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High-performance liquid chromatographic determination of sulfonylureas in soil and water

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Abstract

Isocratic and gradient conditions for the separation of four sulfonylurea herbicides, namely chlorsulfuron, metsulfuron, chlorimuron and thifensulfuron, by reversed-phase high-performance liquid chromatography (HPLC) on C_6 and C_{18} columns were established. Liquid–liquid (LL) and solid-phase extraction (SPE) procedures for the extraction and concentration of the herbicides from water and soil samples were tested. LL and SPE recoveries, HPLC detection limits and repeatability and dependence of the capacity factor on mobile phase composition are discussed. Typical chromatograms are shown.

1. Introduction

Sulfonylureas are a class of herbicides characterized by low application rates (typically in the range 10–100 g ha^{-1}) and low toxicity to mammals. Such molecules are formed by three moieties, generally (i) a monosubstituted benzene ring, (ii) a diazinic or triazinic ring with various substituents and (iii) a sulfonylurea bridge (Fig. 1). In some instances, a disubstituted benzene, a thiophene, a pyridine or a non-aromatic moiety is present as moiety (i) (Fig. 1).

Various methods have been published for the determination of sulfonylureas. The most recent papers include bioassay [1], enzyme immunoassay [2], gas chromatography [3,4], capillary electrophoresis [5] and high-performance liquid chromatography (HPLC) [6,7]. Each has its own advantages and disadvantages.

Bioassays reach very low detection limits (0.1 ppb), but are aspecific. Immunoassays show similar sensitivity and reduce sample work-up and analysis time, but are expensive and not yet commercially available. Two recent papers showed an elegant way to form stable N,N′-dimethyl derivatives of sulfonylureas in soil and water using diazomethane in ethyl acetate [3,4]. However, gas chromatographic analysis contrasts with the low volatility and thermal instability of underivatized and monomethylated sulfonylureas, and is uncommon for such a class of herbicides. Capillary electrophoresis has been used to determine chlorsulfuron and metsulfuron in tap water [5], but has yet to be applied to soil, its main problem being the low sample loadability.

HPLC is the most commonly adopted method

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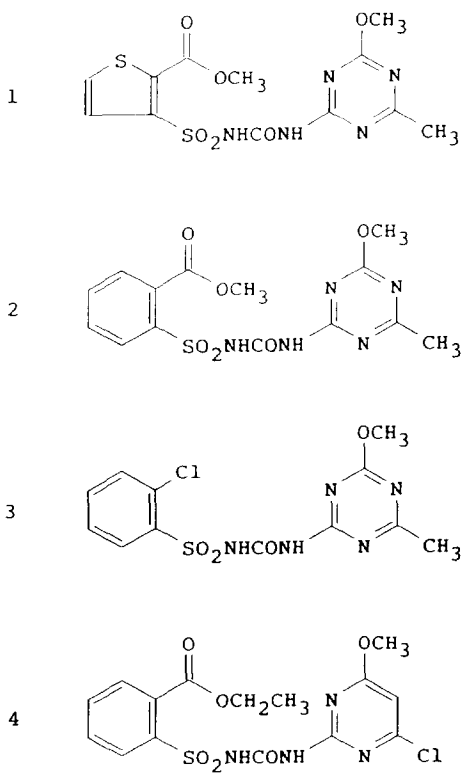

Fig. 1. Structures of sulfonylureas: 1 = thifensulfuron; 2 = metsulfuron; 3 = chlorsulfuron; 4 = chlorimuron.

for sulfonylurea determination in soil and water [6,7]. Chromatographic techniques, including HPLC, need preliminary enrichment steps when analyte concentrations in the sample are below the minimum injectable level. Minimum concentrations of sulfonylurea standard solutions for HPLC with UV detection are about 1 ppm. Photoconductivity detectors lower such detection limits by about one order of magnitude. Although sulfonylurea concentrations as low as 0.2 ppb have been determined in soil using HPLC with photoconductivity detection [7], careful control of various operating parameters is needed to optimize sensitivity and baseline stability [8–10]. In conclusion, photoconductivity detectors are not commonly adopted in HPLC.

Since 1982, when the first sulfonylurea herbicide, chlorsulfuron, became commercially available, at least sixteen different herbicide products containing different sulfonylureic active ingredients have appeared on market. Surprisingly, most HPLC publications have dealt with the simultaneous determination of one or two sulfonylureas only, aimed at improving the detection limit rather than increasing the number of detected molecules.

Prior to research on sulfonylurea degradation in soil, we decided to test some extraction and HPLC conditions in an attempt to increase the number of sulfonylureas detectable in one run. Four sulfonylureas (Fig. 1) were selected among those commercially available. Three compounds, chlorsulfuron, metsulfuron and chlorimuron, are monosubstituted benzenic sulfonylureas. Thifensulfuron is characterized by a monosubstituted thiophene instead of a benzene ring. The former compounds are characterized by long residence times in soil. The latter is representative of a category of sulfonylureas more easily degraded in soil. Such molecules are of less environmental impact, but are more elusive, because they decompose faster.

2. Experimental

2.1. Reagents

Reagents for HPLC separations and extraction were pesticide-free and supplied by Sigma (St. Louis, MO, USA). The sample concentration column for solid-phase extraction consisted in a Bakerbond (Phillipsburg, NJ, USA) C_{18} (1 g, 40-μm silica particles). Sulfonylurea commercial products were kindly provided by Professor P. Catizone and Dr. A. Vicari, Department of Agronomy, University of Bologna.

2.2. Sulfonylurea samples

Chlorsulfuron, metsulfuron, chlorimuron and thifensulfuron were extracted from commercial formulates with freshly redistilled dichloromethane in a Soxhlet extractor for 3 h. After dehydration with anhydrous sodium sulfate, dichloromethane was distilled off in a rotary evaporator. The residual sulfonylureas were sub-

jected to nuclear magnetic resonance, infrared and mass spectral analyses to confirm their identity and used for subsequent experiments without further purification. Sulfonylurea yields from the commercial formulates ranged from 24 to 71% (Table 1).

2.3. Standard solutions

A stock standard solution at a concentration of 100 ppm was prepared by dissolving 10 mg each of the four sulfonylureas in 100 ml of methanol–water (40:60). Appropriate dilutions of this stock standard solution were made with methanol–water (40:60) to obtain working standard solutions of 0.25, 0.5, 1, 2, 4, 5 and 10 ppm.

A similar procedure was adopted for (a) thifensulfuron, metsulfuron and chlorsulfuron in one stock solution and (b) chlorimuron in a separate stock solution, in order to run "isocratic 2 and 3" respectively (see Section 2.7).

2.4. Water sample fortification and extraction

Water (100 ml) containing the four sulfonylureas (4 ppb each) was passed through a disposable C_{18} column previously conditioned with methanol (5 ml) and water (5 ml). Adsorbed sulfonylureas were eluted with methanol (5 ml). Excess of solvent was removed in a rotary evaporator. The residue was dissolved in 0.01% $HClO_4$–methanol (1:1, 100 μl). An aliquot of this solution was injected into the HPLC system. The whole procedure was done in triplicate.

Table 1
Sulfonylurea yield (%) after duplicate Soxhlet extraction from commercial formulations

Compound	Declared	Found	
		Sample 1	Sample 2
Chlorsulfuron	75	71	73
Metsulfuron	20	24	24
Chlorimuron	Not declared	27	26
Thifensulfuron	Not declared	66	66

2.5. Soil sample fortification

The soil used for the trials was a sandy loam soil (58% sand, 15% silt, 27% clay, 1.3% organic matter, pH 6.5) from Cadriano, Bologna, sieved to 3 mm.

A stock standard solution containing 1 ppm of the four sulfonylureas was obtained by dissolving 10 mg of each compound in 10 l of doubly distilled water. A 500-g amount of soil (on an oven-dry basis) was treated by uniform spraying of 25 ml of the stock standard solution to obtain a final concentration of 50 ppb. The same procedure was effected for the soil samples at 20 and 10 ppb, spraying 10 and 5 ml of the stock standard solution on 500 g of soil (on an oven-dry basis). After the fortification, the soil samples were mixed for 5 min in a blender and frozen at −20°C.

2.6. Soil extraction

A liquid–liquid and a solid-phase extraction were employed and compared.

Liquid–liquid extraction (in duplicate) of the fortified soil samples was performed according to Zahnow [11]. Briefly, the buffer for extraction was methanol–0.1 *M* NaOH (1:1, v/v) (pH 11). Purification of extract was performed using methylene chloride. The solvent was discarded and the aqueous phase was adjusted to pH 3–4 by adding 10% HCl dropwise. Again, methylene chloride was added, shaken, separated from the aqueous phase and evaporated to dryness in a Rotavapor at 45°C. A 50-g amount of soil (on an oven-dry basis) for the 50 and 20 ppb levels and 100 g for the 10 ppb level were used. The dry residues after all extraction steps were dissolved in 1 ml of methanol–water (60:40). In this way, an enrichment of 50-fold was obtained for the samples at 50 and 20 ppb and 100-fold for the sample at 10 ppb.

Solid-phase extraction was performed in duplicate according to Dinelli et al. [5]. Briefly, 100 ml of sodium hydrogencarbonate solution (0.1 *M*, pH 7.8) was added to 50 g of soil (50 and 20 ppb fortifications) and to 100 g of soil for the 10 ppb level. The suspension was shaken for 1 h.

The slurry was centrifuged at 12 000 rpm for 5 min. The extraction procedure was repeated twice and the liquid extracts were combined. The extracts were adjusted to pH 2.5 with 0.1 *M* HCl and passed through the solid-phase extraction column. The dry residues were reconstituted with 1 ml of methanol–water (60:40), thus obtaining an enrichment of 50-fold for the 50 and 20 ppb samples and 100-fold for the 10 ppb sample.

2.7. High-performance liquid chromatography

The HPLC system was a Beckman (Palo Alto, CA, USA) System Gold 126 with two pumps and a Rheodyne Model 7725-i valve (20-μl loop). A Beckman Model 168 diode array detector was used.

Reversed-phase C_6 and C_{18} columns were tested using both isocratic and gradient elution modes. The dependence of the capacity factors on the mobile phase composition was checked for both columns. Response and retention time repeatabilities were checked for the C_{18} column, which was used more generally.

The C_6 column was a Viospher (5 μm, 120 × 4.6 mm I.D.) (Violet, Rome, Italy). The mobile phase was (A) 0.01% $HClO_4$ in water and (B) methanol at a flow-rate of 1 ml/min. The A:B ratio was 55:45 (v/v) for isocratic elution (hereafter called "isocratic 1"). For gradient eleution, the A:B ratio was varied from 60:40 to 40:60 (v/v) in 20 min, holding the final conditions for 5 min (hereafter called "gradient 1").

The C_{18} column was a Beckman C_{18} Ultrasphere (25 cm × 4.6 mm I.D., 5 μm particle size). Analyses were performed in isocratic and gradient modes. For the first isocratic separation (hereafter called "isocratic 2") the mobile phase was (A) water (pH 2.5, adjusted phosphoric acid) and (B) methanol in the ratio 60:40 (v/v) at 1 a flow-rate of ml/min. For the second isocratic condition ("isocratic 3") the mobile phase was the same as above but in ratio 40:60. For the gradient separation, the gradient was performed by maintaining initial conditions at water (pH 2.5, adjusted with 85% phosphoric acid)–methanol (60:40) for 5 min, then increasing the B content linearly to reach a final water:methanol ratio of 30:70, which was maintained for 5 min before resetting. The injections volume was 20 μl and detection was performed at 224 and 234 nm.

3. Results and discussion

3.1. Reversed-phase C_6 column

This column was tested first because it was expected that the analysis times would be faster than those with C_{18} columns. Actually, separations of standard mixtures of the four sulfonylureas were completed in about 25 min adopting both isocratic 1 and gradient 1 conditions (Fig. 2a and c). Responses (data not shown) were linear in the 0.1–2 ppm range ($R^2 > 0.999$).

The retention time of chlorimuron was much longer than those of the other three compounds. This observation can be explained by considering that its structure bears a chlorine-substituted diazinic ring instead of the relatively more polar methoxy-substituted triazinic ring of the other sulfonylureas, the other features not differing substantially.

Both isocratic and gradient conditions were chosen as the best compromise between rapidity of analysis and separation efficiency. This consideration is better explained in Fig. 3a, in which the capacity factors of the four sulfonylureas are plotted against mobile phase composition. The efficiency of the C_6 column used did not allow the separation of the four sulfonylureas with organic modifier contents in the mobile phase higher than 50%. Under such circumstances, the C_6 column was applied to the analysis of water samples only, as explained in the following section.

3.2. Reversed-phase C_{18} column

As expected, the sulfonylurea retention times were much longer using a C_{18} column, the analysis of the three earlier eluting compounds requiring about 35 min. Under such conditions,

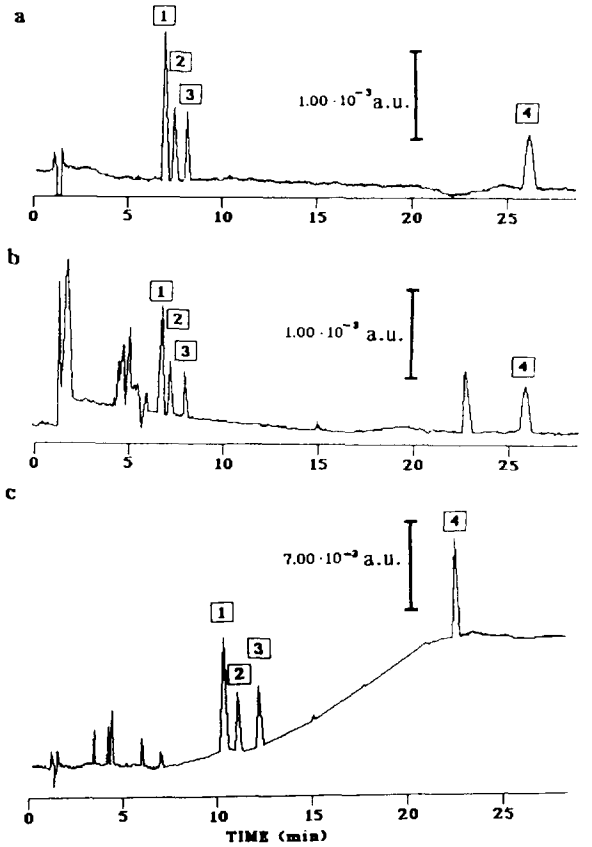

Fig. 2. Separation of sulfonylureas on a C_6 column using isocratic 1 conditions for (a) the standard mixture and (b) a spiked water extract and gradient 1 conditions for (c) the standard mixture. Detection at 234 nm. Peak numbers: compounds as in Fig. 1.

the retention time of chlorimuron was very delayed and useless for practical applications. This problem was overcome by (a) determining chlorimuron separately from the other three molecules and (b) using gradient conditions. Fig. 4a–c shows the separation of sulfonylurea standard mixtures under isocratic and gradient eluting conditions, namely (a) isocratic 2, (b) isocratic 3 and (c) gradient 2.

Isocratic conditions 2 and 3 were those adopted for the determination of sulfonylureas in soil in this work, as discussed in the next section. However, the capacity factors were linear and the compounds were well resolved in a range of mobile phase compositions wider than that with the C_6 column (Fig. 3b), allowing the possibility of further separations, depending on the sample nature, the sulfonylurea and the interferent concentrations.

Given the more general application of the reversed-phase C_{18} column, the retention time and peak area repeatabilities and response linearity were checked. With regard to retention time repeatability, Table 2 shows the results obtained after ten replicate injections on the same day (intra-day) and during 1 month (inter-day). The retention time fluctuations were within a maximum of 2.8% (R.S.D.) and did not appear much larger in 1 month than in 1 day.

Peak-area variability (Table 3) measured in the same way as above showed R.S.D.s in the range 3.7–8.4%, which did not differ at two detection wavelengths. Finally, the responses of all sulfonylureas were highly linear in the range 0.25–10 ppm injected (Table 4).

3.3. *Sample clean-up, sulfonylurea enrichment and analysis*

Water, C_6 HPLC column

Table 5 shows the recoveries of sulfonylureas after triplicate solid-phase extractions of aqueous solutions at the 5 ppb level, obtaining a 10^3-fold enrichment. At such concentrations, i.e., 5 ppm, sulfonylureas were well above the detection limits and typical chromatograms appeared were obtained such as that shown in Fig. 2b, in which the four sulfonylureas are well separated and free from water interferences.

Soil, C_{18} HPLC column

Two different soil clean-ups were tested, one based on liquid–liquid sulfonylurea partitioning and the other on a solid-phase extraction. Sulfonylurea recoveries as determined after duplicate extractions of soil samples spiked in the range 10–50 ppb are given in Tables 6 and 7.

The method based on liquid–liquid partioning seemed unsatisfactory (Table 6), in that the extraction recoveries were low when the sulfonylurea concentrations in the sample were lower than 50 ppb. The thifensulfuron recoveries were particularly low at all concentrations tested. This observation is consistent with the reported

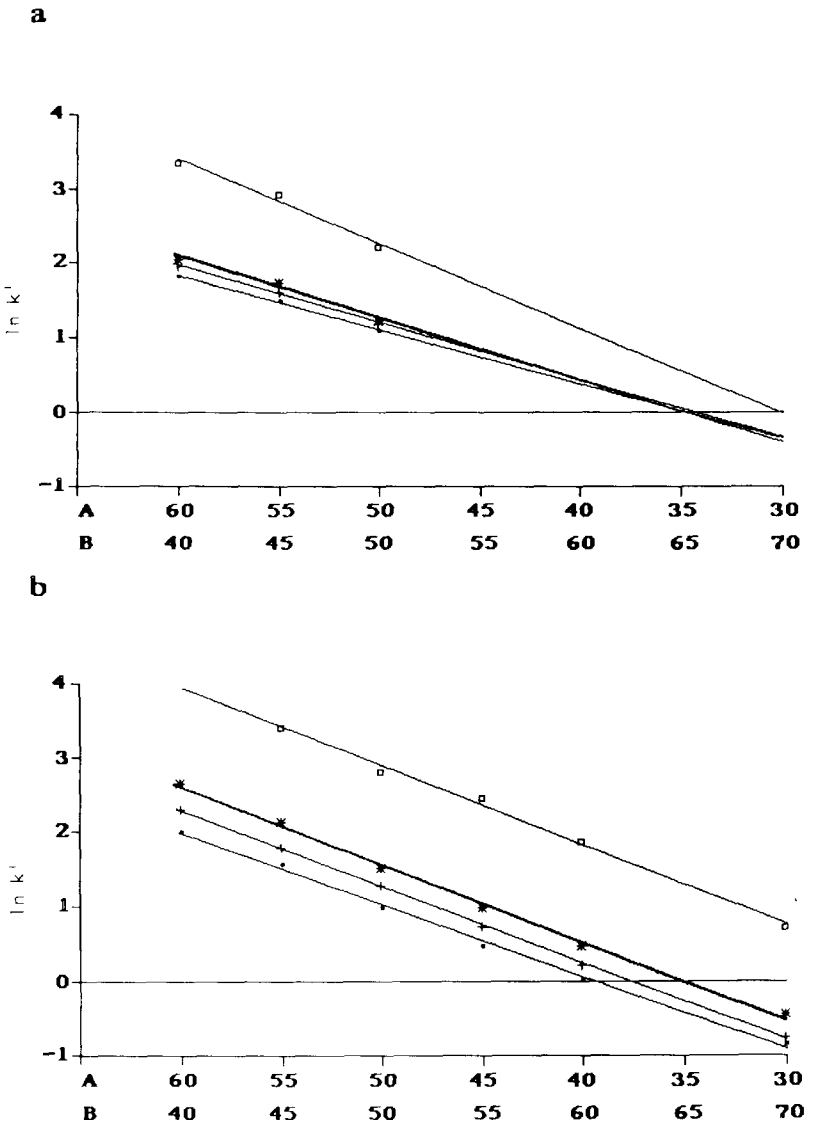

Fig. 3. Dependence of capacity factors on mobile phase composition for (a) C_6 column and (b) C_{18} column. □ = Thifensulfuron; * = metsulfuron; + = chlorsulfuron; ■ = chlorimuron.

relatively labile nature of thifensulfuron compared with the other three molecules and with the very fast degradation of sulfonylureas at low and high pH in aqueous systems [12–15].

Solid-phase extraction (Table 7), more rapid than the previous one, improved the recovery of thifensulfuron, owing to the milder pH conditions. The recoveries of all sulfonylureas did not seem to be affected by sample concentration.

Fig. 5 shows the separations under isocratic 2 and 3 conditions of sulfonylureas from soils spiked at 10 ppb levels after solid-phase extraction and 100-fold enrichment. The early-eluting and large soil interferences corroborate the previous statement about the need to use a C_{18} instead of a C_6 column, in order to separate sulfonylureas properly from interferences. While gradient elution was effective in separating all

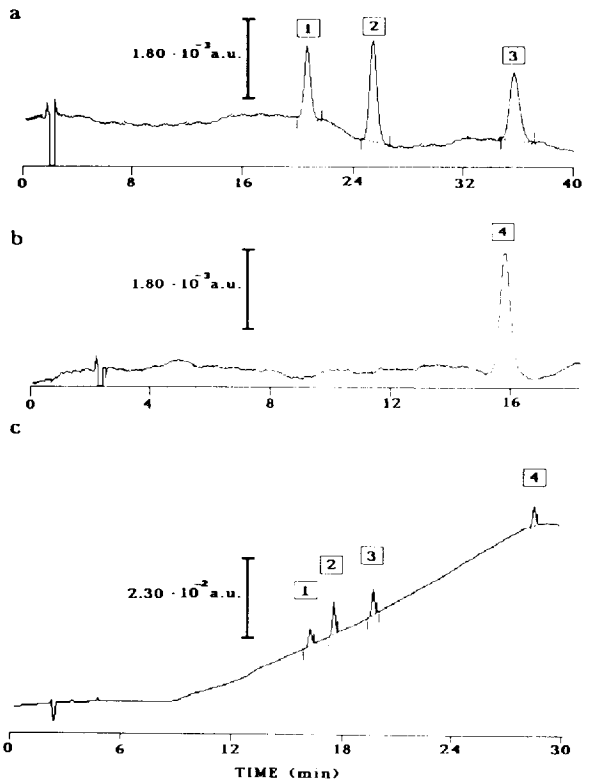

Fig. 4. Separation of standard sulfonylureas on a C_{18} column using various elution conditions: (a) isocratic 2. (b) isocratic 3 and (c) gradient 2. Detection at 234 nm. Peak numbers: compounds as in Fig. 1.

sulfonylureas in about 30 min (Fig. 4c), some soil interferences co-eluted with peaks of thifensulfuron and metsulfuron, suggesting that the use of two isocratic conditions was safer. In fact, the high correlation coefficients between the UV spectra scanned over the sulfonylurea peaks from soil and standard mixtures (lower and upper curve, respectively, in Fig. 6) suggest that little if any interference was from the soil matrix.

3.4. Method sensitivity

Table 8 compares the minimum concentrations at which sulfonylureas were detected in this work with the detection limits reported by other workers in different substrates and using different chromatographic techniques. The orders of magnitude only are reported for such detection limits, given the variable concept of definition of detection limit used by different workers.

The overall method sensitivity appears to be governed by essentially two factors: (i) sensitivity inherent to the analytical technique and (ii) enrichment coefficient applicable to a particular substrate.

Concerning sensitivity, a final concentration of 1–5 ppm is the lower limit for solutions to be analyzed by gas chromatography and HPLC with UV detection. Such techniques are therefore substantially equivalent to this respect. A tenfold improvement to 0.1 ppm (order of magnitude) can be achieved by capillary electrophoresis and by HPLC with photoconductivity detection. Detection limits of 0.01 ppm have been reported for the latter after accurate optimization of the chromatographic conditions.

Concerning sample effects, limits may differ

Table 2
Intra-day and inter-day retention time (t_R) and repeatability [standard deviation (in parentheses) and relative standard deviation (R.S.D.)]

Compound	Intra-day		Inter-day	
	t_r (min)	R.S.D. (%)	t_R (min)	R.S.D. (%)
Thifensulfuron[a]	21.3 (0.4)	1.9	21.0 (0.5)	2.5
Metsulfuron[a]	25.4 (1.1)	2.1	24.9 (0.7)	2.7
Chlorsulfuron[a]	35.7 (0.8)	2.2	35.5 (1.0)	2.8
Chlorimuron[b]	16.5 (0.3)	1.6	16.3 (0.3)	2.0

Average of ten injections of 1 ppm sulfonylurea solutions on the same day (intra-day) and on ten different days during 1 month (inter-day). Detection at 234 nm.

[a] Analysis according to isocratic 2 conditions.

[b] Separate analysis to the other three compounds, according to isocratic 3 conditions.

Table 3
Intra-day and inter-day peak area (arbitrary units) and repeatability [standard deviation (in parentheses) and R.S.D.]

Compound	Detection wavelength (nm)	Intra-day		Inter-day	
		Area	R.S.D. (%)	Area	R.S.D. (%)
Thifensulfuron[a]	234	0.58 (0.03)	4.7	0.59 (0.04)	6.1
	224	0.93 (0.04)	4.6	0.96 (0.06)	6.5
Metsulfuron[a]	234	1.11 (0.04)	3.7	1.06 (0.04)	3.8
	224	1.59 (0.06)	3.7	1.48 (0.07)	4.5
Chlorsulfuron[a]	234	0.75 (0.05)	6.1	0.75 (0.06)	8.4
	224	1.12 (0.07)	6.1	1.13 (0.09)	7.9
Chlorimuron[b]	234	1.15 (0.04)	3.7	1.14 (0.06)	5.5
	224	0.95 (0.04)	3.9	0.94 (0.05)	5.6

Average of ten injections of 1 ppm sulfonylurea solutions on the same day (intra-day) and on ten different days during 1 month (inter-day). Detection at 234 and 224 nm.
[a,b] See Table 2.

Table 4
Calibration graphs for the four sulfonylureas in the range 0.25–10 ppm [injected solutions 0.25, 0.5, 1, 2, 4, 5 and 10 ppm; y = ppm; x = area (arbitrary units)]

Compound	Detection at 224 nm		Detection at 234 nm	
	y	R^2	y	R^2
Thifensulfuron[a]	$1.027x + 0.045$	0.991	$1.750x - 0.062$	0.990
Metsulfuron[a]	$0.671x + 0.057$	0.999	$1.010x - 0.058$	0.999
Chlorsulfuron[a]	$0.795x - 0.138$	0.999	$1.221x - 0.068$	0.999
Chlorimuron[b]	$1.094x - 0.056$	0.994	$0.947x - 0.069$	0.997

[a,b] See Table 2.

by up to a factor of 10^3 depending on (i) whether the sample extracts can be concentrated without the risk of concentrating impurities that may interfere with the analytes and (ii) which sample size is easier to manipulate. Water samples in the litre range can be enriched by a factor 10^3–10^4, whereas enrichments of 10–50-fold are more common for 10–100-g samples of soil and plant materials. Gas chromatography allows enrichments from soil extracts of 10^3-fold, possibly owing to the "filter effect" of both derivatization and volatility. Consequently, while the determination of sulfonylureas at sub-ppb levels in water is relatively straightforward, soil samples are more commonly analysed in the 1–10 ppb range.

In conclusion, detection limits of 1 ppb and even 0.2 ppb have been reported but, as stated by Beyer et al. [13], "conducting routine analysis at these levels is very difficult".

Table 5
Sulfonylurea recoveries with standard deviations (in parentheses) after triplicate solid-phase extraction from a water sample at 5 ppb

Compound	Recovery (%)
Chlorsulfuron	84.0 (4.5)
Metsulfuron	82.0 (4.2)
Chlorimuron	90.0 (3.8)
Thifensulfuron	90.0 (8.5)

Table 6
Sulfonylurea recoveries with standard deviations (in parentheses) after duplicate liquid–liquid extraction from soil samples at different herbicide concentrations (detection at 224 nm)

Concentration (ppb)	Recovery (%)			
	Thifensulfuron	Metsulfuron	Chlorsulfuron	Chlorimuron
50	56.4 (6.6)	94.5 (6.5)	95.5 (1.3)	87.4 (3.1)
20	40.6 (4.4)	65.2 (4.9)	64.4 (1.5)	60.1 (3.4)
10	41.7 (3.5)	47.0 (4.0)	70.6 (16.4)	63.4 (4.9)

Table 7
Sulfonylurea recoveries with standard deviations (in parentheses) after duplicate solid-phase extraction from soil samples at different herbicide concentrations (detection at 224 nm)

Concentration (ppb)	Recovery (%)			
	Thifensulfuron	Metsulfuron	Chlorsulfuron	Chlorimuron
50	75.8 (8.4)	90.4 (0.5)	91.3 (5.7)	97.3 (11.1)
20	83.4 (3.3)	108.4 (1.2)	91.9 (20.8)	75.8 (2.4)
10	71.1 (1.5)	95.6 (3.4)	88.4 (7.6)	97.8 (4.6)

4. Conclusions

Sulfonylurea application rates of 10–100 g ha^{-1} correspond to initial nominal soil concentrations of 0.1–1 ppm. Sulfonylurea concentrations of 10–50 ppb in soil and above 1 ppb in water were adopted in this work as more suitable limits for setting up a rapid, simple and routine method to screen several sulfonylureas in tests about their degradation rate in soil, where the expected residue levels will be above the detection limit. Although no attempt was made to lower the detection limits reported in the literature, improved recovery of sulfonylureas from soil was demonstrated with solid-phase extraction, and isocratic HPLC with diode-array detection performed satisfactorily for our intended purposes. We believe we have demonstrated the validity of solid-phase extraction and the applicability of various HPLC conditions to the determination of four sulfonylureas.

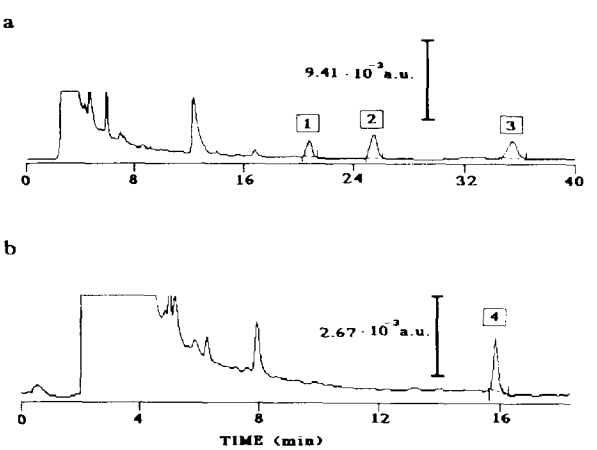

Fig. 5. Separation of sulfonylureas from a soil spiked at 10 ppb using (a) isocratic 2 and (b) isocratic 3 conditions and a C_{18} column. Peak numbers: compounds in Fig. 1.

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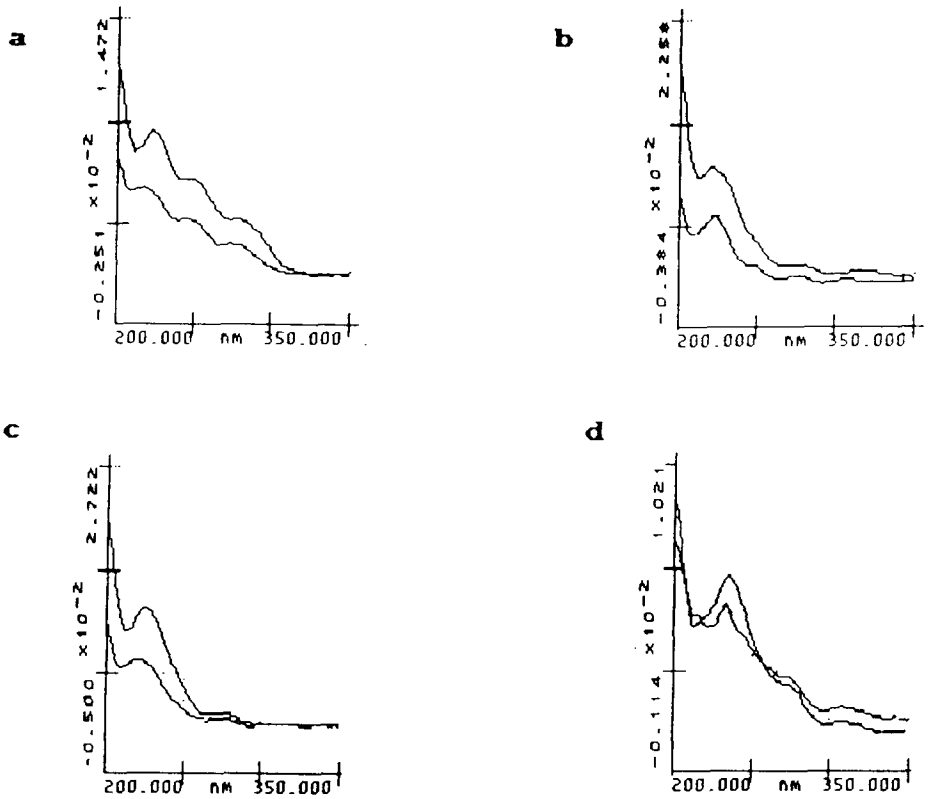

Fig. 6. UV spectral scans for (a) thifensulfuron, (b) metsulfuron, (c) chlorsulfuron and (d) chlorimuron. Upper curves, standard; lower curves, soil extract.

Table 8
Selected examples of minimum sulfonylurea concentrations (order of magnitude) as reported in literature compared with the levels used in this work

Sample	Sample amount	Initial concentration (ppb)	Enrichment factor	Final concentration (ppm)	Analytical method[a]	Ref.
Water	1 l	0.1	10^4	1	CE–UV	[5]
Water	1 l	0.1	10^4	1	GC–ECD	[4]
Water	100 ml	5	10^3	5	HPLC–UV	This work
Soil	50 g	0.2	50	0.01	HPLC–PID	[7]
Soil	100 g	1	10^3	1	GC–ECD	[4]
Soil	100 g	10	100	1	HPLC–UV	This work
Soil	50 g	50	50	2.5	HPLC–UV	[16]
Plant	10 g	10	10	0.1	HPLC–PID	[17]

[a]CE–UV = capillary electrophoresis with ultraviolet detection; GC–ECD = gas chromatography with electron-capture detection; HPLC–UV = high-performance liquid chromatography with ultraviolet detection; HPLC–PID = high-performance liquid chromatography with photoionization detection.

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