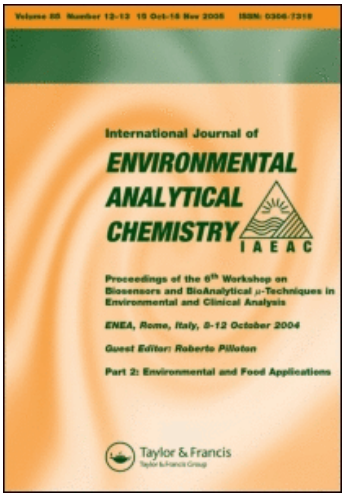


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# A REVIEW OF ANALYTICAL METHODS FOR SULFONYLUREA HERBICIDES IN SOIL

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The sulfonylurea herbicides are a group of about twenty compounds used for the control of broad-leaved weeds and some grasses in cereal crops. These herbicides are non-volatile, and their water solubilities are pH dependent being greater in alkaline than in acidic solutions. Their soil adsorption is generally low, with leaching potential in alkaline field soils. Sulfonylurea herbicides are degraded in soils by both chemical and biochemical mechanisms. Chemical degradation is particularly important in acidic soils where herbicide degradation is considerably more rapid that in soils of pH >7. Application rates in the order of 10 g $ha^{-1}$ necessitate analytical techniques capable of quantifying soil based residues in the sub μg $kg^{-1}$ levels. Analytical methodologies based on plant bioassays, and chemical extraction followed by gas chromatographic (GC), high performance liquid chromatographic (HPLC), and enzyme immunoassay techniques are described and discussed.

**KEY WORDS:** Bioassays, chemical analysis, immunoassays, soils, sulfonylurea herbicides.



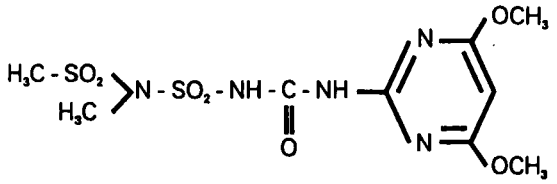
## INTRODUCTION

The sulfonylurea herbicides are a relatively new class of compounds used worldwide for the control of broad-leaved weeds and certain grasses in cereal crops[1-3]. Currently there are about 20 such herbicides either in general use, or in the process of being developed and registered, for weed control. Their mode of action results from inhibition of acetolactate synthase, a key enzyme in the biosynthesis of branch-chained amino acids[1,2]. Sulfonylureas are based on the general structure:

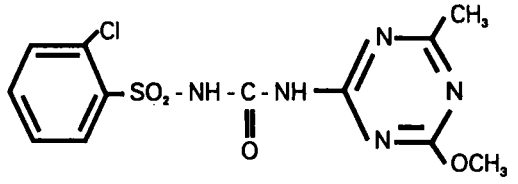
$$R_1 - SO_2 - NH - CO - NH - R_2$$

where the $R_1$ moiety can be an aliphatic, aromatic, or heterocyclic grouping connected by the sulfonylurea bridge to the $R_2$ moiety which can be either a substituted triazine or pyrimidine[1-4] system. Common and chemical names of the sulfonylureas referred to in this manuscript are summarized in Table 1. The structures of amidosulfuron, chlorsulfuron, and thifensulfuron are shown in Figure 1.

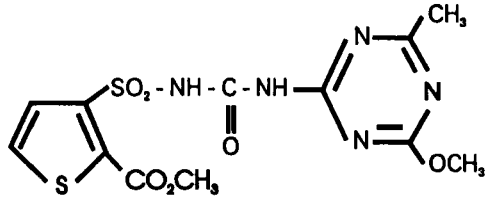
Sulfonylurea herbicides are applied as post-emergence treatments of wettable powders or water-dispersible granules at rates[1] of between 10 and 20 g (a.i.) $ha^{-1}$. Resulting soil residues can exhibit activity in the soil against sensitive plants for more than a year[1-3]. Because of their very low application rates and their mobility in the soil profile due to leaching, analysis of sulfonylurea residues in the soil necessitates their detection at levels of < 1 μg $kg^{-1}$.




AMIDOSULFURON




CHLORSULFURON




THIFENSULFURON

**Figure 1** Structures of amidosulfuron, chlorsulfuron, and thifensulfuron.

**Table 1** Common and chemical names of sulfonylureas mentioned in the text.

| *Common name* | *Chemical name* |
|---|---|
| Amidosulfuron | 3-(4,6-Dimethoxypyrimidin-2-yl)-1-(N-methyl-N-methyl-sulfonyl)aminosulfonylurea |
| Bensulfuron methyl | Methyl 2-[[[(4,6-dimethoxypyrimidin-2-yl)aminocarbon-yl]aminosulfonyl]methyl]benzoate |
| Chlorimuron ethyl | Ethyl 2-[[(4-chloro-6-methoxypyrimidin-2-yl)amino-carbonyl]aminosulfonyl]benzoate |
| Chlorsulfuron | 2-Chloro-N-[4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]benzenesulfonamide |
| Metsulfuron methyl | Methyl 2-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]aminosulfonyl]benzoate |
| Nicosulfuron | 2-[[[[(4,6-Dimethoxypyrimidin-2-yl)amino]carbonyl]-amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide |
| Rimriduron | N-[[(4,6-dimethoxypyrimidin-2-yl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide |
| Sulfometuron methyl | Methyl 2-[[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-aminosulfonyl]benzoate |
| Thifensulfuron | Methyl 3-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]aminosulfonyl]-2-thiophenecarboxylate |
| Triasulfuron | 1-[2-(2-Chloroethoxy)phenylsulfonyl]-3-(4-methoxy-6-methyl)-1,3,5-triazin-2-yl) urea |

In this review, the physical and chemical properties of sulfonylurea herbicides as well as their degradation and persistence in soil will briefly be described. Subsequently, their detection and analysis in soils using plant bioassay, chemical methods, and enzyme immunoassays will be discussed.

## PROPERTIES OF SULFONYLUREA HERBICIDES

### *Physical properties*

The sulfonylurea herbicides are non-volatile compounds with vapor pressures of less than $10^{-10}$ mm of mercury[1,2,4]. They all contain an ionizable proton on the amido group adjacent to the sulfonyl group:

$$-SO_2-NH-CO-NH- \rightleftharpoons -SO_2-N^--CO-NH-$$

and behave as weak acids possessing $pK_a$ values ranging from 3 to 5[1,2,4]. For this reason, their water solubilities at pH 7 are approximately ten fold greater than at pH 5[1,3,4]. Thus, the solubilities of chlorsulfuron, sulfometuron methyl, and metsulfuron methyl in aqueous media (at 25°C) at pH 5 are 60, 8, and 1100 μg $ml^{-1}$, while at pH 7 their solubilities are 7000, 70, and 9500 μg $ml^{-1}$, respectively[1,4].

The effect of pH on the octanol-water partition coefficient ($K_{ow}$) is the reverse of its effect on water solubility since greater partitioning of the neutral molecules occurs in acidic than neutral solutions[1,4]. At 25°C, the $K_{ow}$ values for chlorsulfuron, sulfometuron methyl, and metsulfuron methyl at pH 5 are 5.5, 15, and 1.0; in solutions at pH 7 the values are 0.046, 0.31, and 0.014, respectively[1,4].

### *Chemical properties*

Sulfonylureas undergo hydrolysis in aqueous media at a rate dependent upon both temperature and pH[1,3–6]. Solution pH controls the rate of hydrolysis since the neutral form of the sulfonylurea bridge is considerably more susceptible to hydrolysis than the ionic form[3]. At 45°C, the half-lives of chlorsulfuron, chlorimuron ethyl, metsulfuron methyl, and sulfometuron methyl in aqueous media at pH 5 were 1.7, 0.6, 2.1, and 0.4 days while, under similar conditions at a pH of 7, the half-life data were 51, 14, 33, and 6 days, respectively[1].

Under hydrolytic conditions, cleavage of the sulfonylurea bridge occurs[1,3–6] with the resulting formation of a sulfonamide and an aminotriazine or aminopyrimidine:

$$R_1-SO_2-NH-CO-NH-R_2 \rightarrow R_1-SO_2NH_2 + {}_2HN-R_2$$

For chlorsulfuron and metsulfuron methyl, a second hydrolytic pathway involving the conversion of the methoxy moiety on the triazine ring to a hydroxyl group, prior to cleavage of the sulfonylurea bridge, has been reported[5,6]. The hydrolysis products may also undergo further hydrolytic degradation[1,3–6].

### *Soil adsorption and mobility*

Being weak acids, the sulfonylurea herbicides will exist in their ionic forms in most agricultural soils (pH >6) and as a result be only minimally adsorbed to soil colloids.

Low soil adsorption, with $K_d$ values of <1, has been reported[7-11] for chlorsulfuron, metsulfuron methyl, sulfometuron methyl, and triasulfuron. Their adsorption is not only dependent upon soil pH but also on soil organic matter content. Thus, increased soil adsorption has been reported to acidic soils and to soils with greater amounts of organic matter[3,7,10,11].

As a result of their weak soil adsorption and high water solubilities in neutral and alkaline soils there is great potential for leaching under field conditions of high rainfall[11].

### *Degradation in soil*

Sulfonylurea herbicides undergo degradation in the soil by both chemical hydrolytic and microbiological processes[1-3,12]. The former mechanism follows the same pH dependence noted in buffered aqueous solutions; and is particularly important in soils with acidic pH values where herbicide degradation is considerably more rapid than in soils of pH >7[1-3,9,11]. With the exception of thifensulfuron, which loses its phytotoxic properties very quickly in soil[3,13] as a result of hydrolysis of the ester to the corresponding non-active acid, the sulfonylurea herbicides can persist in the soil under field conditions for more than one crop year[1-3].

Since the sulfonylureas are both persistent and mobile in alkaline soils, they may leach into soil layers of reduced microbiological activity where degradation rates can be further reduced[11]. Thus, it is important to have reliable analytical methods for the detection and monitoring of these herbicides in the soil environment.



## ANALYTICAL METHODOLOGIES

The normal agricultural application rates[1] of the sulfonylureas are of the order of 10 to 20 g $ha^{-1}$. These rates represent a soil concentration of approximately 20 to 40 μg $kg^{-1}$ if the herbicides are assumed to be located within the top 5 cm of field soil[13], or 10 to 20 μg $kg^{-1}$ if distributed throughout the 0 – 10 cm soil layer. Since several sulfonylureas can adversely affect sensitive plants in soil at rates of 1 g $ha^{-1}$, analytical detection at 1 μg $kg^{-1}$, and preferably less, is desirable.

The analysis of such infinitesimal residues is a test of the ingenuity and skill of the analyst. Much of the research conducted on soil adsorption, leaching, and laboratory persistence and environmental fate studies has relied on [$^{14}$C]labelled sulfonylureas to facilitate detection and quantitation. Routine analysis of sulfonylureas in soils at concentrations of <l μg $kg^{-1}$ has involved three main methodologies: bioassays, chemical analyses, and enzyme immunoassays.

### *Bioassay*

The use of plant responses based on plant growth, weight, root and/or shoot growth to determine the residue level of herbicides in soils is well established[14-16]. The advantages of plant bioassays are that the soil can be assayed directly without prior extraction of the residues; bioassays can be very sensitive and exhibit responses to small amounts of the residues; and sophisticated instrumentation is not required. However, their main disadvantages are that the assay results are only semiquantitative; the residue detection limit is soil dependent; there is no compound specificity so that results can be influenced

by other herbicide residues present in the soil; and separate calibration curves are necessary for each sulfonylurea, plant species, and soil type.

The tolerance of crops to soil residues of sulfonylureas are indicated in Table 2 and a summary of selected published bioassay tests, with detection limits, in Table 3. Thus, using plant bioassays, the detection of most sulfonylurea herbicides is possible at concentrations <1 $\mu g\ kg^{-1}$ providing the soils contain no other residues that might interfere with the assay. In soils where increased acidity and/or organic content result in increased herbicide adsorption, the availability of the sulfonylurea to the indicator plant will be reduced and the sensitivity thus decreased.

The limits of detection could be improved by using varieties and cultivars of indicator plant species demonstrating increased sensitivity to this class of herbicides. Plant bioassays are very useful for determining whether a particular rotational crop can be grown in fields previously treated with sulfonylureas[1].

## *Chemical methods*

### *Extraction*

The recovery of sulfonylurea compounds from soils does not seem to present any difficulties and several extraction procedures, based on acidic, neutral, and mildly alkaline solvent systems have been reported. These are summarized in Table 4. Because of their acidic nature, cleanup of the extracts usually involves partitioning between aqueous solutions with final extraction of the neutral forms into chloroform or dichloromethane prior to concentration and quantification.



**Table 2** Tolerance of crops to soil residues of sulfonylureas (Adapted from Reference 1).

| *Moderately Sensitive* | *Sensitive* | *Very sensitive* |
|---|---|---|
| Pea (*Pisum sativum*) | Alfalfa (*Medicago sativa*) | Lentil (*Lens culinaris*) |
| Safflower (*Carthamus tinctorius*) | Canola (*Brassica campestris*) | Sugarbeet (*Beta vulgaris*) |
| Sorghum (*Sorghum bicolor*) | Corn (*Zea mays*) | Turnip (*Brassica rapa*) |
| Soybean (*Glycine max*) | Flax (*Linum usitatissimum*) | |
| | Garden cress (*Lepidum sativum*) | |
| | Lettuce (*Lactuca sativa*) | |
| | Mustard (*Sinapis alba*) | |
| | Sunflower (*Helianthus annuus*) | |

**Table 3** Bioassay tests with detection limits reported for selected sulfonylureas in soils.

| *Sulfonylurea* | *Test* | *Detn. limit* $\mu g\ k^{-1}$ | *Refs.* |
|---|---|---|---|
| Chlorsulfuron | Maize root growth | <1 | 8, 17–20 |
| Chlorsulfuron | Turnip root fresh weight | <1 | 21 |
| Metsulfuron methyl | Turnip root fresh weight | <2 | 21 |
| Sulfometuron methyl | Turnip root fresh weight | <0.5 | 21 |
| Thifensulfuron | Turnip root fresh weight | <7 | 21 |
| Triasulfuron | Turnip root fresh weight | <4 | 21 |
| Triasulfuron | Sugarbeet weight reduction | <1 | 22 |
| Chlorsulfuron | Pea shoot fresh weight | <1 | 12 |
| Chlorsulfuron | Alfalfa root and shoot growth | <1 | 23 |
| Chlorsulfuron | Lentil dry matter weight | <1 | 23 |
| Thifensulfuron | Lentil root length | <10 | 13 |
| Thifensulfuron | Sugarbeet dry shoot weight | <10 | 13 |
| Chlorimuron ethyl | Maize root; sorghum root | <2 | 20 |
| Triasulfuron | Maize root growth | <1 | 20 |
| Chlorsulfuron | Lettuce shoot growth | <1 | 10, 24 |
| Metsulfuron methyl | Lettuce shoot growth | <1 | 10 |
| Triasulfuron | Lettuce shoot growth | <1 | 10 |



**Table 4** Extraction methods for the recovery of sulfonylures from soils.

| *Sulfonylurea* | *Extraction procedure* | *Detection* | *Refs.* |
|---|---|---|---|
| Amidosulfuron<br>Chlorsulfuron<br>Metsulfuron methyl<br>Thifensulfuron | $CH_3CN/H_2O/CH_3COOH$ (80:20:2.5); extended shake | $^{14}C$ | 13, 25, 26 |
| Chlorsulfuron | $CH_3OH/CH_3COOH$ (49:1); shake 1 hr | GC | 27 |
| Chlorsulfuron | $CH_3OH/H_2O$ (70:30); shake 1 hr | HPLC | 24 |
| Chlorsulfuron | 2M $(NH_4)_2CO_3$ (pH 9):$CH_3OH$ (1:3); shake 1 hr | $^{14}C$ | 12 |
| Chlorsulfuron | 0. lM $HCO_3$; sonicate | GC | 28 |
| Chlorsulfuron<br>Metsulfuron methyl | $CH_3OH/H_2O/CH_3COOH$ (80:20:0.5); shake 1 hr | HPLC | 11, 30 |
| Chlorsulfuron<br>Sulfometuron methyl | 0. lM $CO_3/HCO_3$ (pH 10); shake 1 hr | $^{14}C$ or HPLC | 9, 29, 31 |
| Nicosulfuron<br>Rimriduron | $CH_3CN/H_2O$ (80:20); sonicate | HPLC | 32 |
| Sulfometuron methyl<br>Thifensulfuron | $H_2O/CH_3OH/CH_3COOH$ (20:5:0.2); shake 1 hr | $^{14}C$ or HPLC | 33, 34 |
| Sulfometuron methyl | $CH_2Cl_2/CH_3OH$/2M $(NH_4)_2CO_3$ (3:4:1); stir 1 hr | $^{14}C$ | 35 |
| Triasulfuron | 0.07M phosphate buffer (pH 7)/$CH_3OH$ (1:2); shake | HPLC | 22 |

*Gas chromatographic analysis*

Due to their low volatilities and thermal instability, sulfonylureas are not suitable for direct gas chromatographic analysis, though studies indicate that supercritical fluid extraction in conjunction with supercritical fluid chromatography may have some potential[36]. To increase the volatility of chlorsulfuron, derivatization with diazomethane to yield a product methylated on the sulfonamide nitrogen has been reported[28,37]. The methylating conditions require careful control since there is a tendency for the second nitrogen of the sulfonylurea bridge to also be methylated[28,37]. The monomethylated chlorsulfuron, following cleanup on a Florisil column, can be quantified using capillary column GC with electron-capture detection. Using this procedure[28], recoveries of chlorsulfuron from fortified soils were over 80% with an experimental detection limit (3 X background noise) of 1 $\mu g\ kg^{-1}$.

Methylation of chlorsulfuron and metsulfuron methyl using diazomethane in ethyl acetate solution has been found to produce the corresponding di -*N*, *N'*-methylated derivatives in high yields[38]. Such derivatives appear to be both volatile and stable under gas chromatographic conditions and give reproducible responses to electron-capture and nitrogen-phosphorus detectors. Using a soil extraction, based on sonication with sodium bicarbonate and followed by cleanup and derivatization with diazomethane in ethyl acetate, recoveries of chlorsulfuron and metsulfuron methyl from a soil fortified at the 1 and 5 $\mu g\ kg^{-1}$ were reported to be over 69%[39].

The gas chromatographic analysis of chlorsulfuron and metsulfuron methyl as their pentafluorobenzyl derivatives has been investigated[27] since such derivatives greatly increase sensitivity to electron-capture detection. Gas chromatography of the pentafluorobenzyl derivatives prepared using ethyl piperidine and pentafluorobenzyl bromide resulted in single reproducible peaks for both sulfonylureas on either packed or capillary columns using gas chromatography[27]. However, the reaction products were identified by mass spectroscopy as the respective *N,N*-bis(pentafluorobenzyl)-2-benzenesulfonamides indicating that chemical hydrolysis had occurred during derivatization[27]. With 10 fluorine atoms, these derivatives exhibit great sensitivity to the electron-capture detector and provide the basis for an analytical procedure. Following extraction of fortified soils by shaking with a mixture of methanol and acetic acid, with cleanup of the evaporated extracts using solid-phase extraction columns, derivatized extracts were examined gas chromatographically[27]. Using this procedure recoveries of chlorsulfuron and metsulfuron methyl from two different soils fortified at the 0.5 and 0.1 $\mu g\ kg^{-1}$ levels ranged from 88 to 95% with good reproducibility[27]. This analytical procedure offers great sensitivity and general applicability for sulfonylureas, but interferences from extracted soil metabolites which form the same pentafluorobenzyl derivatives as the parent compounds can occur, making the method non-herbicide specific.

*High performance liquid chromatography*

Sulfonylureas are very amenable to separation and assay using normal-phase and reverse-phase HPLC, and the method is particularly suited to the analysis of technical grade sulfonylureas and their formulations[1]. Table 5 summarizes HPLC conditions reported for the analysis of these compounds in soil using various means of detection and their detection limits. The sulfonylureas all have ultraviolet adsorption maxima in the range 220-232 nm[1], but unfortunately UV detection at the 254 nm fixed wavelength featured in

several detection systems is not sufficiently sensitive for the quantitation of amounts that may be present in many soil samples. Use of the more sensitive fluorescence detector is not possible since the sulfonylureas do not show any apparent fluorescence[40]. For triasulfuron, an extraction procedure involving shaking of treated soils with methanolic phosphate buffers followed by column cleanup through ion-pair partition and column chromatography and assay using a three column HPLC switching system with UV-detection (set at the herbicide adsorption maximum of 232 nm) has been reported[22]. This analytical method can detect triasulfuron at concentrations of 0.04 μg $kg^{-1}$.

To achieve adequate sensitivity and to eliminate undesirable responses from coextracted materials the photoconductivity detector has been used. This detector is selective for molecules containing sulfur, halogen, nitrogen, and phosphorus atoms[29,31] and its sensitivity for chlorsulfuron is 15 times greater than that achievable by UV detection at 254 nm. For sulfometuron methyl, the photoconductivity detector is 50 times more sensitive than UV absorbance at 254 nm. This has allowed residue analysis of chlorsulfuron and sulfometuron methyl in soils with detection limits of 0.2 μg $kg^{-1}$ (Table 5)[29,31].

More recently, a trace level analytical method has been reported for nicosulfuron and rimriduron in soil using thermospray liquid chromatography interfaced with a mass



**Table 5** HPLC conditions for analysis of sulfonylurea residues in soils.

| *Sulfonylurea* | *Column* | *Mobile phase* | *Detector* | *Detn. μg $k^{-1}$* | *Refs.* |
|---|---|---|---|---|---|
| Chlorsulfuron | Spherisorb ODS | $CH_3OH/H_2O$ | UV 250 nm | –[a] | 24 |
| Chlorsulfuron Metsulfuron methyl | Lichrosorb RP18 | $CH_3OH/H_2O/CH_3COOH$ | UV 245 nm | – | 11 |
| Chlorsulfuron Sulfometuron methyl | Zorbax SIL | $C_6H_{12}$/2–PrOH/ $CH_3OH/H_2O/CH_3COOH$ | Photocond. | 0.2 | 29, 31 |
| Nicosulfuron Rimriduron | Partisil C8 | $CH_3CN/H_2O/CH_3COOH$ | MS ion monit. | 20 | 32 |
| Sulfometuron methyl | Zorbax C8 | $CH_3CN/H_2O$ pH 2. 2 | $^{14}C$ | – | 35 |
| Sulfometuron methyl | Zorbax SIL | $CH_2Cl_2/H_2O/CH_3COOH$ | $^{14}C$ | – | 35 |
| Thifensulfuron | Ultrabase Si–C8 | $CH_3CN/H_2O/CH_3COOH$ | UV 259 nm | – | 34 |
| Thifensulfuron | Spherisorb S5 $NH_2$ | $CH_3CN/H_3PO_4$ | UV 259 nm | – | 34 |
| Triasulfuron | (1) PRP 1<br>(2) Lichrosorb RP 18<br>(3) Nucleosil Phenyl | $PO_4$ buffers + $CH_3CN$ + TBAB[b] | UV 232 nm | 0.04 | 22 |

[a] Not given.

[b] Tetrabutylammonium bromide.

spectrometer as detector[32]. Recoveries of the two sulfonylureas, ranging from 74–96% with satisfactory reproducibilities, have been achieved from soil fortified at the 20–200 $\mu g\ kg^{-1}$ levels. LC/MS requires minimal sample processing and cleanup prior to chromatographic and spectroscopic quantitation and, with selective ion monitoring, is perhaps applicable to multiresidue sulfonylurea analysis with structural confirmation.

### *Immunoassay*

Enzyme-linked immunosorbent assay (ELISA) is becoming increasingly popular for the analysis of pesticide residues in a variety of substrates and offers an alternative approach to conventional residue analysis[41–45]. The procedure is quick and can offer specificity for individual herbicides with little crossreactivity with structurally related compounds.

ELISA techniques are based on the ability of animals to produce highly specific antibodies to foreign materials. Antibody is usually collected from rabbit serum and becomes one reagent in a rapid, solid phase assay that is both specific and sensitive. The detection is such that the more color observed in the assay, the less analyte present in the sample.

An analytical method using ELISA and based on a polyclonal antibody has been developed for chlorsulfuron using a diazonium derivative covalently linked to a protein as immunogen[46]. This assay showed a sensitivity of 0.4 $\mu g\ kg^{-1}$ which was subsequently improved[46,47] to 0.05 $\mu g\ kg^{-1}$. In both cases, soil samples (10 g) were sonicated with aqueous buffer and the supernatant used directly in the assay. Little cross-reaction was observed with the structurally related bensulfuron methyl and sulfometuron methyl indicating the specificity of the analysis[46].

The determination of triasulfuron in soils by monoclonal antibody based enzyme immunoassay has also been reported[48]. In this study, five different fortified soils were extracted with methanolic phosphate buffer and, after addition of tetrabutylammonium hydroxide, the aqueous phase was transferred to a liquid/liquid partitioning cartridge from which the triasulfuron was eluted with a mixture of dichloromethane and hexane. The organic solvent was evaporated and the residue taken up into phosphate buffer prior to assay. The ion-pair partition stage reduced interference from soil matrix effects allowing recoveries ranging from 53 to 120% (average 78%) from samples fortified with 0.1 to 10 μg triasulfuron per kg soil[48].

These preliminary data indicate that it is possible to analyse for sulfonylureas in soils at very low levels without extensive cleanup procedures. It has been noted that the immunoassay is both specific and rapid with analysis of 50 samples a day being possible compared to 4 a day using HPLC procedures[46]. Thus, given the availability of the necessary antibodies, immunoassays would seem to offer the greatest potential for the routine analysis of sulfonylurea residues in soils.

### *References*

1. E. M. Beyer, M. J. Duffy, J. V. Hay and D. D. Schlueter. In: *Herbicides: Chemistry, Degradation, and Mode of Action* (P. C. Kearney and D. D. Kaufman, Eds., Marcel Dekker, New York, 1988), Vol. 3, Chap. 3, pp. 117–189.
2. A. M. Blair and T. D. Martin. *Pestic. Sci.* **22**, 195–219 (1988).
3. H. M. Brown. *Pestic. Sci.* **29**, 263–281 (1990).
4. J. V. Hay. *Pestic. Sci.* **29**, 247–261 (1990).
5. J. Sabadie. *Weed Res.* **30**, 413–419 (1990).

6. J. Sabadie. *Weed Res.* **31**, 309–316 (1991).
7. J. Harvey, J. J. Dulka and J. J. Anderson. *J. Agric. Food Chem.* **33**, 590–596 (1985).
8. W. Mersie and C. L. Foy. *Weed Sci.* **33**, 564–568 (1985).
9. K. Thirunarayanan, R. L. Zimdahl and D. E. Smika. *Weed Sci.* **33**, 558–563 (1985).
10. A. Walker and S. J. Welch. *Weed Res.* **29**, 375–383 (1989).
11. A. Walker, E. G. Cotterill and S. J. Welch. *Weed Res.* **29**, 281–287 (1989).
12. M. M. Joshi, H. M. Brown and J. A. Romesser. *Weed Sci.* **33**, 888–893 (1985).
13. A. E. Smith, M. P. Sharma and A. J. Aubin. *Can. J. Soil Sci.* **70**, 485–491 (1990).
14. D. O. Eberle and H. R. Gerber. *Arch. Environ. Contam. Toxicol.* **4**, 101–118 (1976).
15. R. Hance and C. E. McKone. In: *Herbicides, Physiology, Biochemistry, Ecology* (L. J. Audus, Ed., Academic Press, London, 1976), 2nd Ed., Vol. 2, pp. 394–402.
16. P. W. Santelmann. In: *Research Methods in Weed Science* (B. Truelove, Ed., Southern Weed Science Society, U.S.A., 1977), 2nd Ed., pp. 79–87.
17. I. G. Eleftherohorinos. *Weed Res.* **27**, 443–452 (1987).
18. K. E. M. Groves and R. K. Foster. *Weed Sci.* **33**, 825–828 (1985).
19. A. I. Hsiao and A. E. Smith. *Weed Res.* **23**, 231–236 (1983).
20. S. L. Sunderland, P. W. Santelmann and T. A. Baughman. *Weed Sci.* **39**, 296–298 (1991).
21. P. Günther, A. Rahman and W. Pestemer. *Weed Res.* **29**, 141–146 (1989).
22. W. Iwanzik and H. Egli. *Proc. Br. Crop Prot. Conf. Weeds.* 1145–1150 (1989).
23. J. R. Moyer, P. Bergen and G. C. Kozub. *J. Environ. Sci. Health.* **B24**, 37–56 (1989).
24. A. Walker and P. A. Brown. *Bull. Environ. Contam. Toxicol.* **30**, 365–372 (1983).
25. A. E. Smith and A. J. Aubin. *J. Agric. Food Chem.* **40**, 2500–2504 (1992).
26. A. E. Smith. *Bull. Environ. Contam. Toxicol.* **37**, 698–704 (1986).
27. E. G. Cotterill. *Pestic. Sci.* **34**, 291–296 (1992).
28. I. Ahmed and G. Crawford. *J. Agric. Food Chem.* **38**, 138–141 (1990).
29. E. W. Zanhow. *J. Agric. Food Chem.* **30**, 854–857 (1982).
30. D. Vega, J. Bastide and C. Poulain. *Weed Res.* **32**, 149–155 (1992).
31. E. W. Zanhow. *J. Agric. Food Chem.* **33**, 479–483 (1985).
32. L. M. Shalaby, F. Q. Bramble and P. W. Lee. *J. Agric. Food Chem.* **40**, 513–517 (1992).
33. J. P. Cambon, S. Q. Zheng and J. Bastide. *Weed Res.* **32**, 1–7 (1992).
34. J. P. Cambon and J. Bastide. *Weed Res.* **32**, 357–362 (1992).
35. J. J. Anderson and J. J. Dulka. *J. Agric. Food Chem.* **33**, 596–602 (1985).
36. J. R. Wheeler and M. E. McNally. *J. Chromatogr.* **410**, 343–353 (1987).
37. I. Ahmed. *J. Assoc. Off. Anal Chem.* **70**, 745–748 (1987).
38. P. Klaffenbach, P. T. Holland and D. R. Lauren. *J. Agric. Food Chem.* **41**, 388–395 (1993).
39. P. Klaffenbach and P. T. Holland. *J. Agric. Food Chem.* **41**, 396–401 (1993).
40. T. C. Mueller, T. B. Moorman and M. A. Locke. *Weed Sci.* **40**, 270–274 (1992).
41. J. C. Hall, R. J. A. Deschamps and M. R. McDermott. *Weed Technol.* **4**, 226–234 (1990).
42. R. J. Schneider, L. Weil and R. Niessner. *Intern. J. Environ. Anal. Chem.* **46**, 129–140 (1992).
43. M. Vandelaan, B. E. Watkins and L. Stanker. *Environ. Sci. Technol.* **22**, 247–254 (1988).
44. J. M. Van Emon, J. N. Seiber and B. D. Hammock. In: *Analytical Methods for Pesticides and Plant Growth Regulators: Advanced Analytical Techniques* (J. Sherma, Ed., Academic Press, New York, 1989), Vol. 17, pp. 217–263.
45. H. Van Vunakis. In: *Immunochemical Methods for Environmental Analysis* (J. M. Van Emon and R. O. Mumma Eds., ACS Symposium Series 442, American Chemical Society, Washington, 1990), pp. 1–12.
46. M. M. Kelley, E. W. Zahnow, W. C. Petersen and S. T. Toy. *J. Agric. Food Chem.* **33**, 962–965 (1985).
47. J. K. Sharp, F. S. Lueng, D. P. O'Brien and T. H. Carski. 198th ACS National Meeting, Miami Beach, Florida, Abstract AGRO 7 (1989).
48. J.-M. A. Schlaeppi, W. Meyer and K. A. Ramsteiner. *J. Agric. Food Chem.* **40**, 1093–1098 (1992).