Anal. Chem. **2000,** *72,* 481−488

Static Subcritical Water Extraction Combined with Anion Exchange Disk Sorption for Determining Chlorinated Acid Herbicides in Soil

Xianwen Lou, David J. Miller, and Steven B. Hawthorne*

Energy and Environmental Research Center, University of North Dakota, Box 9018, Grand Forks, North Dakota 58202-9018

Static subcritical water extraction (SbWE) was coupled with collection on a strong anion exchange (SAX) disk for the determination of chlorinated acid herbicides and their esters in soil. With 100−150 °C water, esters were hydrolyzed into their acid form, and the herbicide acids extracted by subcritical water were trapped onto/into a SAX disk as the extraction cell was cooled. The trapped solutes were then derivatized for gas chromatographic (GC) analysis by placing the disk into a GC autosampler vial containing 1 mL of *N,O*-bis(trimethylsilyl)trifluoroacetamide derivatizing reagent. With the static SbWE/SAX disk extraction, nearly quantitative recoveries (typically over 80%) were obtained at 100 °C for 30 min in the extraction of herbicide acids and esters spiked on several different soils covering a range of organic content from 0.3 to 12%. Good agreements were reached between this method and EPA method 8151 for aged spiked soils. Detection limits of the static SbWE/SAX disk extraction were from 0.05 to 0.5 ppm and from 0.01 to 0.5 ppm using GC/electron capture detector and GC/mass spectrometry, respectively. The method is fast and simple and uses a small amount of organic solvent.

Herbicides are important tools for suppressing unwanted species of plants. In the United States, millions of pounds of various herbicides are used annually. Among these, the chlorinated acid herbicides constitute a major class that has found wide applications in agriculture.[1,2] The conventional methods for analyzing the chlorinated acid herbicides can be complicated, especially for solid samples such as soil. Prior to chromatographic analysis, repeated operations of extraction, concentration, and cleanup can be required, which are both time- and solvent-consuming. In the past few years, various new sample preparation techniques, such as microwave-assisted extraction (MAE)[3,4] sonication extraction,[5,6] supercritical fluid extraction (SFE),[7,8] and accelerated solvent extraction (ASE)[9,10] have been developed, aiming to reduce the solvent required and/or shorten the sample preparation time. Unfortunately, only limited applications of these new methods in the analysis of chlorinated acid herbicides have been reported.[11,12]

Recently, subcritical water has been demonstrated to be a useful analytical fluid for a range of polar and nonpolar organics in environmental solid samples.[13,14] Water is inexpensive and environmentally friendly, and its polarity (measured by its dielectric constant) can be adjusted simply by changing the temperature. For the extraction of chlorinated acid herbicides from solid samples, subcritical water may be a good solvent since most of these compounds exhibit fairly high solubility in water. Furthermore, as will be demonstrated later in this report, if herbicide esters are also present in the sample, water can hydrolyze some esters into their acid forms at suitable conditions. This means that the hydrolysis step, if required, might be performed simultaneously during the extraction process. Another potential advantage of using subcritical water extraction (SbWE) is that many standard methods developed for water analysis can be used directly for further pretreatment of the extracts, or the pretreatment steps can be combined with the extraction process. Hageman et al.[15] and Daimon and Pawliszyn[16] showed that coupling SbWE with solid-phase microextraction (SPME) is a rapid method for the analysis of compounds such as polycyclic aromatic hydrocarbons (PAHs). With this method, no organic solvents are required and only simple and inexpensive equipment is utilized. Field et al.[17] combined SbWE with a strong anion extraction (SAX) disk followed by derivatization with ethyl iodide

* Corresponding author: (e-mail) shawthorne@eerc.und.nodak.edu; (fax) +701-777-5181.

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10.1021/ac990787f CCC: $19.00
Published on Web 12/30/1999

for the analysis of Dacthal. No cleanup steps were required, and only small amounts of organic solvent were consumed. Although only Dacthal was reported in their article, the combination of SbWE with an anion extraction disk appears to be a potential method for the analysis of herbicide acids.

In the present contribution, the potential of combined SbWE/SAX disk extraction is further investigated with the objective to develop an easy, robust, and field-portable method for the analysis of chlorinated acid herbicides from contaminated solids. Experiments are performed by simply placing the sample and a SAX disk into an extraction cell, adding water, and heating the system in an oven. The experimental setup is very simple, and no pump is included in the system. After extraction, the cell is cooled and the target compounds trapped in the disk are derivatized. Five derivatizing reagents are studied and compared. The conditions for the extraction are systematically studied and optimized. The method is applied to aged spiked samples, and the results are compared with the data obtained in a contract laboratory using a conventional method. Finally, the detection limits of the method are evaluated by gas chromatography (GC)/electron capture detector (ECD) and GC/mass spectrometry (MS).

EXPERIMENTAL SECTION

Samples. The clean sea sand was purchased from Fisher Scientific (Pittsburgh, PA). The sandy soil (0.3% w/w of organic matter) and agricultural soil (2% w/w of organic matter) were obtained from New Mexico (USA) and Alberta (Canada). The garden soil (∼12% w/w of organic matter) was collected locally and then sieved to <6 mm to remove debris. Neither soil had detectable levels of the target analytes before spiking.

In the preparation of the aged spiked samples, the herbicide acids or esters were first added to a suitable volume of hexane in a wide-mouth bottle. Then a known amount of soil (either agricultural soil or the garden soil) was added carefully to the bottle. The volume of hexane was large enough to entirely immerse the soil. After the addition of soil, the slurry was mixed frequently until the solvent was almost completely evaporated (∼4 h). The bottles were left open for four more hours, then the samples were capped and aged at ambient conditions for 40 days before analysis.

Standards and Materials. The analytical standards of herbicide acids and esters were purchased as ampulized solutions from Absolute Standards (Hamden, CT). The internal standards, 4,4′-dibromooctafluorobiphenyl (DBOB) and 2,4-dichlorophenylacetic acid (DCAA) were obtained from Aldrich (Milwaukee, WI). Methyl iodide and ethyl iodide were purchased from Lancaster (Windham, NH), and BF_3−methanol (10% w/w), *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and BSTFA + trimethylchlorosilane (TMCS) (99:1) from Supelco (Bellefonte, PA). The SAX disks were Empore brand from 3M (St. Paul, MN).

Coupled Subcritical Water/SAX Disk Extraction. SAX disks must be preconditioned to provide good contact between the sorbent and water. A general procedure of conditioning is to wet the disk with acetone, 2-propanol, methanol, and water in succession with applied vacuum.[18] For all experiments, 9 cm diameter disks were conditioned with acetone, 2-propanol, methanol, and water, cut into 1 cm diameter circles, and stored in clean water prior to use.

All extractions were performed using Wheaton V-vials with screw-top lids (Aldrich). Although the supplier designates these as 3 mL vials, they actually have a total volume of 4.6 mL when capped with a solid-top cap with a Teflon-faced, styrene−butadiene rubber liner. Before extraction, the 1.5 g soil sample was loaded into the V-vial, 2.5 mL of HPLC-grade water was added, and a 1 cm diameter SAX disk was placed into the vial. After capping, this left a ∼1 mL headspace in the cell, which serves to maintain the equilibrium pressure during the heating step. (Safety note: A static cell such as those used in this study must **NEVER** be completely filled or excessive pressures will result upon heating. A gas headspace must always be left in the cell so that the internal pressure is controlled by the steam/equilibrium pressure[19]). For extraction, the vial was fixed into a rotator (45 cycles/min; faster rotations can reduce mixing) located in a Hewlett-Packard (Palo Alto, CA) 5890 GC oven and heated to the desired temperature. Once the heating process was complete, the vial was cooled in the GC oven (with rotation) to room temperature (∼15 min). The SAX disk was removed from the vial and partially dried by blotting with a piece of tissue paper. The disk was placed in a 2 mL autosampler vial for derivatization. No additional separation step of the trapped compounds from the disk was employed either before or after derivatization. The disk remained in the autosampler vial, and the vial was placed directly onto the autosampler for GC analysis.

Derivatization of Herbicide Acids from the Disk. *Esterification with Methyl or Ethyl Iodide.* According to the method of Field and Monohan,[20] the disk was placed into an autosampler vial containing 1 mL of acetonitrile and 100 μL of methyl or ethyl iodide. The vial was capped and heated to 100 °C for 1 h.

Esterification with BF_3−Methanol (10% w/w). The disk was placed into an autosampler vial containing 1 mL of reagent. The vial was then capped and heated to 60 °C for 1 h.[21]

Silylation. The disk was added to an autosampler vial containing 1 mL of either BSTFA or TMCS−BSTFA. The vial was capped and heated to 70 °C for 30 min.[22]

Gas Chromatography Analysis. GC separations were carried out with a Hewlett-Packard 5890 series II gas chromatograph equipped with a split/splitless injector (held at 320 °C) and an electron capture detector. The GC/ECD experiments were performed with an HP5 capillary column (20 m × 0.32 mm i.d., 0.25 μm film thickness). The initial temperature was 100 °C (1 min), which was then ramped at 10 °C/min to 280 °C.

In addition to GC/ECD, GC/MS was also employed for the estimation of detection limits. The GC/MS analyses were carried out with a Hewlett-Packard model 5973 GC/MS equipped with a split/splitless injector. The GC column used was an HP5-MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The same temperature programming as that used in GC/ECD was used for GC/MS.

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Table 1. Comparison of the Performances of Different Derivatization Reagents for Chlorinated Herbicide Acids Spiked on an Anion Exchange Disk

	CH_3I	C_2H_5I	CH_3OH (10% BF_3)	BSTFA	BSTFA (1% TMCS)
time (min)	60	60	60	30	30
temp (°C)	100	100	60	70	70
efficiency (%)	0−50[a]	0−50[a]	10−90	>80[b]	>80[b]
resulting solution	clear	clear	turbid	clear	clear
GC compatibility	poor	poor	poor	good	acceptable

[a] Quantitative only for dacthal acid, but not for other herbicides. [b] Except dacthal acid.

RESULTS AND DISCUSSION

Derivatization Strategies. In coupled SbWE/SAX disk extraction, the solutes are first extracted from a solid sample into subcritical water and then transferred from water into the disk. After extraction, the solutes are eluted from the disk, derivatized, and analyzed by GC. In initial experiments, five derivatizing reagents, C_2H_5I, CH_3I, BF_3/CH_3OH (10%), BSTFA, and TMCS−BSTFA (1%) were tested by spiking a standard acid herbicide solution on a disk followed by placing the disk in an autosampler vial and derivatizing directly with the reagents. Results are summarized in Table 1.

Field et al.[17] reported that quantitative derivatization of dacthal acids was obtained by using ethyl iodide, which was also confirmed independently in our experiments. However, for the other herbicide acids tested, the recoveries were very low (<50%). Similar results were also obtained by using methyl iodide. In addition to the poor recoveries, acetonitrile, which shows a serious tailing peak in GC especially with ECD as the detector, was employed as the solvent for the reactions using the iodides.

When the acids were derivatized with BF_3-CH_3OH, recoveries were found to be strongly dependent on the identity of the acids. Among the herbicides tested, good recoveries (>80%) were obtained for 2,4-D, 2,4,5-T, and 2,4,5-TP, but very low recoveries were observed for the other compounds, such as dicamba (∼10%). Furthermore, the resultant solution became turbid, probably because some small particles were released from the disk by BF_3-CH_3OH. Another disadvantage of using BF_3-CH_3OH is that methanol is not a desirable solvent for GC analysis, which means that some additional steps might be required to remove methanol after derivatization and redissolve the residue in other suitable solvents.

Fortunately, good results were obtained by employing BSTFA as the derivatization reagent (see Table 2). It is well known that for the analysis of compounds containing protonic functional groups like organic acids, alkylsilylation is a versatile method. The most common derivatizing reagents are the trimethylsilyl (TMS) reagents. BSTFA is generally the preferred reagent for trimethylsilylation of carboxylic acids because BSTFA and its byproducts are volatile and cause little chromatographic interference.[23] BSTFA can be used without additional organic solvent, and the resultant solution after derivatization can directly be introduced into the GC system without any damage to it. In fact, BSTFA has successfully been used for the deactivation of a wide range of GC and supercritical fluid chromatography (SFC) columns.[24] In our experiments, more than 1000 injections of the BSTFA derivatives have already been made and no noticeable impairment to the GC performance has been observed. (It should be noted that the water content on the disk after the subcritical water extraction may affect the efficiency of some reagents, as discussed later in the text for BSTFA.)

The completeness of derivatization using BSTFA was confirmed in an indirect way since no standard herbicide−TMS derivatives were available. To produce a frame of reference, the reactions were first carried out without a disk according to a standard procedure.[22] About 20 μg of each herbicide acid was added to an empty autosampler vial and derivatized with 0.5 mL of BSTFA at 70 °C for 30 min. Similar experiments were also performed with 1 mL of reagent, or at higher temperatures (100 °C) or longer times (60 min), and no considerable variation was observed in the derivatizing efficiency. In addition, TMCS−BSTFA, which is considered to be a stronger reagent, was also used for silylation. The results are listed in Table 2. It can be seen clearly from this table that very good agreements were obtained between these two reagents. Furthermore, the relative responses of the herbicide−TMS derivatives to an internal standard were found to be quite comparable to the values of their corresponding methyl esters/ethers having the same concentration. From these results, it can be concluded that the herbicide acids can quantitatively be derivatized with 0.5 mL of BSTFA at 70 °C for 30 min. In the following experiments, 1 mL of BSTFA was used because the reagent was purchased in ampulized vials of 1 mL, and 1 mL is a convenient volume for use in the GC autosampler.

The ability of BSTFA to derivatize the herbicide acids directly from a SAX disk was then evaluated by comparing the silylation results to those of the reference (without a disk). It is interesting to see from Table 2 that the results are in very good agreement, except for dacthal acid (a diacid). Therefore, except for dacthal acid, the herbicides spiked on the disk can quantitatively be recovered and derivatized with BSTFA. Another independent support for this is that second derivatization (with new reagent) of the derivatized disk yields no detectable solutes. Hence, the presence of a disk has no apparent influence on the results. No isolation of the herbicides from the disk is required before or after derivatization, and the disk can remain in the autosampler vial, which helps to simplify the analysis. TMCS−BSTFA also gave good recoveries, but its byproduct HCl should be removed before GC analysis. Therefore, in the following sections, BSTFA is used exclusively as the derivatizing reagent. The data of dacthal acid were not included because of its poor recovery from the disk. For its analysis, interested readers are referred to a recent article.[17]

Extraction of Herbicide Acids from Spiked Water at Elevated Temperatures. Originally, the extraction disk was developed for water analysis. By applying vacuum (at room temperature), large amounts of water can rapidly be pulled through the disk while the solutes are being concentrated.[18] However, in static SbWE/SAX disk extraction, the disk is placed into a closed vial together with the soil sample and water and heated. The thermal stability of the disk was investigated by

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Table 2. Relative Peak Areas of Herbicide TMS Derivatives and Their Methyl Esters/Ethers to an Internal Standard in GC/ECD[a]

	herbicide acids			methyl esters/ethers, BSTFA (disk)
	BSTFA (no disk)	TMCS−BSTFA (no disk)	BSTFA (disk)	
phenols				
4-nitrophenol	0.83 (1.0)[b]	0.84 (1.9)	0.81 (0.6)	0.51 (2.1)
pentachlorophenol	5.19 (1.0)	5.22 (1.8)	5.17 (0.6)	4.81 (2.1)
dinoseb[c]	1.32 (5.8)	1.32 (7.9)	1.05 (10)	1.31 (7.0)
chlorinated benzoic acids				
3,5-dichlorobenzoic acid	1.04 (0.6)	1.05 (3.4)	1.00 (1.8)	0.50 (2.6)
dicamba	1.56 (0.8)	1.51 (4.1)	1.46 (1.9)	1.30 (0.4)
chlorinated benzoic diacid				
dacthal acid	1.95 (2.6)	1.92 (6.4)	0.64 (20)	2.57 (4.1)
chlorinated phenoxy acids				
2,4-DP	0.44 (0.8)	0.44 (2.4)	0.47 (1.5)	0.41 (0.5)
2,4-D	0.50 (1.0)	0.50 (4.6)	0.53 (1.7)	0.53 (2.6)
2,4,5-TP	1.87 (1.1)	1.85 (4.3)	1.94 (1.2)	2.09 (1.6)
2,4,5-T	1.93 (1.2)	1.87 (6.0)	1.99 (1.2)	2.09 (1.1)
2,4-DB[c]	0.27 (0.8)	0.29 (1.6)	0.26 (7.3)	0.22 (1.5)
chlorinated acids with amino or nitro substituents				
chloramben	1.17 (1.8)	1.08 (4.0)	1.31 (1.6)	1.59 (3.8)
picloram	2.22 (5.8)	2.09 (6.5)	1.76 (10)	1.60 (8.5)
acifluorfen	1.91 (2.9)	1.81 (2.7)	2.06 (2.8)	1.65 (11)

[a] Internal standard: 4,4′-dibromooctafluorobiphenyl. [b]Relative standard deviations (%) based on triplicate determinations. [c]Tested as single compounds because of the coelution of 2,4-DB and dinoseb.

Table 3. SAX Disk Extraction Recoveries of Herbicide Acids Spiked in Water after Exposure to Elevated Temperatures[a]

	100 °C	125 °C	150 °C
phenols			
4-nitrophenol	73 (1.7)[b]	57 (2.4)	50 (6.8)
pentachlorophenol	94 (0.3)	92 (1.7)	89 (3.2)
dinoseb[c]	43 (15)	53 (9.5)	47 (5.0)
chlorinated benzoic acids			
3,5-dichlorobenzoic acid	92 (0.4)	89 (0.5)	83 (3.2)
dicamba	90 (2.7)	87 (1.7)	80 (3.6)
chlorinated phenoxy acids			
2,4-DP	98 (0.2)	98 (1.2)	92 (4.6)
2,4-D	102 (0.2)	101 (1.0)	99 (5.4)
2,4,5-TP	99 (1.8)	96 (3.0)	92 (3.9)
2,4,5-T	101 (2.2)	99 (2.6)	98 (5.0)
2,4-DB[c]	92 (0.9)	84 (5.3)	67 (1.3)
chlorinated acids with amino or nitro substituents			
chloramben	90 (2.2)	77 (2.5)	63 (3.9)
picloram	63 (15)	69 (12)	67 (25)

[a] Extraction time 30 min, followed by cooling the cell to room temperature before removing the disk for derivatization. [b] Relative standard deviations (%) based on triplicate determinations. [c]Tested as single compounds because of the coelution of 2,4-DB and dinoseb.

extracting spiked herbicide acids from water at various temperatures for 30 min. It should be mentioned here that, unlike directly spiking on the disk where the acids may not be in the ion form and only weakly retained by the disk, the herbicides extracted from water may be more strongly bonded to the disk through ion exchange. The extraction results of the herbicides at different temperatures are listed in Table 3. The data here are the overall recoveries of extraction from water and derivatization. From Table 3 it can be seen that nearly quantitative recoveries were obtained for most herbicide acids even after exposure to the highest temperature tested (150 °C). The lower recoveries in Table 3 were probably due to thermal degradation and not because of the extraction capability of the SAX disk since no compounds were extracted by a second disk placed in the same spiked water solutions. This indicates that the SAX disk can be used at temperatures up to 150 °C. Temperatures above 150 °C were not investigated because of the potential analyte degradation, as well as the maximum allowable temperature of the glass V-vial.

In the experiments above, only the loose water on the disk was dried by a piece of tissue paper. The disk was then directly derivatized with BSFTA. It is interesting to note that if the disk was excessively dried, e.g., by vacuum suction, the herbicide acids trapped on/in the disk could only be poorly (10−20%) recovered. Considerably higher but still not complete recovery of the acids could be obtained with the addition of a few microliters of water to the dried disk. The reason for this is still not fully understood. Most likely, during the process of extraction, the solutes penetrated into the water-swollen disk. If the disk was completely dried, it would shrink, and the BSTFA reagent could not penetrate into it and react with the acids. This is in sharp contrast with the situation where the acids were directly spiked on an unconditioned disk. In this case, the acids were on the disk surface and could readily be derivatized by BSTFA.

Extraction of Herbicide Acids from Spiked Solids. It has been demonstrated above that the SAX disk can be used at elevated water temperatures. To investigate the applicability of the static SbWE/SAX disk extraction method to solid samples, the herbicides were spiked onto four soils with different organic contents, i.e., clean sea sand, sandy soil (0.3% w/w of organic matter), agricultural soil (2% w/w of organic matter), and garden soil (~12% w/w of organic matter).

Table 4 shows the effects of temperature on the extraction of herbicide acids from clean sea sand and agricultural soil in 30 min. For both samples, the extraction recoveries were found to

Table 4. Effects of Extraction Temperature on the Recovery (%) of Herbicide Acids Spiked on Soils[a]

	sea sand				agricultural soil			
	75 °C	100 °C	125 °C	150 °C	75 °C	100 °C	125 °C	150 °C
phenols								
4-nitrophenol	56 (4.3)[b]	85 (1.5)	69 (0.6)	60 (1.6)	56 (2.5)	90 (6.2)	79 (3.2)	50 (6.2)
pentachlorophenol	81 (0.5)	92 (1.0)	94 (1.5)	86 (0.9)	67 (9.4)	88 (7.6)	77 (6.6)	61 (5.6)
dinoseb[c]		42 (12)				47 (11)		
chlorinated benzoic acid								
3,5-dichlorobenzoic acids	87 (4.7)	93 (2.5)	92 (1.8)	84 (1.4)	79 (2.6)	90 (6.1)	87 (1.5)	82 (4.7)
dicamba	78 (0.7)	92 (0.5)	91 (1.8)	79 (2.5)	62 (6.0)	76 (6.8)	72 (1.7)	57 (8.4)
chlorinated phenoxy acids								
2,4-DP	91 (2.1)	99 (0.4)	99 (3.4)	93 (2.0)	80 (5.2)	96 (6.1)	92 (4.5)	81 (8.5)
2,4-D	84 (2.6)	103 (1.2)	107 (1.1)	101 (2.4)	74 (5.9)	93 (6.3)	87 (2.8)	73 (9.3)
2,4,5-TP	87 (1.8)	100 (1.0)	101 (1.5)	92 (1.4)	74 (7.4)	92 (6.3)	92 (2.3)	77 (5.6)
2,4,5-T	83 (2.6)	101 (1.9)	104 (1.8)	96 (1.5)	69 (7.4)	92 (7.6)	91 (3.2)	72 (7.2)
2,4-DB[c]		93 (3.9)				90 (6.1)		
chlorinated acids with amino or nitro substituents								
chloramben	89 (5.0)	90 (2.2)	78 (5.4)	56 (9.1)	68 (10)	90 (8.0)	86 (3.9)	63 (12)
picloram	53 (20)	69 (9.9)	82 (8.8)	76 (12)	50 (7.4)	71 (7.6)	74 (8.9)	31 (44)
acifluorfen	75 (11)	108 (7.3)	119 (4.9)	105 (3.2)	66 (11)	95 (9.5)	94 (3.3)	58 (29)
surrogate								
2,4-dichlorophenylacetic acid	80 (2.1)	92 (2.5)	86 (4.1)	83 (2.8)	67 (3.0)	88 (4.9)	84 (1.4)	76 (3.6)

[a] Extraction time 30 min, followed by cooling the cell to room temperature before removing the disk for derivatization, disk lot number 720006. [b]Relative standard deviations (%) based on triplicate determinations. [c]Only tested at 100 °C as single compounds because of the coelution of 2,4-DB and Dinoseb.

increase when the temperature was raised from 75 to 100 °C, and good results were obtained at 100 °C. When the acids were spiked on sea sand, their recoveries were quite close to those from spiked water. Similar results were also observed from the spiked agricultural soil if the extractions were carried out at 75 and 100 °C. However, at 150 °C, the recoveries from the agricultural soil were considerably lower than those from the spiked water. As discussed above for spiked water samples, degradation of some of the herbicides may occur at high temperatures and such degradation may be accelerated in the presence of soil. In addition, the originally white SAX disks turned dark brown after the 150 °C extractions of the agricultural soil compared to only being lightly colored for lower temperature extractions. The dark color implies that more soil matter is extracted at higher temperatures and trapped in the disk. The matrix compounds might compete with the herbicide acids for the ion exchange sites and unfavorably affect their distribution from water into the disk.

Since the previous results indicated that the efficiency of the method could be affected by the extracted soil compounds, herbicide acids were also spiked on a very rich garden soil (∼12% w/w of organic matter). Here again, the recoveries were found to increase when the extraction temperature was raised from 75 to 100 °C and then decrease at higher temperatures. Reasonable results were also obtained at 100 °C (Table 5), as was the case for sand and agricultural soil (Table 4). Increasing the extraction time from 30 to 60 min showed no significant change in recoveries. Therefore, all subsequent extractions were performed at 100 °C for 30 min.

In the experiments described above, only SAX disks with the lot number of 720006 were used and good results were obtained at 100 °C for all the spiked soils tested. To find out if the same results could also be obtained with different lots of the disks, similar experiments were repeated at 100 °C with disks of lot 720087. For the sea sand, agricultural soil, and sandy soil, no considerable difference in recoveries was observed when SAX disks with different lot numbers were used. However, the recoveries from the garden soil were significantly lower with lot 720087 than with lot 720006 (Table 5). This is probably due to the variation of the disk capacity among different lots. Since only the recoveries from the rich garden soil were affected by the disk lot number, it seems likely that the coextracted matrix compounds may compete with the herbicide acids for the active sites of the disk. Increasing disk size (or adding more disks) might improve the extraction, but it was not practical because the additional water held by the swollen disks would result in a gelled solution with the derivatization reagent (BSTFA).

Fortunately, for the analysis of a complex sample, a surrogate internal standard, which has properties similar to that of the solutes and goes through all the analytical steps, can be useful. According to the EPA method 8151A, DCAA was selected as the surrogate. By spiking DCAA on the soil prior to extraction, the performance of the overall experiment can be monitored. From Table 5 it can be seen that if the surrogate could quantitatively be recovered, so could most of the herbicide acids. A low recovery of the surrogate indicates poor performance of the method for the herbicides. For example, when a disk with lot 720087 was used for the analysis of the garden soil, only ∼50% of the surrogate and the herbicides could be recovered. It is interesting to see from Table 5 that, despite the significantly decreased recoveries in this case, acceptable results could still be obtained if they were calculated relative to the surrogate. Therefore, it is always recommended that, in the analysis of real world samples, a surrogate internal standard should be added.

Extraction of Herbicide Esters and Ethers from Spiked Soils. When herbicide esters and ethers are to be analyzed, they must first be hydrolyzed into the acid form before being trapped to the SAX disk. In pure water, only a small amount (0−40%) of the esters were hydrolyzed even at 150 °C. Fortunately, for some

Table 5. Effects of Extraction Temperature and Disk Lot Number on the Extraction Recovery (%) of Herbicide Acids from a Garden Soil[a]

	disk lot 720006			disk lot 720087, 100 °C	
	75 °C	100 °C	125 °C		relative to surrogate
phenols					
4-nitrophenol	92 (3.2)[b]	93 (3.7)	76 (2.0)	54 (6.4)	113 (0.8)
pentachlorophenol	63 (5.0)	74 (1.6)	65 (4.2)	65 (1.0)	135 (8.2)
dinoseb[c]		51 (3.2)		48 (2.8)	100 (6.8)
chlorinated benzoic acids					
3,5-dichlorobenzoic acid	78 (3.1)	94 (3.6)	80 (0.6)	64 (5.0)	134 (1.0)
dicamba	65 (2.4)	78 (1.5)	63 (1.1)	45 (6.1)	95 (1.2)
chlorinated phenoxy acids					
2,4-DP	81 (1.8)	95 (3.6)	80 (1.0)	65 (2.1)	135 (3.1)
2,4-D	80 (2.1)	97 (2.0)	82 (1.3)	60 (4.5)	126 (2.2)
2,4,5-TP	79 (2.1)	90 (1.5)	83 (2.4)	63 (3.5)	132 (3.3)
2,4,5-T	78 (2.1)	90 (2.3)	80 (3.1)	58 (5.4)	121 (1.6)
2,4-DB[c]		75 (7.8)		51 (9.3)	107 (2.2)
chlorinated acids with amino or nitro substituents					
chloramben	70 (2.7)	80 (3.3)	57 (3.7)	54 (9.4)	112 (0.5)
picloram	52 (6.5)	65 (5.6)	57 (9.8)	27 (30)	57 (15)
acifluorfen	89 (3.7)	98 (6.9)	94 (7.3)	65 (3.3)	136 (4.7)
surrogate					
2,4-dichlorphenylacetic acid	76 (4.3)	86 (1.0)	75 (0.9)	48 (6.3)	

[a] Extraction time 30 min, followed by cooling the cell to room temperature before removing the disk for derivatization. [b]Relative standard deviations (%) based on triplicate experiments. [c] Only tested at 100 °C because of the coelution of 2,4-DB and dinoseb.

Table 6. Recovery (%) of Herbicide Methyl Esters/Ethers Spiked on Different Soils[a]

	sandy soil		agricultural soil		garden soil	
	20 °C, 24 h	100 °C,[b] 30 min	20 °C, 24 h	100 °C,[b] 30 min	20 °C, 24 h	100 °C,[b] 30 min
phenols						
4-nitrophenol	nd[c]	nd	nd	nd	nd	nd
pentachlorophenol	nd	15 (10)[d]	nd	6.5 (2.8)	nd	4.9 (5.2)
dinoseb[e]	nd	nd	nd	nd	nd	nd
chlorinated benzoic acids						
3,5-dichlorobenzoic acid	21 (11)	66 (3.4)	75 (3.6)	58 (7.5)	87 (5.3)	41 (7.5)
dicamba	nd	nd	nd	nd	nd	nd
chlorinated phenoxy acids						
2,4-DP	66 (8.8)	72 (5.9)	85 (1.9)	72 (6.6)	97 (5.3)	76 (6.6)
2,4-D	83 (8.9)	81 (4.4)	81 (4.4)	80 (7.3)	102 (6.2)	92 (7.3)
2,4,5-TP	65 (8.7)	85 (6.2)	79 (5.4)	70 (6.6)	99 (4.1)	77 (3.6)
2,4,5-T	99 (8.4)	96 (4.4)	82 (9.9)	85 (6.8)	108 (5.6)	89 (6.5)
2,4-DB[e]	79 (8.0)	23 (16)	92 (6.0)	48 (6.2)	89 (3.6)	36 (3.6)
chlorinated acids with amino or nitro substituents						
chloramben	nd	15 (5.3)	35 (13)	18 (3.9)	84 (3.6)	11 (3.5)
picloram	3.9 (9.5)	16 (10)	17 (42)	21 (8.1)	47 (20)	18 (16)
acifluorfen	3.8 (11)	59 (4.8)	5.8 (36)	35 (7.1)	19 (15)	7.4 (11)
surrogate						
2,4-dichlorophenylacetic acid	103 (0.8)	86 (5.8)	93 (3.3)	86 (4.7)	95 (4.0)	86 (8.5)

[a] Recoveries based on the acids hydrolyzed from the esters; SAX disk with lot 720006. [b] The extraction cell was cooled before removing the disk for derivatization. [c] nd, not detectable. [d] Relative standard deviations (%) based on triplicate experiments. [e] Tested as single compounds because of the coelution of 2,4-DB and dinoseb.

esters, hydrolysis is considerably easier in the presence of soil. Even at room temperature and simple rotation together with the soil, water, and disk, the chlorinated phenoxy herbicide esters (2,4-DP, 2,4-D, 2,4,5-TP, 2,4,5-T, 2,4-DB) were significantly hydrolyzed in 24 h (Table 6). The results coincide with the findings that the chlorinated phenoxy herbicide esters can fairly quickly (e.g., a few days) be hydrolyzed into acids in agricultural fields.[1,25] Hydrolysis of these compounds could also be achieved during the extraction process (e.g., 100 °C, 30 min). However, for the other groups of herbicides, i.e., the phenol ethers and the esters of chlorinated benzoic acids and of acids substituted with amino or nitro groups, much lower levels of or even no hydrolysis was observed (Table 6).

Fortunately, the chlorinated acid herbicides are usually not applied in the ester/ether form, except for the phenoxy esters.[1,26] As discussed above, the phenoxy esters can readily be hydrolyzed in the presence of soil. Therefore, the herbicide esters applied in agriculture can easily be transformed into the acid form either in

(25) Zepp, R. G.; Wolfe, N. L.; Gordon, J. A.; Baughman, G. L. *Environ. Sci. Technol.* **1975**, *9*, 1144−1150.

Table 7. Comparison of Concentrations (ppm) of Aged Spiked Soils (1 ppm of Each Analyte) Using Static SbWE/SAX Disk Extraction and EPA Method 8151

	agricultural soil		garden soil	
	SbWE/SAX[b]	EPA 8151[c]	SbWE/SAX	EPA 8151
acids/phenols[a]				
4-nitrophenol	1.3 (18)[d]	nd[e]	1.0 (22)	nd
pentachlorophenol	0.75 (8.8)	nd	0.65 (23)	nd
dinoseb [f]	0.42 (9.0)	0.90	0.46 (3.9)	0.75
3,5-dichlorobenzoic acid	0.80 (6.9)	nd	0.85 (14)	nd
dicamba	0.61 (9.6)	0.92	0.75 (8.4)	0.93
2,4-DP	0.89 (2.7)	0.96	1.2 (15)	0.95
2,4-D	0.85 (14)	0.95	1.1 (9.9)	0.96
2,4,5-TP	0.69 (7.2)	0.73	0.76 (10)	0.71
2,4,5-T	0.60 (12)	0.86	0.69 (8.6)	0.79
2,4-DB[f]	0.71 (3.3)	1.0	0.68 (12)	0.96
chloramben	0.60 (5.6)	nd	0.48 (11)	nd
picloram	0.34 (39)	nd	0.64 (7.8)	nd
acifluorfen	0.54 (16)	nd	0.82 (10)	nd
surrogate recovery (%)[g]	88 (4.8)	119	86 (3.6)	122
esters[h]				
2,4-DP	1.3 (8.5)	0.90	1.3 (14)	1.00
2,4-D	1.3 (2.5)	0.90	1.0 (9.7)	1.00
2,4,5-T	0.95 (1.7)	0.68	0.71 (16)	0.77
2,4,5-T	0.93 (3.0)	0.80	0.71 (18)	0.87
2,4-DB [f]	0.70 (10)	0.92	0.75 (8.3)	1.00
surrogate recovery (%)[g]	89 (5.0)	119	86 (2.5)	125

[a] Acids/phenols spiked on agriculture soil and garden soil at ~1 ppm level, respectively, and aged for 40 days. [b] Static SbWE/SAX disk extraction at 100 °C for 30 min, followed by cooling the cell to room temperature before removing the disk for derivatization, determined by GC/ECD. [c]Conventional method carried out in a contract laboratory. [d] Relative standard deviations (%) based on triplicate experiments. [e] Not determined by EPA method 8151. [f] Determined by GC/MS because of the coelution of 2,4-DB and dinoseb. [g] 2,4-Dichlorophenylacetic acid. [h] Esters spiked on agriculture soil and garden soil at ~1 ppm level, respectively, and aged for 40 days.

Table 8. Detection Limits (ppm) To Determine Acidic Herbicides by SbWE/SAX Disk Extraction Using GC/ECD and GC/MS[a]

		GC/MS		
	GC/ECD, ppm	ppm	monitored ion	EPA 8151,[b] ppm
phenols				
4-nitrophenol	0.50	0.01	196	
pentachlorophenol	0.05	0.01	323	
dinoseb	*c*	0.05	297	0.5
chlorinated benzoic acids				
3,5-dichlorobenzoic acid	0.25	0.01	173	
dicamba	0.25	0.05	203	0.2
chlorinated phenoxy acids				
2,4-DP	0.50	0.10	308	0.2
2,4-D	0.50	0.50	233	0.2
2,4,5-TP	0.25	0.10	342	0.04
2,4,5-T	0.25	0.10	326	0.2
2,4-DB	*c*	0.05	159	0.4
chlorinated acids with amino or nitro substituents				
chloramben	0.25	0.01	262	
picloram	0.05	0.01	371	
acifluorfen	0.05	0.01	418	

[a] Herbicide acids spiked on an agriculture soil and extracted at 100 °C for 30 min. [b] Detection limits ("practical quantitation limits") reported by the contract laboratory. [c] Not evaluated because of the coelution of 2,4-DB and dinoseb.

the field or during the extraction process and analyzed by the static SbWE/SAX disk extraction. The optimized conditions for the extraction of acids (100 °C, 30 min) were also found to be suitable for the analysis of these esters.

Extraction of Herbicides from Aged Spiked Samples. In the experiments described above, only freshly spiked samples were extracted. Freshly spiked analytes can typically be extracted more efficiently and rapidly. Therefore, high recoveries of freshly spiked samples do not necessarily yield the same results for real world samples. In the validation of an extraction method, certified samples are frequently used. Unfortunately, suitable certified samples for the chlorinated acid herbicides are not available. Therefore, four different aged spiked samples at the ~1 ppm level were analyzed. These samples were prepared by spiking herbicide acids or esters on the agricultural soil and the garden soil, respectively, and aging for 40 days before extraction. The extraction conditions optimized before, i.e., at 100 °C and 30 min, were applied for these samples and the results compared to those obtained in a contract laboratory using EPA method 8151. As shown in Table 7, the results obtained using the static SbWE/SAX disk extraction are in reasonably good agreement with those obtained using the conventional method for both the herbicide acids and those commonly applied as esters. (Note that none of the data in Table 7 is adjusted for surrogate recovery. If surrogate recoveries were used, the results from the contract laboratory would be lower by −20%, while the results from our method would increase by −10 to +15%.) Unlike the conventional method, which requires multiple steps of extraction, concentration, cleanup, hydrolysis, and diazomethane derivatization, the SbWE/SAX disk extraction technique is a fast method and consumes very small amounts of organic solvents. The total analysis time, including extraction, derivatization, and GC separation, is less than 2 h and the apparatus required is very simple.

Detection Limits. The detection limits were estimated based on a 1.5 g soil sample and the lowest detectable peak that has S/N from 3 to 6. Detection limits are determined by many parameters such as the properties of the analyte, the efficiency of the GC separation and the sensitivity and selectivity of the detector, any interferences from the sample matrix and the reagents, and extraction efficiencies. To determine the detection limits, herbicide acids were spiked on the agricultural soil at several concentrations. Extractions were carried out at 100 °C for 30 min, and the disk was derivatized as before (no changes to the method were made in an effort to increase sensitivity). Detection limits on GC/ECD are listed in Table 8. Depending on the identity of the herbicides, detection limits on GC/ECD were found to be in the range of 0.05−0.5 ppm (μg/g of soil).

For most of the herbicides tested, the detection limits by GC/MS were improved due to the selective MS detector (Table 8). However, for some, like 2,4-DP, the improvement is much smaller because of the lack of intense and unique ions in their MS spectra. For these compounds, the most sensitive ion (m/z) is 73. If this ion is selected for analysis, extracted matrix compounds that can be derivatized by BSTFA will give enormous interferences since this ion is typical for TMS derivatives, as well as for GC column degradation products. Therefore, much less sensitive ions have

(26) Worthing, C. R.; Phil M. A. D. *The Pesticide Manual*, 8th ed.; British Crop Protection Council: Lavenham, Suffolk, U.K.,1987.

to be selected for these compounds, resulting in lower sensitivities and higher detection limits.

In static SbWE/SAX disk extraction, only a very simple device was used, and no cleanup and concentration steps were employed. Evidently, the detection limit could further be improved by employing extra sample preparation steps, such as cleanup and concentration. However, this is outside the scope of this contribution. Despite the simplicity of the method, detection limits of around 0.25 and 0.05 ppm for most herbicides tested were achieved on GC/ECD and GC/MS, respectively, which compares favorably with the detection limits reported by the contract laboratory for EPA method 8151 (Table 8).

CONCLUSIONS

Coupling static SbWE in situ with a SAX disk allows for the simultaneous extraction and trapping of acid herbicides and phenoxy acid esters from soil samples. The SAX disk is stable at water temperatures as high as 150 °C. Trapped solutes can directly be derivatized from the disk by BSTFA. No isolation of the herbicides from the disk is required either before or after derivatization. The whole analysis, including extraction, derivatization, and GC separations, can be completed within 2 h and uses very simple apparatus.

ACKNOWLEDGMENT

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through Grant R82536-01-1 to the University of North Dakota Energy and Environmental Research Center, it has not been subjected to the Agency's required peer and policy review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred. The authors thank Carol Grabanski for carefully editing the manuscript.

Received for review July 16, 1999. Accepted October 26, 1999.

AC990787F