



ELSEVIER

Journal of Chromatography A, 885 (2000) 237–250

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Review

Solid-phase extraction of acidic herbicides

Martha J.M. Wells*, Lan Zhou Yu¹

Center for the Management, Utilization and Protection of Water Resources and Department of Chemistry, Dixie Avenue, Prescott Hall, Room 233, Box 5033, Tennessee Technological University, Cookeville, TN 38505, USA

Abstract

A discussion of solid-phase extraction method development for acidic herbicides is presented that reviews sample matrix modification, extraction sorbent selection, derivatization procedures for gas chromatographic analysis, and clean-up procedures for high-performance liquid chromatographic analysis. Acidic herbicides are families of compounds that include derivatives of phenol (dinoseb, dinoterb and pentachlorophenol), benzoic acid (acifluorfen, chloramben, dicamba, 3,5-dichlorobenzoic acid and dacthal – a dibenzoic acid derivative), acetic acid [2,4-dichlorophenoxyacetic acid (2,4-D), 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)], propanoic acid [dichlorprop, fluazifop, haloxyfop, 2-(4-chloro-2-methylphenoxy)propanoic acid (MCP) and silvex], butanoic acid [4-(2,4-dichlorophenoxy)butanoic acid (2,4-DB) and 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB)], and other miscellaneous acids such as pyridinecarboxylic acid (picloram) and thiadiazine dioxide (bentazon). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Solid-phase extraction; Pesticides

Contents

1. Introduction	238
2. Characterization of acidic herbicides	238
3. Solid-phase extraction method development	240
3.1. Final analytical determination	241
3.2. Solid-phase extraction sorbent–solute interactions	241
3.2.1. Bonded silica sorbents	242
3.2.2. Graphitized carbon black sorbents	242
3.2.3. Polymeric resins	243
3.2.4. Designer resins	243
3.2.5. Anion-exchange sorbents	243
3.2.6. Selective adsorption/desorption	244
3.3. Matrix modification	244
3.3.1. Ion suppression	244
3.3.2. Ion-pairing and silanol masking	245
3.3.3. Neutral pH extraction without ion-pairing	246

*Corresponding author. Fax: +1-931-372-6346.

E-mail address: mjmwells@tntech.edu (M.J.M. Wells)

¹Present address: Analytical Development Department, Biomira Inc., 2011-94th St., Edmonton, Alberta T6N 1H1, Canada.

3.3.4. Hydrolysis	246
3.3.5. Other matrix additives	246
3.4. Elimination of matrix interferences for HPLC analysis of acidic herbicides	247
3.5. Derivatization procedures for GC analysis of acidic herbicides	248
3.6. Online solid-phase extraction	248
3.7. Solid-phase extraction of acidic herbicide metabolites	248
4. Conclusions	249
References	249

1. Introduction

Acidic herbicides (Table 1) are widely used for control of broad-leaved weeds and other vegetation. They are relatively inexpensive and very potent even at low concentrations. After application, they may pass into streams, rivers, or lakes with the possibility of environmental contamination [61]. With increasing public concerns for agrochemicals and their potential movement in the ecosystem, agrochemical residues in our environment and especially in our surface water and groundwater need to be more effectively documented [21].

Solid-phase extraction (SPE) has developed as an alternative to liquid–liquid extraction (LLE) for the separation, purification, concentration and/or solvent exchange of solutes from solution. Acidic herbicides are so widely used throughout the world that various methods for their extraction by SPE began to appear soon after disposable cartridges/columns containing bonded silica sorbents were introduced by Waters Associates in 1977. Research on improved analyses of acidic herbicides by SPE actively continues at present.

2. Characterization of acidic herbicides

Acidic herbicides consist of several families of compounds that are related by similarities in biological activity and chemical properties. The chemical properties of acidic herbicides influence the ways they are extracted and analyzed. These families of compounds are derivatives of acidic functional groups including phenol (dinoseb, dinoterb and pentachlorophenol), benzoic acid (acifluorfen, chloramben, dicamba, 3,5-dichlorobenzoic acid and

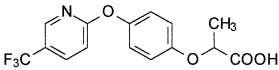
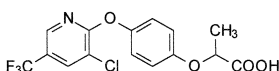
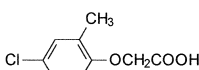
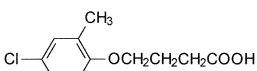
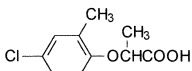
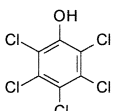
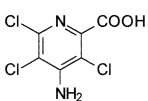
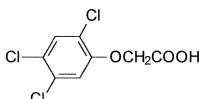
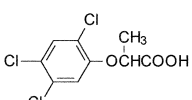
dacthal – a dibenzoic acid derivative), acetic acid [2,4-dichlorophenoxyacetic acid (2,4-D), 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)], propanoic acid [dichlorprop, fluzifop, haloxyfop, 2-(4-chloro-2-methylphenoxy)propanoic acid (MCPB) and silvex], butanoic acid [4-(2,4-dichlorophenoxy)butanoic acid (2,4-DB) and 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB)], and other miscellaneous acids such as pyridinecarboxylic acid (picloram), and thiadiazine dioxide (bentazon). Dozens of acidic herbicides are manufactured. This manuscript does not attempt to provide an exhaustive review of all papers reporting the SPE of acidic herbicides, but does provide comprehensive coverage of the various strategies and approaches taken to conduct the SPE of acidic herbicides and cites leading references to further research on this subject. The acidic herbicides for which developed SPE methods are most commonly reported in the literature are listed in Table 1.

The acidic herbicides are manufactured in formulation as the free acids, as their alkaline salts (such as potassium or dimethylamine salts) or as esters (such as butoxyethyl, isooctyl or 2-ethylhexyl esters), and in herbicide combinations. The unionized free acids vary in water solubility (Table 1), but the acidic herbicides most frequently exist in ionized form at environmental pH values. Acidic herbicides formulated as salts are water soluble while those formulations prepared as esters are not very water soluble. In the environment, acidic herbicides formulated as esters have short hydrolysis half-lives, on the order of 24–48 h [41,62,63], and therefore, are generally present as the corresponding ionized acids. The analyst must either evaluate the herbicides in both the ester and hydrolyzed acid forms, or convert all components present to their free acids before analysis.

Table 1
Identification and properties of selected acidic herbicides analyzed by SPE

Common name/ molecular formula/CAS No.	Systematic name	Structure	SPE Refs.	pK _a	Aqueous solubility (mg/l)	Log P
Acifluorfen C ₁₄ H ₇ ClF ₃ NO ₅ [50594-66-6]	Benzoic acid, 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitro-		[1–4]	1.93 [3] 3.5 [49] 3.86 [50]	120 [50,66]	3.70 [55]
Bentazon C ₁₀ H ₁₂ N ₂ O ₃ S [25057-89-0]	1H-2,1,3-Benzothiazin-4(3H)-one, 3-(1-methyl-ethyl)-,2,2-dioxide		[1–15]		500 [50,66]	2.34 [56] 2.80 [57]
Chloramben C ₇ H ₅ Cl ₂ NO ₂ [133-90-4]	Benzoic acid, 3-amino-2,5-dichloro-		[1,2]	3.40 [66]	700 [54,66]	
2,4-D C ₈ H ₆ Cl ₂ O ₃ [94-75-7]	Acetic acid, (2,4-dichloro-phenoxy)-		[1–7,16–32]	2.6 [15] 2.8 [18,51,66] 3.3 [18]	620 [54] 890 [66] 900 [50]	2.65 [58] 2.8 [50]
2,4-DB C ₁₀ H ₁₀ Cl ₂ O ₃ [94-82-6]	Butanoic acid, 4-(2,4-dichloro-phenoxy)-		[1–4,8,9,16,17]	4.8 [15,50,52,66]	46 [50,54,66]	3.53 [57]
DCPA, Daclhal C ₁₀ H ₆ Cl ₄ O ₄ [1861-32-1]	1,4-Benzene-dicarboxylic acid, 2,3,5,6-tetrachloro-, dimethyl ester		[2–4,33–35]		0.5 [50,66]	4.40 [57]
Dicamba C ₈ H ₆ Cl ₂ O ₃ [1918-00-9]	Benzoic acid, 3,6-dichloro- 2-methoxy-		[1–6,8,9,16,18,19,21,36–38]	1.87 [50] 1.9 [18] 1.91 [66]	4500 [50] 5000-8000; 6150; 6500 [66]	2.21 [57]
3,5-Dichlorobenzoic acid C ₇ H ₄ Cl ₂ O ₂ [51-36-5]	Benzoic acid, 3,5-dichloro-		[2–4]	3.46 [3]		3.00 [57]
Dichlorprop, 2,4-DP C ₉ H ₈ Cl ₂ O ₃ [120-36-5]	Propanoic acid, 2-(2,4-dichloro-phenoxy)-		[1–5,16,17,21,36,39]	2.86 [50,66] 3.5 [15]	350 [54,66] 710 [50,66]	3.43 [57,58]
Dinoseb C ₁₀ H ₁₂ N ₂ O ₅ [88-85-7]	Phenol, 2-(1-methylpropyl)- 4,6-dinitro-		[2–4,10,18,40]	4.5 [66]	52 [50,54]	3.56 [57]
Dinoterb C ₁₀ H ₁₂ N ₂ O ₅ [1420-07-1]	Phenol, 2-(1,1-dimethylethyl)- 4,6-dinitro-		[8–10,40]			

Table 1. Continued

Common name/ molecular formula/CAS No.	Systematic name	Structure	SPE Refs.	pK _a	Aqueous solubility (mg/l)	Log P
Fluazifop C ₁₅ H ₁₂ F ₃ NO ₄ [69335-91-7]	Propanoic acid, 2-[4-[[5-(trifluoromethyl)- 2-pyridinyl]oxy] phenoxy]-		[1,7,41]	2.98 [50] 3.12 [59]	2 [50]	3.08 [50] 3.18 [59]
Haloxifop C ₁₅ H ₁₁ ClF ₃ NO ₄ [69806-34-4]	Propanoic acid, 2-[4-[[3-chloro-5-(trifluoromethyl)- 2-pyridinyl]oxy] phenoxy]-		[1,36,41]	4.33 [50]		
MCPA C ₉ H ₉ ClO ₃ [94-74-6]	Acetic acid, (4-chloro-2- methylphenoxy)-		[1,5-7,10-14,16,17,19,20,36]	3.12 [50,66]	825 [50,54,66]	3.25 [58]
MCPB C ₁₁ H ₁₃ ClO ₃ [94-81-5]	Butanoic acid, 4-(4-chloro-2- methylphenoxy)-		[1,5,17,36]	4.8 [50,66]	44 [50,54,66]	3.47 [58]
MCPP, Mecoprop C ₁₀ H ₁₁ ClO ₃ [7085-19-0]	Propanoic acid, 2-(4-chloro-2- methylphenoxy)-, (±)-		[1,5,8-10,16,17,19,20]	3.11 [50] 3.18 [59] 3.7 [15]	620 [50,54,66]	3.13 [58] 3.22 [59] 3.63 [60]
Pentachlorophenol (PCP) C ₆ HCl ₅ O [87-86-5]	Phenol, pentachloro-		[2-4,20,22,42,45]	4.71 [52]	14 [3] 80 [54]	5.12 [57]
Picloram C ₆ H ₃ Cl ₃ N ₂ O ₂ [1918-02-1]	2-pyridine- carboxylic acid, 4- amino-3,5,6- trichloro-		[1-4,16,26-28,37,46,47]	1.97 [53] 2.3 [50]	430 [50,54,66]	0.30 [57] 1.92 [50]
2,4,5-T C ₈ H ₅ Cl ₃ O ₃ [93-76-5]	Acetic acid, (2,4,5- trichlorophenoxy)-		[1-5,17,18,22-25]	2.2 [15] 2.8; 3.5 [18]	238 [50] 150; 278 [66]	3.13 [58] 3.31 [57]
2,4,5-TP, Silvex C ₉ H ₇ Cl ₃ O ₃ [93-72-1]	Propanoic acid, 2-(2,4,5-trichlorophenoxy)-		[2-4,8,9,16-18,23-25,48]	3.0 [18]	140 [50]	3.80 [57]

3. Solid-phase extraction method development

A schematic (Fig. 1) outlines the most common approaches to utilizing SPE for analysis of acidic

herbicides. For most analytes and especially for the acidic herbicides, the choice of instrumentation and method for the chromatographic separation and detection of components to be isolated by SPE must

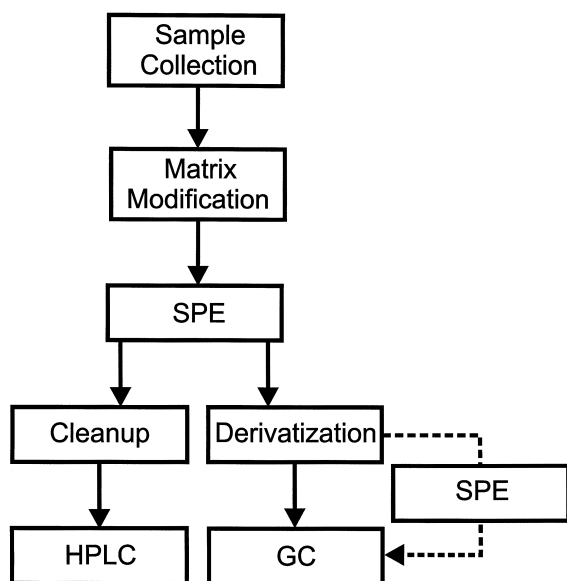


Fig. 1. General schematic for analysis of acidic herbicides by SPE.

be made before the SPE procedure can be tested. The choice of SPE sorbents, techniques, and subsequent sample treatment employed for acidic herbicides is dependent on the analytical instrumentation used for final determination. Cserhati and Forgacs [64] evaluated SPE for gas chromatographic and high-performance liquid chromatographic analysis of phenoxyacetic acids. Whether high-performance liquid chromatography (HPLC) or gas chromatography (GC) is selected, either choice has advantages and disadvantages for the determination of acidic herbicides.

3.1. Final analytical determination

Most SPE methods developed for acidic herbicides utilize HPLC [5–8,10–13,17–21,23,24,26–28,31,32,36–39,41,43,44,46,47] or GC [1–4,16,22,29,31–34,40,45,48] instrumental analysis for final analytical determination, although methods using thin-layer chromatography (TLC) [25] or supercritical fluid chromatography (SFC) [42] are also developed. Single-wavelength UV or multi-wavelength diode-array detection (DAD) are commonly used with HPLC. Electrochemical detection [44] and mass spectrometric (MS) [10] detection are also reported.

Electron-capture detection (ECD) and MS detection are widely used for the GC analyses of acidic herbicides. HPLC detection limits can be pushed to sub-ppb levels, and are usually comparable to those obtained by GC–MS. However, neither HPLC–DAD nor GC–MS techniques are usually as sensitive as GC–ECD for these compounds.

Using HPLC, the acidic herbicides can be analyzed in the ionic form (via ion-pairing); the molecular, unionized acid form (via ion suppression); or as the ester; thereby, requiring no chemical derivatization. However, the prime disadvantage to HPLC is its sensitivity to interference from fulvic and humic acids that are co-extracted with the acidic herbicides from environmental waters [11,15,44], making particularly difficult the analysis of the most polar acidic herbicides. When this happens, a large anomalous (amorphous) peak is observed to elute at the beginning of the HPLC chromatogram that reduces the quality of the chromatogram and makes quantitation difficult. Analysts have adopted several approaches to alleviate this problem. Additional clean-up procedures are required prior to HPLC analysis. These techniques are further discussed in Section 3.4.

Alternatively, GC analyses are not as susceptible to interferences from humic substances as are HPLC analyses. However, the acidic herbicides are polar and non-volatile, and do not lend themselves to direct analysis by GC. GC analysis first requires derivatization of the analytes to more volatile compounds. Various derivatives have been prepared for the GC analysis of acidic herbicides and are discussed in Section 3.5.

3.2. Solid-phase extraction sorbent–solute interactions

The selection of an appropriate SPE extraction sorbent depends on understanding the mechanism(s) of interaction between the sorbent and the analyte of interest. That understanding in turn depends on knowledge of the hydrophobic, polar and ionogenic properties of both the solute and the sorbent. SPE sorbents retain solutes by primary and secondary mechanisms. The sorbents used to extract the acidic herbicides from aqueous solution (Table 2) generally do so based on Van der Waals interactions (reversed-phase bonded silica sorbents, graphitized carbon

Table 2
SPE sorbents reported for acidic herbicide analyses

Sorbents	SPE Refs.
<i>Extraction</i>	
Bonded silica, column/cartridge format	[1,3,5–8,10,17,19–21,23,25–29,31,32,36–38,45–48]
Bonded silica, disk format	[2,9,16,30,32,33,36,43]
Graphitized carbon black column/cartridge format	[12,15,19,36,40,41]
Polymeric sorbents, column/cartridge format	[3,9,11,12,15,41,42,44,45]
Polymeric sorbents, disk format	[2,4,9,33,36,41]
Designer polymer	[11–14]
Anion exchange, column/cartridge format	[22,37,38]
Anion exchange, disk format	[33]
<i>Clean-up</i>	
Polar	[8,17,48]

black, polymeric sorbents) or by electrostatic interactions (anion exchange). Silica and Florisil used for HPLC clean-up procedures primarily interact with solutes by polar dipole/dipole interactions. All of these sorbents express secondary interactions, i.e., those primarily exhibiting electrostatic interactions can also have weaker Van der Waals interactions with the solute; conversely, sorbents retaining analytes primarily by Van der Waals interactions can exhibit secondary electrostatic interactions. Such mixed mode retention mechanisms can be beneficial or detrimental to the analysis. A useful review of SPE sorbents for the extraction of polar organic pollutants from environmental waters was recently published by Masque et al. [14].

3.2.1. Bonded silica sorbents

Acidic herbicides are retained on bonded silica as unionized compounds from acidified samples or as ion-pairs. The first SPE procedures developed for acidic herbicides used bonded silica sorbents [21,23,25–29,46,47] in the form of columns or cartridges to generate improved analytical procedures relative to LLE. The acidic herbicides recovered by

these procedures were primarily in the chlorophenoxy acid family and are efficiently extracted from aqueous solution by reversed-phase bonded silica sorbents. As SPE analyses expanded to include other family members of the multiclass group of acidic herbicides, and as the desire for concomitant multiresidue analyses increased, reversed-phase sorbents such as octadecyl silica, C₁₈, were found to be less appropriate for compounds at the polarity extremes of this family of compounds [36] and lead to testing of many other types of sorbents. However, improved extraction and recovery of very polar and very non-polar acidic herbicides can be achieved through increasing sorbent mass and/or by appropriate matrix modification (see Section 3.3). C₁₈ sorbent is still an excellent choice especially when the chlorophenoxyacetic acid family of acidic herbicides are the analytes of primary interest, and is the most frequently reported sorbent used for extraction of all types of acidic herbicides.

Butz et al. [1] tested a reversed-phase, C₁₈, sorbent (60 Å, 20–45 µm, irregular particle) for recovery of 34 phenoxyalkanoic acids and other acidic compounds. Using this sorbent, they determined that SPE recovery unexpectedly decreased with increasing aliphatic chain length (e.g., from 2,4-D to 2,4-DB and from MCPA to MCPB), whereas aliphatic chain branching increased SPE recovery (e.g., dichlorprop was better extracted than 2,4-D and mecoprop better than MCPA).

Bonded silica sorbents have been examined in column/cartridge and disk formats. Johnson et al. [30] demonstrated that the storage stability of 2,4-D on C₁₈ SPE disks was greater than cold storage in water. The advantages of membrane (disk) technology are higher flow-rates and reduced plugging due to the larger cross-sectional areas of disks compared to columns/cartridges, and reduced channeling and improved mass transfer [30,33]. Disadvantages include higher consumption of eluents than for cartridges [36] and a gram-for-gram greater cost.

3.2.2. Graphitized carbon black sorbents

Graphitized carbon black (GCB) exhibits the advantage of simultaneous extraction of neutral, basic and acidic compounds. No pH adjustment was necessary when using GCBs to extract acidic herbicides [15,41]. The versatility of this sorbent is

likely due to its behavior as both a non-specific (i.e., Van der Waals interactions) and an anion-exchange (electrostatic) sorbent. A very retentive sorbent, desorption from graphitized carbon black is reported to be problematic [36], requiring a displacing agent to overcome the electrostatic retention of anions [41].

Nouri et al. [19] demonstrated that acidic herbicides, including dicamba, 2,4-D, MCPA and MCPP, and other pesticides extracted from water with graphitized carbon black, were better recovered when acetonitrile was used as an elution solvent rather than methylene chloride or methanol. Nolte et al. [40] used GCB to extract phenolic hydroxybenzonitriles and 2,4-dinitrophenol derivatives from tap, ground and surface water. The herbicides with a free phenolic OH functional group and corresponding esterified formulations were strongly adsorbed. The esters were easily eluted from the sorbent, while compounds with free phenolic OH groups were difficult to desorb. However, the difficult desorption of these compounds from the sorbent presented the opportunity to derivatize them to the methyl esters directly at the surface of the graphitized carbon black. Lagana et al. [41] conducted SPE of aryloxyphenoxypropionic (ArPPs) acidic herbicides, including fluazifop and haloxyfop, on graphitized carbon black from drinking, spring and ground water. An organic mixture (dichloromethane–methanol) containing formic acid was used to desorb the analytes from the GCB [41]. Lagana et al. [41] report that the ArPPs are less acidic than other acidic herbicides such as dicamba, 2,4,5-T or 2,4-D. The ArPPs are higher in molecular mass among the acidic herbicides listed in Table 1 and are expected to be very non polar.

3.2.3. Polymeric resins

Highly crosslinked polystyrene–divinylbenzene (PS–DVB) and other polymeric resins have been introduced to the market in both column and disk forms and used to extract acidic herbicides. These sorbents are demonstrated to be more retentive, especially toward the polar members of this chemical group, than the bonded silica sorbents. However, polar compounds still have lower breakthrough volumes on these sorbents than nonpolar compounds. Hodgeson et al. [2] demonstrated polymeric resin

disks to be superior to C₁₈ disks for 13 acidic herbicides. They reported that recovery was most problematic for picloram and dacthal, but was better on the polymeric resin. Note from the log *P* values given in Table 1 that picloram is very hydrophilic and dacthal is very hydrophobic. Researchers [2,14,36] attribute the better performance of the PS–DVB resin to the aromatic, polymeric structure, which can interact with aromatic analytes via π – π interactions. Pichon et al. [9] determined that a PS–DVB sorbent with a specific surface area of about 1000 m² per gram yielded higher retention than sorbents with half as much specific surface area, so much higher that adequate recoveries were obtained from nonacidified, i.e., pH 7, water samples.

The US Environmental Protection Agency (EPA) regulates several standard methods for the determination of chlorinated acids in drinking water, and industrial and municipal wastewater. In method 515.2, a 250-ml measured volume of sample is adjusted to pH 12 with 6 *M* sodium hydroxide for 1 h to hydrolyze derivatives. Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with a 47 mm resin based PS–DVB extraction disk. The acids are converted to their methyl esters using diazomethane. Excess derivatizing reagent is removed, and the esters are determined by GC–ECD.

3.2.4. Designer resins

Masque and co-workers [11–14] prepared chemically modified polymeric resins producing functionalized PS–DVB sorbents developed particularly for SPE of polar compounds of environmental interest. They chemically introduced polar functional groups including acetyl, hydroxymethyl, benzoyl and *o*-carboxybenzoyl into the structural backbone of polymeric resins and demonstrated higher breakthrough volumes for the most polar compounds than with classical hydrophobic bonded silicas or non-functionalized polymeric resins.

3.2.5. Anion-exchange sorbents

Chatfield et al. [22] tested two strong quaternary ammonium resins in the fluoride, hydroxide, cyanide, acetate, propionate and butyrate forms, and found the fluoride form most suitable for extraction of 2,4-D and 2,4,5-T. Krzyszkowska and Vance [37] used

aminopropyl weak anion-exchange sorbent for SPE analysis of dicamba, conditioned with 1 M acetic acid and water. Arjmand et al. [38] conditioned amino ion-exchange columns with 1 M nitric acid and water for analysis of dicamba. Monohan et al. [33] used strong anion-exchange disks to extract dacthal (DCPA) and its mono- and diacid metabolites from water. The disks were first preconditioned with acetone, then with 1 M HCl–methanol, and finally conditioned with water. Strong anion exchange was demonstrated to be superior to C₁₈ bonded phase silica disks or PS–DVB polymeric disks for this application.

3.2.6. Selective adsorption/desorption

Because the acidic herbicides differ widely in their properties (over four orders of magnitude in log *P*) the opportunity is presented to selectively adsorb or desorb compounds within this group during SPE. Class separation or distinct fractionation of analytes can facilitate subsequent analyses. Picloram and 2,4-D are selectively desorbed from C₁₈ sorbent by using two elution solvents that differ in eluotropic strength [28]; picloram is desorbed with 25% acetic acid followed by desorption of 2,4-D with methanol. Monohan et al. [33] fractionated the parent compound, DCPA, from its mono- and diacid metabolites using a two-phase desorption from a strong anion-exchange disk. DCPA was first desorbed with methanol followed by elution of the metabolites by 10% (v/v) H₂SO₄ in methanol.

Schulein et al. [36] and Crescenzi et al. [15] retained simultaneously basic/neutral and acidic/phenolic compounds on graphitized carbon black from aqueous samples and performed a two-step differential elution. Basic/neutral compounds were eluted with dichloromethane–methanol. Acidic compounds were eluted with a dichloromethane–methanol–trifluoroacetic acid mixture [36] or a dichloromethane–methanol–tetrabutylammonium chloride solvent [15]. Crescenzi et al. [15] observed some carryover for 2,4-DB. Wang and Huang [48] compare step-wise or simultaneous desorption of acidic herbicides as methyl esters from reversed-phase and Florisil sorbents.

3.3. Matrix modification

The acidic herbicides are ionizable compounds

that exist in the ionic state at most environmental pH values. SPE recovery of acidic herbicides can be accomplished in either the unionized state or as anions. The pH-dependent dissociation of acidic herbicides in water is a function of the p*K*_a (the logarithm of the ratio of ionized to unionized analyte). The relative concentrations of dissociated and non-dissociated forms of ionizable analytes in aqueous solution are equal when the solution pH is equal to the p*K*_a (Table 1). In aqueous solution, the acidic herbicides are 99% unionized when the pH of the sample is two log units below the p*K*_a. SPE recovery may be incomplete unless the pH of the sample is two log units below the p*K*_a, but the sorbent properties and the hydrophobicity and size of the ionized form of the analyte can influence this generalization, as is demonstrated in the SPE literature for the acidic herbicides.

3.3.1. Ion suppression

For those researchers that attempt to retain the acidic herbicides on sorbents in unionized form, the pH of the solution is most commonly adjusted to 2.5 [11,13,46,47], 2.2 [21], 2.1 [20], 2 [3,16,24,25,31–33,37,41,43,44], <2 [30,40] or 1 [2,4] to achieve ion suppression. For those compounds in Table 1 for which data were available, the p*K*_a values are plotted against log *P* (Fig. 2). When more than one value was cited, the average value was plotted. A relationship between p*K*_a and log *P* is not anticipated. Plotting these parameters in a two-dimensional grid enables visualization of the dual importance of p*K*_a and log *P* to the SPE of acidic herbicides. The purpose of the scatter plot is to identify compounds for which problems would potentially be encountered during SPE. On the graph an area is identified that is bounded by a log *P* of 1, below which compounds are very hydrophilic; a log *P* of 4, above which compounds are very hydrophobic; and a p*K*_a of 2, allowing for the lowest p*K*_a at which a solution pH of 1 would yield at least 90% unionized analyte. Within these boundaries data are plotted for compounds that have been demonstrated to produce adequate SPE recoveries on hydrophobic sorbents. Compounds that have data points near or outside of these boundaries can be expected to be more difficultly extracted, and indeed, this supposition is supported by the literature on acidic herbicides. Of the compounds in Table 1, bentazon, picloram,

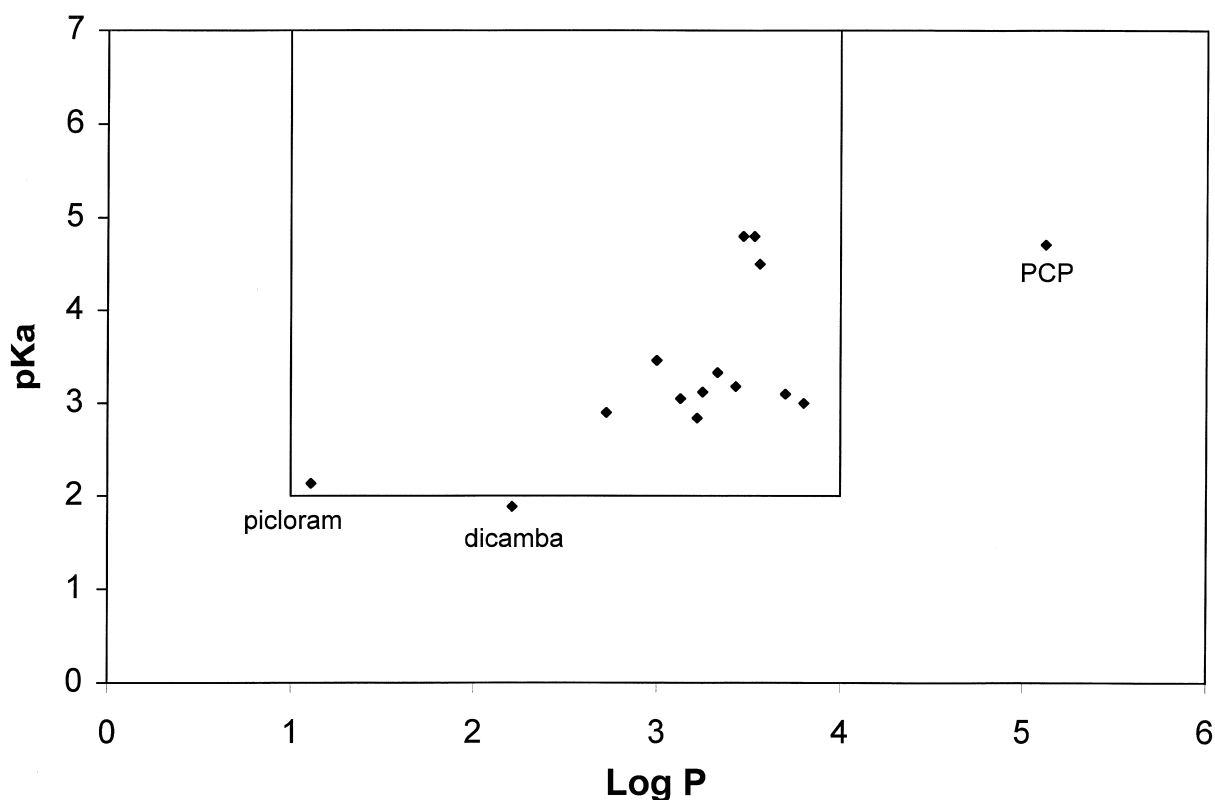


Fig. 2. Comparison of hydrophobicity and ionogenicity for acidic herbicides.

dicamba, dinoseb, dacthal and PCP are more often reported as difficult to recover by SPE. From the log P given for dacthal (4.40) it is seen that its data point in Fig. 2 would lie outside the drawn boundary. At the hydrophobic extremes, picloram is very hydrophilic and pentachlorophenol is very hydrophobic, making them each difficult to extract without additional matrix and/or sorbent modification.

3.3.2. Ion-pairing and silanol masking

Since the ionic form of acidic herbicides is negatively charged, ion-pairing and silanol masking probably occur at the same time and cannot really be distinguished from each other. Both effects may contribute to the improved recovery observed when bulky hydrophobic counterions are added to the sample.

In aqueous solution, the acidic herbicides are 99% ionized when the pH of the sample is two log units above the pK_a . SPE recovery by ion pairing may be incomplete unless the pH of the sample is two log

units above the pK_a . At neutral pH, the pK_a values for all of the compounds depicted in Fig. 2 are two log units below the solution pH.

Bonded silica sorbents exhibit secondary polar interactions due to the silica backbone and unreacted surface silanol groups. In some manufactured sorbents, surface silanol groups are “endcapped” by further reaction with a short-chain hydrocarbon. Even so, some free silanol groups remain, but can be “masked” by addition of positively charged, hydrophobic counterions.

Balinova [6] used an ion-pairing reagent (triethylamine) to retain acidic herbicides on C_{18} bonded silica at neutral pH (6.9). The approach was found to be particularly useful for increasing the recovery of weakly retained compounds such as dicamba. Tetrabutylammonium hydrogensulfate (TBAHS) was added to samples containing picloram and improved SPE recovery at pH 2.5 was observed [46]. Increased recovery probably resulted from the dual effects of silanol masking at the sorbent surface as well as

ion-pair formation between picloram and the lipophilic quaternary ammonium counterion. A combined pK_a of 1.97 was assigned to picloram by Osteryoung and Whittaker [53] representing the dissociation of both the neutral and zwitterionic forms.

3.3.3. Neutral pH extraction without ion-pairing

As earlier described, anion-exchange sorbents allowed the extraction of acidic herbicides at neutral pH. Pichon et al. [9] report experiments in which the sorbent (styrene–divinylbenzene) was so retentive that no adjustment of pH was necessary at all in order to achieve retention. Some researchers [15,36,41] found that no pH adjustment was necessary when using GCB.

3.3.4. Hydrolysis

Initial adjustment of environmental samples to pH 11 [23] or pH 12 [4,24] is reported. In the methods

developed by Mallinckrodt Baker [4] and Myers [24], the sample is allowed to stand for an hour before an LLE wash step using methylene chloride is conducted after which the organic phase is discarded. Presumably there are two reasons for this procedure: (1) to remove interferences that are unionized at high pH, and (2) to convert the acidic herbicides formulated as esters to the free acids. Hoke et al. [23] adjusted the pH to 2.5 after hydrolysis of the ester and extracted the sample with reversed-phase sorbents.

3.3.5. Other matrix additives

The acidic herbicides featured in Table 1 represent a multiclass group that varies widely in aqueous solubility and in hydrophobicity (Fig. 3). Aqueous solubility and hydrophobicity are two parameters that do not measure the same phenomenon, yet they are often observed to trend toward an inverse relationship, i.e., when hydrophobicity, represented by $\log P$

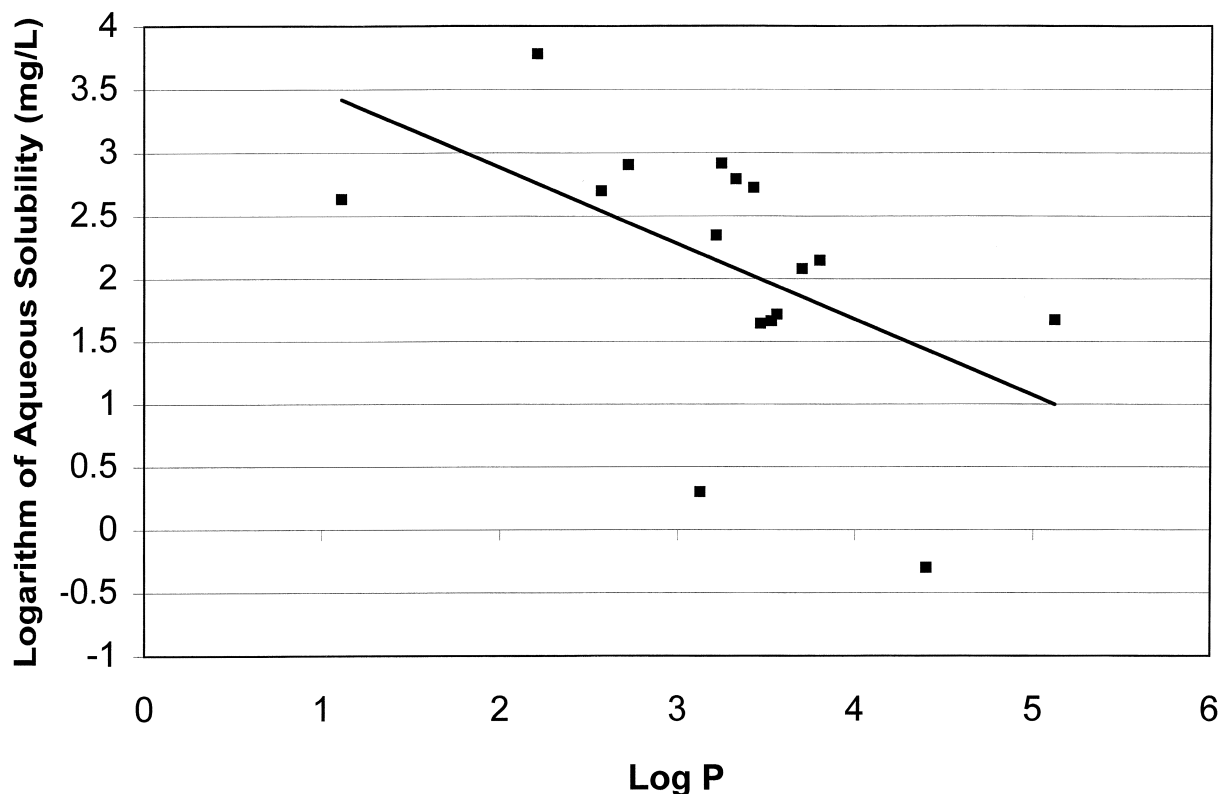


Fig. 3. Comparison of hydrophobicity and aqueous solubility for acidic herbicides.

is large, aqueous solubility is reduced. That is the case when these values are plotted for the acidic herbicides (Fig. 3). A general trend is demonstrated, albeit with a poor correlation coefficient.

The recovery of highly hydrophobic compounds ($\log P$ of 4 or greater) as unionized solutes can benefit from the addition of organic modifier to the sample. The solubility of hydrophilic members of this group can be reduced from the addition of salts to the sample to favor extraction by the sorbent. Sometimes the addition of both organic modifiers and salts to the sample can improve analyses of compound groups that vary widely in hydrophobicity [65].

Small amounts of organic modifiers are often added to aqueous samples to improve flow characteristics and sorbent penetration. Addition of organic modifiers on the order of 5–20% are used to promote the solubility of hydrophobic compounds in the mobile phase and alter the selectivity characteristics of the sorbent. Thompson and Miller [16] and Schulein et al. [36] added 5 ml of methanol per liter of water extracted in order to maintain the conditioning (wettability) of the adsorbent during extraction, while Johnson et al. [30] added 2 ml of methanol per 250 ml of sample.

Hodgeson et al. [2] determined that recovery of acidic herbicides was markedly increased by the addition of salt to increase the ionic strength of the sample. The addition of sodium sulfate (20%, w/w) generated higher recoveries than addition of a comparable amount of sodium chloride. Addition of 20% sodium sulfate was also reported in the Mallinckrodt Baker procedure [4] and 10% sodium sulfate by Monohan et al. [33]. Krzyszowska and Vance [37] added 2.5 g of sodium chloride to 50 ml water samples, and Zhou [3] compared the addition of 17.4% and 32% sodium chloride to the effect of adding no salt to samples containing acidic herbicides. Balinova [7] adjusted sample ionic strength by addition of 2.5 *M* sulfuric acid and 10 g of sodium chloride per liter.

3.4. Elimination of matrix interferences for HPLC analysis of acidic herbicides

Clean-up strategies reported for the acidic herbicides appear to follow several paths: (1) chemical

treatment of the sample to degrade humic substance interferences; (2) using a second extraction with a polar sorbent such as silica or Florisil to remove matrix interferences that were co-extracted with the analytes of interest from the initial extraction procedure; or (3) comparing all sorbents listed in Table 2 to improve sample suitability, such as retaining the analytes in the ionized form at neutral pH on anion-exchange or otherwise strongly retentive sorbents, thereby minimizing humic substance interferences retained at acidic pH values.

Masque and co-workers [12,13] decreased the initial HPLC–UV peak due to fulvic and humic acids by adding sodium sulfite to tap and river waters. The interfering matrix peak was reduced with no losses in the compounds studied when 500 or 1000 μl of 10% Na_2SO_3 solution were added prior to SPE for every 100 ml of tap or river water, respectively. Bernal et al. [42] and Jauregui and Galceran [44] added 300 μl of a 10% solution of Na_2SO_3 to each 100 ml of tap water samples to eliminate free chlorine. Using SFC–DAD, interferences were observed [42] to be extracted from environmental waters, but none interfered with quantitation of the analytes of interest.

Pichon et al. [8] conducted multiresidue analyses in natural waters with analysis by HPLC–DAD and developed a clean-up procedure by performing SPE on a Florisil cartridge. At pH 2 co-extraction of humic and fulvic acids on C_{18} bonded silica generated a large, early eluting peak in the HPLC chromatogram. However, in a subsequent SPE clean-up procedure, the polar humic and fulvic substances were strongly sorbed on Florisil while the analytes of interest were quantitatively desorbed. Wang and Huang [48] used Florisil as a clean-up sorbent following extraction with C_{18} sorbent. Sancho-Llopis et al. [17] performed silica column clean-up of C_{18} extracts of chlorophenoxy acid herbicides from environmental water samples. They also utilized an HPLC precolumn containing internal surface reversed-phase material.

Lagana et al. [41] demonstrated that extracts from graphitized carbon black yielded humic acid interferences by HPLC–DAD analyses that were slightly less than those obtained with polymeric sorbents, due, they reasoned, to strong interactions between humic substances and positively charged sites on the graphitized carbon black sorbent. Krzyszowska and

Vance [37] noted that when samples adjusted to pH 1 were eluted through octadecyl SPE cartridges some octadecyl material was stripped from the stationary phase and interfered with HPLC analyses of samples containing dicamba. They achieved improved recovery by developing an ion-exchange SPE procedure using aminopropyl SPE sorbent. Pichon et al. [9] demonstrated that humic and fulvic acid interferences could be eliminated by using a highly retentive styrene–divinylbenzene sorbent that adsorbed the acidic herbicides in their ionic form at pH 7. No further clean-up was necessary to determine the analytes in surface water samples.

3.5. Derivatization procedures for GC analysis of acidic herbicides

Analysis by GC requires converting the acidic herbicides to ester or ether derivatives that are less polar and more volatile than the parent compound. Homogeneous derivatization, in which both the derivative and the derivatizing reagent are in the liquid phase, was reported using diazomethane [2,4,16] to convert the carboxylic acid derivatives to methyl esters and phenolic compounds to their methyl ethers. Extracts were dried with anhydrous sodium sulfate before reacting with diazomethane. Butz et al. [1] derivatized extracted acidic compounds with pentafluorobenzyl bromide.

Swineford and Belisle [29] and Sutherland [31] developed procedures in which SPE both preceded and followed homogeneous derivatization (adding an extra step following the dotted line path in Fig. 1). The C_{18} column extracts of 2,4-D were converted to the methyl ester with boron trifluoride in methanol, then the 2,4-D methyl ester was subjected to a second SPE procedure to quench the derivatizing reagent and recover the methyl ester in a solvent suitable for subsequent GC analysis.

Monohan et al. [33] derivatized the mono- and diacid metabolites of dacthal with diazomethane, but prior to analysis by GC it was first necessary to perform a liquid–liquid microextraction of the SPE eluate with diethyl ether. Krause and Niemczyk [34] analyzed the dacthal metabolites as the ethyl esters. Louter et al. [45] first acetylated phenols, including pentachlorophenol, with acetic anhydride directly in the aqueous sample then conducted SPE on the

derivatized analytes, thereby eliminating the SPE step prior to derivatization.

Heterogeneous derivatization, in which the derivative is adsorbed on the sorbent and the derivatizing reagent is in the liquid phase, has been reported for selected acidic herbicides. Chatfield et al. [22] converted 2,4-D and 2,4,5-T to their methyl esters using supercritical carbon dioxide containing methyl iodide while the analytes were adsorbed onto an anion-exchange resin. Nolte et al. [40] derivatized 2,4-dinitrophenol herbicides, including dinoseb and dinoterb, to their corresponding methyl ethers by direct methylation at the surface of graphitized carbon black using diazomethane or trimethylsulfonium hydroxide (TMSH). He [32] conducted solid-phase derivatization of 2,4-D sorbed on C_{18} columns or C_{18} disks by reaction with BF_3 –methanol. Zhou [3] examined solid-phase derivatization of 13 chlorinated herbicide acids on two types of extraction sorbents – octadecyl bonded silica and styrene–divinylbenzene in column format – using BF_3 –methanol and trimethylsilyldiazomethane as derivatizing reagents.

3.6. Online solid-phase extraction

Some researchers [10–14,39,42,44] used online SPE–chromatographic procedures for the analysis of acidic herbicides. The advantages of online SPE include better sensitivity, lower organic solvent consumption, greater automation potential and simplicity [11–13], and reduced sample manipulation [44]. Using SPE online with HPLC–DAD allowed quantitation of groups of pesticides in a single analysis [39]. Bernal et al. [42] coupled SPE online with SFC–DAD. Louter et al. [45] coupled SPE online with GC using flame ionization detection (FID). Aguilar et al. [10] analyzed priority pesticides using online SPE–HPLC–MS.

3.7. Solid-phase extraction of acidic herbicide metabolites

Acidic herbicide parent compounds range widely in polarity (Table 1). Additionally, metabolites of the acidic herbicides are often (but not always) more polar than the parent compound making it more challenging for the analyst to deal with a spectrum of

polarities in the same sample. Less research is reported for SPE of the acidic herbicide metabolites than for the parent compounds. Arjmand et al. [38] developed SPE procedures for dicamba and its metabolite, 3,6-dichlorosalicylic acid, that is formed by the hydrolysis of the methoxy ether group of dicamba to a hydroxyl group. Dacthal (dimethyl tetrachloroterephthalate) degrades into mono- and dicarboxylic acid metabolites for which concomitant analyses by SPE were developed by Monohan et al. [33] and Krause and Niemczyk [34].

4. Conclusions

For the acidic herbicides, a combination of physico-chemical parameters influence their extraction from aqueous solution. Ionogenicity (pK_a) and hydrophobicity ($\log P$) are especially important in determining the approach to SPE for these compounds.

The chlorophenoxy acid herbicides in this family are the most easily extracted by SPE sorbents that exhibit Van der Waals forces as the primary mechanism of interaction. From this review it is obvious that researchers have tried virtually every sorbent type on the market for SPE as well as custom-designing sorbents for the extraction of acidic herbicides. Of the compounds reported, most often researchers cite difficulty in the extraction of bentazon, dacthal, dicamba, dinoseb, pentachlorophenol and picloram. Although not a certainty, it is highly probable that because many of these compounds exhibit characteristics of low hydrophobicity or high hydrophobicity and/or a low pK_a value, they are poorly extracted as unionized solutes.

The SPE literature for acidic herbicides is approximately equally divided among final analysis of the compounds by HPLC or GC. Very polar components are difficult to analyze by HPLC because of co-extracted interferents at low pH values. Innovations in ion exchange, ion pairing and other “neutral pH” SPE approaches help to improve extracts analyzed by HPLC methods. Analysis by GC requires that these compounds be converted to the corresponding ester or ether, adding to the overall difficulty level of the procedure, but GC is not as sensitive to the presence of humic material interferences.

Despite the analytical difficulties, the body of literature reviewed here makes it clear that SPE procedures have improved the ease, reproducibility, and sample throughput for analysis of acidic herbicides as compared to other approaches. SPE methods have been applied to the analysis of thousands of samples, thereby improving our overall understanding of the fate and transport of acidic herbicides in the environment.

References

- [1] S. Butz, Th. Heberer, H.-J. Stan, J. Chromatogr. A 677 (1994) 63.
- [2] J. Hodgson, J. Collins, W. Bashe, J. Chromatogr. A 659 (1994) 395.
- [3] L. Zhou, Masters Thesis, Tennessee Technological University, Cookeville, TN, 1997.
- [4] Mallinckrodt Baker, SPD-008 Extraction of Chlorinated Acids from Water (EPA Method 515.2), 1999, [On-Line]. Available web: <http://www.jtbaker.com/applica/spd008.htm>
- [5] J.M. Sanchis-Mallols, S. Sagrado, M.J. Medina-Hernandez, R.M. Villanueva Camanas, E. Bonet-Domingo, J. Liq. Chromatogr. Rel. Technol. 21 (1998) 1871.
- [6] A. Balinova, J. Chromatogr. A 728 (1996) 319.
- [7] A. Balinova, J. Chromatogr. 643 (1993) 203.
- [8] V. Pichon, C. Cau Dit Coumes, L. Chen, M.C. Hennion, Int. J. Environ. Anal. Chem. 65 (1996) 11.
- [9] V. Pichon, C. Cau Dit Coumes, L. Chem, S. Guenu, M.-C. Hennion, J. Chromatogr. A 737 (1996) 25.
- [10] C. Aguilar, I. Ferrer, F. Borrull, R.M. Marce, D. Barcelo, J. Chromatogr. A 794 (1998) 147.
- [11] N. Masque, M. Galia, R.M. Marce, F. Borrull, Analyst 122 (1997) 425.
- [12] N. Masque, R.M. Marce, F. Borrull, J. Chromatogr. A 793 (1998) 257.
- [13] N. Masque, M. Galia, R.M. Marce, F. Borrull, J. Chromatogr. A 803 (1998) 147.
- [14] N. Masque, R.M. Marce, F. Borrull, Trends Anal. Chem. 17 (1998) 384.
- [15] C. Crescenzi, A. Di Corcia, G. Passariello, R. Samperi, M.I.T. Carou, J. Chromatogr. A 733 (1996) 41.
- [16] T.S. Thompson, B.D. Miller, Chemosphere 36 (1998) 2867.
- [17] J.V. Sancho-Llopis, F. Hernandez-Hernandez, E.A. Hogendoorn, P. van Zoonen, Anal. Chim. Acta 283 (1993) 287.
- [18] P.R. Loconto, J. Liq. Chromatogr. 14 (1991) 1297.
- [19] B. Nouri, B. Fouillet, G. Toussaint, P. Chambon, R. Chambon, Analyst 120 (1995) 1133.
- [20] J. Frebortova, Fresenius Environ. Bull. 4 (1995) 209.
- [21] E.R. Bogus, T.L. Watschke, R.O. Mumma, J. Agric. Food Chem. 38 (1990) 142.
- [22] S.N. Chatfield, M.Y. Croft, T. Dang, E.J. Murby, G.Y.F. Yu, R.J. Wells, Anal. Chem. 67 (1995) 945.

- [23] S.H. Hoke, E.E. Brueggemann, L.J. Baxter, T. Trybus, *J. Chromatogr.* 357 (1986) 429.
- [24] K.F. Myers, Determination of chlorinated phenoxyacid herbicides in water and sediment by solid-phase extraction and high-performance liquid chromatography, Report WES/TR/W-92-3; Order No. AD-A260201, from: Gov. Rep. Announcement. Index (US) 1993, 93(11), Abstr. No. 332,211, 1992.
- [25] J. Sherma, *J. Liq. Chromatogr.* 9 (1986) 3433.
- [26] M.J.M. Wells, in: Proceedings of the 2nd Annual International Symposium on Sample Preparation and Isolation Using Bonded Silicas, Analytichem International, Harbor City, CA, 1985, pp. 63–68.
- [27] M.J.M. Wells, in: Proceedings of the 3rd Annual International Symposium on Sample Preparation and Isolation Using Bonded Silicas, Analytichem International, Harbor City, CA, 1986, pp. 117–135.
- [28] M.J.M. Wells, J.L. Michael, *Anal. Chem.* 59 (1987) 1739–1742.
- [29] D.M. Swineford, A.A. Belisle, *Environ. Toxicol. Chem.* 8 (1989) 465.
- [30] W.G. Johnson, T.L. Lavy, S.A. Senseman, *J. Environ. Qual.* 23 (1994) 1027.
- [31] D.J. Sutherland, Masters Thesis, Tennessee Technological University, Cookeville, TN, 1994.
- [32] X. He, Masters Thesis, Tennessee Technological University, Cookeville, TN, 1995.
- [33] K. Monohan, I.J. Tinsley, S.F. Shepherd, J.A. Field, *J. Agric. Food Chem.* 43 (1995) 2418.
- [34] A.A. Krause, H.D. Niemczyk, *J. Environ. Sci. Health, Part B* B25 (1990) 587.
- [35] J. Manes, Y. Pico, J.C. Molto, G. Font, *J. High Resolut. Chromatogr.* 13 (1990) 843.
- [36] J. Schulein, D. Martens, P. Spitzauer, A. Ketrup, *Fresenius' J. Anal. Chem.* 352 (1995) 565.
- [37] A.J. Krzyszkowska, G.F. Vance, *J. Agric. Food Chem.* 42 (1994) 1693.
- [38] M. Arjmand, T.D. Spittler, R.O. Mumma, *J. Agric. Food Chem.* 36 (1988) 492.
- [39] J.M. Huen, R. Gillard, A.G. Mayer, B. Baltensperger, H. Kern, *Fresenius' J. Anal. Chem.* 348 (1994) 606.
- [40] J. Nolte, B. Grass, F. Heimlich, D. Klockow, *Fresenius' J. Anal. Chem.* 357 (1997) 763.
- [41] A. Lagana, G. Fago, A. Marino, *J. Chromatogr. A* 796 (1998) 309.
- [42] J.L. Bernal, M.J. Nozal, L. Toribio, M.L. Serna, F. Borrull, R.M. Marce, E. Pocurull, *Chromatographia* 46 (1997) 295.
- [43] K.-K. Chee, M.-K. Wong, H.-K. Lee, *Mikrochim. Acta* 126 (1997) 97.
- [44] O. Jauregui, M.T. Galceran, *Anal. Chim. Acta* 340 (1997) 191.
- [45] A.J.H. Louter, P.A. Jones, J.D. Jorritsma, J.J. Vreuls, U.A.Th. Brinkman, *J. High Resolut. Chromatogr.* 20 (1997) 363.
- [46] M.J.M. Wells, *J. Liq. Chromatogr.* 5 (1982) 2293–2309.
- [47] M.J.M. Wells, J.L. Michael, D.G. Neary, *Arch. Environ. Contam. Toxicol.* 13 (1984) 231–235.
- [48] W.K. Wang, S.D. Huang, *J. Chromatogr.* 483 (1989) 121.
- [49] L. Celi, M. Negre, M. Gennari, *J. Agric. Food Chem.* 44 (1996) 3388.
- [50] *Herbicide Handbook*, 5th Edition (1983); 7th Edition (1994), and [On-Line]. Available web: <http://www.orst.edu/dept/hort/weeds/agrichem.htm>, Weed Science Society of America, Champaign, IL.
- [51] R.J. Musser, *Integrated Case Studies in Natural Resource Analysis*, Duke University, 1981.
- [52] Supelco, Bellefonte, PA, personal communication.
- [53] J. Osteryoung, J.W. Whittaker, *J. Agric. Food Chem.* 28 (1980) 95.
- [54] H. Kidd, D.R. James (Eds.), *The Agrochemicals Handbook*, 3rd Edition, Royal Society of Chemistry Information Services, Cambridge, 1991.
- [55] U.B. Nandihalli, M.V. Duke, S.O. Duke, *Pestic. Biochem. Physiol.* 43 (1992) 193.
- [56] H. Saito, J. Koyasu, K. Yoshida, T. Shigeoka, S. Koike, *Chemosphere* 26 (1993) 1015.
- [57] C. Hansch, A. Leo, D.H. Hoekman, *Exploring QSAR: [2]. Hydrophobic, Electronic, and Steric Constants*, American Chemical Society, Washington, DC, 1995.
- [58] A. Ilchmann, G. Wienke, T. Meyer, J. Gmehling, *Chem.-Ing.-Tech.* 65 (No. 1) (1993) S72.
- [59] J. Comer, K. Chamberlain, A. Evans, *SAR QSAR Environ. Res.* 3 (1995) 307.
- [60] M. Nakamura, M. Nakamura, S. Yamada, *Analyst* 121 (1996) 469.
- [61] N. Fung, T. Ikesaki, *J. Chromatogr.* 537 (1991) 385.
- [62] A.J. Cessna, R. Grover, L.A. Kerr, M.L. Aldred, *J. Agric. Food Chem.* 33 (1985) 504.
- [63] E.A. Smith, *J. Agric. Food Chem.* 33 (1985) 483.
- [64] T. Cserhati, E. Forgacs, *J. Chromatogr. B* 717 (1998) 157.
- [65] M.J.M. Wells, D.D. Riemer, M.C. Wells-Knecht, *J. Chromatogr. A* 659 (1994) 337.
- [66] R.D. Wauchope, T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers, J.P. Burt, in: G.W. Ware (Ed.), *Reviews of Environmental Contamination and Toxicology*, Vol. 123, Springer-Verlag, New York, 1992.