



# Polydimethylsiloxane/MIL-100(Fe) coated stir bar sorptive extraction-high performance liquid chromatography for the determination of triazines in environmental water samples



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## ABSTRACT

Polydimethylsiloxane (PDMS)/MIL-100(Fe) coated stir bar was prepared by sol gel technique, and good preparation reproducibility was achieved with relative standard deviations (RSDs) ranging from 2.6% to 7.5% (n=7) and 3.6% to 10.8% (n=7) for bar-to-bar and batch-to-batch, respectively. Compared with commercial PDMS coated stir bar (Gerstel) and PEG coated stir bar (Gerstel), the prepared PDMS/MIL-100(Fe) stir bar showed better extraction efficiency for target triazines compounds. It also exhibited relatively fast extraction/desorption kinetics and long lifespan. Based on it, a method of PDMS/MIL-100(Fe) coated stir bar sorptive extraction (SBSE)-high performance liquid chromatography-ultraviolet detector (HPLC-UV) was developed for the determination of six triazines (simazine, atrazine, prometon, ametryn, prometryne and prebane) in environmental water samples. Several parameters affecting SBSE of six target triazines including extraction time, stirring rate, sample pH, ionic strength, desorption solvent and desorption time were investigated. Under the optimal experimental conditions, the limits of detection (LODs, S/N=3) were found to be in the range of 0.021–0.079  $\mu\text{g L}^{-1}$ . The repeatability RSDs were in the range of 2.3–6.3% (n=7, c=0.5  $\mu\text{g L}^{-1}$ ) and the enrichment factors (EFs) ranged from 51.1 to 102-fold (theoretical EF was 200-fold). The proposed method was applied to the analysis of target triazines in environmental water samples, with recoveries of 98.0–118% and 94.0–107% for spiked East Lake water and local pond water samples, respectively.

## 1. Introduction

To satisfy the increasing need of food, pesticides have been widely used in the agriculture products. As a kind of high effective and selective pesticides, triazines can control the growth of broadleaf weeds and have been extensively used in many agricultural crops such as rice, grapes and maize [1]. Due to the widespread and prolonged use, high chemical stability and water solubility, the residues of triazines herbicides would enter surface water and other environmental water through the ecological chain [2,3]. It has been reported that triazines and its degradation products are very toxic, they can disturb and damage endocrine and reproductive systems of animals, and cause birth defects, weight loss of embryos and even multiple kinds of cancer [4]. Therefore, triazines have been considered as one kind of endocrine disrupters in many countries, and European Union (UN) has limited the concentration of residues level of triazines in surface water, established a maximum permitted concentration as 0.5  $\mu\text{g L}^{-1}$  for total triazines and 0.1  $\mu\text{g L}^{-1}$  for their individual concentration [5].

Considering human may be exposed to triazines in food chain, it is of great importance to develop effective and sensitive methods for monitoring and detection of triazines in environmental water samples.

Many analytical instruments have been applied for the analysis of trace triazines in environmental samples such as gas chromatography (GC) [6,7], high performance liquid chromatography (HPLC) [8–10], and capillary electrophoresis (CE) [11]. However, the determination of triazines in real samples is challenging because of their low concentration and the complexity of real sample matrix. Sample pretreatment techniques are usually needed prior to instrumental measurement. Various methods have been applied for the pretreatment of triazines, including conventional solid phase extraction (SPE) [12,13] and liquid-liquid extraction (LLE). However, the operating procedure in traditional LLE is time-consuming and large amount of organic solvents are needed. New types of SPE, such as dispersive solid phase extraction (d-SPE) [14] and magnetic solid phase extraction (MSPE) [15] have also been used for the analysis of triazines. In recent years, new sample preparation techniques aim to simplify the operating procedure and be

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friendly to environment, solid phase microextraction (SPME) [16], liquid phase microextraction (LPME) [17] and stir bar sorptive extraction (SBSE) [18] have been developed accordingly.

Among them, SBSE is an equilibrium technique which was developed based on SPME in 1999 by Baltussen and co-workers [19]. It is featured with higher adsorption capacity and recovery than SPME due to the coating amount of stir bar 50–250 times higher than that of SPME fiber. Besides, SBSE merits good reproducibility, anti-interference ability and easy-to-operate, and has been widely applied for the analysis of various analytes in different matrix [20]. The coating of stir bar is the key point of SBSE, however, the commercial coating in SBSE available is still rare, only three kinds of coating including polydimethylsiloxane (PDMS), ethyleneglycol (EG)-silicone and polyacrylate (PA) are available at present. Among them, EG-silicone and PA coatings are suitable for the extraction of semi-polar compounds, and PDMS coating is suitable for apolar compounds. Accordingly, further development of SBSE is focusing on the preparation of new stir bar coatings, especially those with high stability and efficiency for the analysis of polar analytes. Coatings of stir bar applied for the analysis of triazines were relatively few, including commercial PDMS, polyurethane (PU) foams and molecular imprinted coating. Commercial PDMS-coated stir bar was used for the preconcentration of ten triazines from underground waters, and a relatively long extraction time (2 h) was needed to achieve the extraction equilibrium [18]. PU foam was used as the polymeric phases for SBSE of seven triazines from ground and superficial water, while the extraction kinetics was very slow, and a long extraction time about 6 h was needed [21]. Besides, evaporation of desorption solvent was needed before HPLC analysis, which may result in the loss of target analytes and complicate the operation procedure. Li and co-workers prepared a molecular imprinted polymer (MIP)-based stir bar for SBSE of triazine herbicides in complex samples such as soils, rice and lettuce [22,23]. The selectivity for target analytes was greatly improved, but it still needed 60 min to achieve extraction equilibrium. Thus, it is of great significance to develop novel SBSE coatings with high extraction efficiency and fast kinetics for the extraction and preconcentration of triazines from real samples.

Metal-organic frameworks (MOFs) are a new type of hybrid inorganic-organic porous material, which merit diverse structures, pore topologies, accessible cages and tunnels. They have been widely used in gas storage/capture [24], catalysis [25], magnetic materials [26], luminescent material [27], battery [28], and drug delivery [29]. Besides, because of their high surface area, easy-to-modify and high adsorption capacity, MOFs are very attractive in stationary phases in GC, HPLC and coating of capillary tube of CE [30] for the separation of organics and chiral compounds. Recently, great efforts have been made in applying MOFs as adsorption materials in sample pretreatment techniques such as SPME [31], SPE [32,33], MSPE [34] and SBSE [35]. In our previous work, a PDMS/IRMOF-3 coated stir bar [36] and PDMS/Al-MIL-53-NH<sub>2</sub> coated stir bar [37] were prepared for SBSE of seven estrogens and polycyclic aromatic hydrocarbons from environmental water samples; a PDMS/MIL-101-Cr-NH<sub>2</sub> coated stir bar was fabricated for the analysis of organophosphorus pesticides [38]. Moreover, covalent triazine frameworks were employed as the stir bar coating for the extraction of eight phenols from environmental water samples [39]. The application potential of MOFs in SBSE has been demonstrated and relatively fast extraction/desorption kinetics was achieved probably due to the porous structure of MOFs.

In this work, three water stable MOFs (MIL-100(Fe), MIL-101(Cr) and UiO-66) were chosen for the preparation of PDMS/MOFs coated stir bar through sol-gel method. Considering triazines consist of amino group bonded directly to a carbon atom in an aromatic heterocyclic ring, while these MOFs contain benzene ring and carboxyl groups, the selected MOFs were expected to be efficient coatings for SBSE of triazines based on  $\pi$ - $\pi$  stacking, hydrophobic interaction and intermolecular hydrogen. The extraction efficiency of three home-made

coated stir bars for six target triazines was compared, and PDMS/MIL-100(Fe) coated stir bar exhibited the highest extraction efficiency. Based on it, a method of PDMS/MIL-100(Fe)-SBSE-ultrasonic assisted liquid desorption (LD)-HPLC-UV was developed for the determination of triazines in environmental water samples. The experimental parameters affecting the extraction efficiency of triazines by PDMS/MIL-100(Fe)-SBSE were optimized, and the analytical performance and application potential of the proposed method was evaluated.

## 2. Experimental

### 2.1. Reagents and standards

Hydroxyl-terminated polydimethylsiloxane (OH-PDMS) was purchased from Sigma-Aldrich (Milwaukee, WI, USA). Methyltrimethoxysilane (MTMS) and poly(methylhydrosiloxane) (PMHS) were purchased from the WD Silicone Co. Ltd. (Wuhan, China). Methanol, ethanol, acetonitrile, sodium chloride (NaCl), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), hydrochloric acid (HCl), sodium hydroxide (NaOH), nitric acid (HNO<sub>3</sub>), hydrofluoric acid (HF), iron powder, chromium nitrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), zirconium chloride (ZrCl<sub>4</sub>), trichloromethane (CHCl<sub>3</sub>), N, N-dimethylformamide (DMF) and trifluoroacetic acid (TFA, 95%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Trimesic acid (1, 3, 5-BTC), terephthalic acid were purchased from Shanghai Aladdin Chemistry Co., Ltd. (Shanghai, China). The capillary glass bars were obtained from Apparatus Factory of West China University of Medical Sciences (Chengdu, China). Solid reagents and all solvents used in this work were of analytical grade. High purity water obtained by a Milli-Q water purification system (18.25 M $\Omega$  cm, Millipore, Molsheim, France) was used throughout the whole experiment. Commercial PDMS stir bar (20 mm long, 0.5 mm thick, Twister™) and EG-Silicone stir bar (10 mm long, 0.5 mm thick, Twister™) was purchased from Gerstel GmbH (Mülheim an der Ruhr, Germany).

Standards of simazine, atrazine, ametryn, prometon, prometryne, prebana were purchased from Aldrich Chemistry Co., Ltd. (Shanghai, China). The structure and properties of target analytes are listed in Table 1. The individual standard stock solutions of each analyte (100 mg L<sup>-1</sup>) were prepared by dissolving a specific amount of corresponding triazines in methanol, and then stored at 4 °C in a refrigerator. The working solutions were prepared by diluting the standard stock solution to required concentration daily using high-purity water.

### 2.2. Instrumentation

An Agilent 1100 HPLC (Agilent Technologies, Waldbronn, Germany) equipped with a degassing device, a quaternary pump, a 100- $\mu$ L sample loop, and a variable wavelength UV-Visible detector was used for separation and detection of triazines. A reversed phase-C<sub>18</sub> column (250 mm×4.6 mm, 5  $\mu$ m, Merck KGaA, Germany) was used for the analysis of target triazines. The isocratic elution was performed with a mixture of methanol, acetonitrile, H<sub>2</sub>O at a volume ratio of 20/48/32 at a flow rate of 1 mL min<sup>-1</sup>. UV detection was performed at 220 nm.

IKA color squid magnetic stir (Baden-Württemberg, Germany) and SY 1200-T ultrasonic processor (Shengyuan Instrument Factory, Shanghai, China) were used for SBSE procedures. FEI Quanta 200 scanning electron microscope (SEM, FEI Company, Hillsboro, OR, USA) and Nicolet iS10 Fourier transform infrared spectrometer (FT-IR, Thermal Fisher Scientific, USA) were employed for the characterization of the prepared MIL-100(Fe) and home-made stir bar coating. Powder X-ray diffraction (PXRD) data was collected on PANalytical EMPYREA with CuK $\alpha$ 1 ( $\lambda$ =1.54056 Å) radiation operated at 40 kV and 40 mA.

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