



# Cobalt oxide nanoparticles as a novel high-efficiency fiber coating for solid phase microextraction of benzene, toluene, ethylbenzene and xylene from aqueous solutions



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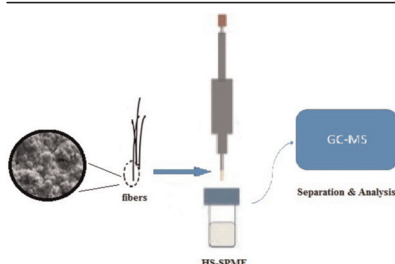
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## HIGHLIGHTS

- Co<sub>3</sub>O<sub>4</sub> nanoparticles were introduced as a novel SPME fiber coating.
- The fiber was evaluated for the extraction of BTEX in combination with GC–MS.
- The fiber showed extraction efficiencies better than a PDMS fiber toward BTEX.
- The fiber was successfully applied to the determination of BTEX in real samples.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work cobalt oxide nanoparticles were introduced for preparation of a novel solid phase microextraction (SPME) fiber coating. Chemical bath deposition (CBD) technique was used in order for synthesis and immobilization of the Co<sub>3</sub>O<sub>4</sub> nanomaterials on a Pt wire for fabrication of SPME fiber. The prepared cobalt oxide coating was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. The fiber was evaluated for the extraction of benzene, toluene, ethylbenzene and xylene (BTEX) in combination with GC–MS. A simplex optimization method was used to optimize the factors affecting the extraction efficiency. Under optimized conditions, the proposed fiber showed extraction efficiencies comparable to those of a commercial polydimethylsiloxane (PDMS) fiber toward the BTEX compounds. The repeatability of the fiber and its reproducibility, expressed as relative standard deviation (RSD), were lower than about 11%. No significant change was observed in the extraction efficiency of the new SPME fiber after over 50 extractions. The fiber was successfully applied to the determination of BTEX compounds in real samples. The proposed nanostructure cobalt oxide fiber is a promising alternative to the commercial fibers as it is robust, inexpensive and easily prepared.

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## 1. Introduction

Solid-phase microextraction (SPME) has been introduced by the research group of Arthur and Pawliszyn [1]. Because of the simplicity of use, relatively short sample processing time and fiber re-usability of SPME, it has been widely applied to the analysis of

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food [2], environmental [3,4], medicinal [5], medicinal plants [6] and biological and pharmaceutical samples [7]. SPME can combine sampling, extraction and sample introduction into a single step and thus has become an attractive alternative to most of the conventional sampling techniques. A common belief is that the development and further extension of SPME application greatly depend on new breakthroughs in coating technology [7]. SPME is predominantly performed on commercially available SPME fibers coated with different sorbents having various polarities. The extraction efficiency of SPME is determined by the distribution of analytes between the matrix and the coating. Therefore, the most important part of the SPME device is the fiber coating itself. Fused silica has been widely used as a support for SPME coatings; however, it has the disadvantage of being fragile. The use of metal wires as SPME supports with high mechanical stability makes this technique more robust for routine analysis [8].

Several studies have been reported by using different material coatings over the traditional fused silica or metallic supports; these include platinum [9], anodized aluminum [10], gold [11,12], stainless steel [13,14] and copper [15] wires. Further development of SPME is related intimately to the preparation and characterization of new sorbent materials such as molecular imprinted polymers [16], mesoporous materials [17], nanomaterials [18,19] and some organic polymers [20] as coatings over fused-silica fiber or metal wire supports.

Nanomaterials possessing excellent physical and chemical properties have attracted great attention lately for use in the separation science.  $\text{Co}_3\text{O}_4$  has many applications in heterogeneous catalysis under specific conditions, such as the elimination of nitrogen oxides [21], the oxidation of CO [22,23] and the remediation of toxic compounds such as acetaldehyde [24]. For all these applications, the preparation of oxide nanocrystals exhibiting a large surface-to-volume ratio, good adsorption ability and high thermal stability have been targeted by many research programs. These properties of  $\text{Co}_3\text{O}_4$  oxide nanocrystals make them suitable for removal of extractable compounds. Therefore, in the present work, the cobalt oxide nanoparticles ( $\text{Co}_3\text{O}_4$ ) were synthesized by chemical bath deposition and, for the first time, used as a suitable fiber coating onto platinum wires and applied to SPME of polar phenolic compounds (such as phenol, 2-nitrophenol and 4-chlorophenol) and nonpolar benzene, toluene, ethylbenzene and xylene (BTEX) compounds. The obtained results revealed the suitability of the new fiber for extraction of nonpolar compounds.

It is worth mentioning that BTEX are presented in environment because of industrial use of these compounds and also due to their presence in petroleum products (e.g., gasoline, diesel fuel, and heating oil). BTEX are hazardous to the environment and to public health, and it is the reason why environmental organizations regarded these compounds as priority pollutants. The permissible levels for chemical contaminants in drinking water, called maximum contaminant levels (MCLs), have been established by the US environmental protection agency (EPA). In the case of known or suspected carcinogens, the MCL is calculated based on assumption of an average adult weighing 70 kg and drinking approximately 2 L of water per day over a lifetime of 70 years. The MCL is set so that a lifetime exposure to the contaminant at the MCL concentration would result in no more than 1–100 (depending on the chemical) excess cases of cancer per million people exposed. According to this statement, the maximum contaminant levels for BTEX in drinking water are 0.005, 1.0, 0.7, and  $10.0 \mu\text{g mL}^{-1}$ , respectively [25].

To determine trace levels of BTEX in real samples, isolation and preconcentration steps are often necessary before analysis. In the current work, the new fiber was evaluated for the extraction of BTEX in combination with GC–MS. For optimization of the factors affecting the extraction efficiency, a simplex optimization method

was used. Under optimal conditions the fiber was successfully applied to the determination of BTEX compounds in real samples.

## 2. Experimental

### 2.1. Reagents and materials

Analytical grade benzene, toluene, ethylbenzene, xylenes (*o*-, *m*- and *p*-) (BTEX), polyethylene glycol and ammonia were obtained from Merck. Single standard solutions ( $500 \text{ mg L}^{-1}$ ) of BTEX compounds were prepared by spiking of each compound in methanol (HPLC grade, Merck), stored at  $4^\circ\text{C}$  and used within two weeks. Working aqueous solutions, prepared just before use, were made from the dilution of the stock methanolic solutions. An appropriate volume of the aqueous sample solution was introduced into a 20 mL SPME vial for the headspace-solid phase micro-extraction (HS-SPME) of the target compounds. Pt wires with  $100 \mu\text{m}$  diameter were obtained from Labor-Platina Company.

### 2.2. Preparation of SPME fiber using chemical bath deposition

The nanostructure  $\text{Co}_3\text{O}_4$  SPME fiber coating was prepared using chemical bath deposition (CBD) method, according to the procedure by Shim et al. [26]. Prior to the CBD, the Pt wires were subjected to acetone cleaning in an ultrasonic bath to remove the organic contaminants on their surface. In a typical synthesis process, cobalt acetate (0.5 g) was dissolved in 25 mL water/methanol (50% v/v) mixture. After being stirred vigorously for 15 min, a solution of polyethylene glycol (0.002 g in 10 mL water/methanol (50% v/v)) was added to the initial cobalt solution and stirred for 15 min while 1-cm length of Pt wires with  $100 \mu\text{m}$  diameter were immersed in the solution. The mixture was refluxed at  $40^\circ\text{C}$ ; during the reflux, 2.5 mL ammonia was added drop wise to the mixture. After adding ammonia the temperature was increased to  $80^\circ\text{C}$  and left for 2 h. Then the wires were removed, washed by water and methanol and dried. Finally, the resulted coating was calcined at  $400^\circ\text{C}$  for 3 h to obtain  $\text{Co}_3\text{O}_4$  nanostructure.

### 2.3. Characterization

The morphology and microstructure of the annealed films were characterized by X-ray diffraction (XRD) using an X'Pert PPO MPD apparatus with  $\text{CuK}\alpha$  emission, at 40 kV and 40 mA. The average crystallite size was calculated from the Scherrer equation after fitting the experimental profiles.

The scanning electron microscopy (SEM) images were obtained by a Kyky-EM 3200 scanning electron microscope. Uniform coating of  $\text{Co}_3\text{O}_4$  on the fiber is evident.

### 2.4. Headspace SPME procedure

The prepared fiber was conditioned prior to each extraction by leaving it in the injection port for 10 min at  $270^\circ\text{C}$ . A special SPME device (Azar Electrode Co., Oroumie, Iran) was used for holding and injection of the proposed fiber into the GC–MS injection port.

A 20 mL glass bottle sealed with rubber septum was used as a sample container. The bottle was held in the ultrasonic bath during the extraction. Then, the SPME device was fixed on top of the capped vial and the fabricated fiber was exposed to the sample head space after a sonicating step. After sample extraction, the fiber was withdrawn from the bottle and inserted into the GC–MS injection port in order to evaporate absorbed analytes for analysis.

### 2.5. GC/MS analysis procedure

GC/MS analysis was performed using an Agilent 6890N GC instrument coupled to 5973N mass detector. The analytes were

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