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CONTENT

SULFONYLUREA HERBICIDES RESIDUES ANALYSIS IN SOIL

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ABSTRACT

Prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron are widely used sulfonylurea herbicides (SUs), applied in low-dose rates. However, these herbicides under specific conditions as low temperature, poor rainfall, microbial activity, high pH of soil, can remain at low concentrations in soil and can affect the growth of sensitive plants. This paper presents the method that we developed for determination of prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron residues in soil. Determination and quantification were performed by HPLC/DAD using Agilent Zorbax SB-C18 column (3.0 mm×250 mm, 5 μm particle size). Mobile phase was acetonitrile/0.1% CH_3COOH solution. Analyzed SUs showed linear calibrations from 0.05 to 0.2 mg/ml with correlation coefficient (r^2) above 0.990%. The recovery data were obtained by spiking blank soil samples at two concentration levels (2.5-5.0 mg/kg), yielding average recovery between 95.56 and 99.79%. Precision values expressed as relative standard deviation (RSD) were between 0.91-1.11% for all SUs herbicides for the intraday precision. Considering the obtained values of analytical parameters, the proposed method proved to be an efficient and sensitive method for the determination of prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron in soil samples.

INTRODUCTION

Sulfonylurea herbicides are extremely active in low-dose rates of 10-100 g/ha against many grasses and broadleaf weeds in the agriculture production. This feature means that under specific conditions, such as high pH of soil, low temperatures, poor rainfall and microbial activity, remaining low concentrations of these analytes can still affect the growth of sensitive plants (Font et al., 1998). Various methods for the residue analysis of sulfonylurea herbicides in different matrices have been reported, as gas chromatography (GC) or liquid chromatography (LC) (Thompson and MacDonald, 1992; Ahmad, 1987; Zahnow, 1982; Bernal et al., 1997). Sulfonylurea herbicides are polar compounds (p*K* 3.5) with low vapor pressure, and need derivatisation prior to GC analysis. In that reason, LC is preferable technique for the analysis of sulfonylurea herbicides in matrices such as water and soil.
Several methods for the extraction of sulfonylureas in soil have been described. In order to enhance solubility of acidic analytes, a basic aqueous solvent is frequently applied (Font et al., 1998), followed with solid-phase or liquid-liquid extraction (Bernal et al., 1997). Recently, for determination of sulfonyurea herbicides extraction procedures like solid-phase microextraction (SPME), supercritical fluid extraction (SFE), and matrix solid-phase dispersion (MSPD) have been described.

MATERIALS and METHODS

Standard and Solutions.
Ultra pure water was produced by a water purification system TKA, Germany. Acetonitrile and acetic acid of analytical grade, were obtained from J.T. Baker (USA). Certificated analytical standards of prosulfuron (95%), rimsulfuron (97%), tifensulfuron-methyl (97%) and tritosulfuron (98%) were purchased from Dr Ehrenstorfer GmbH, Germany. QuEChERS dispersive SP extraction kits were from Agilent, USA.
The sulfonylurea herbicide standards stock solutions were individually prepared in acetonitrile at a concentration level of 100 μg/ml and stored in dark at 4°C. Suitable concentrations of working standards were prepared from the stock solutions by dilution with acetonitrile, immediately before sample preparation.

Extraction Procedure.
Control soil sample was from area without SUs application. The extraction procedure was done using modified method Wang at al. (2012). Freshly-spiked soil samples were prepared by weighing 10.0 g of soil into polypropylene tube 50 ml volume and fortified by adding SUs standards solution in concentrations of 2.5 and 5.0 mg/kg. The mixture was then homogenized and the sample was allowed to stand at room temperature for 30 min, 3 ml of deionized water and 10 ml of acidified acetonitrile were added. The tube was shaken and vortexed for a 1 min. A mix of buffered salts (1000 mg of sodium citrate, 500 mg of sodium hydrogen citrate sesquihydrate, 4000 mg magnesium sulphate and 1000 mg sodium chloride) from separate pouches was added, shaken for 1 min and vortexed 1 min. The tube was placed in an ultrasonic bath for 10 min and centrifuged at 4000 rpm for 5 min. The supernatant was filtered through a 0.45 μm membrane filter and transferred into an autosampler vial for HPLC-DAD analyses.

Chromatographic Parameters.
The HPLC-DAD system Agilent Technologies was used with Zorbax SB-C18 column (3.0 mm × 250 mm and particle size 5 μm). The detector wavelength was 230 nm. The mobile phase was acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) at flow rate of 0.9 ml/min. The following gradient profile was used: 0–10 min linear from 52% to 47% (A). The external standard and calibration on five levels were used.

Method for the analysis four investigated sulfonylurea herbicides in soil was validated in terms of linearity, reproducibility, LOQ and recovery, according to the SANCO 3029/99 criteria.

RESULTS

Herbicides were analyzed under previously described conditions. The retention times of prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron were 2.012 min, 2.382 min, 4.604 min and 4.920 min, respectively. The HPLC-DAD chromatogram of prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron are illustrated in Figure 1.

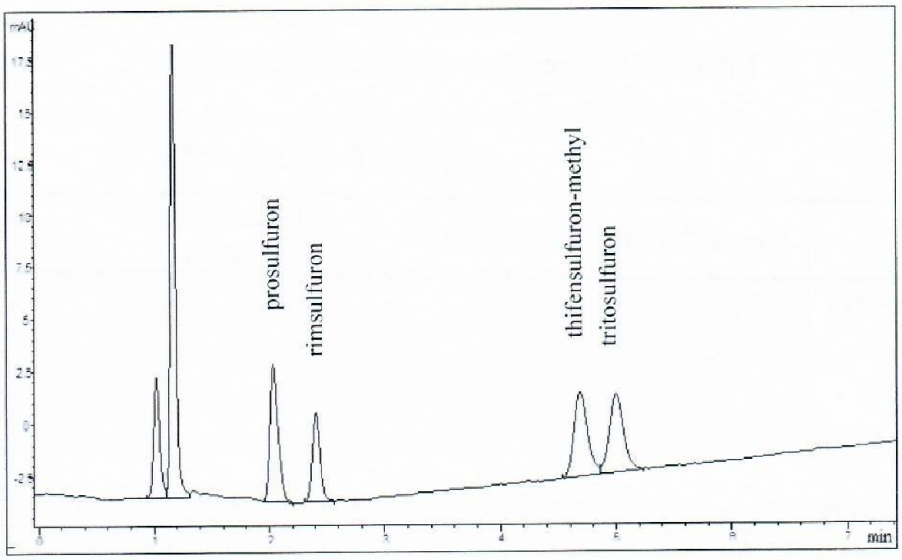

Figure 1. HPLC/DAD chromatogram of soil sample spiked with prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron

To validate the method, the linearity of the calibration curves in working standard SUs solution were generated from 0.01 up to 0.2 mg/ml (Figure 2). They showed a linear behavior with the following coefficients of determination (r^2): prosulfuron $r^2 = 0.997$; rimsulfuron $r^2 = 0.998$, thifensulfuron-methyl $r^2 = 0.998$ and tritosulfuron $r^2 = 0.998$.

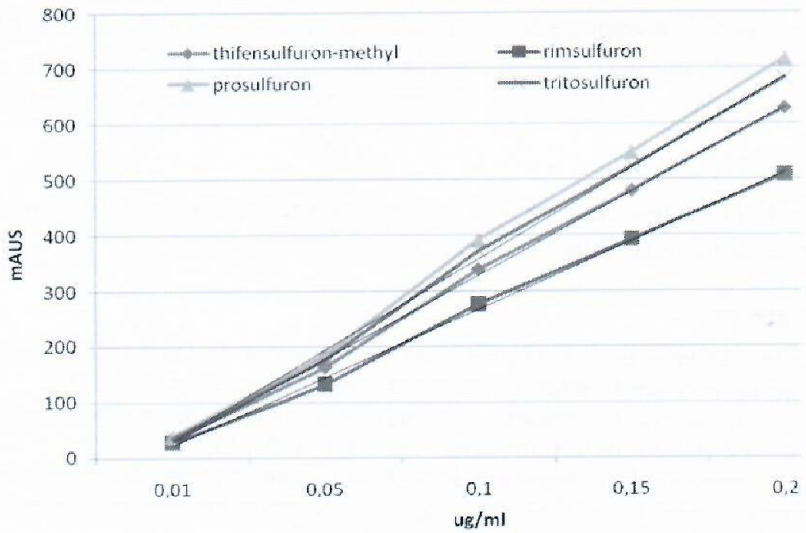

Figure 2. Representative calibration curve of sulfonylurea herbicides

Precision was expressed as the repeatability of the peak area. Repeatability was checked by injecting mixed standard solution at concentration of 0.1 mg/ml five times. The RSD values were within the range of 0.91-1.11% for all SUs herbicide. Limit of quantification (LOQ) for analyzed SUs herbicides were established as 0.05 mg/kg.

The mean recoveries of analyzed SUs were between 95.56% and 99.79% at these two spiking levels with associated relative standard deviations (RSDs) in the range of 0.21-0.63%. Results are shown in Table 1.

Table 1. Mean recovery of spiked soil samples

	2.5 and 5.0 mg/kg of SUs			
SU	**Prosulfuron**	**Rimsulfuron**	**Thifensulfuron-methyl**	**Tritosulfuron**
Average recovery %	95.56	99.79	97.31	94.14
RSD%	0.63	0.30	0.30	0.21

The mean recoveries of analyzed SUs were between 95.56% and 99.79% at these two spiking levels with associated relative standard deviations (RSDs) in the range of 0.21-0.63%. Results are shown in Table 1. The average recoveries and RSDs of the analyzed samples complied with the SANCO/3029/99 criteria; mean recoveries for each level should be in the range 70-110%, ideally with the mean in the range of 80-100%.

CONCLUSIONS

An analytical method for the quantification of widely used, prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron in soil was developed. Spiked soil samples showed mean recoveries between 95.56 and 99.79%. Calibration curves established between 0.01 and 0.2 mg/kg showed r^2 values above 0.997. The limits of quantification of the method were 0.05 mg/kg for all investigated compounds. Considering the obtained values of analytical parameters, the proposed method proved to be an efficient and sensitive method for determination of prosulfuron, rimsulfuron, thifensulfuron-methyl and tritosulfuron in soil samples.

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