30, 31, 39, 41, 74, 96
Bensulphuron-methyl	VI	83
Bentazone	X	63, 73, 74, 96, 112
Bromacil	VIII	5, 57, 60, 61, 74, 96
Buturon	II	34, 38
Chlorbromuron	II	31, 32, 34, 41, 42, 47, 49, 74
Chloridazone	IX	19, 31, 56, 59, 61, 74, 96
Chlorimuron-ethyl	VI	84
Chloroxuron	II	30, 31, 34, 37, 38, 47, 49, 74, 96
Chorpropham	III	30, 32, 61, 74, 96
Chlorsulphuron	VI	49, 82, 86, 88, 89, 90
Chlortoluron	II	30–32, 34, 36, 38, 39, 47, 49, 74
Cyanazine	Ia	7, 9, 10, 27, 30, 39, 41, 74
Desmedipham	III	31, 55
Desmetryn	Ia	7, 9, 26
Dichlorprop	IV	62–64, 66, 73, 74
Diphenoxuron	II	34, 74
Diquat	VII	91–95
Diuron	II	30, 32, 34, 36, 38, 47, 48, 74
Fenoprop (2,4,5-TP)	IV	62, 64–66, 69, 74, 96
Fenuron	II	30, 34, 36, 38, 39, 47
Fluazifop-butyl	V	61, 76–80
Fluometuron	II	34, 36, 47, 74
Haloxyfop-ethoxyethyl	V	63, 76, 77
Isoproturon	II	30, 31, 34, 36, 37, 38, 41, 47, 74
Lenacil	VIII	19, 31, 58, 61
Linuron	II	30–32, 34, 36, 38, 39, 41, 42, 47, 49, 74, 96
MCPA	IV	62–66, 68, 69, 72–74
MCPB	IV	62, 63, 65, 73, 74, 96
Mecoprop (MCPP)	IV	62–64, 66, 68, 69, 72–74, 96
Metabenzthiazuron	II	30, 31, 38, 39, 54
Metamitron	Ib	29, 30, 56, 61
Metobromuron	II	30, 34, 36, 38, 42, 47
Metoprotryn	Ia	9, 26, 39
Metoxuron	II	30, 31, 34, 36, 37, 38, 39, 41, 46, 47, 74, 96
Metribuzine	Ib	26, 28, 30, 31, 41, 61, 74, 96
Metsulphuron-methyl	VI	90
Monolinuron	II	30–32, 38, 39, 41, 42, 47, 49, 74, 96
Monuron	II	34, 36, 38, 47, 74, 96
Neburon	II	34, 38, 39, 47, 48, 74
Paraquat	VII	91–95
Phenmedipham	III	31, 32, 53–56
Prometryn	Ia	7, 9, 10, 26, 27, 30, 31, 39, 41
Propazine	Ia	9, 26, 27, 30, 39, 74
Propham	III	96
Quazalofop-ethyl	V	76, 77
Siduron	II	47
Simazine	Ia	7, 9, 10, 26, 27, 30, 31, 39, 41, 74
Sulphometuron-methyl	VI	85

(Continued on p. 294)

TABLE 1 *(continued)*

Common name	Class (see Table 2)	Refs.
Terbacil	VIII	6
Terbutryn	Ia	7, 9, 10, 26, 27, 30, 31, 41
Terbuthylazine	Ia	7, 9, 30, 31, 74
Thiazafluron	II	31, 54
2,4-D	IV	62–66, 68, 69, 72–74, 96
2,4,5-T	IV	62–66, 68, 69, 74, 96
2,4-DB	IV	62, 64–66, 73, 74, 96
2,4,5-TB	IV	74
2,4-DP	IV	65, 66, 68, 69, 72

used for determining their residues. Recently published methods involve almost exclusively capillary GC columns. Víden *et al.* [9] determined residues of triazines in forage and milk, the identity of the residues being confirmed by GC–mass spectrometry (MS). Tekel' and co-workers used GC–NPD on OV-1 for the determination of triazine residues in butter [10] and sugar [19]. There are several methods permitting the simultaneous determination of the parent compounds and their degradation products, *e.g.*, those described by Bardalaye and co-workers for the determination of prometryn in parsley [20] and ametryn in tropical root crops [21], or the method [22] for the determination of terbutryn and its metabolites in sorghum grain. In the last study, the identity of the residues was confirmed by MS.

LC offers another possibility for the determination of residues of triazines. Ultraviolet (UV) detection is very suitable as *s*-triazines exhibit strong absorbance at 220–240 nm. The chlorotriazine herbicides atrazine, cyanazine and simazine and their dealkylated degradation products have been determined in soil by LC with diode-array detection (DAD) and by GC–NPD [23]. GC–MS and thermospray LC–MS were employed as confirmatory characterization techniques. With LC–DAD, the detection limit was much higher than with GC–NPD (0.3–0.5 mg kg^{-1} *vs.* 5–10 $\mu g\ kg^{-1}$), but the other advantages of LC–DAD, such as the possibility of choosing different wavelengths to avoid matrix interferences, and partial degradation of some chlorotriazines under GC conditions, were pointed out. A lower detection limit in the LC–UV determination of eight triazines in soil, *i.e.*, 1 $\mu g\ kg^{-1}$, was reported by Battista *et al.* [24]. They used a special extraction–isolation procedure on two minicolumns connected in series. A one order of magnitude lower sensitivity for LC–UV determination compared with GC–NPD was also reported by Hajšlová *et al.* [7] in a comparative study of chromatographic methods for the determination of *s*-triazines in milk. Moreover, an additional clean-up step had to be included prior to the LC–UV determination. The detection limit with GC–MS was comparable to that achieved with GC–NPD.

In the determination of residues of triazines in water, the detection limit of the method seems to depend more on the isolation and enrichment procedure chosen than on the method adopted for the

TABLE 2

STRUCTURAL GROUPS OF HERBICIDAL COMPOUNDS

Class	Structural group
Ia	1,3,5-Triazines
Ib	1,2,4-Triazines
II	Phenylureas
III	Carbamates
IV	Phenoxyalkanoic acids
V	Aryloxyphenoxypropanoic acids
VI	Sulphonylureas
VII	Bipyridylium cations
VIII	Uracils
IX	Pyridazines
X	Others

TABLE 3

MULTI-RESIDUE METHODS FOR THE DETERMINATION OF DIFFERENT HERBICIDE GROUPS IN ENVIRONMENTAL AND FOOD MATERIALS

Herbicide group	Method	Commodity	Ref.	Notes (Derivatization)
1,3,5-Triazines	GC–NPD (SE-30)	Milk	9	
1,3,5-Triazines	GC–NPD (OV-1)	Butter	10	
1,3,5- and 1,2,4-triazines Dealkylated atrazine Phenylureas Carbamates	LC–DAD (RP C_{18})	Water (ground, drinking, surface)	30	
1,3,5-Triazines Phenylureas Uracils Pyridazone Carbamates Phenoxyalkanoic acids	Environmental (RP C_{18})	LC–DAD water	74	
Phenylureas Substituted anilines	GC–ECD, GC–NPD (CP Sil 5) LC–ECD (RP C_{18})	Environmental samples	33, 34	Hydrolysis on silica gel HFBA
1,3,5- and 1,2,4-triazines Dealkylated products of atrazine	GC–NPD (DB-17)	Water	26	
Phenylureas Substituted anilines	GC–NPD (SE-54)	Water	42	
Phenylureas	GC–NPD (DB-5)	Water	36	Methyl iodide
Phenylureas	LC–photodegradation (RP C_{18})	Crops	47	After UV photodegradation, OPA (postcolumn)
1,3,5- and 1,2,4-triazines Phenylureas Carbamates Uracils Pyridazone Bentazone	TLC on silica gel	Crops Foods Water Soil	31	Only for inhibitors of Hill reaction
Phenoxyalkanoic acids Chlorophenols	GC–ECD (SE-54)	Cereal grain	68	PFBB
Aryloxyphenoxypropanoic acids (esters, free acids)	GC–ECD (HP-5)	Crops	77	PFBB
Phenoxyalkanoic acids	GC–NPD (DE-1 or DB-5)	Water Soil	72	CEMDSDEA
1,2,4-Triazines Carbamates Uracils Pyridazone Aryloxyphenoxypropanoic acids (esters)	GC–MS	Crops	61	

final determination. When classical liquid–liquid extraction with methylene chloride was used followed by clean-up on a Floriril column and GC–NPD determination, a detection limit of 25 ng l^{-1} was obtained for eleven triazines [25]. Grandet *et al.* [26] reported a detection limit of < 100 ng l^{-1} for the GC–NPD determination of triazines and their metabolites in drinking water after liquid–liquid extraction. On the other hand, a detection limit of < 10 ng l^{-1} was achieved in the determination of seven triazine herbicides in drinking water and ground water when solid-phase extraction (SPE) was employed [27].

The non-symmetrical 1,3,4-triazines can be also determined by GC–NPD. Jarczyk determined metribuzine in water, soil, cereals and vegetables [28] and metamitron in soil, water, sugar and fodder beet, strawberries and peas [29]. Metribuzine and metamitron, along with several *s*-triazines, were determined in water by LC–DAD [30].

2.2. Phenylureas

The use of this herbicide group is growing, partially because they are gradually replacing the more persistent triazine herbicides. The lower stability of phenylurea herbicides contributes to their faster degradation in crops and the environment but it also makes their analysis more complicated.

For the determination of both phenylurea herbicides and their degradation products, substituted anilines, GC or HPLC methods are almost exclusively used. TLC with selective biochemical detection [31] has a limited applicability to the parent compounds only.

The GC determination of phenylurea herbicides has to cope with the problem of thermal instability of these compounds. This is usually overcome either by derivatizing them to more stable products or by hydrolysing them to their corresponding anilines, which are subsequently measured. The latter approach was used by Dornseiffen and Verwaal [32], who determined the anilines obtained by alkaline hydrolysis of the parent herbicides. The anilines were determined after bromination to 2,4,6-tribromo derivatives by GC with electron-capture detection (ECD). The method is not suitable for the determination of metoxuron and difenoxuron but it covers some carbamate herbicides. De Kok and co-workers [33,34] developed a technique of catalytic hydrolysis on silica gel. The anilines obtained were again determined by cGC–ECD following derivatization with heptafluorobutyric anhydride (HFBA). The anilines originally present in the sample were determined in parallel. The advantage of this approach is the possibility of determining degradation products (anilines) in addition to parent herbicides. However, most methods involve derivatization of the phenylureas and the use of GC–NPD. Ogierman [35] used derivatization with trimethylanilinium hydroxide (TMAH), Oehmichen *et al.* [36] alkylation with methyl iodide and Pérez *et al.* [37] alkylation with ethyl iodide. Stan and Klaffenbach [38] determined phenylurea herbicides by GC–ECD after derivatization with HFBA. To avoid derivatization of both the phenylureas and the substituted anilines prior to the final GC determination, attempts have been made to find conditions for direct GC analysis. This was first done by Deleu and Copin [39] for the parent compounds only and later by Böer *et al.* [40] for the substituted anilines in water. Tekel' and co-workers [41,42] established conditions for the simultaneous determination of seven phenylureas and four anilines in water by GC–NPD without derivatization.

All urea herbicides can be determined by HPLC. Without derivatization and after thorough clean-up of the extracts, determination limits in the range 0.015–0.02 mg kg^{-1} could be achieved for plant materials using UV detection [43–45]. Three linuron metabolites, including 3,4-dichloroaniline, could be determined simultaneously with the parent compounds [45]. The sensitivity of the analysis can be improved by derivatizing the analytes and using a selective detector. Fluorescence detection was used by Lantos *et al.* [46] for the determination of metoxuron in potatoes, soil and water. The compound was first hydrolysed and the product converted into a fluorescent derivative with dansyl chloride. Luchtefeld [47] inserted a module for photodegradation of the separated phenylureas between the LC column and the fluorescence detector. The photodegradation products were then derivatized with *o*-phthalaldehyde (OPA). Limits of detection for the six phenylureas investigated ranged between 0.001 and 0.006 mg kg^{-1} for eight different crops and the limits of determination between 0.003 and 0.022 mg kg^{-1}. Zahnow [48] used photocon-

ductivity detection (PCD) in the LC determination of linuron, diuron and three diuron metabolites in crops with a detection limit of 0.01 mg kg^{-1}. An improved sensitivity of LC–UV measurement was reported for the micro-HPLC technique used in the determination of linuron and monolinuron in milk [49]. Liu *et al.* [50] determined the residues of six phenylureas in fruits and vegetables by LC with thermospray MS single-ion monitoring.

2.3. Carbamates, uracils, pyridazines

In earlier reviews [51,52], information was summarized on analytical methods for carbamate pesticides in general, which, apart from herbicides, include insecticides, acaricides and fungicides. Only a small proportion of analytical work on carbamate residues concerns the carbamate herbicides. The most important carbamate herbicides are phenmedipham, desmedipham, propham and chlorpropham. Bromacil, lenacil and terbacil are uracil-type herbicides and chloridazone belongs to the pyridazine group. Their residues are determined mostly by GC.

Dornseiffen and Verwaal [32] included propham, chlorpropham and phenmedipham in a multi-residue method for herbicides that generate anilines on alkaline hydrolysis. The corresponding anilines are determined by GC–ECD after bromination. The method has been tested for the determination of herbicide residues in various crops, with a detection limit of *ca.* 0.01 mg kg^{-1}. Alkaline hydrolysis to *m*-toluidine has been also used in a method [53] for the determination of phenmedipham in spinach, but in this instance the *m*-toluidine was determined directly without derivatization by GC with flame ionization detection (FID). A determination limit of 0.03 mg kg^{-1} was reported. Stan and Klaffenbach [54] used GC–MS for the determination of thermolabile carbamates (phenmedipham) and ureas (metabenzthiazuron, thiazafluron) after derivatization with acetic anhydride. Residues of desmedipham and phenmedipham in drinking water were determined by LC–UV after enrichment by SPE [55]. LC–DAD was applied to residues of phenmedipham and chloridazone in soil [56].

GC–NPD was described for the determination of bromacil residues in strawberries [57], lenacil in sugar beet roots and tops [58] and in sugar [19] and chloridazone residues in sugar beet [59] and sugar [19]. Residues of bromacil [5] and terbacil [6] in milk were determined by GC–ECD. Goewie and Hogendoorn [60] determined residues of bromacil and other herbicides in well water by LC–UV. Tuinstra *et al.* [61] worked out a multi-residue–multi-matrix method for the determination of nitrogen-containing herbicides. The method, which is based on GC–MS determination, has been evaluated for bromacil, lenacil, chlorpropham, chloridazone, fluazifop-ethyl, metamitron and metribuzine.

2.4. Phenoxyalkanoic acids

Phenoxyalkanoic acids are the oldest group of synthetic herbicides, introduced in agriculture as early as the 1940s. They still retain an important position, especially in the control of weeds in cereal crops.

Because of their highly polar nature and low volatility, phenoxyalkanoic acids cannot be directly determined by GC at residue levels and they have to be derivatized to esters, usually methyl or pentafluorobenzyl (PFB) esters. Chlorophenols, which are important degradation products of phenoxyalkanoic acids, are derivatized to the corresponding methyl and PFB ethers. Methylation is conveniently done with methanol and sulphuric acid [62,63]. Diazomethane is an efficient methylating agent [63,64] but less convenient for toxicity reasons. The residues in the form of methyl esters are determined by GC–ECD [63] or GC–MS [62], which is less demanding with respect to the clean-up and has a lower determination limit. Derivatization with pentafluorobenzyl bromide (PFBB) has been reported [65–68]. This method results in a higher sensitivity of GC–ECD analysis, but a comparative evaluation showed that the results obtained with the methylation method were in general more reliable. The PFB method may be advantageous if lower detection limits are required and if a narrower GC–ECD quantification range can be tolerated [66]. Other derivatization agents have been used for phenoxyalkanoic acids, such as trifluoroethanol [69], acetyl chloride [70] and iodoethane [63]. Derivatization with 2-cyanoethyldimethyldiethylaminosilane (CEDMSDEA) has been reported for use with GC–NPD [71] and was applied to the determination of acidic herbicides in water and soil [72]. The advantage of this method is an almost instantaneous

formation of the CEDMSDEA derivative and its detectability by NPD, which is much more selective than ECD.

Phenoxyalkanoic acids in water were also determined by HPLC with simultaneous UV, fluorescence and electrochemical detection [73]. The herbicides could be detected at levels between 20 and 90 ng l^{-1} without the necessity for derivatization. Di Corcia and Marchetti [74] determined phenoxyalkanoic acids and other herbicides (triazines, ureas, carbamates, uracils) in environmental waters by LC–UV. Novel clean-up techniques for a polymeric precolumn for the subsequent determination of eight phenoxy acid herbicides and bentazone in surface water by HPLC–UV were described [75]. Detection limits of 50–100 ng l^{-1} were reported and, owing to automation, the total analysis time was *ca.* 30 min.

2.5. *Aryloxyphenoxypropanoic acids*

Esters of aryloxyphenoxypropanoic acids are a new series of highly selective post-emergence herbicides often termed "phenoxyphenoxys". In the treated plants they decompose fairly rapidly, yielding the corresponding free acids as the main metabolites. Fluazifop-butyl, haloxyfop-methyl and -ethoxyethyl, quazalofop-ethyl and others belong to this group.

The number of studies dealing with trace analysis for aryloxyphenoxypropanoates in plant materials is limited. The residues are hydrolysed to their corresponding acids directly in the matrix and then extracted together with the free acids present as degradation products. The free acids are converted into methyl esters by methylation with diazomethane and determined by GC–MS or GC–ECD [76,77]. For ECD, fluazifop esters had to be brominated prior to GC analysis. NPD detection was also used [77,78], but the determination limit was higher (0.05 mg kg^{-1} for NPD, 0.01 mg kg^{-1} for ECD and MS).

Worobey and Shields [79] determined fluazifop-butyl and fluazifop acid using LC with oxidative amperometric detection (LC–AD). Fluazifop-butyl was hydrolysed to fluazifop acid prior to the extraction, similarly to the procedures used with GC analysis, but no methylation of the free acid was needed for the LC separation. Extracts of soybeans and soybean oil could also be analysed using LC–UV detection and no adverse effects of co-extracted compounds were observed; however, the sensitivity was approximately one order of magnitude less than with LC–AD where the limit of detection was $\leqslant$0.01 mg kg^{-1}. To improve the sensitivity of detection, fluazifop-butyl was derivatized with 4-bromoethyl-7-methoxycoumarin to give a fluorescent derivative that was determined by HPLC [80]. A detection limit of 0.5 ng for the derivative was reported, but no real samples were analysed with this method.

2.6. *Sulphonylureas*

Herbicides of the sulphonylurea group were developed by DuPont in the 1970s for weed control in cereal crops. They are characterized by high effectiveness, resulting in low application doses, usually of the order of 10–150 g of active ingredient per hectare. Their herbicidal properties, mode of action, degradation and persistence in soil were thoroughly reviewed by Blair and Martin [81].

Owing to the low application doses, low residue levels in soil, water and crops can be expected. Hence methods for residue analysis should exhibit an adequate sensitivity.

For the determination of the residues of chlorsulphuron in cereal crops, Slates [82] developed an LC method with photoconductivity detection. The detection limits were 0.01 mg kg^{-1} for grain and 0.05 mg kg^{-1} for straw and green plants. No residues were detected in grain and straw even at treatment up to 2240 g of active ingredient per hectare. In green plants, residues were detected shortly after the post-emergence treatment. The same author later determined the residues of bensulphuron-methyl in rice grain and straw by LC–photoconductivity detection (PCD) [83], with similar detection limits. Chlorimuron-ethyl was determined by LC–PCD in soybeans and some soybean rotational crops [84] and sulphometuron-methyl in fish and in green plants (alfalfa, corn, rice, wheat) [85].

For the analysis of sulphonyl urea herbicides in runoff water, a detection limit of $\leqslant$50 ng l^{-1} is required. Ahmed [86] found this impossible to reach with LC–UV for chlorsulphuron and used GC–ECD. However, due to the polar nature of the compound, GC of chlorsulphuron was poor and

methylation with diazomethane was needed. Methylation conditions could be optimized to obtain mainly monomethyl chlorsulphuron and a detection limit of 25 ng l^{-1} was reached. The same principle was applied in the analysis of chlorsulphuron in soil [87]. In this case, the detection limit was 0.001 mg kg^{-1}.

A different approach was adopted by Long *et al.* [88] who determined chlorsulphuron residues in milk by GC–NPD. Chlorsulphuron was found to undergo a thermally induced decomposition to give 2-amino-4-methoxy-1,3,5-triazine which was detected and quantitated. The products of thermal decomposition of chlorsulphuron were characterized by GC–MS [89]. Cotterill [90] determined the residues of chlorsulphuron and metsulphuron-methyl by GC–ECD following derivatization with PFEB. The PFB derivative was characterized by GC–MS as N,N-bis(pentafluorobenzyl)-2-chlorobenzene sulphonamide. The method was more sensitive than those described above and was found to be suitable for the determination of these residues in soil and water. However, it was less successful in plant materials for which the clean-up method used was inadequate.

2.7. Diquat and paraquat

The bipyridinium derivative diquat and paraquat are widely used general non-selective weed killers. Both are quite toxic for man and warm-blooded animals. Owing to their cationic nature, bipyridinium herbicides are prone to sorption interactions and their displacement from the bonding sites of an organic matrix requires special conditions, mostly achieved by refluxing with strong sulphuric or hydrochloric acid. This results in large amounts of co-extractives which may interfere with the determination. The older methods were often based on spectrophotometric determination and lacked specificity and sensitivity. At present, LC methods are most commonly used. GC determination is only possible after conversion into volatile products.

Worobey [91] analyzed the residues of diquat and paraquat simultaneously in potatoes by HPLC–UV on a reversed-phase column. The method works with 5-g samples and a detection limit of approximately 0.05 ppm was achieved. Nagayama *et al.* [92] reported a detection limit of approximately 0.02 ppm for their method which was also based on reversed-phase LC–UV. The method which includes clean-up on an Amberlite CG-50 column is relatively simple and rapid and it was tested for a variety of crops (cereal grains, potatoes, peaches, cabbage). Chichila and Walters [93] developed a method with a detection limit of 0.01 mg kg^{-1} which was achieved by using pH-controlled silica SPE, clean-up of the hydrochloric acid (6 *M*) digest and ion-pairing LC–DAD for the final determination. The method is suitable for the analysis of high-moisture crops. For the analysis of diquat and paraquat in well water, Simon and Taylor [94] used HPLC–DAD after SPE on bare silica columns. Followig the direct detection with DAD, postcolumn reaction with sodium hydroxide and sodium hydrosulphite was performed and the derivatives were detected with a variable-wavelength UV detector. The detection limit of 0.1 μg l^{-1} was achieved with 100-ml samples, 1 μg l^{-1} can be detected in 20-ml samples.

For the GC analysis, diquat and paraquat have to be volatilized, usually by hydrogenation. Hajšlová *et al.* [95] analyzed diquat and paraquat in potatoes and rapeseed by GC–NPD and GC–MS following hydrogenation with sodium borohydride–nickel(II) chloride. Comparable detection limits (0.005 ppm) were achieved with NPD and mass fragmentography; for the analyses of rapeseed the latter method was preferred owing to higher selectivity.

3. PRESENT TRENDS IN THE ANALYSIS OF HERBICIDE RESIDUES

Multiresidue methods are a response to the demand for decreasing the cost of analyses and increasing the productivity of laboratories. Most such procedures have been developed for the particular structural groups of herbicides in different commodities. Multiresidue methods require universality of the isolation and clean-up procedure and, as far as possible, unification of the conditions of the chromatographic separation.

In isolation of residues, efforts have been devoted to optimize the extraction and clean-up procedures [15–17]. Apart from the classical solvent extractions, other processes are being introduced. In the determination of herbicides in water, SPE became generally accepted for all major herbicide groups [27,30,36,40, 55,74]. In addition to the regularly used C_{18}-bonded

silica cartridges, graphitized carbon black cartridges seem to be advantageous for specific applications [96].

This technique makes it possible to concentrate the residues so that levels below 0.1 $\mu g\ l^{-1}$ can be determined, 0.1 $\mu g\ l^{-1}$ being the maximum residue limit of many herbicides in drinking water [117]. In the determination of herbicide residues in solid matrices, supercritical fluid extraction (SFE) has recently been introduced [97–99]. This technique contributes to decreasing the use of hazardous organic solvents and to giving shorter extraction times. SFE can be coupled with cGC. With this on-line modification, lower detection limits may be reached.

For clean-up, gel permeation chromatography (GPC) is increasingly being used whereas traditional column chromatography on alumina, silica and Florisil, which had been almost ubiquitous in the earlier clean-up procedures, is gradually losing its exclusive position. Detailed information on the utilization of GPC on Bio-Beads SX-3 has been published [100–102].

Unification can be observed in the types of columns used for GC and also for HPLC. Wall-coated open-tubular (WCOT) columns are used for GC where capillary columns and operation with optimized temperature programming are currently a standard requirement. For the determination of herbicide residues, capillary columns with immobilized or cross-linked stationary phases are employed. WCOT columns of length 15–30 m and I.D. *ca.* 0.3 mm and with a stationary phase film thickness of 0.2–0.4 μm are most frequently encountered. Capillary columns with non-polar or low-polarity stationary phases (SE-30, SE-54, OV-1, DB-1, DB-5 or equivalent) dominate.

Of the different GC detector types, those used for pesticide residue analysis have been reviewed [103]. For herbicide residue analysis, the two detection methods most frequently used are nitrogen–phosphorus-selective detection (NPD) and electron-capture detection (ECD). Both can be used either for direct detection (the procedures not requiring derivatization), or after conversion of the analytes into suitable derivatives. The derivatization in turn is employed for two reasons: (1) to improve the chromatographic behaviour of the analyte (*e.g.*, for thermolabile or highly polar compounds), or (2) to increase the sensitivity and/or selectivity of the detection (*e.g.*, by introducing more halogen atoms into the molecule).

It is essential for a derivatization technique that well defined reaction product(s) are formed with the derivatizing agent in a reasonable time and in sufficiently high and reproducible yields.

NPD is routinely used for most herbicidal compounds and their important degradation products in crops, foods of plant and animal origin, soils and water. It predominates in the determination of residues of triazines and is often used for phenylureas and uracils. In the determination of residues of phenoxyalkanoic acids and aryloxyphenoxypropanoic acids, ECD is the method of choice. For some herbicides that have both nitrogen and halogen atoms in their structures, both NPD and ECD can be used.

LC is a good method for the determination of a wide variety of different herbicides, especially in water samples. DAD is effective for the identification of the compounds. LC–DAD after SPE can serve as a means of determining polar, non-polar or thermolabile compounds in a simple run. The universal UV detector is usually insufficiently selective for this purpose. Fluorescence detection is highly sensitive but pre- or postcolumn derivatization of the analyte to fluorescent products is necessary in most instance. In the LC determination of sulphonylurea herbicides, PCD proved useful [82–85]. This method is highly sensitive and selective for sulphur, halogens, nitrogen and phosphorus. In the determination of phenylurea herbicides and substituted anilines, LC–ECD has also been applied [33,34], but it requires derivatization and technical adjustment of the LC equipment. Recently, the combination of reversed-phase LC or GC with NPD has been described for the determination of herbicide residues [104]. The sensitivity and selectivity of the LC determination can be increased by column switching. Comprehensive information on the application of this technique in the HPLC of pesticide residues was presented by Hogendoorn *et al.* [105].

Most of the LC work on herbicide residues is done on a C_{18} reversed-phase. Amino- and cyano-bonded stationary phases are less common. Both isocratic and gradient elution are employed.

As indicated earlier, TLC, even though of only marginal importance in modern residue analysis,

may still be of value especially as an inexpensive routine screening method not requiring sophisticated instrumentation. Technical developments (automated sample application and other high-performance TLC techniques, densitometric evaluation) have contributed to the value of TLC results. The use of HPTLC for the identification and determination of pesticide residues was evaluated by Gardyan and Thier [106], but only a few of th *ca.* 150 compounds discussed are herbicides. They also used HPTLC for confirmation of the identities of the residues [107]. The separation of phenylurea and triazine herbicides has been optimized using overpressured layer chromatography [108]. TLC methods in pesticide residue analysis have been thoroughly reviewed by Sherma [109–111].

For the TLC of herbicide residues, biochemical detection based on their ability to inhibit the enzyme systems of isolated chloroplasts, known as the Hill reaction inhibition, proved to be very sensitive and selective. This biochemical detection even permits quantification by evaluating the dependence between the lifetime of the spots and the amount herbicide present in them. The utilization of this chronometric technique for the determination of herbicide residues in soil, water, food commodities and plant materials has been summarized [31]. Residues of herbicides inhibiting the Hill reaction can be determined by this method, *i.e.*, triazines, phenylureas, carbamates, uracils and pyridazone. The method has been used for the determination of bentazone in soil, water and crops [112] and of thiazafluron in drinking water [113].

4. CONCLUSIONS

Chromatographic methods are indispensable in the determination of herbicide residues. A variety of selective detectors permit the analysis of compound mixtures or mixtures of parent compounds and degradation products. cGC–NPD and –ECD are the dominant methods for routine control analyses. The use of LC is growing, especially for the analysis of less complex matrices, *e.g.*, water. In spite of technical improvements, TLC is losing importance and is used, if at all, as a screening method.

In research work, the mass-selective detector is indispensable for identity confirmation studies, especially using GC–MS, whereas LC–MS has so far been applied less frequently. For the characterization of the chromatographic and spectral properties of the compounds investigated, GC–Fourier transform infrared spectrophotometry (FT-IR) has been applied [114]. Two-dimensional chromatography broadens the potential of the GC method [115].

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