

DOI: <http://doi.org/10.21698/simi.2020.ab38>

SIMULTANEOUS DETERMINATION OF THREE SULFONYLUREAS HERBICIDES FROMS ENVIRONMENTAL SAMPLES BY HPLC-DAD

Gabriel-Valentin Serban, Vasile-Ion Iancu, Marcela Niculescu, Florentina-Laura Chiriac, Roxana-Elena Scutariu, Toma Galaon

National Research and Development Institute for Industrial Ecology-ECOIND, 71-73 Drumul Podu Dambovitei Street, 060652, Bucharest, vasileiancu10@gmail.com, Romania

Keywords: *environmental samples, determination, HPLC-DAD, sulfonylureas herbicides*

Introduction

Sulfonylurea herbicides (SUHs) are one of the largest classes of herbicides in the world used for the control of many grasses and broad-leafed species in all agronomic crops and vegetables. Sulfonylurea herbicides are the second most common class of herbicides after glyphosates used in over 80 crops in the form of 30 commercial products. These herbicides, which have low toxicity to mammals, are highly toxic to plants, especially for crops, aquatic plants and microorganisms, affecting the entire food chain. SUHs are weak acids with pKa from 3 to 5, and in water they exist in mainly in the ionised form (anionic). Intense use of herbicides has led to contamination of various types of water, soil, sediment and agricultural crops (wheat, corn, fruits, vegetables). Thus, the European Commission has set maximum limits for each pesticide class in water intended for human consumption (0.1 µg/L).

Materials and methods

In this work, a simple, fast and sensitive analytical method was developed, optimized and validated for surface and waste water samples. Firstly, the method included the isolation and clean-up of the SUHs (metsulfuron-methyl, triasulfuron, chlorosulfuron) by solid phase extraction (SPE) from river and effluent water samples using the automated instrument Autotrace 280 (Thermo) with Strata C18 cartridges. The water sample (250 mL) was filtrated by the 0.45 µm glass membrane (Merck, 47mm diameter) and pH was adjuted to 3 with H₃PO₄ 0.1%. The all sample volume was passed trough the conditioned sorbent after that the analytes were eluted with metanol. The organic extract was concentrated to dryness in nitrogen stream and he was reconstituted to 1 mL with mobile phase. The extract was intected (20 µL) into 1200 HPLC-DAD (Agilent Technologies). The compounds were separated on the Eclipse XDB C18 LC column (150x4.6 mm, 5 µm) using a gradient of mobile phase (ACN: H₃PO₄ 0.1%: 0-4min 40% ACN, 4-7 min 40-50% ACN) at a flow rate of 0.8 mL/min. The contaminants were detected at 230 nm in 8 minutes.

Results and conclusions

The method was validated for surface and waste water (effluent) samples by considering the next parameters: limit of cuantitation (LOQ), calibration range (determination coefficient), recovery rate, repeatabily and reproducibility (precision).

The standard calibration curves of the analytes were constructed by plotting of compound concentrations against peak area. The calibrations curves for each compound were obtained by injecting of the five calibration standards in the range of 10-500 $\mu\text{g/L}$ (Table 1). The calibration regressions were linear in the selected range having good determination coefficients higher than 0.996. Recovery rates ranged between 76.8% and 92.5% (Figure 1). The LOQ were low (0.016-0.022 $\mu\text{g/L}$) proving the sensitivity of the new developed method. The analytical procedure was precise, repeatability was situated below 5.6% and reproducibility has values lower than 10.5%.

Table 1. Analytical performance of the SPE-LC-MS/MS method for detection of sulfonylurea herbicides in environmental samples

	Calibration range, $\mu\text{g/L}$	R^2	Recovery %	LOQ $\mu\text{g/L}$	Precision, %	
					RSD _F	RSD _R
Metsulfuron-methyl	10-500	0.9964	92.5	0.022	3.4	6.1
Trialsulfuron	10-500	0.9970	82.9	0.016	4.3	10.5
Clorosulfuron	10-500	0.9977	76.8	0.019	5.6	9.1

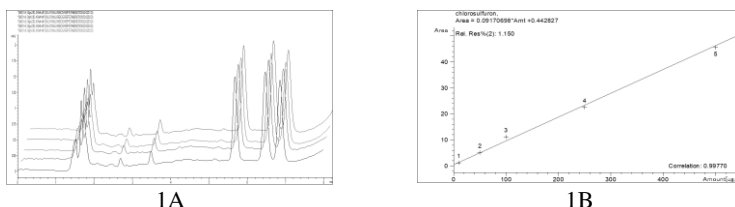


Figure 1. Sulfonylurea herbicides overlapping chromatograms for samples tested for recovery (1A); Calibration curve obtained for chlorsulfuron 10-500 $\mu\text{g/L}$ (2B)

The method was successfully applied for analysis of surface water and effluent samples. The sulfonylurea compounds were detected only in effluent samples in the range of 0.52 $\mu\text{g/L}$ metsulfuron-methyl and 0.12 $\mu\text{g/L}$ chlorsulfuron (Figure 2).

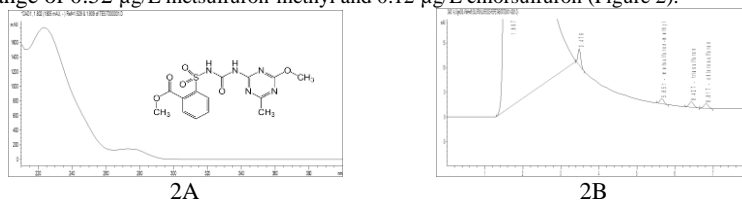


Figure 2. UV absorption spectrum and structural formula of metsulfuron-methyl (2A); Effluent wastewater treatment plant sample chromatogram indicating the presence of sulfonylureas herbicides (2B)

Acknowledgement

This work has been conducted within the framework of the National Research Program "Nucleu", contract number 20N/2019, PN 19 04 01 01.