Extraction and preconcentration of simazine and atrazine using cloud point extraction

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Introduction

Monitoring of herbicide residues in soils and waters has become essential for reducing environmental impacts. The use of surfactant micelles is an alternative to the organic solvents commonly used in conventional methods for extraction and preconcentration of herbicides in analyses of water and soil samples. Cloud point extraction is defined as the process of transferring of a non-ionic surfactant from one liquid phase to another by heating and increasing ionic strength. If the surfactant is present at a suitable concentration, as the temperature of the solution rises, the surfactant molecules form micelles and if the temperature increases above the cloud point the micelles become dehydrated and aggregate, leading to macroscopic phase separation of the solution into a surfactant-rich phase and a solvent phase. As the core of the micelles is predominantly hydrophobic, it is able to dissolve herbicides that are poorly soluble in aqueous solutions. The present work employed a 5% (w/v) Triton X-114 surfactant (tert-octylphenol polyethylene glycol ether). Surfactant solution (5 mL), 30% (w/v) NaCl (1 mL) and sample solution (9.0 mL) were added to 15 mL centrifuge tubes. Then the centrifuge tubes were shaken vigorously for one minute and taken to a water bath for 30 min at 60 °C. After this time they were centrifuged at 5000 rpm for 10 min. The supernatant (water-rich phase) was discarded and 1 mL of a 80% solution of methanol:water (v/v) was added to the surfactant-rich phase. The tubes were centrifuged at 13,000 rpm for 10 min. The final volume (2 mL) was transferred to vials and submitted to chromatographic analyses.

Results and Discussion

The chromatographic analyses were carried out employing a Dionex® UltiMate 3000 HPLC system, fitted out to a monolithic C_{18} column (100 x 4.6 mm). Separation was achieved by gradient elution using mobile phases: (A) 2.5 mM NH_4Ac/HAc (pH 4.2), and (B) acetonitrile (ACN). Elution gradient: 13-90% of B in 16,5 min, UV detection at 223 and 238 nm and sample volume of 20 µL. Calibration curves were constructed for simazine and atrazine at concentrations ranging from 25 to 250 µg L^{-1}. The results obtained for simulated samples free of herbicides are shown in Table 1.

Table 1. Recoveries found in cloud point extracted simulated samples spiked with simazine and atrazine (n=3)

Herbicide	Concentration (µg L^{-1})			Recovery (%)
	Spiked	Expected	Obtained	
Simazine	10	50	63	125±5
	15	75	88	117±2
	20	100	97	97±1
	50	250	207	83±1
Atrazine	10	50	30	61±2
	15	75	67	90±1
	20	100	85	85±1
	50	250	229	92±1

Additionally to promote the extraction of compounds of interest, the micelles of Triton X-114 surfactant concentrated the analytes, since the concentrations obtained for the most samples were around 5 times greater than the simulated initially spiked concentrations. The recovery percentages were mostly within the range recommended for spiking and recovery studies (between 70 and 120%)[1]. Atrazine metabolites such as deisopropylatrazine, deethylatrazine and hydroxyatrazine, which are more hydrophilic than atrazine and simazine, were not efficiently extracted by the proposed procedure. Cloud point extraction for determination of simazine and atrazine in water samples has not yet been extensively described in the literature, although prometryn, another triazine herbicide, was successfully extracted from water and soil samples with recoveries between 85 and 99%[2].

Conclusion

The cloud point extraction proved to be an efficient and easy to perform method. The results demonstrated the feasibility of the use of Triton X 114 in the extraction step and preconcentration of simazine and atrazine in water samples, without the use of toxic organic solvents, attending the demand for greener analytical methods.

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