Screening Method for Nine Sulfonylurea Herbicides in Soil and Water by Liquid Chromatography with Ultraviolet Detection

Charles R. Powley* and Patricia A. de Bernard

E. I. du Pont de Nemours and Company, DuPont Agricultural Products, Experimental Station, Wilmington, Delaware 19880-0402

An analytical method is described for the preliminary analysis of azimsulfuron, chlorimuron-ethyl, chlorsulfuron, ethametsulfuron-methyl, flupyrsulfuron-methyl, metsulfuron-methyl, sulfometuron-methyl, thifensulfuron-methyl, and tribenuron-methyl in soil (LOQ = 1 ppb) and in water (LOQ = 0.1 ppb). HPLC chromatograms show little to no response for control samples when compared to the lowest fortifications. Average recoveries at the limit of quantitation and above are in the 70−120% range, with relative standard deviations of <20%. Extraction efficiency experiments demonstrated the ability of this method to extract sulfonylureas from soil samples. This method is suitable for screening of samples; however, LC/MS would be required for a definitive confirmation.

Keywords: *Sulfonylurea; herbicide; soil; water; liquid chromatography*

INTRODUCTION

Sulfonylurea herbicides were first introduced in 1982 by DuPont Agricultural Products; they are typically applied at rates less than 100 g/ha, have low mammalian toxicity, and degrade to innocuous compounds after application (Beyer et al., 1987). Analytical methods are needed to evaluate their presence and persistence in soil and water. Determination of sulfonylureas at low levels is very challenging, owing to their thermal and chemical instability, and many different approaches have been reported. Some methods for soil analysis have been reviewed (Smith, 1995). The earliest approaches utilized normal-phase liquid chromatography with photoconductivity detection (Zahnow, 1982, 1985); this detector has undesirably long equilibration times. Sulfonylureas are not directly amenable to gas chromatography (GC) because of their extremely low volatility and thermal instability. GC has been used in conjunction with diazomethane derivatization (Ahmad and Crawford, 1990; Klaffenbach and Holland, 1993), pentafluorobenzyl bromide derivatization (Cotterill, 1992), and hydrolysis followed by analysis of the aryl sulfonamides (Thompson and MacDonald, 1992). These approaches have not become widely accepted most likely because none of them perform well for the entire family of sulfonylureas. Capillary electrophoresis has been evaluated for water (Dinelli et al., 1993; Krynitsky, 1997; Berger and Wolfe, 1996) and soil (Dinelli et al., 1995). The low injection volumes required may not yield the required sensitivity for certain applications. Enzyme immunoassay has been reported for chlorsulfuron (Kelley et al., 1985) and triasulfuron (Schlaeppi et al., 1994; Brady et al., 1995), with limits of detection ranging from 20 to 100 ppt in soil and water.

The most common approaches to sulfonylurea determinations currently involve reversed-phase high-performance liquid chromatography (HPLC) with either ultraviolet (UV) or mass spectrometric (MS) detection. HPLC−MS has been reported using thermospray (Shalaby et al., 1992), fast-atom bombardment (Reiser et al., 1991; Reiser and Fogiel, 1994), and direct liquid introduction (Shalaby, 1985). More recently, electrospray (Volmer et al., 1995; Marek and Koskinen, 1996; Krynitsky, 1997) and tandem mass spectrometry (Li et al., 1996) have been reported. An HPLC−UV method for determination of thifensulfuron-methyl, metsulfuron-methyl, chlorsulfuron, and chlorimuron-ethyl in soil and water was reported with detection limits of 10−50 and 1 ppb, respectively (Galletti et al., 1995). In this work, liquid−liquid extraction and reversed-phase solid-phase extraction (SPE) were compared. Another HPLC−UV method reported used an on-line supported liquid membrane for concentration and cleanup of natural water samples with detection limits of 50−100 ppt (Nilvé et al., 1994).

The purpose of our work was to develop HPLC−UV methodology for determination of nine sulfonylureas in soil and water, which uses commonly available equipment and has sufficient sensitivity for most investigative and regulatory purposes. This paper describes methods that use conventional extraction, solid-phase extraction (SPE) cleanup, and reversed-phase HPLC−UV detection. This method is meant to be used as a screening technique, with confirmation by LC−MS or LC−MS−MS according to published criteria (e.g., Li et al., 1996).

MATERIALS AND METHODS

Chemicals. Analytical standards (>95% pure) of azimsulfuron, chlorimuron-ethyl, chlorsulfuron, ethametsulfuron-methyl, flupyrsulfuron-methyl, metsulfuron-methyl, sulfometuron-methyl, thifensulfuron-methyl, and tribenuron-methyl were obtained from DuPont Agricultural Products (Experimental Station, Wilmington, DE). HPLC-grade solvents (acetone, ethyl acetate, acetonitrile, methanol, and hexane) were obtained from EM Scientific (Gibbstown, NJ). Deionized−distilled water was obtained from a Milli-Q water purification system (Millipore Corp, Milford, MA). Reagents (potassium phosphate (monobasic), glacial acetic acid, phosphoric acid,

* Author to whom correspondence should be addressed [fax (302) 695-4296; e-mail chuck.powley@usa.dupont.com].

S0021-8561(97)00543-8 CCC: $15.00 © 1998 American Chemical Society
Published on Web 01/16/1998

ammonium hydroxide, ammonium carbonate) were obtained from J. T. Baker (Phillipsburg, NJ) and were reagent grade or better.

Soil Samples. Four different soils were evaluated in this work. These soils were obtained from Fargo, ND (pH 7.8, 5.6% organic matter (OM), silty clay loam); Middletown, DE (pH 5.3, 1.9% OM, silt loam); Cambridge, U.K. (pH 7.4, 2.9% OM, sandy loam); and Rochelle, IL (pH 5.7, 5.2% OM, clay loam).

Water Samples. Tap water (chlorinated), water from a natural spring (15 grains hardness), river water, and pond water with algae visibly present were all evaluated.

Equipment. A Hewlett-Packard model 1090 series II liquid chromatograph with ternary solvent capability was used for this work (Hewlett-Packard Co, Little Falls, DE). The UV detector was obtained from Applied Biosystems (Ramsey, NJ), model 783A. The column was a Zorbax SB-Phenyl analytical column (4.6 mm × 250 mm, P/N 880975-912, MAC-MOD Analytical, Chadds Ford, PA) with a Zorbax SB-Phenyl guard cartridge (P/N 820674-917, MAC-MOD Analytical).

Soil samples were extracted using a wrist-action shaker (Burrell Corp, Pittsburgh, PA). Centrifugation was done on a Sorvall model RC-5B centrifuge equipped with a model H5-4 rotor (Sorvall Inc., Newtown, CT). Solvent evaporation was done on a RapidVap evaporation system (model 79000, Labconco, Kansas City, MO) and a nitrogen evaporator (N-EVAP model 111, Organomation Assoc., Berlin, MA).

Solid-phase extraction was done using a Visiprep SPE Manifold (catalog no. 5-7030M, Supelco Inc., Bellefonte, PA). The cartridges used were C18 (1 g/6 mL, catalog no. AI-122560-01, Varian, Sugarland, TX) and silica (1 g/6 mL, catalog no. AI-122560−08, Varian).

Procedures to Prevent Contamination. Soil plots were sampled according to procedures recommended in Carter (1993). Soil sampling equipment was cleaned with bleaching solutions thoroughly after each plot was sampled. Precleaned plastic jugs (water samples) or new cloth bags (soil samples) were used for storage of samples. Once samples were taken, they were kept in ice until they could be stored frozen. The effectiveness of the cleaning procedure used was demonstrated by preparation and analysis of reagent blanks with each set of samples. A set of glassware was dedicated for trace sulfonylurea analysis in soil and water while this work was being done.

Preparation of Standards. Approximately 10 mg of each individual sulfonylurea analytical standard was accurately weighed and brought to 100-mL volume with acetonitrile to make individual stock standard solutions at approximately 100 μg/mL. These stock standard solutions were kept in the freezer for storage and were stable for 6 months at freezer temperatures. Intermediate dilutions in acetonitrile at 10.0 and 1.0 μg/mL of all nine sulfonylureas mixed together were then made; these were useful for fortifications and preparation of chromatographic standards. At least four chromatographic standards ranging from 0.02 to 0.15 μg/mL (or concentrations expected to cover the range of sulfonylurea concentrations in the samples) were prepared by diluting intermediate standards with the pH 6.2, 30 mM phosphate buffer so that the concentration of acetonitrile in each standard was no greater than 5% (v/v). These standards were prepared daily.

Sample Preprocessing. Soil samples were received and stored frozen. Water samples were collected and stored frozen in polypropylene bottles not more than two-thirds full to prevent breakage. Soil was sieved through a $^1/_4$-in. screen to remove stones and plant debris. Samples were composited and homogenized using a Hobart chopper or a ball mill. Water samples were thawed at room temperature or in a refrigerator overnight. Water samples with a high degree of turbidity (e.g., pond-water samples containing algae) were centrifuged (instead of filtered) to remove particulate matter.

Sample Fortification Procedure. Fortifications were prepared using the 1 μg/mL intermediate standard. A syringe was used to add 50, 100, or 250 μL of the standard solution to 50 g soil, resulting in fortification levels of 1.0, 2.0, and 5.0 ppb. Similarly, either 20, 40, or 100 μL of the standard solution was added to 200 mL of water sample, resulting in fortification levels of 0.1, 0.2, or 0.5 ppb. To demonstrate soil extraction efficiency, the fortification was made to 15 mL of purified water, which was then added to 50 g of soil in a centrifuge bottle. The samples were mixed well to form a slurry, then evaporated to dryness overnight under a stream of nitrogen.

Soil Extraction. (1) Fifty grams of homogenized soil was weighed into a 250-mL polypropylene centrifuge bottle. Any necessary fortifications were made at this time, and the sample was air-dried for 15 min to evaporate the acetonitrile from the sample before proceeding.

(2) A quantity of 100 mL of 80/20 (v/v) 0.1 M ammonium carbonate/acetone (soil-extracting solution) was added to the sample. The sample was capped and shaken vigorously by hand for several seconds in order to make sure that the soil was thoroughly wetted. Samples were placed on a wrist-action shaker, set at maximum deflection, for 20 min, then centrifuged at 11 000 rpm for 20 min.

(3) The supernatant was decanted through a funnel containing a plug of glass wool into a 250-mL beaker. A separate funnel and glass wool plug was used for each sample. (Note: if the supernatant was cloudy, which is often the case when a high-speed centrifuge is not used, filter paper was used instead of glass wool. Glass microfiber filter paper grade GF/D was found to be the best choice. Note: when screening for flupyrsulfuron-methyl, the supernatant was placed on ice or refrigerated until combined with the supernatant from the second extract.)

(4) A spatula was used to break up the pellet, then steps 2 and 3 were repeated, combining the supernatants. One-fifth of the total volume of the combined supernatants was evaporated using a rotary evaporator or RapidVap. The temperature bath or heating block was set at 35 °C.

(5) An equal volume of water was added to the sample and mixed well. The extract was found to be stable if stored overnight at refrigerator temperature, or frozen for several days.

Water Extraction and Soil and Water Cleanup. (1) A quantity of 200 mL of water sample was measured out, using a graduated cylinder, into a 250-mL beaker. Any necessary fortifications were made at this time.

(2) *Two* 1-g C18 SPE cartridges were preconditioned for each water sample to be analyzed by passing 5 mL of methanol through each cartridge followed by 10 mL of water. A light vacuum and a flow rate of 5−10 mL/min were used (individual drops could be seen forming at the outlet of each cartridge) for all SPE procedures. The cartridge packing was not allowed to go dry during or after the preconditioning steps. *One* 1-g C18 cartridge was preconditioned for each soil extract to be analyzed in a similar manner.

(3) The pH of the entire water sample (*or* one-half of the soil extract) was adjusted to 3.0−3.5 using dilute (1:10 dilution of reagent grade) phosphoric acid (with stirring). The pH was not adjusted until just before the samples were applied to the SPE cartridge(s), since tribenuron-methyl is not stable under acidic conditions.

(4) Water samples were divided into two equal portions and each portion was passed through one of the two preconditioned C18 cartridges. *Alternatively,* one-half of the soil extract was passed through the single preconditioned C18 cartridge. After the sample went through, 5 mL of distilled deionized water was passed through each cartridge. The cartridges were not allowed to go dry until all of the sample and wash solutions passed through. The effluent was discarded.

(5) Each cartridge was eluted with 10 mL of 0.1% (v/v) glacial acetic acid in ethyl acetate. The eluate was collected in a 13-mL glass graduated centrifuge tube. Some residual water from the cartridge (<0.5 mL) was often seen at the bottom of the tube; this water was removed and discarded using a long-stemmed Pasteur pipet. The eluate was evaporated to dryness under a stream of dry nitrogen using a water bath set at 35 °C (the eluates from the two cartridges used for water samples were combined halfway through this evaporation).

Table 1. Sample Gradient Program

action	time (min)	%B	%C	eluent
injection	0.00	75	0	1
	10.50	75	0	
switch eluent	10.55	0	95	2 → 3
end gradient	40.50	0	80	3
End hold	47.00	0	80	3
begin wash	47.05	0	50	
end wash	54.00		50	
reequilibrate	54.10	75	0	1

(6) A quantity of 2 mL of ethyl acetate was added to the centrifuge tube. Samples were reconstituted using a vortex mixer and ultrasonication for 5 min. A volume of 8 mL of hexane was added, and samples were mixed again using a vortex mixer.

(7) A 1-g silica SPE cartridge was preconditioned with 5 mL of ethyl acetate followed by 5 mL of 80/20 (v/v) hexane/ethyl acetate. The cartridge packing was not allowed to go dry during these steps.

(8) The sample from step 6 was passed through the cartridge. The sample centrifuge tube was rinsed with 5 mL of 80/20 (v/v) hexane/ethyl acetate, and the rinsate was passed through the cartridge. The effluent was discarded, and the cartridge was not allowed to go dry until all of the sample and wash solution passed through. The cartridge was eluted with 5 mL of 0.1% (v/v) glacial acetic acid in ethyl acetate, which was evaporated to dryness using a stream of nitrogen.

(9) To reconstitute the sample, 0.5 mL of methanol was added. The sample was ultrasonicated for 5 min, then mixed well on a vortex mixer. A volume of 1 mL of the 30 mM, pH 6.2 phosphate buffer was added, and a stream of dry nitrogen and a water bath set at 35 °C was used to reduce the volume to just under 1 mL. Samples were then diluted to the 1-mL mark with water. The samples were ready for analysis and were stable for at least 24 h if kept refrigerated.

HPLC Analysis. In this study, a liquid chromatograph with three proportioning pumps was used to mix the eluents. HPLC instruments that use solenoid valves to proportion solvents may require that three eluents be premixed. The need for premixing will be determined by the amount of baseline fluctuation observed. The HPLC system was set up using the following parameters:

column: Zorbax SB-Phenyl, 4.6 m × 250 mm

oven temperature: 35 °C

injection volume: 250 μL

detection: UV at 245 nm

flow rate: 1.5 mL/min

mobile phase reservoir A: acetonitrile

reservoir B: 30 mM, pH 2.7 pot. phosphate buffer

reservoir C: 30 mM, pH 6.2 pot. phosphate buffer

Example gradient program is shown in Table 1 (see table for details on setting time points).

If Eluents 1, 2 and 3 are premixed, three appropriate eluents are the following:

eluent 1: 25/75 (v/v) acetonitrile/pH 2.7 buffer

eluent 2: 7.5/92.5 (v/v) acetonitrile/pH 6.2 buffer

eluent 3: 17.5/82.5 (v/v) acetonitrile/pH 6.2 buffer

and the time to switch from eluent 2 to eluent 3 would be approximately 5 min after chlorsulfuron elutes.

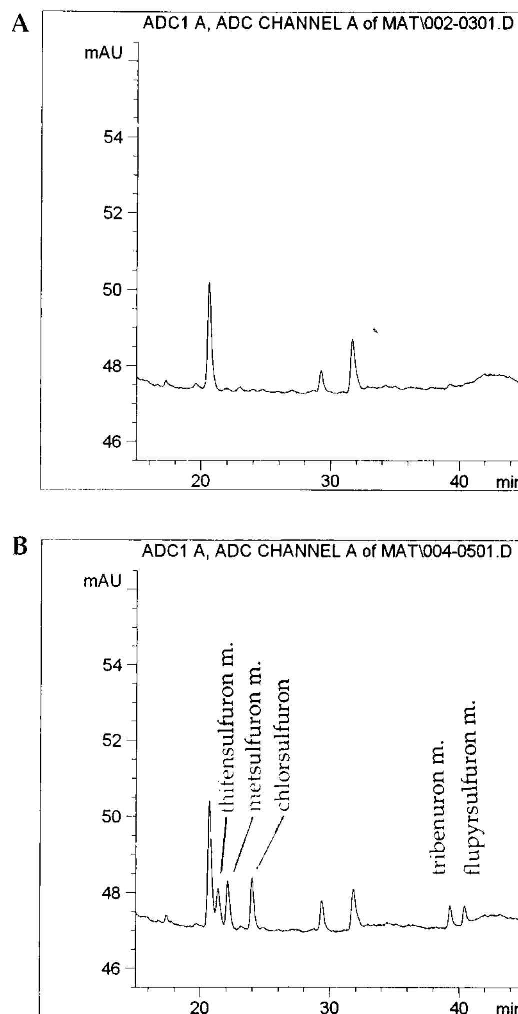

Figure 1. HPLC−UV chromatogram of (A) control silt loam soil extract and (B) silt loam soil fortified with 1 ppb each thifensulfuron-methyl, metsulfuron-methyl, chlorsulfuron, tribenuron-methyl, and flupyrsulfuron-methyl.

The column was allowed to equilibrate for at least 15 min with the starting mobile phase (eluent 1). A 1.0 μg/mL standard of metsulfuron-methyl was injected while maintaining eluent 1 isocratically. The retention time was noted; the "switch-eluent" time corresponded to one-half the metsulfuron-methyl retention time. The "end-gradient" time was 30 min later, as shown in Table 1. (Note: if metsulfuron-methyl was not being analyzed, a standard of the earliest-eluting sulfonylurea, which was to be analyzed, was used for determination of the switching time.)

The data acquisition program was set to step from eluent 1 to eluent 2 at the appropriate "switch-eluent" time. A 1.0 μg/mL mixed standard containing all the sulfonylureas to be analyzed was injected. The "end-hold" time was after the last peak (chlorimuron-ethyl) eluted.

Each set of samples analyzed included at least one control (a sample that matched the investigation samples as closely as possible) and a reagent blank. A reagent blank was prepared by carrying a 200-mL sample of purified water or soil-extracting solution through the same procedure as that of the samples.

Calculations. The response factor for each peak was calculated using

$$\text{response factor} = \frac{\text{peak height or area}}{\text{concentration } (\mu\text{g/mL})} \qquad (1)$$

The average response factor used to calculate a sample concentration was the average of response factors for the

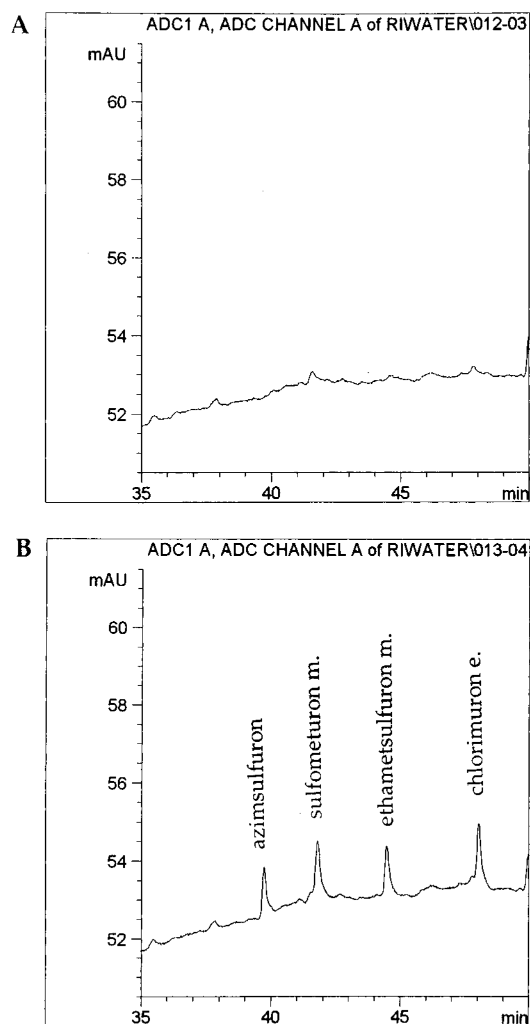

Figure 2. HPLC–UV chromatogram of (A) control river-water extract and (B) river water fortified with 0.1 ppb each of azimsulfuron, sulfometuron-methyl, ethametsulfuron-methyl, and chlorimuron-ethyl.

standards analyzed during the course of sample analysis. The sulfonylurea level in a treated or recovery sample was calculated using

$$\text{ppb sulfonylurea} = \frac{\text{peak height or area} \times \text{AF} \times 1\ \text{mL} \times 1000}{\text{avg response factor} \times \text{g sample}} \quad (2)$$

where AF = aliquot factor (2 for soil samples, because only half the original sample was used, 1 for water samples).

RESULTS AND DISCUSSION

The eluent-switching program used for this work provided better resolution of sulfonylureas from matrix constituents than that of a simple binary gradient. When the mobile phase was switched to an eluent with a higher pH and lower organic modifier concentration, matrix interferences were retained on the column. However, the sulfonylureas converted to their anionic forms (pK_a values range from approximately 3.5 to 5), which were much less strongly retained on the phenyl column, and continued to migrate.

Calibration curves of each of the nine sulfonylureas all had good linearity with correlation coefficients of 0.999–1.000; in all cases the intercept values were not statistically different from zero, which enabled the use

Table 2. Recovery Data for Sulfonylureas in Soil[a]

fortification level	% recovery levels 1 ppb	2 ppb	5 ppb	10 ppb[b]
	Azimsulfuron			
range	73–108	75–101	80–98	79–88
average	95	87	90	84
%RSD (*n*)	15(6)	13(6)	10(3)	5(3)
	Chlorimuron-ethyl			
range	85–116	90–107	85–98	88–96
average	107	99	101	93
%RSD (*n*)	11(6)	7(6)	7(3)	4(3)
	Chlorsulfuron			
range	64–88	86–96	89–104	90–96
average	80	91	97	92
%RSD (*n*)	10(6)	4(6)	8(3)	2(3)
	Ethametsulfuron-methyl			
range	98–115	85–103	94–104	87–96
average	106	96	100	92
%RSD (*n*)	5(6)	9(6)	6(3)	5(3)
	Flupyrsulfuron-methyl			
range	62–98	72–98	77–116	88–96
average	79	87	94	92
%RSD (*n*)	19(6)	12(6)	21(3)	5(3)
	Metsulfuron-methyl			
range	65–92	87–99	93–104	88–98
average	81	93	98	94
%RSD (*n*)	11(6)	5(6)	6(3)	6(3)
	Sulfometuron-methyl			
range	81–114	76–102	95–106	87–97
average	97	91	101	93
%RSD (*n*)	13(6)	12(6)	6(3)	6(3)
	Thifensulfuron-methyl			
range	59–89	82–92	80–101	80–82
average	76	86	91	81
%RSD (*n*)	13(6)	4(6)	12(3)	1(3)
	Tribenuron-methyl			
range	70–101	76–97	79–100	87–96
average	81	86	91	92
%RSD (*n*)	17(6)	9(6)	12(3)	6(3)

[a] Data from fortification experiments conducted with four different soil types. [b] Results from extraction-efficiency experiments.

of response factors. Representative chromatograms of unfortified and fortified soil and water samples are shown as Figures 1 and 2. Chromatograms for control samples are generally free from matrix interference in the regions of sulfonylurea elution. Recovery data for the nine sulfonylureas investigated in soil and water are given in Tables 2 and 3, respectively. These results are based on 15–20 recovery determinations for each SU, using three different soil types and three or four different water sources on different days. For each soil or water source, a sample set consisting of a control, two LOQ fortifications, two 2 × LOQ fortifications, and one 5 × LOQ fortification was prepared and analyzed. The results indicate acceptable recovery levels (averages and most individual values within 70–120%) and repeatability (<20% RSD). A few of the sulfonylureas did show different recovery levels in different soils. No such differences were observed for different water sources. Table 2 also includes results for extraction efficiency studies, where the slurry fortification and drying technique described above was used to simulate field application and weathering conditions in a soil with high clay and organic matter content. In our experience, this soil would represent a “worst-case” scenario from an extractability standpoint. The results indicate that the extraction procedure can release and recover weathered residues of sulfonylurea herbicides.

Table 3. Recovery Data for Sulfonylureas in Water[a]

fortification level	% recovery levels		
	0.1 ppb	0.2 ppb	0.5 ppb
Azimsulfuron			
range	67−83	67−86	70−73
average	73	79	72
%RSD (*n*)	10(8)	8(8)	3(4)
Chlorimuron-ethyl			
range	80−101	91−106	88−92
average	88	95	90
%RSD (*n*)	8(8)	6(8)	2(4)
Chlorsulfuron			
range	86−108	91−107	86−96
average	95	98	92
%RSD (*n*)	8(6)	6(6)	6(3)
Ethametsulfuron-methyl			
range	81−107	87−107	89−91
average	93	95	90
%RSD (*n*)	12(8)	6(8)	1(4)
Flupyrsulfuron-methyl			
range	87−116	66−102	80−100
average	99	81	88
%RSD (*n*)	12(6)	15(6)	13(3)
Metsulfuron-methyl			
range	87−115	81−108	87−93
average	95	98	91
%RSD (*n*)	11(6)	10(6)	4(3)
Sulfometuron-methyl			
range	76−98	79−100	82−90
average	85	90	86
%RSD (*n*)	7(8)	8(8)	3(4)
Thifensulfuron-methyl			
range	86−119	94−107	91−96
average	104	102	93
%RSD (*n*)	13(6)	5(6)	2(3)
Tribenuron-methyl			
range	82−129	87−114	85−95
average	101	98	92
%RSD (*n*)	18(6)	12(6)	8(3)

[a] Data from fortification experiments conducted with four different water sources (tap, spring, river, pond).

Sensitivity. The limit of quantitation (determination) for each of the analytes was determined to be 1 ppb in soil and 0.1 ppb in water. This limit was defined as the lowest fortification level evaluated at which acceptable average recoveries and precision were obtained. This quantitation limit also reflects the fortification level at which an analyte peak is consistently generated at a level approximately 10 times the background noise (or 5 times the background peaks) in the chromatograms, using the complete residue method.

Specificity. Other readily available sulfonylureas (nicosulfuron, rimsulfuron, bensulfuron-methyl, triflusulfuron-methyl, primisulfuron-methyl, and triasulfuron) were found not to interfere with the compounds determined by this method. If a response for one of the analytes being determined is obtained in a sample (other than a fortified sample or a soil sample that was recently treated with sulfonylurea herbicides), the possibilities of contamination and interference must immediately be addressed. If a reliable control sample has not been obtained and analyzed concurrently, a reagent blank should have been run. If an analyte response is present in the reagent blank, the equipment used to prepare the sample should be thoroughly cleaned and checked by preparation of another reagent blank before repeating the analysis; the previous data should be discarded as false positive results. If the possibility of contamination has been ruled out, then the possibility of a coeluting interference must be considered.

Confirmatory Methods. The degree of confirmation required for a potential positive finding depends on both the intended use of the results and on the history of the sample. In cases where a positive detection is obtained for a soil sample known to have recently been exposed to the analyte found, confirmatory analysis may not be required. However, if a sulfonylurea herbicide that was not recently used in the general area from which the sample was collected is detected, confirmation by LC/MS would be required. Nonspecific detection systems, such as LC/UV, have limited utility as confirmation methods, especially since reliable control samples are not always available when contamination of soil or water is suspected. In LC/MS or LC/MS/MS, selected ion monitoring of the molecular ion and at least two fragment ions should be used to confirm findings according to established criteria (Cairns et al., 1989; Cairns, 1996; Li et al. 1996).

CONCLUSION

This method is suitable for the preliminary determination of azimsulfuron, chlorimuron-ethyl, chlorsulfuron, ethametsulfuron-methyl, flupyrsulfuron-methyl, metsulfuron-methyl, sulfometuron-methyl, thifensulfuron-methyl, and tribenuron-methyl in soil at levels down to 1 ppb and in water at levels down to 0.1 ppb. This method is not applicable to the determination of nicosulfuron and rimsulfuron because these compounds are not quantitatively eluted from the silica cartridge.

LITERATURE CITED

Ahmad, I.; Crawford, G. Trace Residue Analysis of the Herbicide Chlorsulfuron in Soil by Gas Chromatography-Electron Capture Detection. *J. Agric. Food Chem.* **1990**, *38*, 138−141.

Brady, J. F.; Turner, J.; Skinner, D. H. Application of a Triasulfuron Enzyme Immunoassay to the Analysis of Incurred Residues in Soil and Water Samples. *J. Agric. Food Chem.* **1995**, *43*, 2542−2547.

Berger, B. M.; Wolfe, N. L. Multiresidue Determination of Sulfonylurea Herbicides by Capillary Electrophoresis for Hydrolysis Studies in Water and Sediments. *Fresenius J. Anal. Chem.* **1996**, *356*, 508−511.

Beyer, E. M.; Duffy, M. J.; Hay, J. V.; Schlueter, D. D. Sulfonylureas. In *Herbicides: Chemistry, Degradation, and Mode of Action*; Kearney, P. C., Kaufmann, D. D., Eds.; Dekker: New York, 1987; pp 117−189.

Cairns, T.; Siegmund, E. G.; Stamp, J. J. Evolving Criteria for Confirmation of Trace Level Residues in Food and Drugs by Mass Spectrometry. Part I. *Mass Spectrom. Rev.* **1989**, *8*, 93−117.

Cairns, T. Development of Guidelines for Detection, Confirmation, and Quantitation by GC/MS, LC/MS, and MS/MS. ASMS Workshop, November, 1996.

Carter, M. R., Ed. *Soil Sampling and Methods of Analysis;* Lewis Publishers: New York, 1993.

Cotterill, E. G. Determination of the Sulfonylurea Herbicides Chlorsulfuron and Metsulfuron-methyl in Soil, Water, and Plant Material by Gas Chromatography of Their Pentafluorobenzyl Derivatives. *Pestic. Sci.* **1992**, *34,* 291−296.

Dinelli, G.; Vicari, A.; Catizone, P. Use of Capillary Electrophoresis for Detection of Metsulfuron and Chlorsulfuron in Tap Water. *J. Agric. Food Chem.* **1993**, *41*, 742−746.

Dinelli, G.; Vicari, A.; Brandolini, V. Detection and Quantitation of Sulfonylurea Herbicides in Soil at the ppb Level by Capillary Electrophoresis. *J. Chromatogr. A* **1995**, *700,* 201−207.

Galletti, G. C.; Bonetti, A.; Dinelli, G. High-Performance Liquid Chromatographic Determination of Sulfonylureas in Soil and Water. *J. Chromatogr. A* **1995**, *692,* 27−37.

Kelley, M. M.; Zahnow, E. W.; Petersen, W. C.; Toy, S. T. Chlorsulfuron Determination in Soil Extracts by Enzyme Immunoassay. *J. Agric. Food Chem.* **1985**, *33*, 962−965.

Klaffenbach, P.; Holland, P. T. Analysis of Sulfonylurea Herbicides by Gas-Liquid Chromatography III-Mass Spectrometry and Multiresidue Determination. *Biol. Mass Spectrom.* **1993**, *22*, 565−578.

Krynitsky, A. J. Determination of Sulfonylurea Herbicides in Water by Capillary Electrophoresis and by Liquid Chromatography/Mass Spectrometry. *J. AOAC Int.* **1997**, *80*, 392−400.

Li, L. Y. T.; Campbell, D. A.; Bennett, P. K.; Henion, J. Acceptance Criteria for Ultratrace HPLC−Tandem Mass Spectrometry; Quantitative and Qualitative Determination of Sulfonylurea Herbicides in Soil. *Anal. Chem.* **1996**, *68*, 3397−3404.

Marek, L. J.; Koskinen, W. C. LC/MS Analysis of 4-Methoxy-6-methyl-1,3,5-triazin-2-yl-Containing Sulfonylurea Herbicides in Soil. *J. Agric. Food Chem.* **1996**, *44*, 3878−3881.

Nilvé, G.; Knutsson, M.; Jönsson, J. Å. Liquid Chromatographic Determination of Sulfonylurea Herbicides in Natural Waters after Automated Sample Pretreatment using Supported Liquid Membranes. *J. Chromatogr. A* **1994**, *688,* 75−82.

Reiser, R. W.; Barefoot, A. C.; Dietrich, R. F.; Fogiel, A. J.; Johnson, W. R.; Scott, M. T. Application of Microcolumn Liquid Chromatography-Continuous-Flow Fast Atom Bombardment Mass Spectrometry in Environmental Studies of Sulfonylurea Herbicides. *J. Chromatogr.* **1991**, *554,* 91−101.

Reiser, R. W.; Fogiel, A. J. Liquid Chromatography/Mass Spectrometry Analyses of Small Molecules Using Electrospray and Fast-atom Bombardment Ionization. *Rapid Commun. Mass Spectrom.* **1994**, *8,* 252−257.

Schlaeppi, J. A.; Kessler, A.; Föry, W. Development of a Magnetic Particle-Based Automated Chemiluminescent Immunoassay for Triasulfuron. *J. Agric. Food Chem.* **1994**, *42*, 1914−1919.

Shalaby, L. M. Liquid Chromatography/Mass Spectrometry of the Thermally Labile Herbicides, Chlorsulfuron and Sulfometuron Methyl. *Biomed. Mass Spectrom.* **1985**, *12,* 261−268.

Shalaby, L. M.; Bramble, F. Q.; Lee, P. W. Application of Thermospray LC/MS for Residue Analysis of Sulfonylurea Herbicides and Their Degradation Products. *J. Agric. Food Chem.* **1992**, *40,* 513−517.

Smith, A. E. A Review of Analytical Methods for Sulfonylureas in Soil. *Int. J. Environ. Anal. Chem.* **1995**, *59*, 97−106.

Thompson, D. G.; MacDonald, L. M. Trace-Level Quantitation of Sulfonylurea Herbicides in Natural Water. *J. AOAC Int.* **1992**, *75,* 1084−1090.

Volmer, D.; Wilkes, J. G.; Levsen, K. Liquid Chromatography/Mass Spectrometry Multiresidue Determination of Sulfonylureas after On-line Trace Enrichment. *Rapid Commun. Mass Spectrom.* **1995**, *9,* 767−771.

Zahnow, E. W. Analysis of the Herbicide Chlorsulfuron in Soil by Liquid Chromatography. *J. Agric. Food Chem.* **1982**, *30*, 854−857.

Zahnow, E. W. Analysis of the Herbicide Sulfometuron Methyl in Soil and Water by Liquid Chromatography. *J. Agric. Food Chem.* **1985**, *33*, 479−483.

Received for review June 24, 1997. Revised manuscript received November 3, 1997. Accepted November 6, 1997.

JF9705431