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Optimization of headspace solid phase microextraction based on nano-structured ZnO combined with gas chromatography–mass spectrometry for preconcentration and determination of ultra-traces of chlorobenzenes in environmental samples

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ABSTRACT

In this study, a simple, novel and efficient preconcentration method for the determination of some chlorobenzenes (monochlorobenzene (MCB), three isomeric forms of dichlorobenzene (diCB), 1,3,5-trichlorobenzene (triCB) and hexachlorobenzene (hexaCB)) has been developed using a headspace solid phase microextraction (HS-SPME) based on nano-structured ZnO combined with capillary gas chromatography–mass spectrometry (GC–MS). ZnO nanorods have been grown on fused silica fibers using a hydrothermal process. The diameter of ZnO nanorods was in the range of 50–80 nm. The effect of different variables on the extraction efficiency was studied simultaneously using an experimental design. The variables of interest in the HS-SPME were stirring rate, desorption time and temperature, ionic strength, extraction time and temperature. For this purpose, a multivariate strategy was applied based on an experimental design using a Plackett–Burman design for screening and a Box–Behnken design for optimizing of the significant factors. The detection limit and relative standard deviation (RSD) ($n=5$) for the target analytes were in the range of 0.01–0.1 ng L⁻¹ and 4.3–7.6%, respectively. The developed technique was found to be successfully applicable to preconcentration and determination of the target analytes in environmental water and soil samples.

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1. Introduction

Chlorobenzene compounds, as a main class of environmental pollutants, have been widely used as industrial solvents, pesticides, dielectric fluids, deodorant and chemical intermediates [1,2]. They can enter the aquatic environment through solid and liquid effluents and atmospheric discharges [3]. They have toxic characteristics and potential harmfulness to the receiving aqueous environment [4]. Therefore, they are identified as priority pollutants by EPA [5]. The excessive exposure to these compounds can exert dangerous effects on the central nervous system, irritation of the eyes, irritation of the upper respiratory tract, hardening of skin, and hematological disorders including anemia [6]. Therefore, the separation and analysis of traces and ultra-traces of chlorobenzenes in environmental samples is important.

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Chlorobenzenes are usually determined by gas chromatography–electron capture detector (GC–ECD) or (GC–MS) gas chromatography–mass spectrometry [6–9]. However, low concentration and matrix interference are two problems in the determination of chlorobenzene compounds. Thus, beside of developments in modern analytical instruments, sample preparation processes are needed for the extraction and preconcentration of the desired components prior to determination. In the literatures, several sample treatment methods such as liquid–liquid extraction (LLE) [10], solid phase extraction (SPE) [11], liquid phase microextraction (LPME) [12–16] and solid phase microextraction (SPME) [17,18] have been developed to solve these problems. Each of them has advantages and disadvantages and should be chosen according to the analytical problem.

Solid-phase microextraction (SPME), introduced by Pawliszyn and co-workers [19,20], is a fast, simple, efficient, inexpensive and solvent free extraction technique [21]. SPME allows complete elimination of organic solvents in the pretreatment step, decreasing the steps for sample preparation and has become an accepted method for the determination of volatile and semi-volatile substances. Also, it could be easily coupled with different

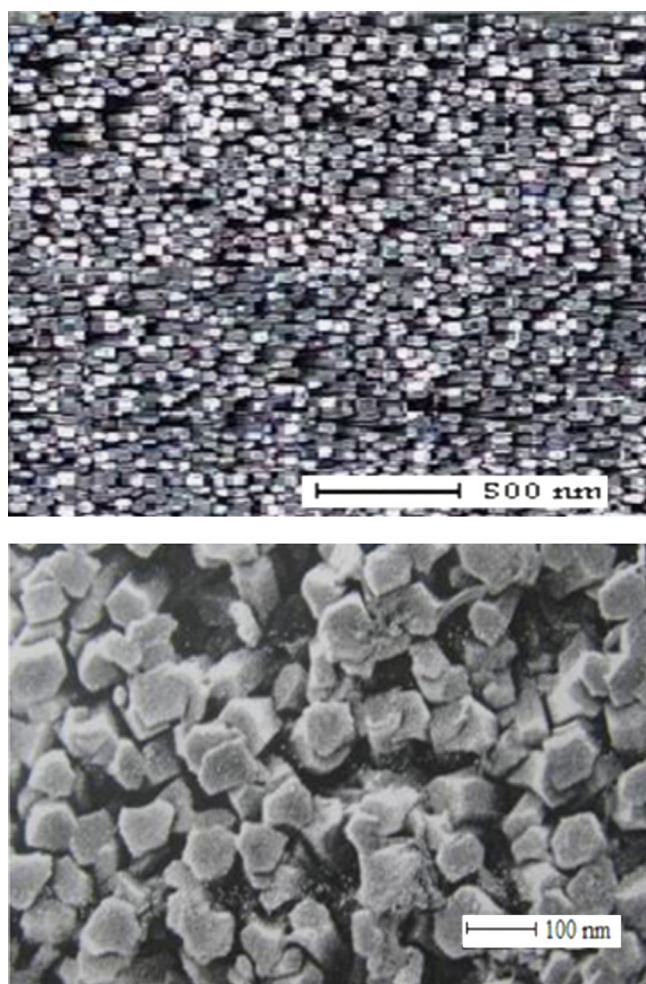


Fig. 1. Longitudinal SEM image of ZnO nanorod coated fused silica by hydrothermal process from solution containing of 0.01 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMT for 4 h at 80 °C.

determination techniques such GC and HPLC. There are different types of commercial SPME fibers; however, they usually have drawbacks of low thermal and chemical stability besides of the high cost and poor reusability. Recently some researchers have used nano-metal oxides as a coating of SPME fibers for analyte extraction and preconcentration in biological and environmental analysis [22–26]. Compared with traditional SPME fibers, nano-materials possess large surface area and high diffusion rate, which may result in high extraction efficiency and rapid equilibrium establishment. It was reported that ZnO nanostructured can be easily synthesized in various shapes and sizes using different chemical method [27–30]. The synthesized ZnO nanostructures as a coating of fibers in SPME have some advantages such as low cost, good conductivity, high stability in acidic media and proper adsorption properties [24]. Therefore, this fiber could be used to adsorption of a wide range of organic compounds with suitable sensitivity and high reproducibility.

The aim of this study was to develop a simple, highly effective and sensitive method for the preconcentration and determination of some chlorobenzene compounds in environmental samples. Therefore, the headspace solid phase microextraction based on the nanostructured ZnO as a coating followed by GC–MS was applied for this purpose. The experimental variables such as stirring rate, desorption time and temperature, ionic strength, time and temperature of extraction were optimized by a multivariate strategy based on an experimental design using a Plackett–Burman design

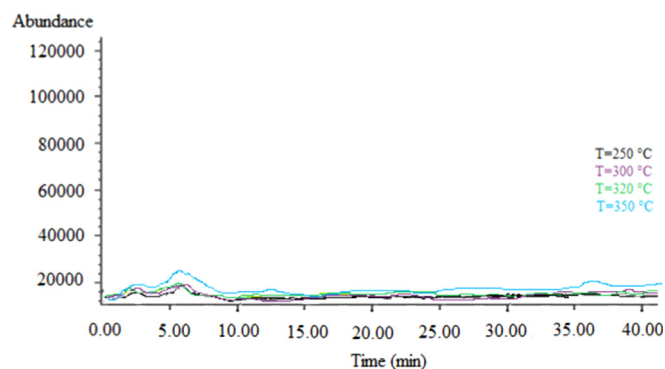


Fig. 2. Chromatograms showing baselines during conditioning of ZnO coating at 250, 300, 320 and 350 °C.

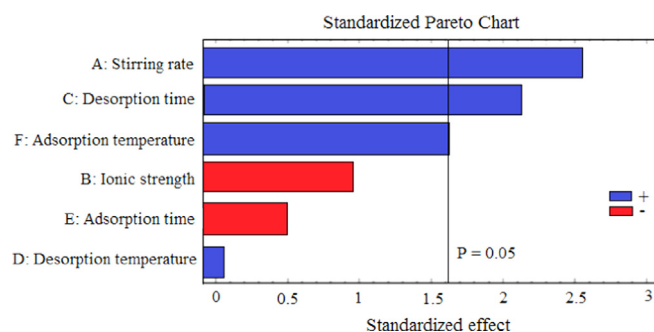


Fig. 3. Standardized ($P=0.05$) pareto chart, representing the estimated effects of parameters obtained from the Plackett–Burman design for CBzs compounds.

(PBD) for screening and a Box–Behnken design (BBD) for optimizing of the significant factors. The optimized procedure was applied to determine chlorobenzene compounds in environmental water and soil samples.

2. Experimental

2.1. Reagents and analytical standards

All chemicals were of analytical reagent grade. Reagent grade water was collected from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The studied CBzs (monochlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene and hexachlorobenzene) were purchased from Sigma Aldrich (St. Louis, MO, USA). All of the organic solvents such as methanol and acetone were obtained from Merck (Darmstadt, Germany). Zinc Nitrate and hexamethylenetetramine (HMT) were also purchased from Fluka. Sodium chloride (Merck, Darmstadt, Germany) was used to adjust the ionic strength of the aqueous samples. The SPME syringe and fused silica optical fiber were purchased from Azar Electrode Company (Tabriz, Iran) and Poly micro Technologies Inc. (Tucson, USA), respectively. Standard stock solutions of 500 mg L^{-1} of target compounds were prepared in methanol. All solutions were stored in the dark at 4 °C. Working solutions were prepared by dilution of standard stock solutions with deionized water.

2.2. Instrumentation

GC–MS separations were carried out by an Agilent (Santa Clara, CA, USA) Technologies 6890N Network GC System and Agilent Technologies 5973 Network Mass Spectrometer. GC was equipped with DB-624 fused silica capillary column ($60 \text{ m} \times 0.25 \text{ mm}$

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