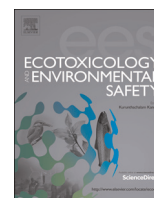




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## Extraction and determination of sulfonylurea herbicides in water and soil samples by using ultrasound-assisted surfactant-enhanced emulsification microextraction and analysis by high-performance liquid chromatography



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## ABSTRACT

An ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) with low-density extraction solvents was developed for the extraction of sulfonylurea herbicides from water and soil samples prior to high-performance liquid chromatography coupled with ultraviolet detection (HPLC–UV). In this technique, a surfactant was used as emulsifier which could enhance the dispersion of water-immiscible extraction solvent into aqueous phase and was favorable for the mass-transfer of the analytes from aqueous phase to organic phase. The target analytes were extracted into an extraction phase (Aliquat-336 in 1-octanol) and dispersed in an aqueous solution. After extraction and phase separation, the organic solvent on top of the solution was withdrawn into a syringe and 20  $\mu\text{L}$  of it was injected into a HPLC instrument for analysis. Influential factors in extraction were investigated and optimized. Under optimum experimental conditions, calibration curve was linear in the concentration range from 1 to 100  $\mu\text{g/L}$ , with coefficients of estimation ( $R^2$  values) varying from 0.9928 to 0.9952, and satisfactory repeatabilities ( $4.7 < \text{RSDs\%} < 6.1$ ) were attained. High preconcentration factors were achieved ranging from 103 to 153. Applicability of the method to the extraction of sulfonylurea herbicides from different types of complicated matrices, such as water and soil samples, was studied. The obtained results indicated that the proposed method is efficient, fast and inexpensive for extraction and determination of sulfonylurea herbicides in environmental aqueous and soil samples.

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### 1. Introduction

Sulfonylurea herbicides (SUHs), introduced in 1982 by the Dupont Corporation, were developed for weed control in cereal crops all around the world. Due to their low application rates (in the range of 10–100 g/ha), unprecedented herbicidal activity and low mammalian toxicity ( $\text{LD}_{50} > 4000 \text{ mg/kg}$ ), these herbicides have become very popular around the world (Niu et al., 2009; Gallitendorfer et al., 2011). Sulfonylurea compounds, which are composed of a sulfonyl structure linked to a urea group, represent one of the largest classes of herbicides (Fang et al., 2010a, 2010b). However, the relatively high water solubility of these herbicides may result in their leaching into deeper soils and potentially entering surface waters (Fang et al., 2010a, 2010b).

Simultaneous monitoring of sulfonylurea herbicides in complex environmental samples is very difficult because of their active

physical–chemical properties. Usually, the residues of these herbicides in environmental waters or soils are found at very low concentrations (parts per billion levels). Therefore, monitoring the trace amounts of these herbicides in environmental waters is a challenging task and demands highly efficient, selective, and sensitive analytical techniques (Zhang et al., 2011).

Several methods for quantifying sulfonylurea residues have been recently innovated that include high-performance liquid chromatography (HPLC) using reversed-phase column followed either by conventional ultraviolet (UV) or diode array (DAD), or mass spectrometric (MS) detectors utilizing various ionization techniques (Zhou et al., 2006; Wu et al., 2009; Perreau et al., 2007; Ouyang et al., 2009; Liu et al., 2003), gas chromatography (GC) along with mass spectrometry (GC–MS) (Klaffenbach et al., 1993; Marek, 1996), capillary electrophoresis (CE) (Rodriguez et al., 2001; Quesada–Molina et al., 2010) and enzyme-linked immunosorbent assay (ELISA) (Brady et al., 1995). Polar characteristics, low volatility, or thermal instability of some SUHs avoid their direct analysis by GC. Thus, HPLC has been the most frequent technique employed for analyzing SUHs.

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Because of low abundance of sulfonylurea residues in environmental waters and their complexity as sample constituents, it is required to develop high enrichment methods for further chromatographic analyzes. Several sample preparation procedures have been suggested for the determination of sulfonylurea herbicides in soil and aqueous samples, comprising liquid–liquid extraction (LLE) (Zhou et al., 2003), solid-phase extraction (SPE) [Gallitzendorfer et al., 2011; Perreau et al., 2007; Rodriguez et al., 2001; Gervais et al., 2008], molecularly imprinted SPE (MISPE) (Tang et al., 2008; Fu et al., 2012), single-walled carbon nanotubes SPE (Niu et al., 2009), multi-walled carbon nanotubes SPE (Fang et al., 2010a, 2010b), cloud point extraction (Wu et al., 2011), ionic liquids supported on magnetic nanoparticles (IL-MNPs), solid-phase extraction with magnetic nanoparticles (Bouri et al., 2012), microwave-assisted solvent extraction (MASE) (Font et al., 1998) and dispersive solid-phase extraction followed by dispersive liquid–liquid microextraction (DSPE-DLLME) (Zhang et al., 2011; Wu et al., 2009).

In 2006, Assadi and coworkers (Rezaee et al., 2006) reported a new liquid-phase microextraction technique, namely dispersive liquid–liquid microextraction (DLLME). This method is based on a ternary component solvent system in which extraction solvent and disperser solvent are rapidly injected into aqueous sample by a syringe to form a cloudy solution. The analyte in the sample is extracted into the fine droplets of extraction solvent. After extraction, phase separation is performed by centrifugation and the enriched analyte in the sedimented phase is determined by chromatographic techniques. After formation of cloudy solution, the surface area between extraction solvent and aqueous sample is enlarged and equilibrium state is reached quickly that leads to a short extraction time. So, advantages of this method include very short extraction time, ease of operation, low cost, and high enrichment factor. DLLME technique has also been used for doping the Er or Yb into the fiber grating for realizing high performance optical switching (Zhang and Zhang, 2012a, 2012b; Zang and Yang, 2011).

In 2008, ultrasound-assisted emulsification microextraction (USAEME) was presented for extraction of organic compounds from water samples (Regueiro et al., 2008). In this process, the extractant is dispersed into an aqueous solution without any dispersant under ultrasound irradiation. Hence, the consumption of toxic organic solvents is greatly reduced. The needed time for emulsification in USAEME is in the range of 5–10 min; consequently, the method does not provide a fast analysis.

The use of surfactants as emulsifiers in the above USAEME technique introduced a new sample pretreatment method called ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) for determination of some carbamates in water samples (Wu et al., 2010). In the UASEME technique, the extraction procedure takes place under the synchronized actions of ultrasound irradiation and surfactant; in this way, the analysis time is appreciably shortened. Surfactants are organic compounds that are amphiphilic; so that they contain both hydrophobic and hydrophilic groups. As a result, they are soluble in organic solvents and water. Surfactants decrease the surface tension of water via adsorption at the liquid–gas interface. They also diminish the interfacial tension between oil and water by adsorbing at the liquid–liquid interface. Thus, surfactants could serve as emulsifiers to enhance the dispersion of a water-immiscible phase in an aqueous phase and accelerate the construction of fine droplets of extraction solvent in an aqueous sample solution under ultrasound irradiation, thereby, reducing the extraction time. The application of a surfactant as an emulsifier in UASEME would combine the advantages of both DLLME and USAEME.

In this paper, an ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) coupled to HPLC–UV

detection was explored and developed for the determination of three SUHs including metsulfuron-methyl (MSM), chlorsulfuron (CS) and bensulfuron-methyl (BSM) in water and soil samples. The effects of various experimental parameters, for example kind and volume of extraction solvent, type and concentration of surfactant, ultrasound emulsification time and salt addition, were scrutinized and optimized.

## 2. Experimental

### 2.1. Chemicals and reagents

Standards of the sulfonylurea herbicides (metsulfuron-methyl, chlorsulfuron and bensulfuron-methyl) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Chemical structures and physicochemical features of the drugs are figured in Table S1. Analytical grade toluene, 1-octanol and dihexyl ether were acquired from Merck (Darmstadt, Germany) and exploited as extraction solvents. Cetyltrimethylammonium bromide, CTAB ( $C_{19}H_{42}BrN$ ), was obtained from Merck. Tetradecyl trimethyl ammonium bromide, TTAB ( $C_{17}H_{38}BrN$ ), sodium dodecyl sulfate, SDS ( $C_{12}H_{25}OSO_3Na$ ), and tricaprylyl methyl ammonium chloride, Aliquat-336 ( $C_{25}H_{54}ClN$ ), were supplied by Sigma-Aldrich. Sodium hexadecyl sulfate, SHS ( $C_{16}H_{33}OSO_3Na$ ), was obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Triton X-114 was obtained from Fluka (Buchs, Switzerland). Ultra-pure water was prepared by an Aqua Max-Ultra Youngling ultra-pure water purification system (Dong-gan-gu, South Korea). Microliter syringes (25–500  $\mu$ L) were purchased from Hamilton (Bonaduz, Switzerland). A centrifuge from Sepand Teb Azema (Tehran, Iran) was applied to phase separation.

### 2.2. Preparation of standards and real samples

Stock standard solution of each analyte was prepared separately, by dissolving appropriate amount of each SUH in acetonitrile to gain a concentration of 1000 mg/L, and stored at 4 °C. The stock solutions were then diluted with acetonitrile to reach secondary mixed stock solutions of the desired concentrations (1–200 mg/L). Mixtures of efficient standard solutions were prepared through the dilution of the secondary mixed stock solutions in ultra-pure water. Natural water samples were collected from the Caspian Sea (Mahmoud abad, Iran), tap water at Tarbiat Modares University (Tehran, Iran) and Haraz River (Mazandaran, Iran). No filtration or further treatment was done for any of the samples before extraction. Soil samples were gathered from two green houses in Marand (Azarbaijan, Iran) and Tehran, and dried at room temperature.

### 2.3. Apparatus

A 40 kHz, 0.138 kW ultrasonic water bath with temperature control from Tecno-Gaz SpA (Sala Baganza, Italy) was utilized to emulsify the organic solvent in aqueous solution.

Chromatographic analysis was carried out with a HPLC system consisting of a Varian 9012 HPLC pump (CA, USA) and a six-port Cheminert HPLC valve from Valco (Houston, USA) with a 20  $\mu$ L sample loop, and equipped with a Varian 9050 UV–vis detector. Chromatographic data were recorded and analyzed by using Chromana software (version 3.6.4). An ODS-3 column (250 mm  $\times$  4.6 mm, with 5  $\mu$ m particle size) from HECTOR (Daejeon, Korea) was employed to separate the SUHs under isocratic elution conditions. Mobile phase was a mixture of acetonitrile and deionized water (53:47, v/v), the pH of which was fixed at 3.0 with 1 mol/L  $HNO_3$ , at a flow rate of 1.0 mL/min. Elution time of the

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