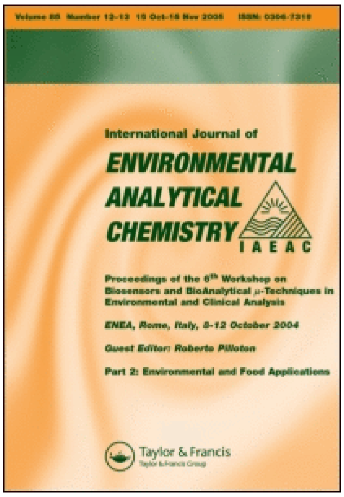

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SUPERCRITICAL FLUID EXTRACTION OF METSULFURON METHYL, SULFOMETURON METHYL, AND NICOSULFURON FROM SOILS

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Sulfonylurea herbicides are usually extracted from soils with batch liquid techniques. The objective of this study was to develop a general supercritical fluid extraction (SFE) procedure for sulfonylurea herbicides in soils. The procedure was optimized for metsulfuron methyl, and the parameters investigated included: SF-CO_2 density, extraction time, and methanol modifier addition. Quantitative extraction could only be performed at high densities (i.e., 0.9 g ml^{-1}) and with 2% (w/w) modifier addition. ^{14}C-labeled metsulfuron methyl, sulfometuron methyl, and nicosulfuron were extracted from sandy loam, silt loam, and clay loam soils spiked at two levels (0.4 and 4 $\mu g\ g^{-1}$) of herbicide. Under the conditions used, good recoveries of metsulfuron methyl and sulfometuron methyl (75–89%) were obtained. However, nicosulfuron was difficult to extract (1–4%). The results show that an optimized method cannot always be directly applied to similar compounds without further method development.

Keywords: SFE; sulfonylurea herbicides; metsulfuron methyl; sulfometuron methyl; nicosulfuron; soils

INTRODUCTION

Sulfonylurea herbicides (SUs), often referred to as low dose herbicides, are a group of medium polarity compounds with very strong systemic herbicidal activity. Due to the high herbicidal activity, they are applied in low doses (10–40 g ha^{-1}, typically less than 100 g ha^{-1}) in the field, thus decreasing application rates of active ingredient by a factor of 10–100 compared to traditional chemicals. SUs are used to control broad leaf and grass weeds, and act by inhibiting plant growth; they inactivate the enzyme acetolactate synthase, which is needed in the

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synthesis of some essential amino acids. They are variously used pre-plant, pre-emergence of crop, or shortly after emergence. Depending on soil characteristics, SUs can persist in soil from 1–6 weeks, to more than one year [1].

SUs are usually extracted from soils with conventional solvent extraction techniques followed by analysis by liquid chromatography (LC) [2], lately in combination with mass spectrometry (MS) [3,4]. SUs are generally thermolabile with low vapor pressure and therefore, can not be analyzed by gas chromatography (GC) without a derivatization step [5]. Traditional liquid extraction techniques are often time-consuming, labor-intensive, and require large volumes of organic solvents.

Supercritical fluid extraction (SFE) is increasing being used as an alternative extraction technique. The main advantages of SFE are the replacement of organic solvents with environmentally-friendly supercritical fluids such as carbon dioxide (CO_2), and highly efficient extraction (high recovery and short extraction time due to the low viscosity and high sample penetration capacity). Also, some selectivity can be obtained using SFE methods by varying the density of the extraction medium and adding modifiers. These properties give SFE the potential to serve as an ideal sample extraction technique, and SFE has been used for quantitative extraction of organic compounds such as pesticides from a variety of environmental matrices [6–11]. SFE has also been used for extraction of SUs from support material and solid phase extraction disks [12–14], soils [15–16], plant materials and cell culture media [16]. However, each new analytical problem requires extensive method development.

The aim of this study was to develop a general SFE method to extract SUs from soil samples. Metsulfuron methyl was used as a model compound, after which sulfometuron methyl and nicosulfuron were used to verify the method. These three compounds were chosen as typical SUS with properties that comprise much of SUs characteristics. They cover, for instance, the whole range of SU acidity (pK_a 3.3–5.2) [17].

EXPERIMENTAL

Chemicals

Metsulfuron methyl (>99% purity), sulfometuron methyl (>99% purity), and nicosulfuron (>94% purity), and ^{14}C-uniformly-ring-labeled metsulfuron methyl (1.4×10^9 Bq g^{-1}), sulfometuron methyl (1.8×10^9Bq g^{-1}), and nicosulfuron (2.3×10^9Bq g^{-1}) were supplied by DuPont Agricultural Products* (Wilmington, Delaware, USA). SFC/SFE-grade carbon dioxide was obtained from Air Products and Chemicals, Inc. (Allentown, Pennsylvania, USA). SFE pump and collecting trap were cooled with industrial purity carbon dioxide. Pesticide grade methanol and $CaCl_2$ were obtained from Fisher Scientific (Fair Lawn, New Jersey, USA), and Ecolite scintillation cocktail was from ICN (Costa Mesa, California, USA).

Soils

Three Minnesota soils, including the surface soils (0–15 cm) of a Webster clay loam (Typic Haploquoll), a Verndale sandy loam (coarse loamy over sandy, mixed frigid Udic Argiboroll), and a Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed mesic Typic Hapludoll), were used in this study. Selected physical and chemical properties of the soils are listed in Table I.

TABLE I Physical and chemical properties of Minnesota soils used in this study

Soil	*Texture*	*Organic Carbon (%)*	*Clay (%)*	*pH*[*]
Webster	clay loam	4.1	35	6.7
Waukegan	silt loam	1.8	22	5.5
Verndale	sandy loam	1.4	7	6.1

[*] determined in 1:2 (w/w) soil:water

SFE

All SF-CO_2 experiments were performed using a HP7680A supercritical fluid extractor (Hewlett Packard, Little Falls, Delaware, USA). The extractor was equipped for 7-ml extraction thimbles, and octadecylsilane-bonded (C18, 5 μm) silica was used as a trapping material. A second trap consisting of a collection vial filled with methanol was connected to the solid phase trap in order to check for analyte losses from the first trap. The system included two pumps, one of which was used to add the modifier.

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[*] Mention of a company or trade name is for information only and does not imply an endorsement by USDA-Agricultural Research Service.

Method development; optimization of SFE conditions

Subsamples of field-moist soils (5 g) were weighed into aluminum weighing boats, and treated with ^{14}C-labeled metsulfuron methyl (5.5 × 10^3 Bq ml^{-1}) solution in methanol (1 ml, 1.9 and 19 μg ml^{-1}, to give final concentrations of 0.4 and 4 μg g^{-1} soil respectively). The low herbicide concentration falls within normal maximum field application rate, assuming incorporation in the surface 1 cm of soil. The soils were mixed with the spike solution and approximately 0.5 ml water and allowed to dry to their original weights to ensure removal of methanol. Deionized water was added to the spiked soil in the weighing boats (after evaporation of methanol) to obtain 11% water contents, and the soil mixed thoroughly. The 11% water content is ~ 1 bar water potential for the Verndale soil. The water content was kept constant for the other two soils, although potentials would be different. The soil was weighed into the extraction thimbles and equilibrated for 24 h prior to extraction. Sulfometuron methyl and nicosulfuron were spiked using the same procedure and herbicide concentration.

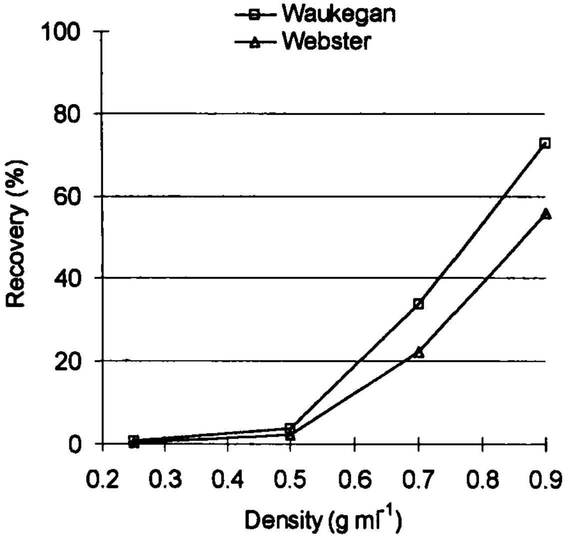

FIGURE 1 Recovery as a function of density for metsulfuron methyl from Webster and Waukegan soils using unmodified carbon dioxide

Densities of 0.25 to 0.90 g ml^{-1}, extraction times of 5 to 60 minutes, and modifier concentrations of 2 and 4 % methanol, were evaluated (Figure 1 and 2). The performance of the SFE procedure such as trapping efficiency and extraction rates was determined by using ^{14}C-labeled compounds. The use of radiolabeled compounds also facilitated mass balance calculations.

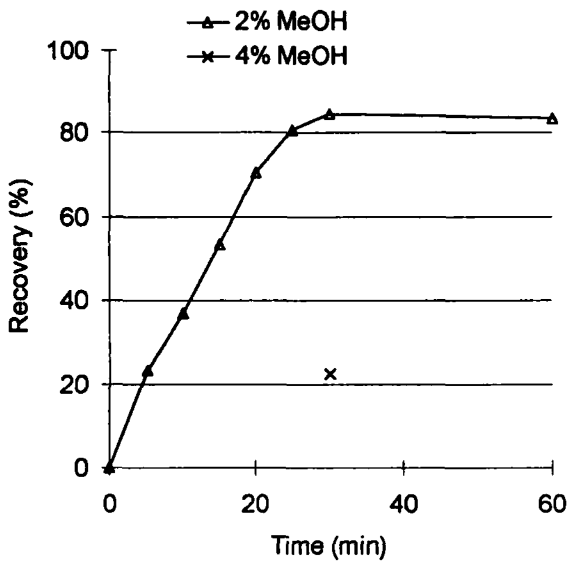

FIGURE 2 Recovery as a function of time for metsulfuron methyl from Webster soil using 2% methanol modified carbon dioxide

To compare extraction efficiencies for the three SUS in the three soils, the soil in the extraction thimble was swept for 30 minutes with CO_2 (8.8 thimble volumes, 61.6 ml, 0.90 g ml^{-1} density, flow rate 2 ml min^{-1} measured at the pump). Methanol (2 % w/w) was added to the SF-CO_2 with the second pump. Thimble, trap, and nozzle temperatures were 40, 10, and 55 °C, respectively. The trap was rinsed twice after extraction with 1.4 ml methanol into two empty vials. Each SFE extract was then combined with scintillation cocktail and counted with a Packard 1500 Tri-carb Liquid Scintillation Analyzer (Downers Grove, Illinois, USA) (more than 99% of the analyte was detected in the first vial).

Mass balances of ^{14}C were determined by combusting triplicate subsamples (0.3 g) of the extracted soil, which had been mixed with equal volumes of microcrystalline cellulose powder, using a Packard 306 sample oxidizer and quantifying the released $^{14}CO_2$ by liquid scintillation counting. Mass balances of metsulfuron methyl for soils before and after SF-CO_2 extraction were 99 ± 5 %, indicating that essentially all of the metsulfuron methyl applied to the soil was recovered from the trap or was still sorbed to the soil.

RESULTS AND DISCUSSION

Optimization of extraction parameters for SFE of metsulfuron methyl from soils

Many experimental variables may affect SFE efficiency, and optimization of instrumental parameters and physical/chemical variables are necessary to establish quantitative and reproducible extraction procedures. Based on previously published research [12–16], the effect of SF-CO_2 density, extraction time/volume of extraction fluid, and methanol modifier addition on extraction efficiency were studied. ^{14}C-labeled metsulfuron methyl was used for optimization of sulfonylurea herbicide extraction from soils. Radiolabeled chemicals provide a simple method to test the extraction procedure by determining the losses at each extraction step with scintillation counting. This is much faster and more reliable than trying to use chromatographic techniques to determine the SU in each step.

Effect of density

Extractions (30 min) at different densities (0.25–0.90 g ml^{-1}) without the addition of modifier were performed on Webster and Waukegan soils. The results showed a pronounced density dependent recovery Figure 1, with higher recovery from Waukegan soil (lower organic carbon and clay contents) than from Webster soil. Only small amounts of metsulfuron methyl could be extracted at lower densities, and a density of 0.90 g ml^{-1}, the maximum attainable by the extractor, was chosen for the rest of the experiments.

Effect of modifier and extraction time

The Webster soil was used for further optimization experiments, due to its higher organic carbon and clay contents. The higher organic carbon and clay contents should lead to higher sorption of the SUs, and consequently, a method developed for the Webster soil would be assumed to perform even better for soils with lower organic carbon and clay contents.

It has been shown that modifier addition, making the SF-CO_2 system more polar, is necessary for quantitative extraction of many medium to polar compounds, such as sulfonylurea herbicides, which have limited solubility in pure CO_2 [13]. However, addition of 4 % methanol (w/w) with a separate modifier pump resulted in recovery of only 22% of added metsulfuron methyl from Webster soil. It appears that methanol becomes a liquid when the pressure drops and can rinse analytes from the sorbent trap [18]. Metsulfuron methyl recoveries were also shown to be time dependent, extraction recovery decreased after longer extraction times, probably due to poor trapping efficiency and stripping of the SU from the trapping sorbent by the methanol modifier during extraction (data not shown).

Burford et al. [19] showed that most of the loss of analytes during the collection step depends on poor trapping in the liquid, not purging of trapped analytes away from the liquid. No traces of metsulfuron methyl could be found in a second methanol filled waste trap. The methanol trap was checked for losses due to purging by adding metsulfuron methyl directly to the solvent, followed by a 30 minute extraction (of thimble filled with soil) under normal conditions. The results showed no losses due to purging and it seems, therefore, that the analyte was transported out of the sorbent trap in a form that could not be trapped by the liquid trap. A third trap containing methanol, dichloromethane, or water as collecting solvent was connected following the second trap, but no traces of analyte could be found in the solvent. This trapping problem was circumvented by using a lower modifier concentration (2 %, w/w) (Figure 2). Recovery then increased with extraction time, and a 30 minute extraction was necessary to obtain quantitative recovery (85%).

Extraction of sulfonylurea herbicides from soils

Results of our recovery experiments are summarized in Table II. The recoveries decreased with increased soil organic carbon and clay contents (Table I), recovery was in the order Verndale = Waukegan > Webster. Sulfonylurea herbicides are weak acids. The pK_avalues of metsulfuron methyl, sulfometuron methyl, and nicosulfuron are 3.3, 5.2 and 4.6 respectively. Their sorption to soil is mainly a function of organic carbon and clay contents, and pH. Sorption is stronger at low pH and high organic matter and clay contents when the chemicals are in the molecular form. However, at high pH, the anion form is only slightly sorbed to soil organic matter and silicate clays, due to repulsion between the sulfonylurea anions and the negative charge of these soil particles. None of the soils are particularly acidic (pH 5.5–6.7), thus, organic carbon and clay content are more important parameters than pH for sorption. Also, water in contact with SF-CO_2 has a pH of 3, due to formation of carbonic acid, therefore during extraction, SUs are in the molecular form [20].

Under the conditions used, good recoveries of metsulfuron methyl and sulfometuron methyl (75–89%) were obtained from all three soils at both spiking levels. However, only 1–4 % of the added nicosulfuron was extracted. This difference in extractability was not expected since the structures and chemical/physical properties of these compounds are relatively similar. It appears that the pyridine group of nicosulfuron interacts with the soil surface resulting in the inability to extract it using SFE. Imidacloprid (1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine) also has an pyridine group and can not be extracted from soil by SFE (unpublished data).

TABLE II Recovery for sulfonylurea herbicides extracted by supercritical carbon dioxide at two different spiking levels

Soil	*SU concentration in freshly spiked soil*				
	0.4 μg g^{-1}		*4 μg g^{-1}*		
	metsulfuron methyl % (SD), n^1	*sulfometuron methyl % (SD), n*	*metsulfuron methyl % (SD), n*	*sulformeturon methyl % (SD), n*	*nicosulfuron % (SD), n*
Webster	75 (5.1)	77 (2.9)	76 (5.2)	79 (2.8)	1 (0), 2
Waukegan	81 (10), 5	89 (8.6), 4	87 (2.9)	83 (3.1)	2 (0), 2
Verndale	83 (3.0)	84 (2.3)	83 (5.8)	84 (1.4)	4 (0.8), 2

[1] n = 3, except when marked

Langenfeld et al. [21] showed that type of modifier generally was more important for extraction efficiency than modifier concentration. Addition of phosphoric acid to the modifier (0.2% w/w of modifier) and including a static extraction step did not improve the extraction rate for nicosulfuron. Addition of a base to the modifier, with increased pH and weaker sorption to the soil, will not solve the problem due to decreased solubility of the SU in the SF-CO_2. Recoveries of the three SUs obtained using extraction conditions outlined by Berdeaux et al. [15], for SFE of metsulfuron methyl and chlorsulfuron from soils were even lower for all three soils. Berdeaux et al. [15], on the other hand, showed that recoveries for metsulfuron methyl was high for all types of soils except for those with high organic content (4.2 % OC).

The results obtained in this study show that an SFE method optimized for specific compounds cannot always be directly applied to similar compounds or to the same compound extracted from a different matrix without further method development. Each new compound-matrix combination usually requires new method optimization. The results also show that it is very difficult to develop general SFE methods, and that SFE is not the universal extraction technique that solves all sample preparation problems. It appears that SFE can not entirely replace classical solvent extraction techniques.

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