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# **SUPERCritical FLUID EXTRACTION OF SULFONYLUREA HERBICIDES IN SOIL SAMPLES**

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The application of supercritical fluid extraction (SFE) with supercritical CO<sub>2</sub> to the analysis of 2 sulfonylurea herbicides in 4 soils is presented. Methanol and water are added to the soil samples as modifiers. After extraction, Chlorsulfuron and Metsulfuron methyl are measured by HPLC-UV at 220 nm. The recovery rates are good (>80%) for all types of the studied soils except for those with high organic carbon content (ca. 50%). According to the characteristics of the soils, recovery with SFE is similar or better than with liquid-solid extraction.

**KEY WORDS:** Supercritical fluid extraction, sulfonylurea herbicides, chlorsulfuron, Metsulfuron methyl, soils.

## **INTRODUCTION**

The application of supercritical fluid extraction (SFE) to the analysis of organic compounds in solid samples has seen increased attention in the last years. This technique is simple, fast, non toxic and selective to many compounds even in complex matrices. SFE can provide equal or better recovery than classical extraction techniques using organic solvents.

Sulfonylurea herbicides are a new class of agrochemicals used in crop protection. Their main characteristics are their great activity at low levels associated to a low toxicity for fauna and a rapid degradation.

The aim of this work was to develop an extraction method for traces of sulfonylurea herbicides from soils in order to study the behaviour of these compounds. A comparison with a liquid-solid extraction (LSE) method is also described.

**Table 1** Physical and chemical properties of the sulfonylurea herbicides<sup>1,2</sup>.

	<i>Chlorsulfuron</i>	<i>Metsulfuron methyl</i>
Commercial names	Glean, Valinate	Allie, Ally, Gropper
Crops	wheat, linseed	cereals, meadow
Dose (g ai/ha)	4–26	1.8–8
DL 50 mg/kg, oral rat	5546	>5000
DL 50 mg/kg, percutaneous rabbit	>3400	>2000
1/2 life (weeks)	<1	1–4
Melting point	174–178°C	158°C
Molecular weight	357.78g	381.37g
Dissociation constant pKa	3,6	3,3
Partition coefficient (oct/water) pH 5	5,5	1,0
Partition coefficient (oct/water) pH 7	0,046	0,014
Vapour pressure at 25°C	2,3 10 <sup>-11</sup> mm Hg	2,5 10 <sup>-12</sup> mm Hg
Water solubility pH 5	60 mg/l	1100 mg/l
Water solubility pH 7	7000 mg/l	9500 mg/l

## EXPERIMENTAL

*Sulfonylurea herbicides:* The physical and chemical properties of the Chlorsulfuron and Metsulfuron methyl are summarized in Table 1<sup>1,2</sup>.

*Soils:* The composition and physico-chemical characteristics of the soil samples used in this study are summarized in Table 2. They were collected from four different regions of Switzerland. All the soils were sieved at 2 mm, dried and sterilized by heating at 120°C.

*Soil spiking:* In order to establish the extraction method, we worked at concentrations of µg/g knowing that for treated soils the concentrations are in the range of ng/g. Aliquots of soils were spiked with a solution of 150 µg/ml of herbicide in methanol. After homogenisation the methanol was evaporated and the soil sample was stored at +4°C for 24 hours.

*Supercritical fluid extraction (SFE):* The equipment was a Hewlett-Packard Model 7680A with liquid carbon dioxide CO<sub>2</sub> (99.99%) as the extraction fluid. Four g of spiked soil were introduced into the extractor cell (volume of 7 ml) with 80 µl of methanol and 200 µl of water as modifiers. The cell was vigorously shaken for 1 min and placed in the extraction

**Table 2** Physical and chemical characteristics of the soil samples.

Soil	Origin	pH KCl	pH H <sub>2</sub> O	Org C %	100 S/T <sup>a</sup> %	Limons %	Clay %	Texture <sup>b</sup>
Alluvial soil	Gordola	5.0	5.9	1.9	97	38	6	Sandy loam
Acid brown soil	St-Cierges	3.5	4.1	3.0	26	26	16	Sandy clay loam
Rubefied argilic soil	Avully	5.4	6.1	1.5	98	35	17	Loam
Cambic gleysol	Courtetelle	5.7	6.6	4.2	100	28	56	Clay

<sup>a</sup> 100 S/T: % of base saturation = sum of exchangeable Ca, Mg, K, Na/total cation exchange capacity

<sup>b</sup> Textural designations according to FAO 1977

chamber of the SF extractor. The temperature of the chamber was set to 50°C and the pressure of the CO<sub>2</sub> was 370 bars. After 10 min of contact between the CO<sub>2</sub> and the matrix (static mode), the flow was set to 4 ml/min and the sample was extracted for 8 min (dynamic mode). The herbicides were trapped on a cartridge of octadecylsilica (C<sub>18</sub>) at 10°C. The temperature of the nozzle was 45°C. After the extraction, the trap was eluted twice with 1 ml/min of methanol and two fractions of 1 ml were collected separately. Both herbicides were in the first vial. The solvent was reduced under nitrogen stream to a final volume of ca. 0.5 ml.

*Liquid-solid extraction (LSE):* Some extraction methods are described in the literature<sup>3-5</sup>. We tested the method described by Cambon *et al.*<sup>5</sup> with some modifications. Briefly, 20 g of dry soil and 25 ml of an extraction mixture composed of water/methanol/phosphoric acid:20/5/0.02, v/v/v, were mechanically stirred for 1 hour. After centrifugation at 2500 rpm the liquid phase was collected and the soil was reextracted. The extracts were recombined and an aliquot was centrifuged at 4500 rpm for 20 min. The supernatant was ready for injection on the HPLC.

*Liquid chromatography (HPLC):* The analysis was performed with a Shimadzu LC-9A pump and a UV detector Applied Biosystems 757 at 220 nm. A 10 µl sample was injected onto a 4.6 × 250 mm Vydac C<sub>18</sub> column with a particle size of 5 µm. The mobile phase was acetonitrile/water:30/70 (v/v) containing 0.04% phosphoric acid. The flow was 2 ml/min on isocratic mode. Under these conditions, detection limits are 5 µg/kg for Chlorsulfuron and Metsulfuron methyl. The detection limit can be improved by further reducing the final volume of the extract or by using a bigger injection loop. A chromatogram is presented in Figure 1.

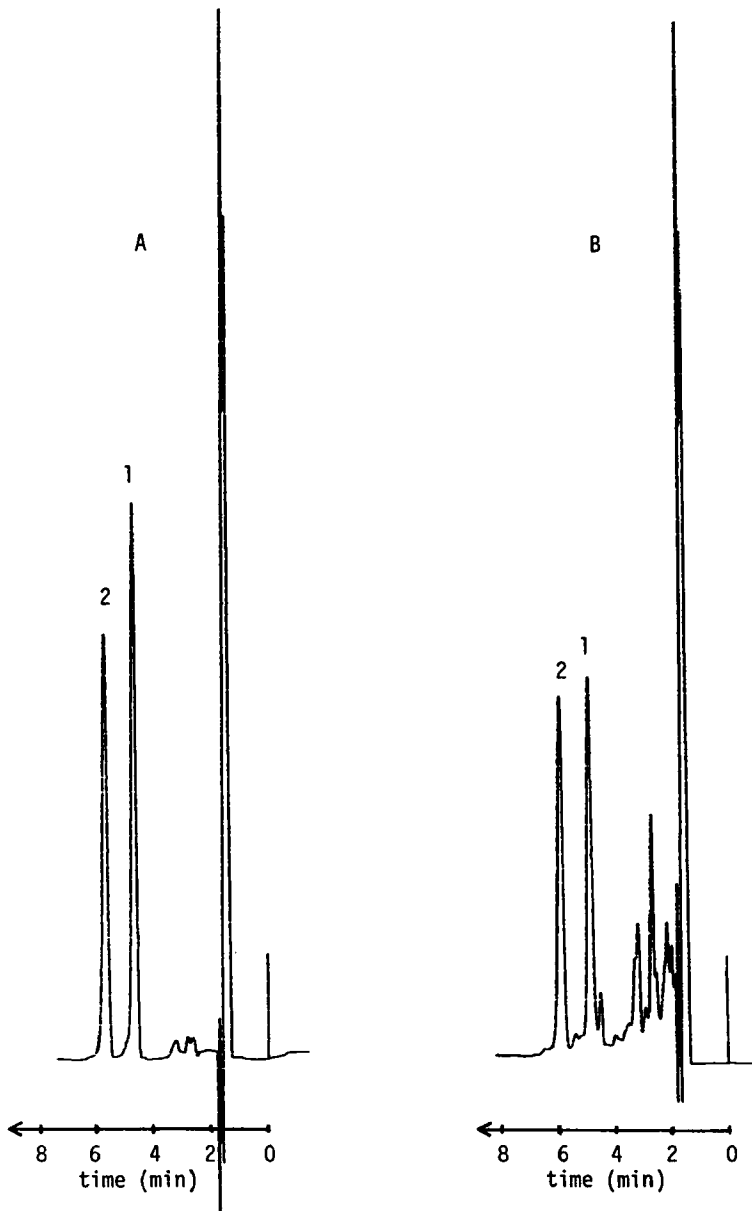
## RESULTS AND DISCUSSION

The critical point of CO<sub>2</sub> is obtained at 31.1°C and 73.8 bars. At temperatures and pressures above this point the CO<sub>2</sub> became a supercritical fluid. By varying the pressure and the temperature we can change the density and consequently the solvation capacity of the fluid. The density of supercritical CO<sub>2</sub> is between 0.2 and 0.9 g/ml. Supercritical CO<sub>2</sub> has a polarity comparable to that of alkanes, being therefore a good extraction medium for non polar compounds. The addition of a polar modifier, e.g. methanol, will favourise the extraction of polar analytes<sup>6-8</sup>.

To establish the best extraction conditions of sulfonylureas with supercritical CO<sub>2</sub>, anhydrous sodium sulphate was used as inert support instead of soil.

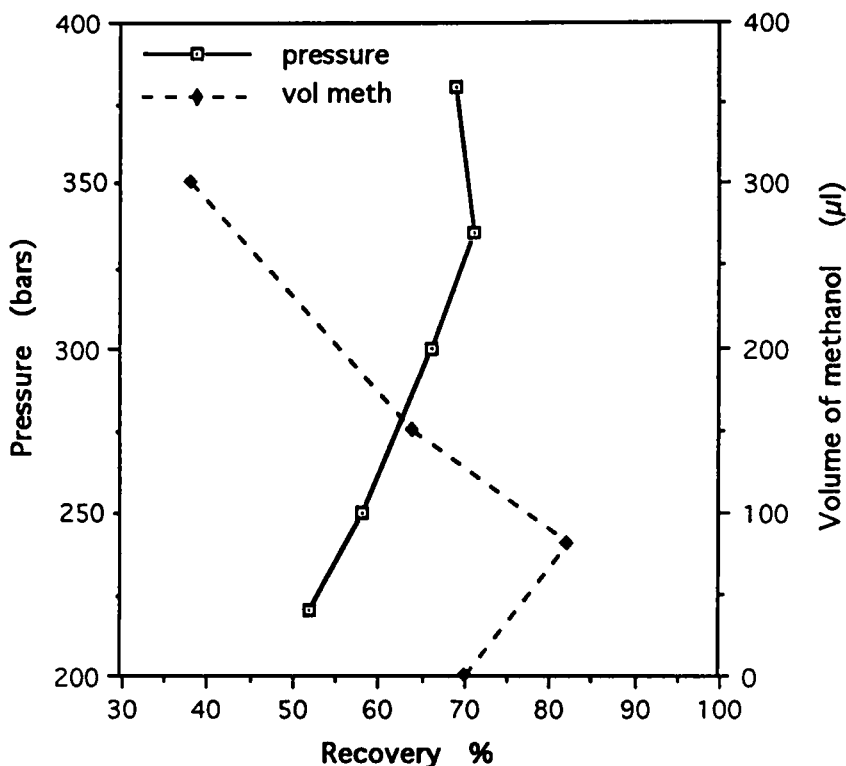
*Influence of the temperature:* Variations between 40 and 50°C did not have a significant influence on the recovery. We chose to work at 50°C.

*Influence of the pressure:* At a constant temperature, we varied the pressure between 220 and 380 bars (maximum permitted by the pump). We observed that below 220 bars, the



**Figure 1** Sulfonylurea chromatograms of a standard mixture (A) and from a spiked soil sample after SFE (B). For HPLC conditions, see text.

1. Metsulfuron methyl 2. Chlorsulfuron

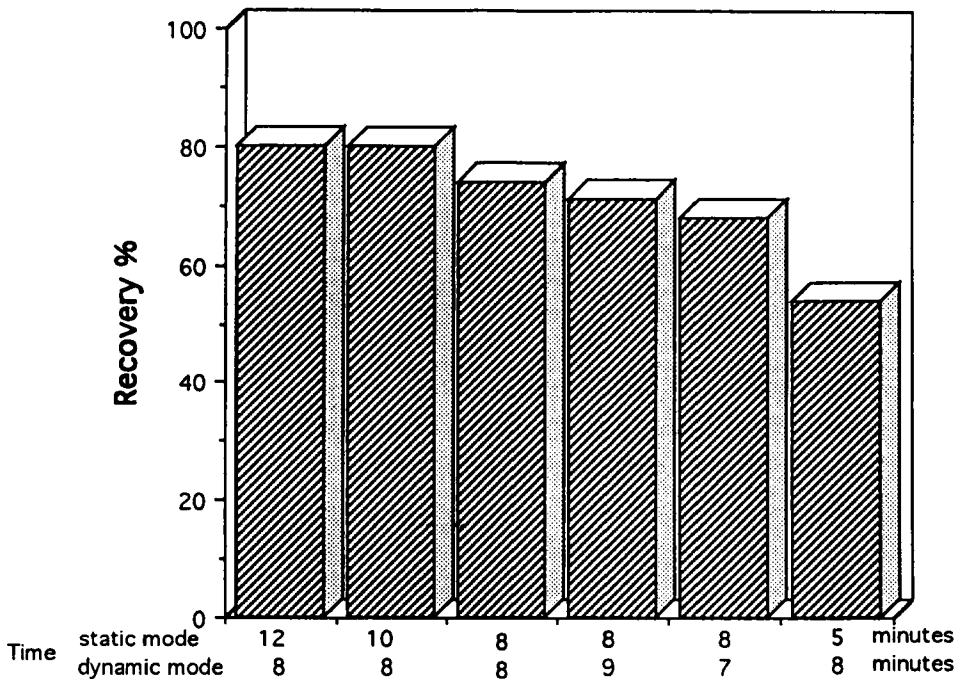


**Figure 2** Influence of the pressure and of the modifier (methanol) on the recovery of Chlorsulfuron.

recovery was poor, less than 50%. The recovery increased until 71% at 340 bars and then remained relatively constant. Therefore, we chose to work close to 370 bars (Figure 2).

*Influence of the polar modifier:* Methanol was selected as modifier. The equipment did not permit to add the modifier to the primary fluid with a second pump. A possibility would have been to work with a premixed and fixed percentage of methanol added to the liquid CO<sub>2</sub> tank. In our case, in order to determine the volume of methanol giving the best recovery, we preferred to add it directly onto the sample in the extraction cell. The cell was then shaken for 30 sec. The best results were obtained by the addition of 80 μl of methanol to 4 g of soil (Figure 2).

*Influence of the extraction time in static mode and in dynamic mode:* During the static phase, fluid CO<sub>2</sub> and the modifier mix and then extract the herbicide from the sample. After that, during the dynamic mode, the fluid CO<sub>2</sub> carries the mixture and extracts the rest of the herbicide. The best recoveries were obtained with at least 10 min static mode and at least 8 min dynamic mode. A second cycle of extraction did not increase the recovery rates (Figure 3).



**Figure 3** Recovery of Chlorsulfuron in soil sample in function of the extraction time in static and dynamic mode.

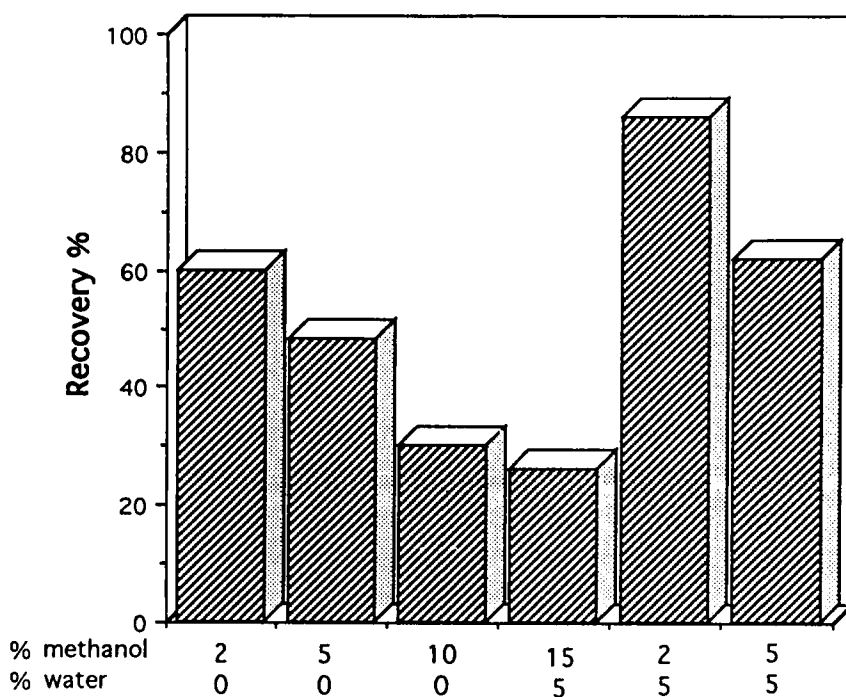
#### *Application to a soil sample (Gordola soil)*

The application of the previously established conditions to extract the herbicides from a spiked Gordola soil sample gave a recovery of only 60%. The modification of any of the parameters did not improve the results. We decided to study the influence of moisture on the recovery and we observed that an addition of 200  $\mu\text{l}$  of deionised water increased the recovery up to 86%. It is therefore important to first dry the soil and then add the appropriate volume of water (Figure 4).

#### *Extraction of herbicides from soils*

**Supercritical fluid extraction (SFE):** The results are summarized in Table 3. For three soils the recovery rate is satisfactory for both herbicides and at two spiking levels. The standard deviation is less than 10%. The differences between the recoveries could be due to the spiking and to losses during extraction or during evaporation.

The recovery efficiencies will be mainly influenced by the solubility of the herbicides in the supercritical fluid, by the diffusion of the analytes from the matrix and by the interactions between the herbicides and the soil matrix.



**Figure 4** Recovery of Chlorsulfuron in soil sample in function of the percentage of moisture and modifier (methanol).

According to the literature<sup>2,9,10</sup>, sulfonylurea herbicides are weak acids, their dissociation constant being  $pK_a = 3.6$  for the Chlorsulfuron and  $pK_a = 3.3$  for the Metsulfuron methyl. Thus, at acidic pH the sulfonylureas are present under their nonionic form, favouring their adsorption onto the soil particles. At neutral or basic pH, they are under their anionic form, which decreases the adsorption. Otherwise, organic carbon is more important than clay fraction for acidic pesticides adsorption<sup>10</sup>. Consequently, it should be difficult to extract these products from soils with low pH and with a high organic matter content.

**Table 3** Recovery rates and standard deviation (SD) for Chlorsulfuron and Metsulfuron methyl by SFE at different spiking levels.

Soil origin	5 $\mu\text{g/g}$						1 $\mu\text{g/g}$					
	Chlorsulfuron			Metsulfuron			Chlorsulfuron			Metsulfuron		
	%	SD	n	%	SD	n	%	SD	n	%	SD	n
Gordola	87	7.6	4	91	8.4	4	84	4.3	10	80	4.9	7
Avully	90	6.5	4	87	3.9	6	89	3.5	4	75	1.8	4
St-Cierges	88	7.7	10	88	5.5	11	82	6.3	5	82	5.8	10
Courtetelle	53	2.0	4	50	3.5	4	47	2.5	4	50	5.2	4



The solubility of the sulfonylureas (in nonionic and anionic forms) is relatively low in supercritical CO<sub>2</sub>. However, the addition of water and methanol to the sample will increase the polarity of the fluid favouring their solubility, which is slightly better for the nonionic form.

Now, according to the characteristics of the studied soils (Table 2), we could expect a lower adsorption on Gordola and Avully soils because their pH is close to neutrality and the percentage of organic carbon is very low (pH = 6 and O.C. <1.9%). On the other hand, the soil from St-Cierges should present the highest adsorption because of its low pH (4.1) and relatively high organic carbon content (3.0%). The fourth soil, Courtetelle, in spite of its neutral pH (6.6), should also present a high adsorption caused by the high organic carbon content (4.2%) and by a high percentage of clay (56%).

The recoveries obtained confirm the hypothesis for Gordola and Avully soils (Table 3). The St-Cierges soil also presents a good recovery because of the good solubility of the nonionic sulfonylurea in the modified fluid CO<sub>2</sub>. Finally, as expected, the Courtetelle soil presents the worst recovery rate, meaning that the organic carbon and the high clay content determine mainly the adsorption of sulfonylurea in this soil.

*Liquid-solid extraction (LSE):* The results are summarized in Table 4. We tested the method only for 2 soils and at 3 different spiking levels. The results agree with the theory, the recoveries being good for Gordola soil (Chlorsulfuron) and poor for St-Cierges soil (Chlorsulfuron and Metsulfuron methyl).

Meanwhile, contrarily as expected, the recoveries of Metsulfuron methyl that should be similar to those of Chlorsulfuron on Gordola soil, are also poor. We have no explanation for this difference.

In comparison with SFE, the recoveries are quite similar between both methods for Chlorsulfuron on Gordola soil (85.5% SFE and 90% LSE). SFE has better recoveries for Metsulfuron methyl on Gordola soil (85.5% SFE and 58% LSE) and also for both herbicides on St-Cierges soil (85% SFE and 42% LSE).

In the future, it would be interesting to establish extraction curves as a function of the pH, of the organic matter content and of the clay level of soils. This would enable to generalize the application of SFE analysis of sulfonylurea herbicides to all types of soils. Experiments with another herbicide, Thifensulfuron methyl, gave almost the same results, suggesting that we can apply this method to other sulfonylureas.

In conclusion, SFE presents good advantages in comparison to traditional liquid-solid extraction techniques. It is easier to use, less toxic, faster and needs a smaller sample

**Table 4** Recovery rates and standard deviation (SD) for Chlorsulfuron and Metsulfuron methyl by liquid-solid extraction at different spiking levels.

Soil origin	0.5 µg/g			1 µg/g			10 µg/g											
	Chlorsulfuron		Metsulfuron		Chlorsulfuron		Metsulfuron		Chlorsulfuron		Metsulfuron							
	%	SD	n	%	SD	n	%	SD	n	%	SD	n						
Gordola	90	3.2	3	58	2.8	2	89	2.5	3	53	3.5	3	92	6.7	3	63	1.3	4
St-Cierges	46	1.7	3	46		1	43	2	3	43	2.8	2	42	2.5	3	37	0.8	3

quantity. The manipulations are reduced, avoiding therefore losses or contaminations. Its selectivity permits direct injection in the HPLC without clean-up. The main limitation is its relatively high cost. It has been shown in this work that this technique is not yet suitable to all kinds of soil and further research is needed in order to solve this problem.

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