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Short communication

# A comparison between emulsification of reverse micelle-based supramolecular solvent and solidification of vesicle-based supramolecular solvent for the microextraction of triazines

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ABSTRACT

Two approaches based on emulsification of reverse micelle-based supramolecular solvent microextraction (ERM-SSME) and solidification of vesicle-based supramolecular solvent microextraction (SV-SSME) were compared for the extraction and preconcentration of four triazines (cyanazine, simazine, prometon and propazine) from water samples. Different ERM-SSME and SV-SSME parameters influencing the extraction efficiency were studied and optimized. The results showed that both extraction methods exhibited good linearity, precision, enrichment factor, and detection limit. Under optimal conditions, the limits of detection were 0.3 and 0.5 $\mu g\,L^{-1}$ for ERM-SSME and SV-SSME, respectively. The enrichment factors were from 330 to 505 and 285 to 421 for ERM-SSME and SV-SSME, respectively. The applicability of the proposed methods was examined by analyzing triazines in water samples and good results were obtained.



## 1. Introduction

Triazines, one type of herbicides with high power for weed control, have been often employed as the selected herbicides for crop protection in agricultural domain over the past years [1]. However, they are in the list of chemical pollutants. Thus, analyses of these compounds are very essential [2]. Gas chromatography (GC) and high-performance liquid chromatography (HPLC) are good techniques for monitoring triazines in water samples [3–5]. These compounds cannot be directly detected in different samples; therefore, suitable extraction methods are required for determining low concentrations of triazines in environmental samples.

Liquid–liquid extraction (LLE) [6] and solid-phase extraction (SPE) [7] are important techniques for extraction of analytes from liquid samples. Recently several different types of liquid-phase microextraction (LPME) methods have been developed, including dispersive liquid–liquid microextraction (DLLME) [8] and solidification of a floating drop (SFD) extraction [9].

Nonetheless, the greenness of microextraction can be enhanced further, so as to adhere more closely to green analytical chemistry principles. From this perspective, ionic liquids (ILs) are appropriate choices. Recently, several research groups have introduced various modes of LPME with ionic liquids [10]. Even though the environmentally friendly nature of ILs is generally accepted, it should be noted that these compounds may be potentially toxic owing to the instability of the $[PF_6]^-$ anion toward hydrolysis upon contact with moisture [11]. Hence, supramolecular solvents (SUPRASs) are excellent candidates to substitute them in many sample treatment procedures [12,13].

The term SUPRASs has been used for two recent alkyl carboxylic acid aggregate-based solvents (water-induced reverse micelle-rich phase and tetrabutylammonium (TBA)-induced vesicle-rich phase) [14,15].

SUPRASs have a unique array of physicochemical properties that render them very attractive to replace organic solvents in analytical extractions. Main intrinsic properties of these solvents include: use of self-assembly based synthetic procedures; ubiquity of amphiphiles in nature and synthetic chemistry which makes them easily accessible; tunability of solvent properties by varying the hydrophobic or polar group of the amphiphile; multiligand ability through the multiple polar groups present in a supramolecular aggregate which is an ideal platform for amplification of solute binding. On the other hand, the large concentration of surfactant and, therefore, of the binding sites it contains (typically 0.1–1 $mg\,\mu L^{-1}$), allows achieving high preconcentration factors by using low solvent volumes. Additional interesting properties for extractions include non-volatility and non-flammability, which permits the implementation of safer processes [16,17].

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To the best of our knowledge, there is no publication related to the comparison between the efficiencies of two types of SUPRAS-based LPMEs (reverse micelle-based solvent and vesicle-based solvent). The goal of this study is to compare the suitability of reverse micellar and vesicular coacervates for the preconcentration and determination of trace amounts of triazines in water samples. Several factors affecting the extraction efficiencies of the methods were scrutinized. Finally, the developed methods were validated through the analysis of target species in real water samples.

## 2. Experimental

### 2.1. Chemicals and reagents

Four selected triazines (cyanazine (CYZ), simazine (SMZ), prometon (PMN) and propazine (PPZ)) were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Tetrahydrofuran (THF) was supplied by Merck (Darmstadt, Germany). Decanoic acid (DeA) was acquired from Fluka (Buchs, Switzerland). Tetrabutylammonium hydroxide ($Bu_4NOH$, 40%, w/v in water) was obtained from Sigma–Aldrich. The ultra-pure water was prepared by an Aqua Max-Ultra Youngling ultra-pure water purification system (Dongan-gu, South Korea).

Stock standard solutions (1000 $\mu g\,mL^{-1}$) of the analytes were prepared by dissolving a proper amount of each triazine in methanol. Mixtures of standard working solutions were prepared by dilution of the stock solutions with ultra-pure water.

### 2.2. Apparatus

Chromatographic separation was performed with a HPLC instrument comprising a Varian 9012 HPLC pump (Walnut Creek, CA, USA) and a six-port Cheminert HPLC valve from Valco (Houston, TX, USA) with a 20-μL sample loop, and equipped with a Varian 9050 UV–vis detector. Chromatographic data were recorded using Chromana CH software (version 3.6.4). An ODS-3 column (150 mm × 4.6 mm, with 5-μm particle size) from MZ-Analysentechnik (Mainz, Germany) was applied to separate the triazines. As the mobile phase, first, a mixture of ultra-pure water, acetonitrile and methanol (45:22:33) for 15 min and then 100% acetonitrile for 5 min were used at a flow rate of 1.0 mL $min^{-1}$, and the analytes were detected at 220 nm.

### 2.3. Vesicular coacervate phase formation

Vesicular coacervate was attained by mixing 5.15 g of decanoic acid and 3.9 g of tetrabutylammonium hydroxide in 200 mL distilled water at pH 7.0 (±0.1). The mixture was stirred and then was centrifuged. The collected vesicular coacervate solvent (about 8 mL) was employed for further experiments.

### 2.4. Extraction procedure

#### 2.4.1. Emulsification of reverse micelle-based supramolecular solvent microextraction (ERM-SSME)

A home-designed centrifuge glass vial was filled with a 40 mL standard sample solution (pH ≈ 3.5), containing 50 $\mu g\,L^{-1}$ of each triazine and NaCl was added to adjust the salinity of the solution. THF (3 mL), containing 30 mg DeA, was rapidly injected into the test tube. Afterwards, the formed emulsion was centrifuged at 5000 rpm for 7 min. After phase separation, the floating SUPRAS was raised to the capillary tube attached to the top of the vial and collected. The volume of floating phase was about 23 μL and then directly injected into HPLC.

#### 2.4.2. Solidification of vesicle-based supramolecular solvent microextraction (SV-SSME)

A 24 mL aqueous sample solution (pH ≈ 7) containing 50 $\mu g\,L^{-1}$ of each triazine was placed in a 25 mL vial and 30 μL of supramolecular solvent was floated on the surface of sample solution and stirred using an IKA multi-position magnetic stirrer (Staufen, Germany) at 800 rpm. At the end of extraction time (70 min), the sample vial was placed into a beaker containing ice pieces until the SUPRAS was solidified. The solidified solvent was subsequently transferred into the conical vial, where it started to melt. Ultimately, 20 μL of the solvent was injected into HPLC.

## 3. Results and discussion

### 3.1. Extraction of triazines by ERM-SSME

#### 3.1.1. Description of reverse micelle-rich solvent

The reverse micelle-based supramolecular solvent applied in this research, spontaneously forms in ternary mixtures of DeA, water and THF at well-defined proportions. Its formation occurs through two sequential self-assembly processes. First, DeA molecules aggregate as reverse micelles in THF and then, upon the addition of water, they rearrange into larger reverse micelles which separate from the bulk solution, as an immiscible liquid, via a mechanism that remains elusive. The immiscible liquid is made up of reverse micelles, THF and minute amounts of water [15].

#### 3.1.2. Optimization of ERM-SSME

The pH of sample solution is one of the most significant factors influencing the stability of the coacervate phase and the extraction efficiency. Carboxylic acid molecules were strongly hydrogen-bonded to each other and it was proposed that intermolecular hydrogen bonding forces intensely increase the cohesion between molecules. Generally, sample solution pH determines the state of DeA in aqueous solution. Because the coacervation phenomenon took place with protonated alkyl carboxylic acids, the extractions had to be conducted at pH values below 4 [15]. Consequently, the impact of pH on the microextraction of analytes was studied in the range 1–4. As can be seen in Fig. 1a, the best extraction efficiencies of the analytes are gained at pH 3.5.

In conventional LLE, extraction efficiency is usually enhanced by increasing salt concentration in the sample solution due to a salting-out effect. The influence of NaCl concentration (ranging from 0 to 10%) on the extraction efficiency was investigated. The results showed an initial increase in the extraction efficiency with a rise in salt concentration, with a maximum being reached at 7.5% (w/v) of NaCl, followed by a decrease in the extraction efficiency with further increase in salt concentration. Hence, according to the obtained results (Fig. 1b), 7.5% (w/v) NaCl was added into the solutions in the next experiments.

The amount of constituents of the coacervate is the most prominent factor which determines the volume of coacervate acquired as well as the extraction efficiency and the preconcentration factor. As mentioned before, in this work, a DeA/THF mixture was used to create the reverse micelle coacervate in the aqueous medium, so both the amount of DeA and the volume of THF had to be optimized. A series of solutions were made by dissolving different amounts of DeA in a fixed volume of THF. As the concentration of DeA increased from 30 to 60 mg (in 4.0 mL THF), the volume of the SUPRAS also increased, whereas the preconcentration factor declined; this might be because the analytes in the floating phase were slightly diluted. Therefore, 30 mg of DeA was chosen as the optimum value in the subsequent experiments.

The dependence of peak areas on THF volume was also examined. As illustrated in Fig. 1c, maximal peak areas are achieved