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SHORT COMMUNICATION

FAST DETERMINATION OF BISPHENOL A IN SPIKED JUICE AND DRINKING WATER SAMPLES BY PIPETTE TIP SOLID PHASE EXTRACTION USING COBALT METAL ORGANIC FRAMEWORK AS SORBENT

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ABSTRACT. A cobalt metal organic framework was prepared with rapid ultrasound assisted method by treatment of cobalt nitrate with pyridine 2,6-dicarboxilic acid dissolved in ethanolic media and used as a sorbent for pipette tip solid phase extraction of Bisphenol A (BPA) and its determination in spiked juice and drinking water samples by HPLC. Parameters which influence extraction efficiency such as pH, sample volume, amount of sorbent, type and volume of eluent, and number of draw/eject cycles for extraction and elusion were tested and optimized. Results showed that best extraction efficiency could be obtained at pH 3, 150 μL of sample volume, 3 mg of adsorbent and 10 μL of methanol as elution solvent. Numbers of draw/eject cycles for both sample extraction and elution were 7 cycles. Limit of detection and limit of quantification of this method were 0.07 and 0.3 μg L^{-1}, respectively, with linear dynamic range of 0.3 to 300 μg L^{-1} for BPA. This method was applied successfully for determination of BPA in five spiked juices and drinking water samples.

KEY WORDS: Cobalt metal organic framework, Bisphenol A, Pipette-tip solid phase extraction, Juice analysis

INTRODUCTION

Bisphenol A (BPA) has many application in the production of polymeric compound such as poly vinyl chloride (PVC) and polycarbonate [1]. This compound is widely applied in very commonly used plastic bottles, medical equipment, children toys, food and drinking packaging, compact discs and infant bottles. Common problem in usage of such devices is migration of BPA to the environmental ecosystems or food samples that can harmful for consumers due to the affecting the hormonal system of humans and animals, even at low concentrations [2-4]. Several lines of investigation have shown that heating times, temperatures and storage time are important factors in influenced migration of BPA from packaged juices. Juice and food product samples are examined in several countries for presence of BPA. It has been found in canned food in concentrations varying from 1 to 69.6 ng.g^{-1} [5].

Several methods such as liquid-liquid extraction [6], dispersive liquid-liquid micoextraction [7-9], stir bar sorptive extraction [10], single drop micro-extraction [11], hallow fiber liquid-liquid micro extraction [12], solid phase microextraction [13] and solid phase extraction [14] were already applied for the extraction and determination of BPA in both environmental and food samples.

Regarding environmental aspects of analytical methods, micro-solid phase extraction techniques were studied and developed in recent decades due to their advantages such as low solvent consumption, speed, high enrichment factor and simplicity. One of them, pipette tip solid phase extraction (PT-SPE), is a micro-SPE method that used for determination and extraction of many analytes such as pharmaceuticals, bioanalytical molecules, proteins, metals and so on. PT-SPE is very simple, fast and environmental friendly method that employs only a

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*Corresponding author. E-mail: rezaei@zbmu.ac.ir pipette tip as extracting column and a variable sampler for turning of sample solution and eluent solvent over the adsorbent [15].

In recent years, a new 3D porous material called metal organic frame work (MOF) were synthesized and used for various application such as gas storage, separation, drug delivery, removal of metal ions and other purposes due to its large porosity, high surface area, tunable pore dimensions and topologies as well as their tailorable physicochemical properties. The porous and ordered structures of MOFs can create well adsorptive sites to adsorption of guest species inside the frameworks. Some metal ions such as Zr and Co were used for synthesize of MOFs that have many promising application in adsorption and as storage for H_2 and CO_2 capturing [16, 17].

The Co-MOF structure have well-coordinated carboxyl and hydroxyl group that connected with pyridine 2,6-dicarboxylic acid as linkers together, showing one dimensional arrangement of parallel hexagonal channels. These unsaturated structure, can offer extra binding sites to the guest molecules [18].

In this work, a Co based metal organic framework is synthesized and used as adsorbent for extraction and high performance liquid chromatographic (HPLC) determination of BPA. After optimizing affecting parameters on extraction efficiency, this method was applied for determination of BPA in juice and drinking water samples.

EXPERIMENTAL

All chemical were of analytical grade and used without more purification. Cobalt nitrate ($Co(NO_3)_2.6H_2O$) and pyridine 2,6-dicarboxilic acid (98%) were purchased from Aldrich (Millipore-Sigma, USA). Ethanol and N,N-dimethyl formamide (DMF) were obtained from Merck KGaA (Germany).

Instrumental analysis. A Cecil HPLC (Cecil, England) system equipped with a UV detector was used for BPA determination. Detector was setup at fix wavelength of 280 nm. An ACE C_{18} column (USA) at temperature of 30 ^oC was employed as analytical column. The mobile phase was a mixture of 60:40 acetonitrile:water at a flow rate of 1 $mL.min^{-1}$. A 20 μL loop was used for injection [19].

Synthesis and characterization of Co-MOF adsorbent. Synthesize of Co-MOF was described in one of our previously reported researches [18]. Briefly, 5.62 mmol of cobalt nitrate and 1.85 mmol of pyridine 2,6-dicarboxilic acid were dissolved in 14 mL of ethanol. Obtained solution was transferred into a Teflon reactor with a tight cap and kept for 7 hour at 85 ^oC. The products were washed with dimethyl formamide (DMF). After mixing and dissolving the reactants, the clear solution radiated in the ultrasound bath for 13 min at working condition of 160 W, 1 kJ, and 21 kHz. Synthesized adsorbent was stored in 4 ^oC.

Pipette tip solid phase extraction procedure. In one of our previous reports, we fully described how the assembly of pipette tip and its uniform packing was performed [20]. 3 mg of Co-MOF sorbent was packed in a 10 μL pipette tip (Dragon, China) as a micro-column and connected to the end of a 200 μL variable sampler (Isolab, Germany). For loading samples, 150 μL aliquot of a sample containing 10 $mg.L^{-1}$ of BPA solution was drawn and ejected for 7 cycles over the adsorbent. The adsorbed BPA was eluted with methanol for same seven cycles and eluent was injected directly in to the HPLC. Peak area of obtained chromatogram was used for quantitative determination of BPA.

RESULTS AND DISCUSSION

Best extraction efficiency of BPA can be obtained at optimum condition of affecting extraction parameters such as pH, amount of adsorbent, type and volume of eluent, sample volume and numbers of draw/eject cycles for both eluent and sample solution. Hence, we tried to optimize all these parameters. In all optimization parameters a standard solution of 10 mg.L^{-1} of BPA was used.

Characterization of Co-MOF adsorbent. Characterization of adsorbent was done and its X-ray diffraction (XRD) pattern and scanning electron microscopy (SEM) image are shown in Figure 1 and Figure 2, respectively. In the XRD pattern, the mean peak at $2\Theta = 6.7$ and 11.7° positions are in good agreement to the crystalline patterns of the Co-MOF product already reported [18]. According to the data obtained from these patterns, the Co-MOF sample had broad peaks that indicate the small size of the crystals (based on the Debye–Scherrer equation) which confirmed the nanometric dimensions of the samples. Moreover, the corresponding XRD patterns were indexed to the cubic crystal system of the pure complex. SEM image (Figure 2) revealed that the average particle size of the Co-MOF is 3.2 µm. Also the morphology is completely homogenous so that there is no evidence for the agglomeration or aggregation of the final structure. The nitrogen adsorption technique (BET) measurements indicated that Co-MOF sorbent has a very large surface area (2983 m^2 g^{-1}) with an average pore size diameter of 63 nm.

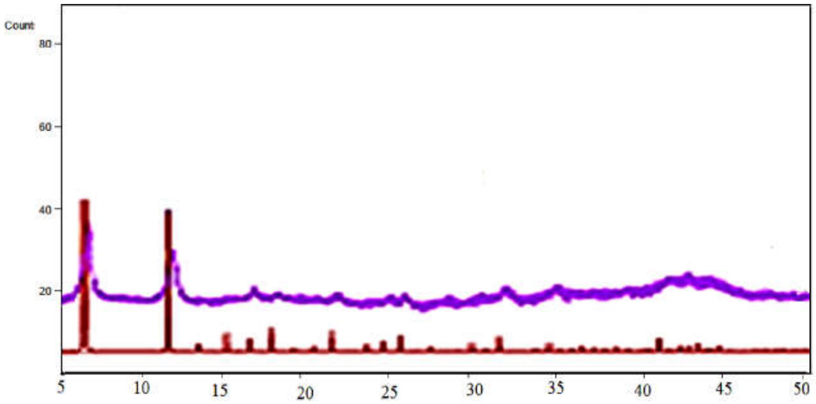


Figure 1. XRD patterns of the Co-MOF synthesized.

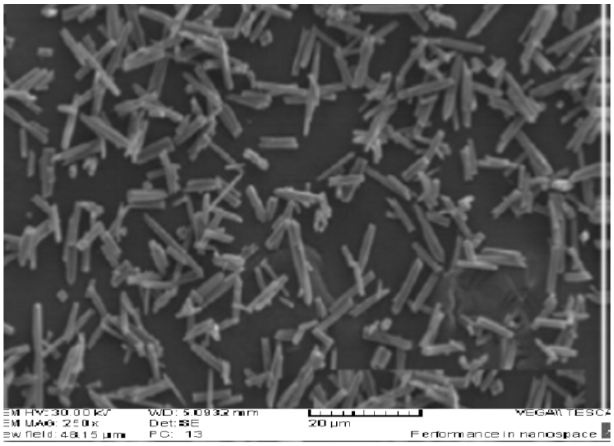


Figure 2. SEM image of the synthesized Co-MOF.

Effect of pH on extraction efficiency. pH is one of the most important parameters on solid phase extraction which determines how adsorption process take places and which form of the analytes (ionic or molecular) will adsorb on Co-MOF. For this purpose, pHs between 3.0 to 11.0 were adjusted with either 0.1 M of HCl or 0.1 M NaOH. The best extraction efficiency is obtained at pH 7.5 that indicates BPA was adsorbed in its molecular form (acidic ionization constant of BPA is $10^{-9.3}$). Therefore, pH of 7.5 was selected for subsequent experiments.

Effect of amount of adsorbent on extraction efficiency. For evaluation of amount of adsorbent on extraction efficiency, amounts of 2.0-5.0 mg of Co-MOF were selected and examined as solid extraction phase. The adsorption ability of PT-SPE was increased with increasing the amount of sorbent, because more adsorption sites were available for the analyte molecules. After 3 mg, the extraction recovery of BPA was decreased because the eluent solvent cannot desorb the absorbed compound completely.

Effect of type of eluent on extraction efficiency. Several eluent solvent including ethanol, methanol, acetonitrille, and 1:1 mixture of aetonitrille:methanol were applied to obtain the best extraction efficiency. Among them, methanol showed the highest extraction efficiency and hence this solvent was selected as proper eluent. The reason for this phenomenon may be the interaction between the BPA and the sorbent is weakened and then, the target molecule is easily eluted.

Effect of sample volume and eluent volume on extraction efficiency. We tried to obtain the highest extraction efficiency by finding the smallest volume of eluent which completely desorbed the target analyte. Also, for achieving best preconcentration factor, the sample volume must be optimized at the largest volume possible. For this purpose, sample volumes between 50.0 to 200.0 µL and eluent volumes between 5.0 to 30.0 µL were evaluated. Results showed that for 150.0 µL of 10.0 mg L^{-1} BPA solution and 10 µL of methanol the best extraction efficiency was obtained. After this optimized point, extraction efficiency was decreased. Decreasing in extraction efficiency is due to the fact the quantitative desorption of BPA from the Co-MOF sorbent became more difficult when the same amount of methanol is used with the same washing cycles.

Effect of draw/eject cycles of sample solution and eluent on extraction efficiency. In PT-SPE, numbers of draw/eject cycles of sample solution and eluent must be optimized to achieve the best extraction efficiency. The number of this procedure is a critical parameter for achieving the highest extraction efficiency [20]. In this regards, number of cycles between 3 to 10 were selected and applied. Results showed that for both sample solution and eluent, highest extraction efficiency will be achieved after seven cycles. This takes 10 min to be completed.

Adsorption capacity. To evaluate the adsorption capacity of Co-MOF, a standard BPA solution containing 1000 mg.L^{-1} of the analyte was extracted by the suggested method. The amount of adsorbed analyte was calculated by determination of difference between its initial concentration and its concentration after performing PT-SPE by Co-MOF [21]. The maximum adsorption capacity was defined as the total amount of adsorbed BPA per gram of the sorbent, which was found to be 23 mg.g^{-1}.

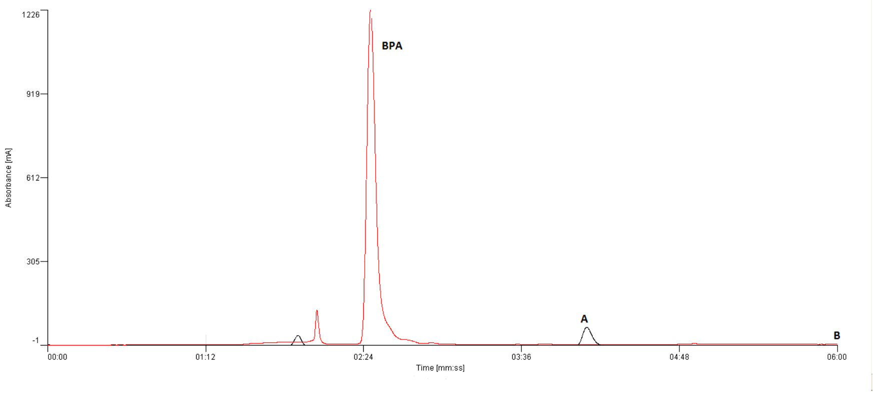
Analytical performance of the suggested method. Limit of detection was calculated to be 0.07 µg.L^{-1} based on $3S_b/m$ criterion for 10 blank measurements, where S_b is the standard deviation of seven replicate measurements of blank and m is the slope of calibration curve. The linear dynamic range (LDR) of calibration curve was studied by increasing concentration of the standard solution of bisphenol A from 0.1 to 500.0 µg.L^{-1} and found to be 0.3–300 µg.L^{-1}. The determination coefficient, R^2 was 0.979. The repeatability of the method, expressed as relative standard deviation (RSD), was calculated for five replicates measurement of a standard at 50 $\mu g.L^{-1}$ of the analyte and found to be 3.2-5.7%. Total extraction time (min) was ≤ 5.0.

Real sample analysis. To demonstrate the applicability of this developed PT-SPE method, four juice samples and one bottled drinking waters were examined for their BPA content. Results are shown in Table 1. As can be seen, no detectable level of BPA was found in samples. Therefore, to evaluate the interference of matrix on the analysis process all samples were spiked with 150 $\mu g.L^{-1}$ of BPA. Result showed that recoveries are good and adequate; therefore, it will be possible to use this PT-SPE method for the analysis of BPA in complicated matrices. Example chromatograms of real samples are showed in Figure 3.

Comparison of proposed methods with other SPE method. Table 2 shows a comparison between the proposed PT-SPE method with other published method for determination of BPA in various samples. As can be seen, this method has a comparable applicability and feasibility which other reported techniques. Shorter extraction time, simplicity of method and ease of automation are also other advantage of this proposed technique. Very large surface area of the synthesized MOF results its very high capacity and fastness of extraction. This sorbent is very robust and can be used for at least 100 times without any changes its power of extraction and can be stored for at least six month.

Table 1. Evaluation of BPA in juice and drinking bottled samples.

Sample	BPA found ($\mu g.L^{-1}$)	Spiked level ($\mu g.L^{-1}$)	Recovery (%) ±0.2%	RSD (%) (n = 5)
Peach juice	-	150	99.1	5.7
Apple juice	-	150	98.6	4.1
Grape juice	-	150	98.7	3.8
Pineapple juice	-	150	98.2	4.5
Drinking water	-	150	98.7	3.2



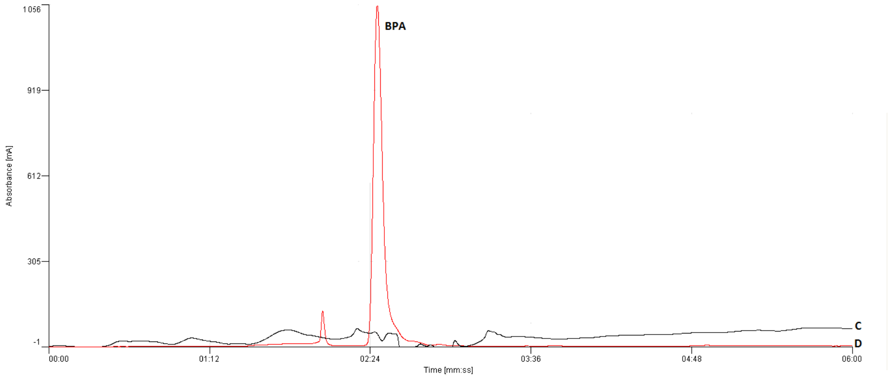


Figure 3. Chromatograms obtained at optimum extraction condition of real samples: A) direct injection of drinking water spiked with 50 μg.L^{-1} of BPA; B) injection of drinking water spiked with 50 μg.L^{-1} of BPA after PT-SPE extraction; C) direct injection of filtered peach juice spiked with 50 μg.L^{-1}of BPA. D) injection of filtered peach juice spiked with 50 μg.L^{-1}of BPA after PT-SPE extraction.

Table 2. Comparison of the proposed method with other methods for BPA analysis.

Method	Instrument	Matrix	LOD	LOQ (μg.L^{-1})	Extraction time (min)	RSD (%)	Ref.
SPE/C_{18} cartridge	GC-MS	Sediment	0.03 (ng.L^{-1})	0.0001		267	19
MSPE/Fe_3O_4@MgAl- LDHs NPs)	HPLC-UV	Juice	0.54 (μg.L^{-1})	-	15	4-7.8	22
SPE/Molecularly imprinted polymer	CE	Tap water, urine	0.8 (μg.L^{-1})	-	15	2-5.6	23
SPE/core shell Fe_3O_4-MIPs	HPLC-UV	Milk	3.7 (μg.L^{-1})	-	40	2.9-3.8	24
Ultrasonic assisted magnetic solid phase dispersive extraction	HPLC/UV	Milk	0.75 (μg.L^{-1})	2.5	-	0.5-3.7	25
ionic liquid paste electrode	Voltammetry	Various food samples	9.0 nmol.L^{-1}	-	-	1.5	26
Nanostructure Carbon Paste Electrode	Cyclic voltammetry, square wave voltammetry, and chronoamperometry	Various food samples	0.1 μM	-	-	1.7	27
PT-SPE/Co-MOF	HPLC-UV	Juice, drinking water	0.07 (μg.L^{-1})	0.25	3.5	3.2-5.7	This work

CONCLUSION

A rapid technique based on ultrasound applied for the synthesis of a novel Co-MOF sorbent which was used for the adsorption and determination of Bisphenol A in juices and drinking water samples based on PT-SPE. Comparison of PT-SPE with other methods showed the applicability and feasibility of the proposed method. Low consumption of sorbent, high adsorption ability and ease of usage are some of the advantages of this PT-SPE technique. The total analysis time was less than 10 min and the calibration curve for BPA was obtained in the concentration range of 0.3 to 300 μg L^{-1} under optimized conditions.

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