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A Novel Ultrasonic Assisted Dispersive Solid Phase Microextraction for Preconcentration of Beryllium Ion in Real Samples Using CeO_2 Nanoparticles and its Determination by Flame Atomic Absorption Spectrometry

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ABSTRACT

A simple and highly sensitive dispersive solid phase microextraction method coupled with flame atomic absorption spectrometry is proposed for preconcentration and determination of beryllium in real water and alloy samples employing cerium oxide nanoparticles as novel DSPME sorbent. This sorbent showed to be very effective for extraction of Be ion at the presence of interfering ions. Different parameters affecting the microextraction procedure such as nanoparticles amounts, pH, stirring and centrifuging times and the type and amount of desorption solvent were thoroughly studied and optimized. Under the optimized conditions, the calibration curve for Be was linear in the range of 0.05-25 μg L^{-1} with a correlation coefficient of 0.99. This method also shows low the relative standard deviation (RSD) and high preconcentration factor for determination of Be ion in real samples. The effects of different interfering ions on the Be determination were investigated and the method was successfully employed for its determination in well, tap and river water samples, and an alloy. The accuracy of method was also evaluated using a standard reference material.

Keywords: ultrasonic assisted dispersive solid phase microextraction, Cerium oxide nanoparticles, Beryllium ion, flame atomic absorption spectrometry

INTRODUCTION

Beryllium (Be) level in natural water is usually very low (0.01 – 0.7 mg L^{-1}) [1]. However, it is known that some acidic river waters or hot spring waters have a high concentration of Be (II) [2]. Because of its high strength and lightness, Be and its alloys are considered as the key components used in aerospace and electronic industries [3-5]. Be has been widely used in specific areas of nuclear technology because of its ability to reflect neutrons and its efficiency in the production of neutrons when exposed to alpha emitters [6]. Be in wastewaters from these industries is a major source of contamination in natural waters and could be hazardous to environment. Be and its compounds can be entered to human body through contaminated water, food and air. Prolonged contact with this element can lead to chronic beryllium disease. Although the mechanism of chronic beryllium disease is not completely understood but it seems that Be is combined with special protein such as ferritin protein in the body and enters into the lungs. These compounds can be taken up by macrophage of lung and caused lesions in the lungs. These problems may occur in other parts of the body including the kidney, nervous system, skin, heart, spleen, bone, skeletal muscles, and liver [7-10]. Moreover, according to the International Agency for Research on Cancer (IARC), Be and its compounds have been classified as Group 1 confirming these compounds are carcinogenic to human and animal. Due to high toxicity of this metal at very low concentrations, highly reliable and sensitive analytical methods are required for determination of this ion in real samples. Several methods such as ETAAS and X-ray fluorescence spectrometry have been used for determination of beryllium [11, 12, 1, 13, 2].

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An important step for determination of an analyte in real samples is sample preparation that affect the selectivity and sensitivity of the analysis method. Nowadays, due to several advantages such as reducing matrix effects and interfering species, and preconcentration of the analyte, microextraction methods are widely used as sample preparation method for real samples such as biological and Pharmaceutical, water and wastewater, industrial and food samples [14-17]. Dispersive solid phase microexrtraction is a new, rapid and practical method for extraction of various analytes using a dispersing solid sorbent to separate then from the sample solution [18, 19]. The main benefit of this method compared to traditional SPME is reducing the time of extraction and the amount of sorbent and also preventing from swelling and breakage of SPME fiber. Moreover, this method is simple and does not require complicated tools. The most important disadvantage of the method is the separation of the sorbent from sample solution after the adsorption of analyte. Although the extraction time is reduced by this method, the time of the sorbent separation from the sample solution increases dramatically compared to traditional solid phase microextraction.

The preparation of nanostructure materials in chemistry and chemical engineering are highly regarded because these materials have unique mechanical, electrical, optical, catalytic, magnetic and photonic properties and many applications in various industries [20, 21]. These materials are widely employed in various branches of analytical chemistry to preconcentrate and separate the analytes [22-24]. Due to the convenient features such as high absorption ability, high strength, simple synthesis and well dispersion of nanomaterials in the solution, nanostructure materials as SPME sorbent have many applications in microextraction methods.

The purpose of the present work is to develop a novel and sensitive DSPME procedure using ceria nanoparticles as DSPME sorbent for extraction of beryllium ion in water and its alloy samples followed their determinations by atomic absorption spectrometry. Based on our knowledge, no work has been reported on the application of nanoparticles for preconcentration of Be so far. Therefore, ceria nanoparticles have been used as a novel and efficient DSPME sorbent for preconcentration and extraction of Be ion at trace levels prior to its determination by nitrous oxide flame atomic adsorption spectrometry.

EXPERIMENTAL

Apparatus

A Shimadzu AA-670 (Shimadzu, Japan) flame atomic absorption spectrometer equipped with a 10-mm nitrous oxide burner head and deuterium background correction was employed. A Be hollow-cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) at a wavelength of 234.9 nm was used as a radiation source. The pH values were measured with a pH meter (Metrohm 827 pH lab, Switzerland) supplied with a glass-combined electrode. Phase separation was assisted using Centurion Scientific Centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany).

Reagents

All reagents were of analytical reagent grade and deionized water was used throughout. A stock solution of 1,000 mg L^{-1} Be was prepared by dissolving appropriate amounts of $BeCl_2$ in deionized water. Cerium oxide nanoparticles as DSPME sorbent was purchased from TECNAN Company with particle average size of 5-10 nm.

Sample Preparation

Tap, well and river water samples were collected from Mashhad, Iran and Golestan River (Torghabeh, Iran), respectively. These samples were acidified with diluted nitric acid and kept in refrigerator at 5 ^{o}C. After adjusting the pH, Be content was measured according to the microextraction procedure.

A Copper-Be alloy (No 175) as a real solid sample was also used for determination of beryllium. 0.01 g of this alloy was treated with 10 mL of a mixture of concentrated nitric and hyrdrochloric acids (3:1 v/v) under heating. After complete dissolution of alloy, it was diluted to the volume of 50 mL using deionized water.

A certified reference material (CRM-TMDW) as liquid was used to validate the accuracy of the method.

Microextraction Procedure

Ten milliliters of sample solution containing 10 μg L^{-1} Be and 6% NaCl was maintained at pH 5 and transferred into a 25 mL beaker followed by addition of 20 mg of cerium oxide nanoparticles. The mixture was placed in an ultrasonic bath for 6 min at room temperature and a turbid suspension was formed from dispersing cerium oxide nanoparticles in the sample solution. The resulting suspension was then centrifuged at 4000 rpm for 7 min to separate the extracting adsorbent from the aqueous solution. The bulk aqueous phase was discarded by a syringe, and Be ion was eluted from the sorbent with 0.5 mL of concentrated formic acid under sonication for 3 min at room

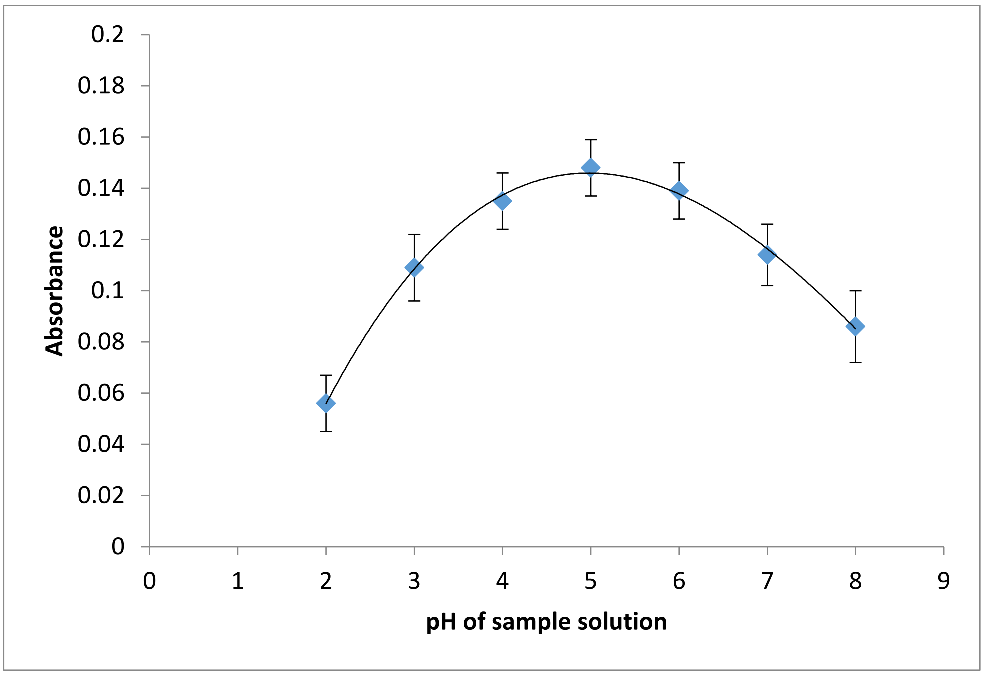

Figure 1. Effect of pH of sample solution

Conditions: analytes concentration,10 μgL^{-1}; amount of sorbent, 10.0mg; desorption solvent, HNO_3; centrifugation time, 5min; extraction time, 4min; desorption time, 4min; amount of NaCl, 8%; temperature 23±0.5 °C.

temperature. The acceptor phase, formic acid, was sprayed into the flame atomic absorption spectrometry for determination of beryllium.

RESULTS AND DISCUSSION

Optimization of Microextraction Procedure

The effects of different parameters affecting the efficiency of microextraction technique such as pH of sample solution, cerium oxide amounts, extraction time, type and concentration of desorption solvent, centrifugation and desorption time, and ionic strength was fully investigated and optimized.

Effect of pH

In order to extract the analyte with DSPME, it is necessary that analyte is adsorbed onto DSPME sorbent surface with a strong physical interaction. Therefore, pH is a critical parameter on the extraction efficiency. To investigate the effects of pH on the absorbance of beryllium, the pH of sample solution was varied in the range of 2-8 by increasing the dilute solution of hydrochloric acid (0.1molL^{-1}) and sodium hydroxide (0.1molL^{-1}). According to the results shown in **Figure 1**, the absorbance of beryllium is maximal at pH 5 and decreases gradually with increasing of the pH. At higher pHs, especially alkaline pH, beryllium ion precipitates with hydroxide ion in the solution, and thus, it would not be extracted. Therefore, pH 5 was selected as the optimum pH value.

Effect of cerium oxide amounts

The effect of amounts of cerium oxide nanoparticles on the absorbance of Be solution was investigated in the range of 5 – 30 mg. The results show that beryllium could be quantitatively adsorbed using 20 mg of cerium oxide nanoparticle and no benefit was noticed at higher amounts (**Figure 2**). Therefore, 20 mg of cerium oxide was chosen as the optimum value.

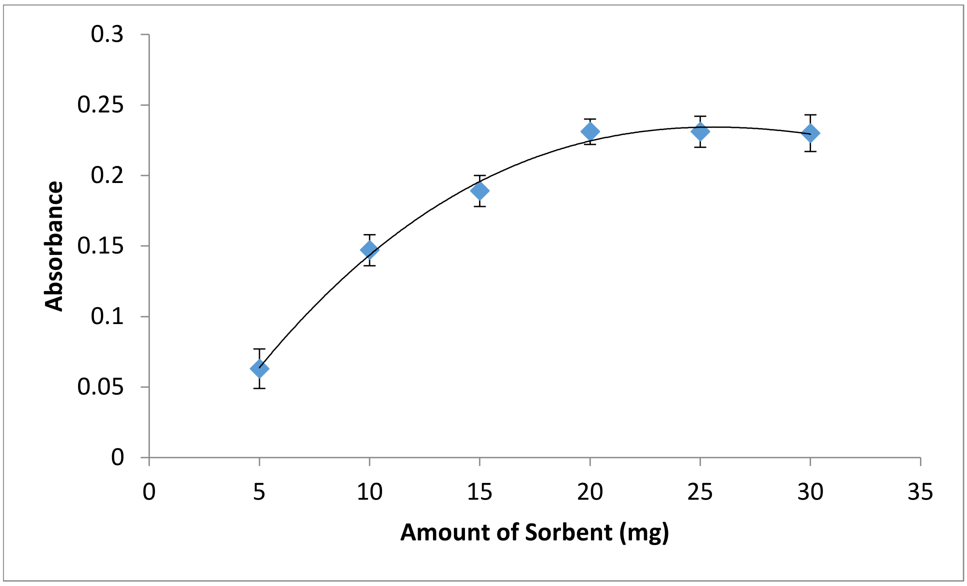

Figure 2. Effect of amount of sorbent

Conditions: analytes concentration, 10 μgL^{-1}; pH of sample solution,5; desorption solvent, HNO_3; centrifugation time,5min; extraction time, 4min; desorption time, 4min; amount of NaCl,8%; temperature 23±0.5 °C.

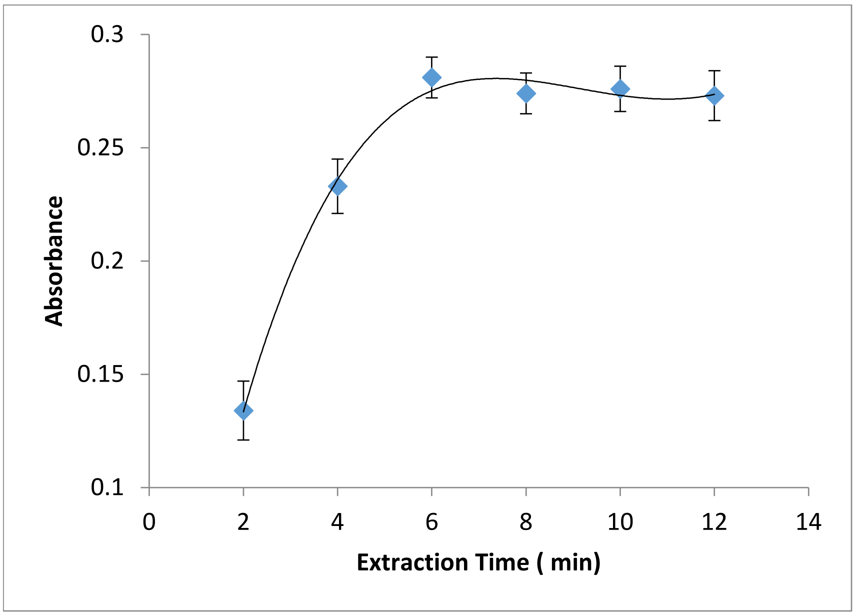

Figure 3. Effect of extraction time

Conditions: analytes concentration, 10 μgL^{-1}; pH of sample solution,5; amount of sorbent, 20.0mg; desorption solvent, HNO_3; centrifugation time, 5min; desorption time, 4min; amount of NaCl,8%; temperature 23±0.5 °C.

Effect of extraction time

Extraction time is an important parameter that affects the extraction efficiency. Generally, the process of solid-phase microextraction involves a dynamic mass transfer and partitioning equilibrium of Be between the SPME sorbent and sample solution. Hence, sufficient extraction time is required to attain adsorption equilibrium to ensure quantitative retention of target ion from the sorbent. The effect of extraction time was studied in the range of 2-12 minutes (**Figure 3**). It is evident that the equilibrium condition was rapidly reached within 6 minutes; and therefore 6 minutes extraction time was selected as the optimum value.

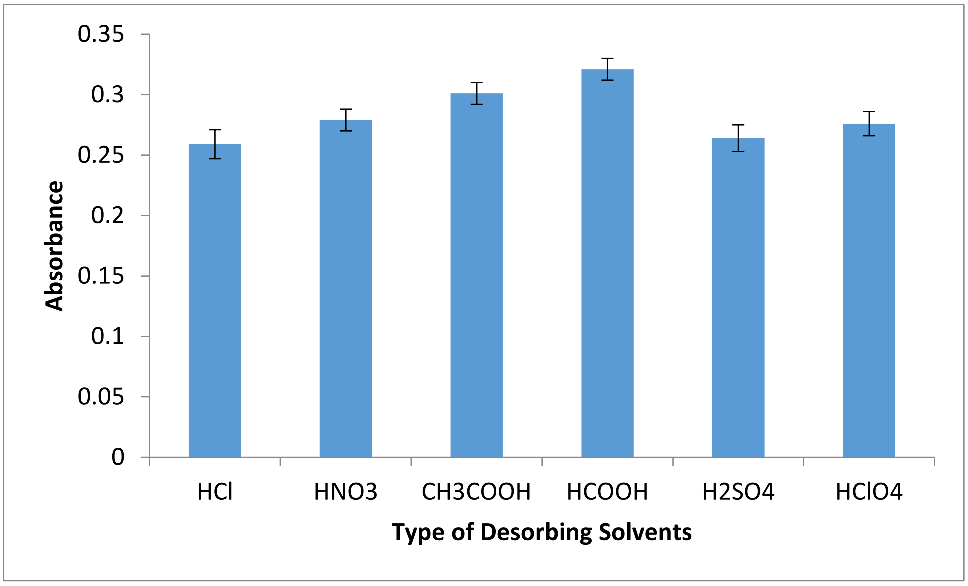

Figure 4. Effect of type of desorption solvent

Conditions: analytes concentration, 10 μgL^{-1}; pH of sample solution,5; amount of sorbent, 20.0mg; centrifugation time,5min; extraction time, 6min; desorption time, 4min; amount of NaCl,8%; temperature 23±0.5 °C.

Effect of desorption condition

After the extraction, it is imperative that the absorbed analyte to be quantitatively eluted from the sorbent surface before injection to AAS for analysis. In desorption process, a partitioning equilibrium is created between the absorbed analyte onto the sorbent surface and desorption solvent as the acceptor phase. Therefore, the two affecting factors in this equilibrium, type and concentration of desorption solvent, and also the time required to achieve equilibrium should be investigated and optimized. Various desorbing solvents such as nitric acid, hydrochloric acid, perchloric acid, sulfuric acid, acetic acid and formic acid were tested and the results are shown in **Figure 4**. According to the results, formic acid produced maximum recovery among other acids studied and therefore, was selected as the eluent solvent. To study the effect of concentration of formic acid in the desorption of Be, formic acid at different concentrations were studied. The results (data not shown) indicated that the highest extraction recovery was obtained by concentrated formic acid and therefore it was used as the optimum concentration.

The effect of desorption time on the absorbance of desorbed beryllium was studied in the range of 2-6 minutes. According to the results (**Figure 5**), 3 minutes desorption time is adequate for quantitative desorption of Be from cerium oxide nanoparticles.

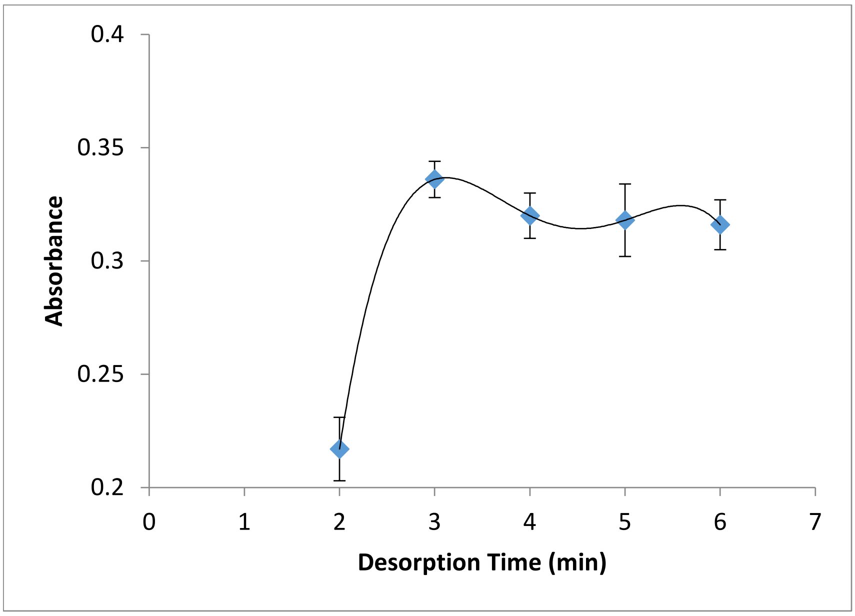

Figure 5. Effect of desorption time

Conditions: analytes concentration, 10 μgL^{-1}; pH of sample solution,5; amount of sorbent, 20.0mg; desorption solvent, HCOOH; centrifugation time, 5min; extraction time, 6min; amount of NaCl, 8%; temperature 23±0.5 °C.

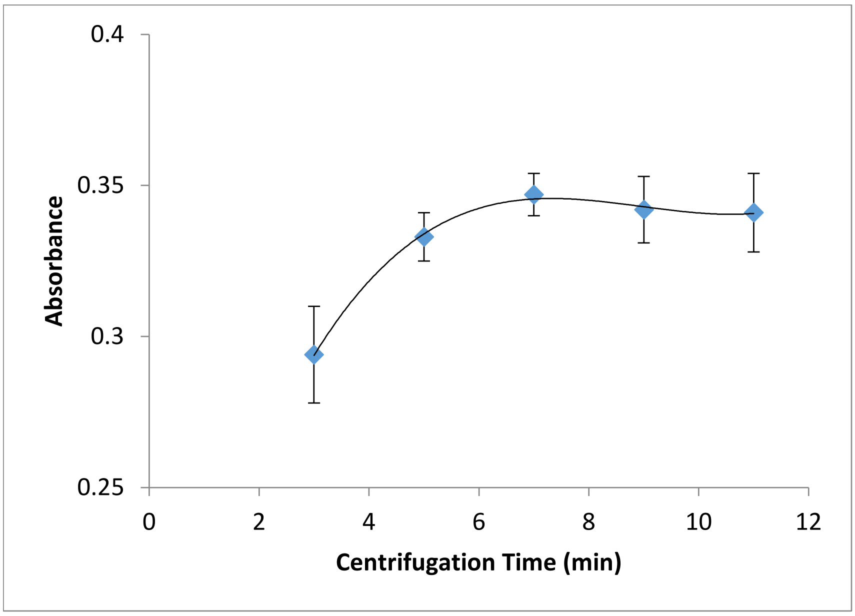

Figure 6. Effect of centrifugation time

Conditions: analytes concentration, 10 μgL^{-1}; pH of sample solution,5; amount of sorbent, 20.0mg; desorption solvent, HCOOH; extraction time, 6min; desorption time, 3min; amount of NaCl,8%; temperature 23±0.5 °C.

Effect of Centrifugation condition

The effect of centrifugation time for separation of nanoceria from the bulk of solution was studied in the range of 3-11 minutes at a constant rate of 4000 rpm. The results show that 5 min centrifuge time is adequate to separate the solid phase extractant from the sample solution (**Figure 6**). Therefore, 7 minutes centrifugation time at 4000 rpm was used as the optimum value.

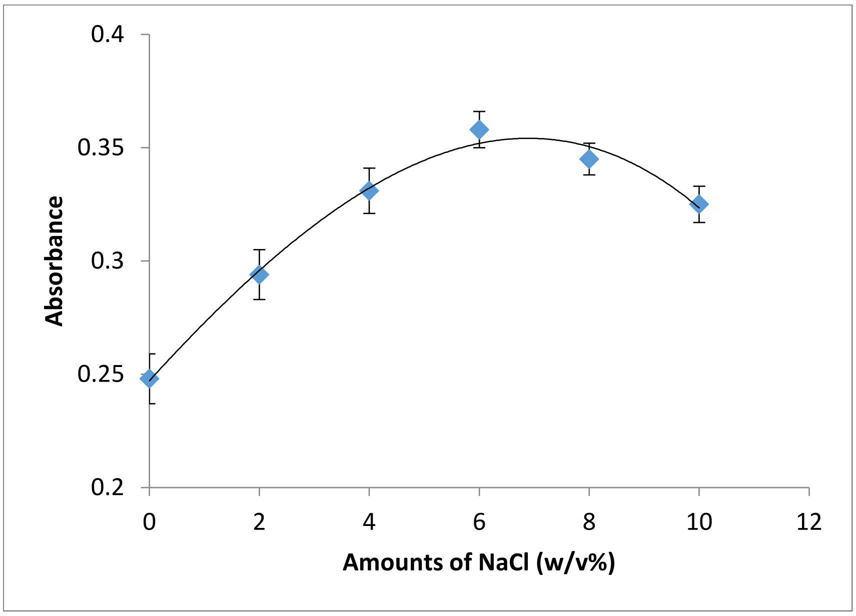

Figure 7. Effect of amount of NaCl
Conditions: analytes concentration, 10 µgL^{-1}; pH of sample solution,5; amount of sorbent, 20.0mg; desorption solvent, HCOOH; centrifugation time,7min; extraction time, 6min; desorption time, 3min; temperature 23±0.5 °C.

Effect of ionic strength

For studying the influence of ionic strength on the adsorption efficiency of Be ion, various experiments were performed by adding varying amounts of NaCl from 0% to 10% (w/v) to the sample solutions while other experimental conditions were kept constant and the results are shown in **Figure 7**. Ionic strength can vary the surface charge and therefore zeta potential of nanoceria. The increase in the adsorption efficiency of Be ion as the result of salting out effect can be explained by engaging water molecules in the hydration spheres around the ionic salt and hence in the reduction of water molecules available to dissolve the analytes. For this reason, the availability of free ions are increased and hence; desorption efficiency is improved. According to the results a salt concentration of 6 % NaCl was used in all solutions as the optimum value.

Effect of Interfering Ions

In order to demonstrate the selectivity of the dispersive solid-phase microextraction method, the effect of different interfering ions on the recovery of Be ion was examined. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample of more than ± 5 %. In order to investigate these effects, 10 mL of the 5 µg L^{-1} Be solution was subjected to 100 fold excess of interfering ions and the extraction procedure was conducted at the optimum conditions. The results are given in **Table 1** and show no obvious influence on the recovery of procedure. Accordingly, it is concluded that the developed method could be performed without any serious interferences from interfering ions in various real samples.

Table 1. Effect of different interfering ions on the absorbance of Be (II)

Interfering ions	**Added**	**Concentration (μg L^{-1})**	**Recovery, %**
K^+	KNO_3	1000	95.2
Na^+	$NaNO_3$	1000	96.1
Zn^{2+}	$Zn(NO_3)_2$	500	97.9
Cu^{2+}	$Cu(NO_3)_2.5H_2O$	500	96.0
Mn^{2+}	$Mn(NO_3)_2.H_2O$	500	96.0
Ni^{2+}	$Ni(NO_3)_2$	500	97.0
Pb^{2+}	$Pb(NO_3)_2$	500	97.6
Cd^{2+}	$Cd(NO_3)_2.H_2O$	500	95.9
Fe^{3+}	$Fe(SO_4)_2.NH_4.H_2O$	500	95.5
Al^{3+}	$Al(NO_3)_3.9H_2O$	500	97.7
Co^{2+}	$Co(NO_3)_2.6H_2O$	500	98.3
SO_4^{2-}	K_2SO_4	1000	97.6
NO_3^-	KNO_3	1000	96.8

Table 2. Extraction recovery for beryllium ion from real samples (N=3)

Analytes		**Beryllium ion**		
Spiked value (μg L^{-1})		0	0.5	2.0
well water	Found (μg L^{-1})	Nd	0.47 ±0.04	1.87 ±0.03
	Recovery percentage	----	94	93.5
Tap water	Found (μg L^{-1})	0.12	0.60 ±0.02	2.06 ±0.03
	Recovery percentage	----	96	97
River water	Found (μg L^{-1})	0.16	0.69 ±0.09	2.05 ±0.08
	Recovery percentage	----	106	94.5
Cu-Be-Alloy(No 175)	Found (w/w%)	0.63± 0.07	---	---
	Recovery percentage	---	---	---
CRM-TMDW[1]	Found (μg L^{-1})	19.2± 0.6	---	---
	Recovery percentage	96.0	---	---

[1] The certified value of Be is 20 μg L^{-1}.

Analytical Figures of Merit

The calibration curve was linear in the range of 0.16 - 25 μgL^{-1} of Be ion. The calibration equation was determined to be A = 0.009 + 0.034C with a correlation coefficient of 0.997 where A is the analytical signal measured as absorbance and C is the concentration of Be ion in μg L^{-1}. The relative standard deviation (RSD, %) for 5 replicate analyses of 5.0 μgL^{-1} of Be ion was 3.4%. The limit of detection (LOD) and the limit of quantitation (LOQ) based on three and ten times of the standard deviation of the blank divided by the slope of calibration curve were 0.05 and 0.16μg L^{-1}, respectively. The preconcentration factor was obtained according to eq.1

$$PC = \frac{A_{fin}}{A_{ini}} * \frac{V_{aq}}{V_f} \tag{1}$$

where A_{fin} and A_{ini} are final and initial absorbances after and before the extraction of Be ion, respectively, and V_{aq} and V_f are sample solution and formic acid volumes, respectively. A preconcentration factor of 171 was obtained for only 15mL of sample solution using 20.0 μgL^{-1} of Be ion by the microextraction method.

Analysis of Real Samples

The proposed solid phase extraction technique was applied for preconcentration and determination of Be ion in real water and an alloy. In order to validate the accuracy of the proposed procedure, recovery experiments were also carried out by spiking the real water samples such as tap, well and river with different amounts of Be before any pretreatment. The results are shown in **Table 2**. The proposed method shows high recovery percentages in the range of 93.5-106 for real water samples. A copper-beryllium alloy (No 175) was analyzed for its beryllium contents according to the proposed method and the result is given in **Table 2**. The accuracy of the proposed method was validated by the analysis of a certified reference material (CRM-TMDW). Be content of this solution was calculated to be 19.2±0.6 which is in good agreement with the certified value of 20 μg L^{-1}.

CONCLUSION

A new, rapid and sensitive DSPME procedure was developed for preconcentration of Be ion using ceria nanoparticles prior to its determination by nitrous oxide flame atomic absorption spectrometry. The ceria nanoparticles as new DSPME sorbent show high suitability for extraction of Be ion without any serious interference from the foreign ions. The most important advantages of ceria nanoparticles as DSPME sorbent are low cost, low sorbent consumption, chemical stability within the pH range and good selectivity for Be ion in the presence of interfering species and real samples. The proposed microextraction method also provides low LOD, high sensitivity and good precision with a wide dynamic range which is applicable for analysis of real samples such as tap water and alloy samples. Analysis of a reference material sample confirmed the accuracy of the method.

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