

# Application of an Ultrasound-assisted Polymer Surfactant-enhanced Emulsification Microextraction for Determination of Aromatic Amines in Water Sample



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**Abstract:** A simple and efficient method, based on ultrasound-assisted polymer surfactant-enhanced emulsification microextraction (SA-USAEME) followed by gas chromatography-mass spectrometry (GC-MS), has been developed for the determination of eight aromatic amines (AAs) in aqueous sample. The main parameters affecting the performance of the proposed method were optimized, and the optimum conditions were obtained as follows: 150  $\mu\text{L}$  of extractive solvent (dichloroethane) 150  $\mu\text{L}$ , polymer surfactant (sodium alginate) of 0.20  $\text{g L}^{-1}$ , pH 7.0, salt addition of 3%, and ultrasound time of 1 min. Under the optimal conditions, the linear ranges were 0.1–200  $\mu\text{g L}^{-1}$  for 3,3'-dichlorobenzidine, 0.3–200  $\mu\text{g L}^{-1}$  for 2,4,5-trimethoxyaniline, 4-chloro-o-toluidine, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 3,3'-dimethylbenzidine and 4,4'-methylene-bis-(2-chloroaniline), and 0.5–200  $\mu\text{g L}^{-1}$  for 4-aminoazobenzene and 3,3'-dimethoxybenzidine. The correlation coefficients ( $R^2$ ) and detection limits were 0.9961–0.9997 and 0.08–0.3  $\mu\text{g L}^{-1}$  respectively. The intra- and inter-RSD were less than 10.3% and 11.9%. Additionally, the proposed method could be applied to the analysis of AAs in water sample respectively collected from tap water and river water. Compared with the common SA-USAEME, conventional surfactant was replaced with water-soluble polymer surfactant in this method to solve the problems of potential pollution and decrease the GC limitation since the polymer surfactant were natural and insoluble in extractive solvent. Compared with solid phase extraction, the proposed method enjoyed simplicity of operation and low cost. Therefore, it is an alternative method that could be widely used for the analysis of trace level of AAs in water sample.

**Key Words:** Polymer surfactant; Ultrasound-assisted emulsification microextraction; Aromatic amines; Gas chromatography-mass spectrometry

## 1 Introduction

Aromatic amines (AAs) can be produced by the decomposition of azo dyes which are intensively used in commercial articles such as textiles, cosmetics, plastics, and food colorants<sup>[1]</sup>. A number of the aromatic amines had been confirmed as cancer risks, for instance, 4-aminoazobenzene and *O*-dianisidine<sup>[2]</sup>. These carcinogenic compounds can easily enter the water systems from different ways such as effluent, supersession and degradation owing to their high

polarity and the corresponding water-solubility<sup>[3]</sup>. Therefore, they must be monitored to adequately assess the potential risk to humans and the environment. Two most used sample preparations, liquid liquid extraction (LLE)<sup>[4]</sup> and solid phase extraction (SPE)<sup>[5,6]</sup> are employed in the extraction of AAs from aqueous samples. However, LLE is time-consuming and requires large consumption of organic solvents. Although SPE consumes less solvent, the presence of the particulate matter in the sample can cause plugging of the cartridges<sup>[7]</sup>. To address the above-mentioned problems, in recent years,

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miniaturized extraction techniques become the noticeable trend of LLE and SPE, for instance, solid phase microextraction (SPME) and liquid phase microextraction (LPME). SPME is a non-exhaustive approach, by which the extracts and concentrates can be carried out in one step and thus it provides a simple route for analyte introduction into a chromatographic instrument<sup>[8]</sup>. However, SPME cannot be satisfactorily used for highly polar analytes because the coatings currently available are either nonpolar or slightly polar<sup>[9]</sup>. LPME, as an alternative to SPME, are increasingly applied for both nonpolar and polar analytes from different matrices recently.

LPME techniques include three categories: dispersive liquid-liquid microextraction (DLLME), hollow-fiber LPME (HF-LPME), and single-drop microextraction (SDME). As the fastest extraction technique<sup>[10,11]</sup>, DLLME first appeared on the analytical scene in 2006 and shortly thereafter sparked intense developments. DLLME can be realized by the following steps. Firstly, a liquid phase is dispersed in the form of small droplets in a second phase quickly by the input of mechanical energy, then the emulsion is broken by centrifugation, finally the sedimented phase is collected for analysis. Apparently, the major advantages of these techniques are quick equilibrium<sup>[12]</sup>, negligible volume of extraction solvent, and simple operation. The developments of DLLME techniques generally can be divided into three stages: organic solvent with miscibility in extraction solvent and aqueous phase is often used to disperse extraction solvent in the first stage. However, the introduction of dispersive solvent can decrease the partition coefficient of the analytes into the extractant<sup>[13]</sup>. Furthermore, the consumption of higher volume (i.e. mL) of dispersive solvent does not benefit environment. Ultrasound is proposed to replace the dispersive solvent to disperse extraction solvent and solve the problems previous indicated in the second stage. However, it is often difficult to ensure the uniformity of ultrasonic energy and consequent emulsion between individual samples and experiments<sup>[14]</sup>. And the heat caused by ultrasound easily evaporates tiny extractive solvent. The mixing mode of emulsification such as ultrasound-assisted surfactant-enhanced microextraction is applied to improve emulsion and further decrease extraction time in the third stage. Currently, some surfactants are often used, such as Tween, Triton X-100, sodium dodecyl sulfate, Quaternary ammonium salt and so on<sup>[15–18]</sup>. Because these surfactants have complicated composition, miscibility with extractive solvent and higher vaporization temperature, gas chromatographic analysis is limited. Furthermore, some surfactants probably contaminate water.

In this work, by using some natural and water-soluble polymers without miscibility with extractive solvent as surfactants, an environment-friendly method based on ultrasound-assisted polymer surfactant-enhanced emulsification microextraction was developed to determinate

eight aromatic amines in aqueous water. The proposed method was evaluated by detecting its linearity, detection limits, precision and applicability in analysis of real water.

## 2 Experimental

### 2.1 Reagents and Instruments

Standards of eight AAs, 2,4,5-trimethylaniline (TMA), 4-chloro-*o*-toluidine (CT), 4-aminoazobenzene (AAB), 3,3'-dimethyl-4,4'-diaminobiphenylmethane (DMDAB), 3,3'-dimethylbenzidine (DMB), 3,3'-dichlorobenzidine (DCB), 4,4'-methylene-bis-(2-chloroaniline) (MBCA) and 3,3'-dimethoxybenzidine (DMOB), were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Methanol (HPLC grade) was obtained from Sigma-Aldrich Company. Tetrachloroethylene (TCE), Dichloroethane (DCE), Carbon tetrachloride (CTC) and chlorobenzene (CB) were analytical grade solvent from Guangzhou Chemical Reagent Factory. Pectin and sodium alginate were obtained from ANPEL Scientific Instrument Co., Ltd (Shanghai, China). The water samples were from real tap water and river water.

Samples emulsification and sediment were respectively carried out on an ultrasonic water bath (40 kHz, 120 W, Crest<sup>®</sup>, USA) and an centrifuge (Anke, China). The analytes separation and detection were carried out by an Agilent 6850-5978B GC-MSD system. A Precision Balance (model no. AB204-S, METTLER TOLEDO) and two syringes (50 and 100  $\mu$ L) from Agilent were used for weighing and injection.

### 2.2 GC-MS analysis

The Analytes were separated by pass through a DB-5 MS fused silica capillary column (30 m  $\times$  0.25 mm inter diameter, 0.25  $\mu$ m film thickness). Helium (purity 99.999%) was employed as the carrier gas at a flow rate of 1.0 mL min<sup>-1</sup>. Samples (1  $\mu$ L) were injected in splitless mode. The injection temperature was set at 250 °C and the interface temperature was maintained at 270 °C. The oven temperature was programmed as follows: 70°C held for 2 min, ramped up to 140 °C at 10 °C min<sup>-1</sup> and held for 1 min, then ramped up to 170 °C at 20 °C min<sup>-1</sup>, successively ramped up to 230 °C at 5 °C min<sup>-1</sup> and held for 6 min, finally ramped up to 310 °C at 20 °C min<sup>-1</sup>. Ions were produced by electron impact with the energy of 70 eV.

### 2.3 Reagents preparation

Standards of eight AAs were dissolved in methanol to obtain stock standard solution with a concentration of 1000 mg L<sup>-1</sup>, which was stored at -18°C in brown bottle to protect from light. Calibration solution for daily use was obtained by

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