

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

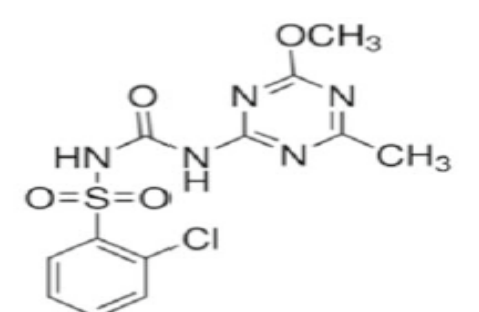
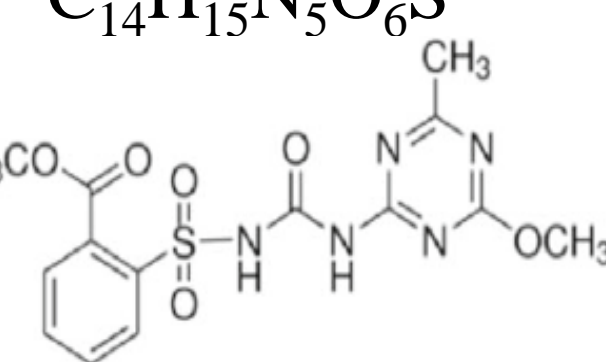
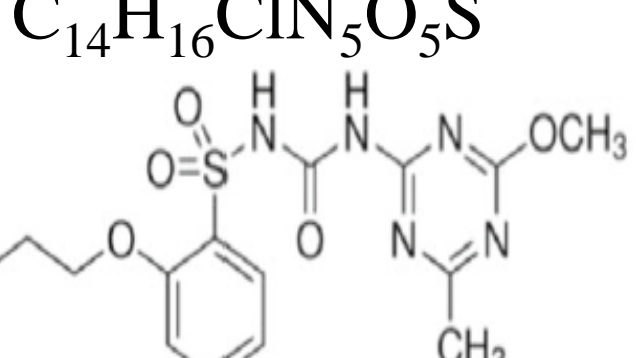
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## INTRODUCTION

Sulfonylurea herbicides (SUHs) are one of the largest classes of herbicides in the world used for the control of many grasses and broad-leaved 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).

Table 1. Physical-chemical characteristics of sulfonylurea herbicides

Sulfonylurea herbicides	Chemical formula and structure	Partition coefficient at pH 7, 20°C (log P)	Dissociation constant (pKa) at 25°C
Chlorsulfuron	<chem>C12H12ClN5O4S</chem> 	-0.99	3.4 (weak acid)
Metsulfuron-methyl	<chem>C14H15N5O6S</chem> 	-1.87	3.75 (weak acid)
Triasulfuron	<chem>C14H16ClN5O5S</chem> 	-0.59	4.64 (weak acid)



## MATERIALS AND METHODS

Table 2. The optimal parameters of the HPLC (Agilent 1200 Series) chromatographic separation

Column	Eclipse XDB with a length of 150 mm, an inner diameter of 4.6 mm and a diameter of the stationary phase particles of 5 µm
Column temperature	300 °C
Injection volume	20 µl
Initial mobile phase	ACN 40%, 60% Phosphoric Acid (0.1%)
Mobile phase flow	0.8 ml/min
Elution	gradient (8 min., 4 min. wash balancing)
Wavelength	230 µm

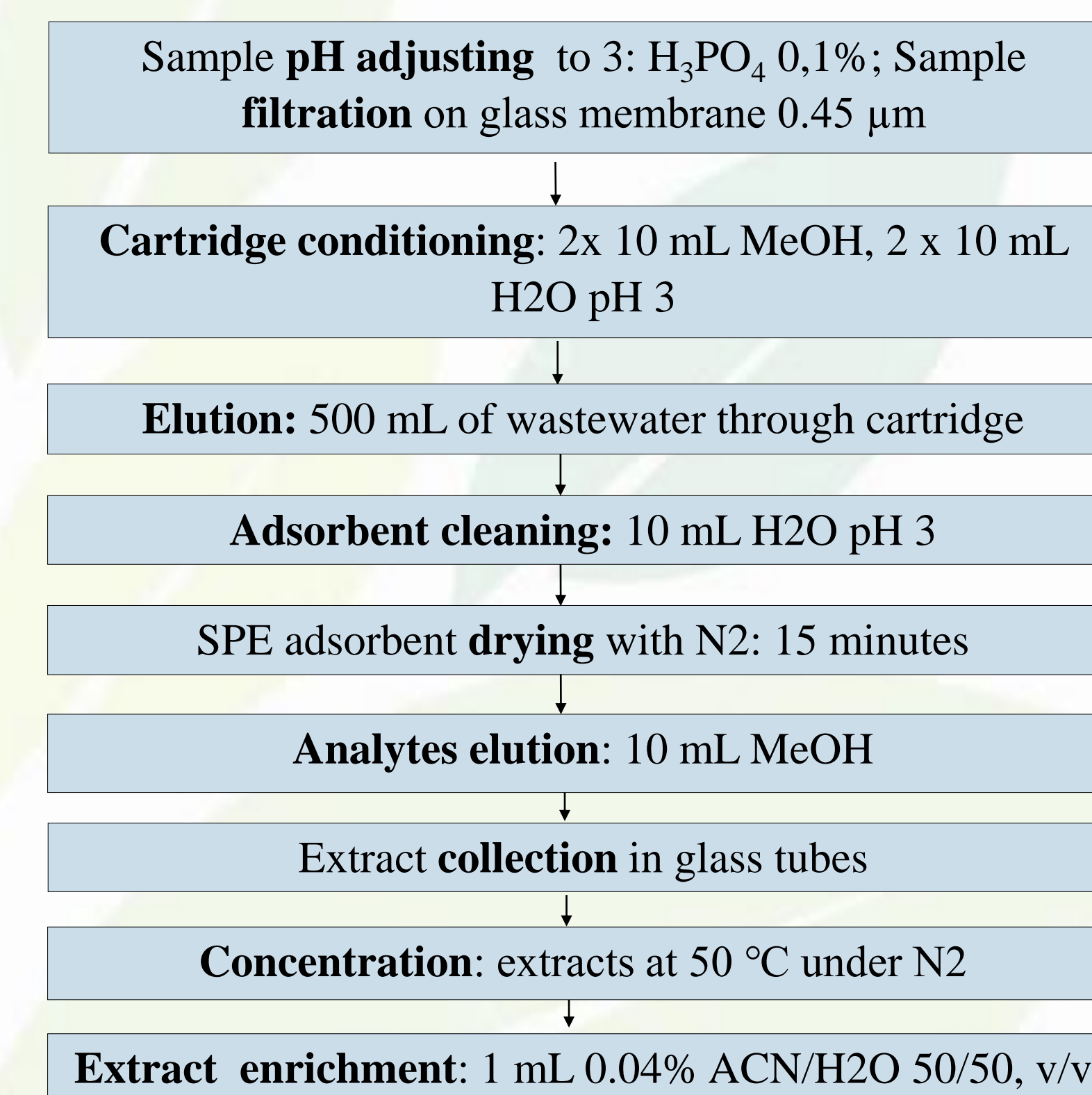


Fig. 2. Optimization of analyte extraction parameters from water samples

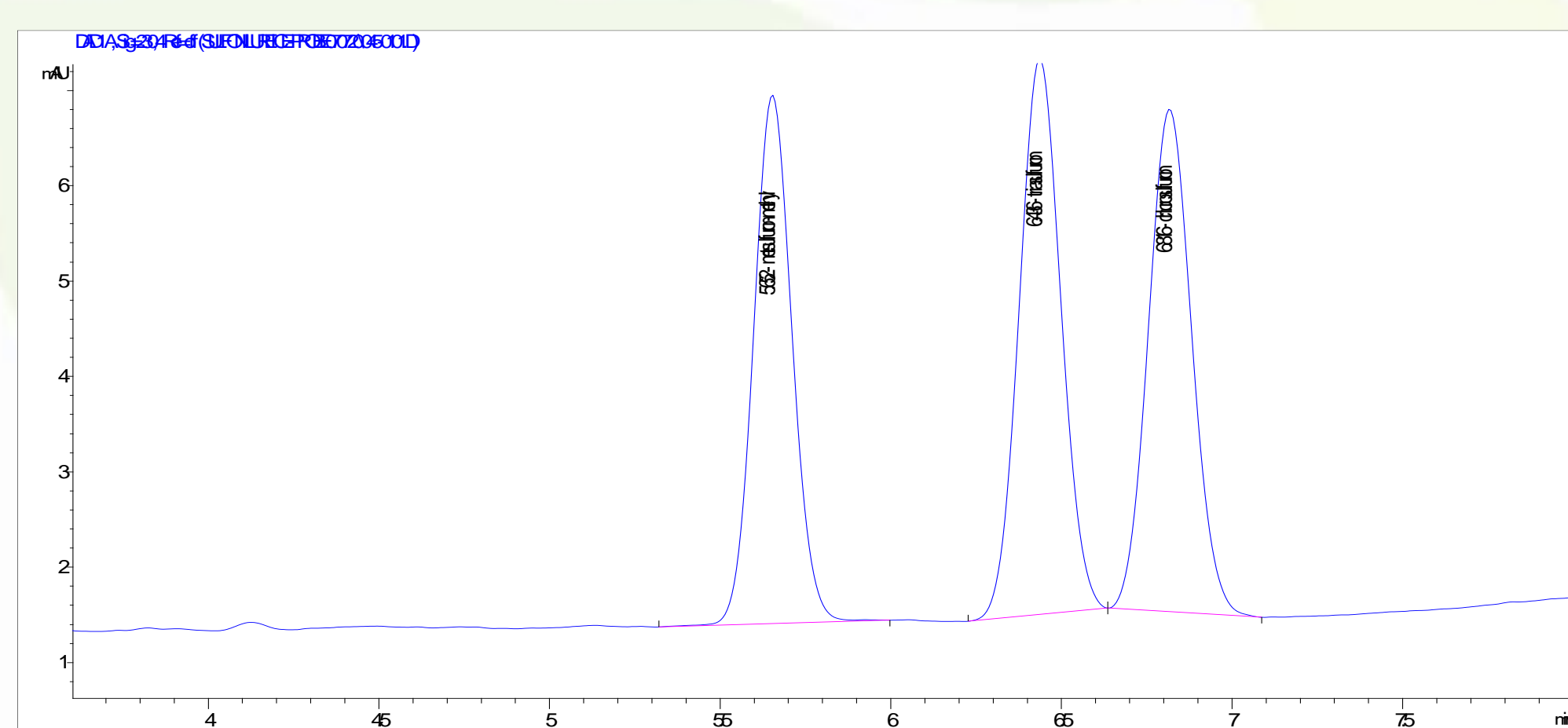


Fig. 1. Chromatogram of a standard mixed solution containing sulfonylureas

## RESULTS AND DISCUSSION

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, chlorsulfuron) by solid phase extraction (SPE) from river and effluent water samples.

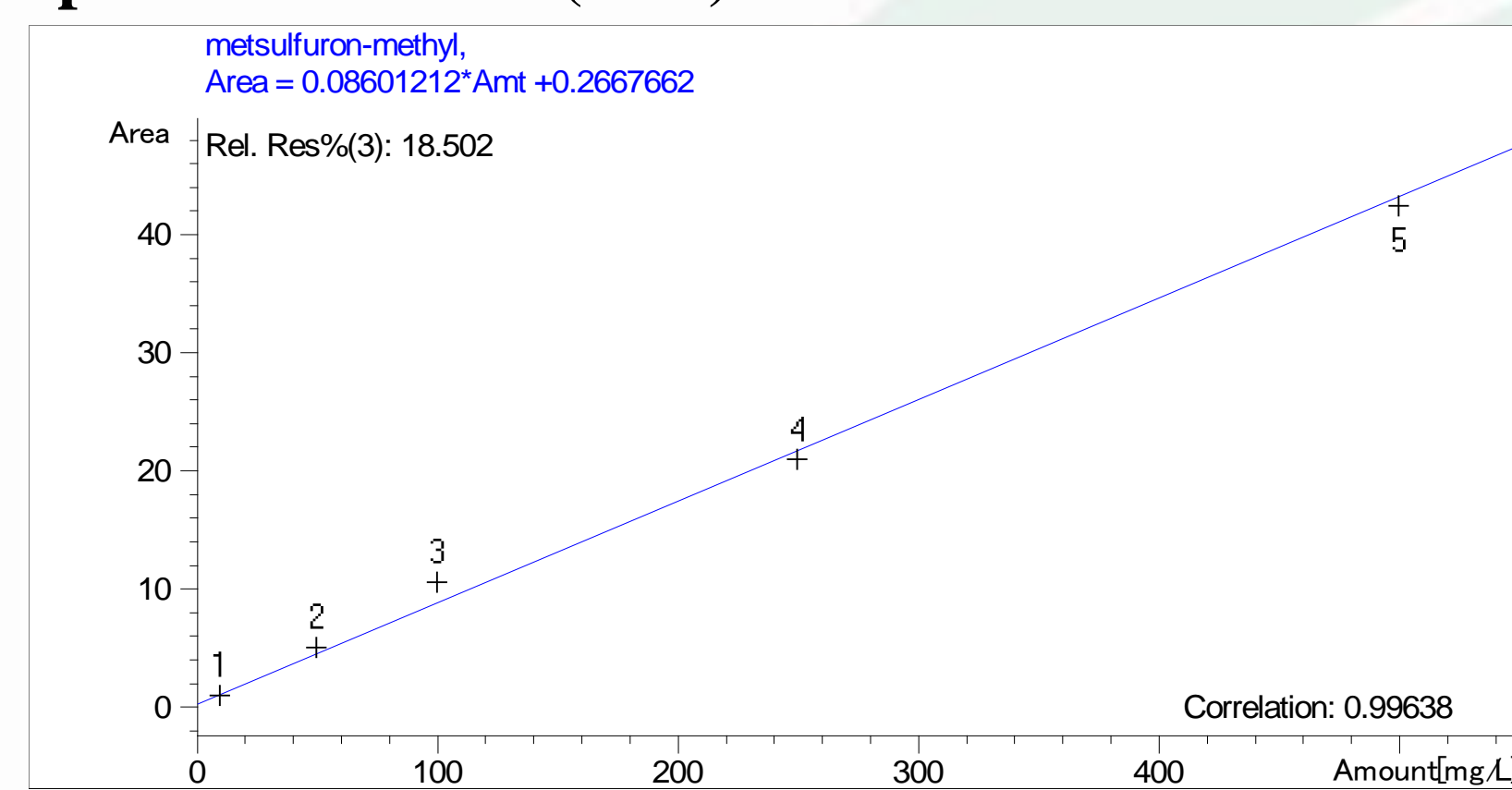


Fig. 3. Linear regression for Metsulfuron-methyl

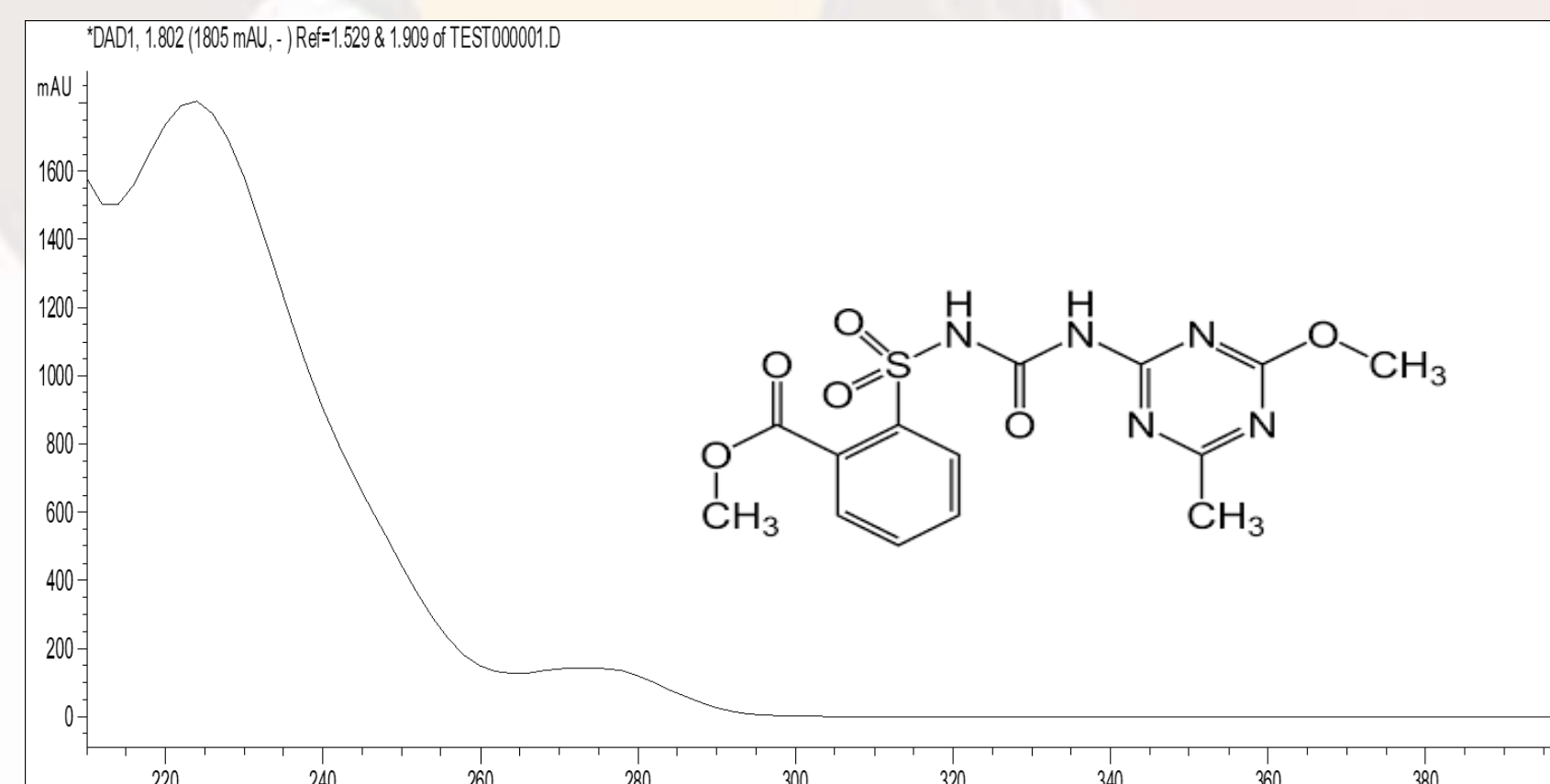


Fig. 4. UV absorption spectrum and structural formula of metsulfuron-methyl

## CONCLUSION

The method was validated for surface and waste water (effluent) samples by considering the next parameters: limit of quantitation (LOQ), calibration range (determination coefficient), recovery rate, repeatability and reproducibility (precision). The calibration regressions were linear in the selected range (10-500 µg/L) having good determination coefficients higher than 0.996. Recovery rates ranged between 76.8% and 92.5%. The LOQ were low (0.016-0.022 µg/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 3. Performance parameters

Compound	Concentration range (µg/kg)	R <sup>2</sup> (%)	Retention time (min)	Line equation	LOD (µg/L)	LOQ (µg/L)	Recovery (%)	RSD <sub>r</sub> %	RSD <sub>R</sub> %
Metsulfuron-methyl	10-500	0.996	5.641	y=0.086x+0.267	0.007	0.022	92.5	3.39	6.12
Triasulfuron	10-500	0.997	6.417	y=0.098x+0.416	0.005	0.016	82.9	4.34	10.56
Clorsulfuron	10-500	0.998	6.806	y=0.092x+0.443	0.006	0.019	76.8	5.57	9.12

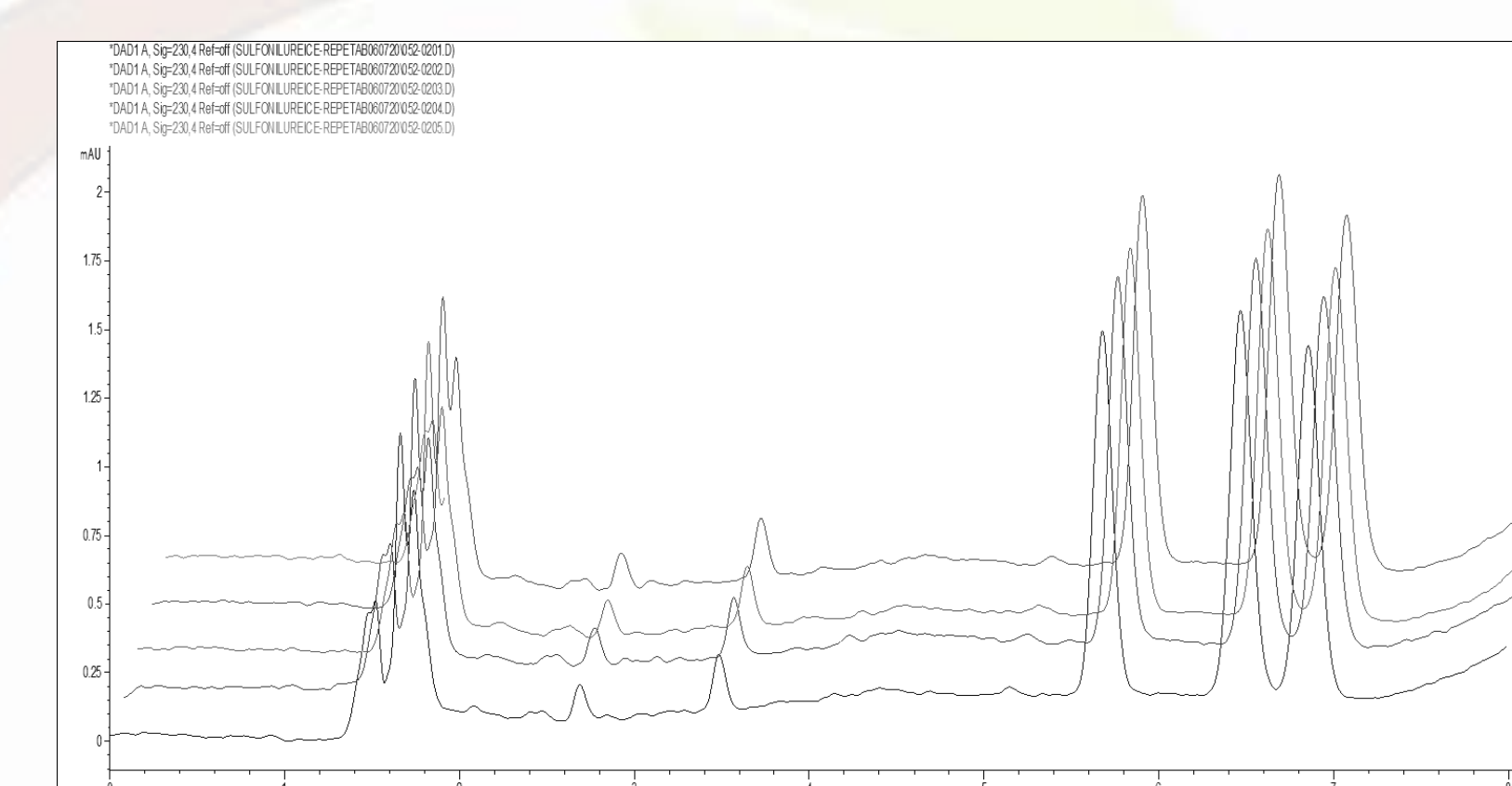


Fig. 5. Sulfonylurea herbicides overlapping chromatograms for samples tested for recovery

Table 4. The presence of sulfonylurea herbicides studied in wastewater and surface water samples (µg/L)

Sample	Metsulfuron-methyl	Triasulfuron	Clorsulfuron
P1 EFL	0.52	0.12	<0.019
P2 AM	<0.022	<0.016	<0.019
P3 AV	0.093	<0.016	<0.019
P4 EFL	0.202	0.226	0.19
P5 AV	<0.022	<0.016	<0.019
P6 AM	<0.022	<0.016	<0.019
P7 AM	<0.022	<0.016	<0.019
P8 AV	<0.022	<0.016	<0.019
Min	0.093	0.12	0.19
Max	0.52	0.226	0.19
Average	0.272	0.173	0.19
Frequency	37.5	25	12.5

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