# Highly sensitive determination of sulfonamides in environmental water samples by sodium dodecylbenzene sulfonate enhanced micro-solid phase extraction combined with high performance liquid chromatography

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ABSTRACT

Sulfonamides are important antibiotics, and have achieved great applications. However they also impose serious threat on the environment and human health when they enter into environment by various ways. Present study developed a new determination method for six sulfonamides such as sulfadiazine, sulfamerazine, sulfamethazine, sulfadimethoxine, sulfamethoxazole and sulfafurazole in water samples, which was based on micro-solid phase extraction (μ-SPE) using $TiO_2$ nanotube arrays as the adsorbent in combination with high performance liquid chromatography. Surfactant sodium dodecylbenzene sulfonate (SDBS) was used to enhance the extraction performance in this enrichment procedure. The parameters that affected the extraction efficiency had been investigated. Under the optimal conditions, it was observed that there were good linear relationships between the peak areas and the concentrations of the sulfonamides. The linear ranges were $1–200 \, \mu g \, L^{-1}$ for the six sulfonamides with the correlation coefficients in the range of 0.998–0.999. The repeatability of the proposed method was satisfactory in the range of 2.1–4.4% (RSD, $n=6$). The limits of detection (LODs) were in the range of $0.27–0.6 \, \mu g \, L^{-1}$. The proposed method was validated with real environmental samples, and the spiked recoveries were satisfied. These results indicated that the proposed method was a good tool for monitoring sulfonamides in the water samples.

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## 1. Introduction

Sulfonamides are one kind of antibiotics used to control a wide variety of bacterial infections in pigs and cattle. They have been in use continuously since the 1930s and posed a serious contamination risk to soil and surface water [1–3]. Intensive researches on sulfonamides have been carried out, which include detection, distribution, transformation, and impact on humans and animals in the surrounding environment [4,5]. However it is still crucial to develop simple and sensitive analytical methods for monitoring and evaluating the environmental safety of the pollutants.

Up to now, many methods have been developed for determination of sulfonamides based on high performance liquid chromatography with an ultraviolet detector (HPLC-UV) [6–8], high performance liquid chromatography with a fluoroscence detector (HPLC-FLD) [9], high performance liquid chromatography coupled

with mass spectrometry (LC–MS) [10], high performance liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) [11], etc. Because of very low concentration levels and complex matrices of environmental samples, sample pretreatment is an indispensable procedure before instrumental analysis. Up to now, many pretreatment techniques have been developed and adopted to extract sulfonamides from various environmental samples [10,12,13] such as hollow fiber supported liquid phase microextraction [6] and solid phase extraction [14]. Hollow fiber supported liquid phase microextraction method was a typical liquid phase microextaction method, which has achieved many applications, and also successfully been used to extract and determine five sulfonamides in environmental water samples with ionic liquid as the liquid membrane and tri-$n$-octylphosphine oxide (TOPO) as the carrier [6]. The results demonstrated that this method was a very sensitive and reliable tool with good repeatability and excellent clean-up. Solid phase extraction (SPE) is another sample pretreatment technique, which has been popular in analytical field due to its merits such as low cost, high enrichment factor, rapidness, easy automation, and wide scope. The key part of solid phase extraction

is the adsorbent. The variety of the adsorbent makes it have wide applicability to screen new materials as the adsorbent for SPE has been hot topics in analytical and related fields. Since nanomaterial was introduced, it was paid more attention. Niu et al. reported a solid phase extraction method with a single-walled carbon nanotubes disk to enrich five sulfonylurea herbicides in water samples [14]. The results exhibited that the adsorption ability of single-walled carbon nanotubes was comparable to C18. $TiO_2$ nanotube array, a novel $TiO_2$ material, possesses unique distinctive semiconducting and catalytic properties that can be used in many fields [15–17]. It has numerous vertical nanotubes and neat surface which can be used for adsorption, and has many potential applications [18–20]. Pan et al. reported a new method for determination of polycyclic aromatic hydrocarbons (PAHs) with $TiO_2$ nanotube arrays fabricated on Ti wire and modified with Au nanoparticles and n-octadecanethiol [21]. Huang et al. used cetyltrimethyl-ammonium bromide modified $TiO_2$ nanotube arrays as the adsorbent to develop a sensitive determination method for PAHs from environmental water samples [22]. They changed the surface properties by adding surfactant into water samples. The cetyltrimethyl-ammonium bromide modified $TiO_2$ nanotube arrays have been proved to have strong adsorption for PAHs. These indicated that $TiO_2$ nanotube arrays had good adsorption and should have more applications.

As sulfonamides were concerned, there were no reports on $TiO_2$ nanotube arrays for enrichment of sulfonamides. So the goal of present study was to develop a μ-SPE method with $TiO_2$ nanotube arrays for determining sulfonamides from environmental water samples. Several parameters including pH values, the content of surfactant, elute solvent, salting-out effect, extraction time and desorption time were optimized.

## 2. Experimental

### 2.1. Reagents and materials

Six sulfonamides including sulfadiazine, sulfamerazine, sulfamethazine, sulfadimethoxine, sulfamethoxazole and sulfafurazole were obtained from Aladdin (Shanghai, China). A series of standard solutions were prepared by mixing appropriate amount of the stock solution with methanol. All the standard solutions were stored at 4 °C. Sodium hydroxide and hydrochloric acid were of analytical grade and obtained from Beijing Chemical Reagents (Beijing, China). Sodium dodecylbenzene sulfonate (SDBS) was purchased from Nanjing Reagent (Nanjing, China). Titanium sheet (0.2 mm) was purchased from Northwest Institute for Nonferrous Metal Research (Xi'an, China). Pt electrode was obtained from INESA (Shanghai, China). 30 V potentiostat was from ATTEN (Shenzhen, China). HPLC-grade acetonitrile and methanol were purchased from Merda Company (Beijing, China). The ultrapure water was used during the experiments.

### 2.2. Preparation and characterization of $TiO_2$ nanotube arrays

$TiO_2$ nanotube arrays were synthesized as described [23]. In brief, a size of $20 \times 20$ mm$^2$ with 0.2 mm thickness Ti sheet was polished by abrasive paper, and then immersed in acetone, isopropanol and methanol by sonicating for 10 min, respectively. The sheet was air-dried after rinsing with ultrapure water. The anodic oxidation was performed with titanium sheet as the anode and platinum electrode as the cathode, and the distance between two electrodes was 3 cm in the experiment. The electrolyte was composed of 0.14 mol L$^{-1}$ NaF and 0.5 mol L$^{-1}$ $H_3PO_4$. The anodic oxidation was carried out at 20 V for 1 h. After electrolysis, titanium sheet was rinsed with ultrapure water and then air-dried. The $TiO_2$ nanotube arrays were analyzed using a field emission

scanning electron microscope (FESEM) (Quanta 200F, FEI, Netherlands) (see (Fig. 1).

### 2.3. μ-SPE procedure

The μ-SPE procedure was similar to our previous work. In brief, the Ti sheet with $TiO_2$ nanotube arrays was cleaned with methanol and acetone before use, and then dipped into the water solution for 40 min to achieve adsorption equilibrium. After that the sheet was taken out, and rinsed with ultrapure water to remove co-adsorbed matrix and air-dried; further the sheet was immersed in a small amount of methanol to desorb the target analytes. The final solution was dried with nitrogen stream, and the residues were dissolved in 200 μL methanol for HPLC analysis.

### 2.4. Chromatographic analysis

The analysis was performed on an Agilent 1260 high-performance liquid chromatography system consisting of a variable wavelength detector, a quaternary pump, a column thermostat, and an automatic sample injector. Agilent Chemstation was used to acquire and process data. A reversed-phase Eclipse XDB-C18 column (250 mm × 4.6 mm, particle size, 5 μm) was used for the separation of sulfonamides. The mobile phase was a mixture of acetonitrile and $KH_2PO_4$–$K_2HPO_4$ buffer solution (pH 5.5) and the flow rate was set at 1 mL min$^{-1}$. The wavelength was set at 272 nm. Gradient elution program used was as follows: initial concentration of acetonitrile at 10%, and then linearly increased to 65% in 15 min.

### 2.5. Water samples

Three river water samples were taken from Shahe River and Wenyu River (Changping District, Beijing), and Tonghui River (Chaoyang District, Beijing). Reservoir water sample was collected from Ming Tombs Reservoir (Changping District, Beijing). These four water samples were filtered through 0.45 μm micropore membranes after sampling and were maintained in glass containers and stored at 4 °C.

## 3. Results and discussion

### 3.1. Optimization of the enrichment parameters

As the μ-SPE procedure was concerned, some parameters would influence the extraction performance. These parameters included sample pH, concentration of the added surfactant, desorption
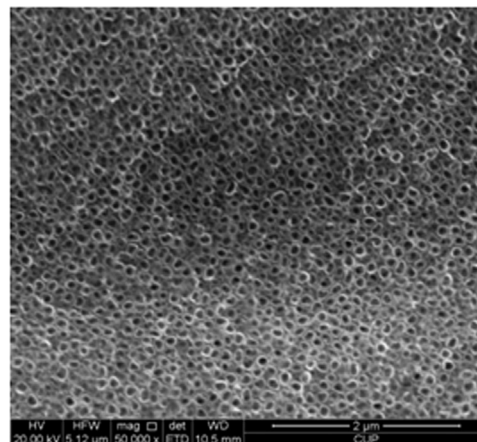


**Fig. 1.** FESEM image of $TiO_2$ nanotube arrays.