



Determination of six sulfonylurea herbicides in environmental water samples by magnetic solid-phase extraction using multi-walled carbon nanotubes as adsorbents coupled with high-performance liquid chromatography



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ABSTRACT

Magnetic solid-phase extraction (MSPE) using magnetic multi-walled carbon nanotubes (mag-MWCNTs) as adsorbents, coupled with high-performance liquid chromatography–diode-array detector (HPLC–DAD), was developed for the simultaneous separation and determination of six types of sulfonylurea herbicides (SUs) in environmental water samples. Several variables affecting MSPE efficiency were systematically investigated, including the type and volume of desorption solvent, sample solution pH, salt concentration, amount of mag-MWCNTs, and extraction and desorption time. Response surface was employed to assist in the MSPE optimization. Under optimized conditions, excellent linearity was achieved in the range of 0.05–5.0 µg/L for all six SUs, with coefficients of correlation $r > 0.9994$, and preconcentration factors ranging from 178 to 210. Limits of detection and quantification were 0.01–0.04 µg/L and 0.03–0.13 µg/L, respectively. The intra-day and inter-day precision (relative standard deviations, $n = 6$, %) at three spiked levels were 2.0–11.0% and 2.1–12.9% in terms of peak area, respectively. The method recoveries at three fortified concentrations were obtained within 76.7–106.9% for reservoir water samples and 78.2–105.4% for tap water samples. The developed MSPE–HPLC method demonstrated high sensitivity, repeatability, simplicity, rapidity, and excellent practical applicability.

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1. Introduction

Sulfonylurea herbicides (SUs) are one class of widely used herbicides with high efficiency and low toxicity. These herbicides provide efficient, broad-spectrum control of broad-leaved weeds and some grasses. To date the class has expanded to include over 30 commercial herbicides. These compounds generally have low mammalian toxicity, but plants demonstrate a wide range of sensitivities to SUs. Some have demonstrated residual phytotoxicity, including rotation crops such as corn, sunflowers, sugar beets and dry beans [1]. SUs can be released into environmental water and endanger human health. Hence, the presence and levels of SUs in environmental water must be monitored and detected.

Determination of trace SUs is very challenging. The most common analytical methods for SUs are high-performance liquid chromatography coupled with an ultraviolet or diode-array detector (HPLC–UV/DAD) [2–6] and mass spectrometry (HPLC–MS) [7,8]. However, for low concentration of SUs in water, UV detectors cannot provide high sensitivity without enrichment prior to analysis. HPLC–MS instrumentation is expensive and not available in every laboratory. Therefore, pretreatment techniques are imperative for the enrichment and cleanup of SUs in environmental samples in order to achieve the ideal sensitivity and effectively eliminate contaminants from complex matrices. Currently reported pretreatment techniques for SUs in environmental water samples mainly include solid-phase extraction (SPE) [2,5,7,8], dispersive liquid–liquid microextraction [4], stir-bar sorptive extraction [9], and salting-out assisted liquid–liquid extraction [10]. SPE, due to its high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, and ease of automation and

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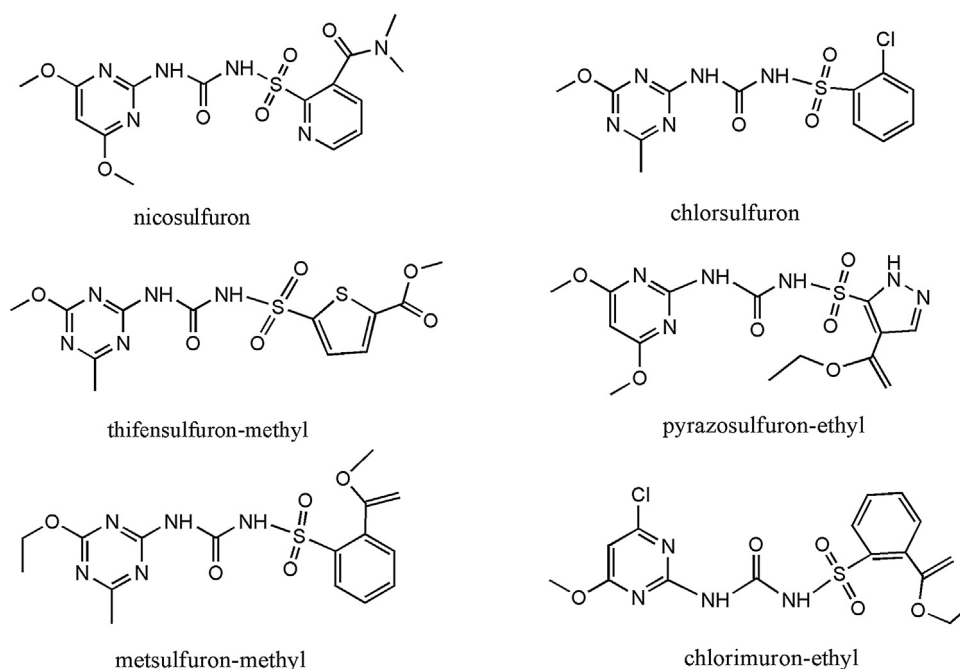


Fig. 1. Chemical structures of six analyzed SUs.

operation, has been widely used to concentrate organic compounds in water samples. In SPE, the choice of adsorbents is very important for obtaining high-enrichment efficiency.

Magnetic SPE (MSPE) has received increasing attention as a relatively new mode of SPE based on the adsorption and release of target analytes by a small amount of magnetic nanoparticles (e.g., Fe₃O₄ nanoparticles) dispersed in solution. The Fe₃O₄ nanoparticle-adsorbed target compounds can be easily collected by an external magnetic field without additional centrifugation or filtration of samples [11,12]. For example, He et al. [13] have used Fe₃O₄@dioctadecyl dimethyl ammonium chloride@silica magnetic particles as MSPE adsorbents for enrichment of SUs in environmental water samples.

Carbon nanotubes (CNTs) have also attracted much interest owing to their unique thermal, mechanical, electronic and chemical properties [14]. Multi-walled CNTs (MWCNTs) composed of several layers of rolled graphite sheets display large specific surface areas and have high adsorption capacities, making them especially useful [15]. As SPE adsorbents, MWCNTs have shown very strong adsorption of phthalate esters [16], chlorophenols [17], 4-*tert*-octylphenol [18], etc. We have used MWCNTs as SPE adsorbents for the successful enrichment of polycyclic aromatic hydrocarbons [19], pyrazole and pyrrole pesticides [20] in environmental water samples.

Inspired by these studies, we used magnetic MWCNTs (mag-MWCNTs) as MSPE adsorbents to enrich six SUs in environmental water samples, followed by HPLC-DAD determination. Several methods have previously been developed using mag-MWCNTs as the adsorbent for analysis of estrogens [21], nerve agents [22], aconitines [23] and so on. However, to the best of our knowledge, no methods based on mag-MWCNTs have been established for determination of SUs. In this work, mag-MWCNTs were prepared and characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). Several key factors influencing MSPE efficiency were investigated in detail, including the type and volume of desorption solvent, sample solution pH, salt concentration, amount of mag-MWCNTs, and extraction and desorption time. Response surface methodology was employed for multi-variable optimization.

The MSPE-HPLC method was validated and applied to the simultaneous separation and determination of six SUs in reservoir and tap water samples.

2. Experimental

2.1. Chemical reagents and materials

Carboxylic MWCNTs (>50 nm I.D., 10–20 μm length) were obtained from Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences (Chengdu, China). Ferric chloride hexahydrate (FeCl₃·6H₂O) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Ethylene glycol was supplied by Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Sodium acetate, sodium hydroxide and absolute ethyl alcohol were purchased from Aibi Chemical Reagent Limited Company (Shanghai, China). Anhydrous sodium chloride was purchased from Jiangsu Powerful Function Chemical Co., Ltd. Phosphoric acid was purchased from Kaixin Chemical Industry Co., Ltd (Tianjin, China). Chemicals were of at least analytical grade. Solvents including methanol, acetonitrile and acetone were of HPLC grade and supplied by TEDIA (USA). Ultrapure water (18.2 MΩ cm) was obtained from a model Synergy 185 ultra-pure water system (Millipore, USA).

Analytical standards of the six SUs (>99% purity), namely, nicosulfuron, thifensulfuron methyl, metsulfuron methyl, chlorsulfuron, pyrazosulfuron-ethyl, and chlorimuron-ethyl (Fig. 1), were purchased from the Testing Center of the Shanghai Pesticide Research Institute (China). A stock solution of each analyte was prepared at 1000 mg/L in acetonitrile, and stored at –18 °C in the dark. Working standard solutions were prepared by appropriate dilution of stock solutions into an acetonitrile-water solution (20:80, v:v).

Surface water samples were collected from the Qingdao Jihongtan Reservoir, and tap water samples were collected from our laboratory. All water samples were filtered through 0.45-μm membranes (Tianjin Jinteng Experiment Equipment Ltd, Co., Tianjin, China) and stored in brown glass bottles at 4 °C prior to analysis.

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