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Green solid phase extraction for preconcentration of Beryllium in aqueous samples

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ABSTRACT

A green solid phase extraction (SPE) based on modified octadecyl silica gel with ellagic acid a sorbent for preconcentration of trace amount of beryllium has been introduced. Parameters affected solid phase exstraction process such as: pH, sample solution and eluant flow rate, type, concentration and volume of eluant, interfering ions and breakthrough volume were investigated. Under optimal condition, the beryllium ions were retained on SPE at pH 6.1-6.7 and 2.0 mL of 0.30 mol L-1 HNO3 can eluate them quantitatively. The limit of detection (LOD) based on 3Sbl is 0.3 µg L-1 for 500 mL sample solution and 2 mL 0.5 mol L-1 HNO3 as an eluent. The accuracy and precision of method was >85% and <10%, respectively. Finally, the proposed method applied successfully for determination of beryllium in aqueous and alloy samples.

KEYWORDS

Oxidative stress;
Lycopene;
Ocular damage;
Carotenoids.

INTRODUCTION

Beryllium, a material valued for its light weight and stiffness, is used in a wide number of applications where these properties are important. Beryllium has physical and chemical properties (such as its stiffness, high resistance to corrosion from acids, and high thermal conductivity) that make it useful for various applications in its alloy, oxide, and metallic forms such as a substrate for high-density electronic circuits for high-speed computers, automotive ignition systems, lasers, and radar electronic countermeasure systems. Because it is transparent to microwaves, microwave communications systems and microwave ovens may use beryllium oxide. Due to application of this element in industries, beryllium-containing wastewaters from these industries can also contaminate natural waters, leading to a serious environmental hazard. Beryllium dust and fumes have been recognized as the cause of chronic beryllium disease (CBD), beryllosis, a serious chronic lung disease[1].

Due to the matrix effects and high detection limit, the determination of elements is usually preceded by their separation from the major components (matrix) of the sample. Thus, separation and preconcentration are important problems in the determination of traces of metals. Preconcentration/separation methods including extraction[2], coprecipitation[3], solid phase extraction[4], ion exchange[5] procedures are a necessity for the determination of the traces beryllium in different media. In addition to commercial chelating resins and ion exchangers used for these purposes, other sorbents have become increasingly popular, and especially interesting are silica gels modified with various reagents[6].

Green chemistry, defined as the use of chemistry for pollution prevention and Green Analytical Chemistry, based on the literature published about clean, environmentally friendly methods [7,8].

Resent reports have shown that ligand such as 2-hydroxyisophthalic acid (HIPA) and 2,3-dihydroxybenzoic acid (DHBA), 1,3,5,8-tetrahydoxyquinoline have a high affinity for beryllium over a wide range of concentrations/pH and consists of one five-member ring and one six-member ring[9]. Ellagic acid is a polyphenol, found in certain fruits and nuts including grapes, strawberries, raspberries, pomegranate, Morinda citrifolia, Terminalia chebula and wallnut. This phenol is one of the most promising chemopreventive agents. Pomegranate (*Punica granatum* L.) is a native species ranging from Iran to the Himalayas in northern India. The Ellagic acid content in pomegranate and berry fruit was reported to be 17.31 and 14.3 $\mu g\ g^{-1}$ in pomegranate juice[10-14]. Ellagic acid and other polyphenol in pomegranate leaf have structure similar to ligand that are intentionally designed to bind polynuclear species of Be based on the Be-O-Be bond, thus can use for extraction of beryllium ion.

In this work, first solid phase extraction based on modified octadecyl silica gel with ellagic acid for preconcentration of trace beryllium has been introduced as a green analytical chemistry method and parameters affected extraction process investigated.

EXPERIMENTAL

Reagents

All reagents were of analytical grade, unless otherwise stated. Analytical-grade Methanol, Ethanol, dimethyl solfoxide (DMSO), HCl, HNO_3, CH_3COOH, NaOH, $Na_2MoO_4\cdot 2H2O$, $ZrOCl_2\cdot 8H_2O$, $NaVO_3\cdot H_2O$, NH_4CH_3COO, NaF, NaCl, Na_2SO_4 and nitrate or chloride salts of other cations prepared from from Merck Co. (Darmstadt, Germany). Ellagic acid (EA) prepared from Sigma Aldrich Co. (St. Louis, MO, USA). Pomegranate leaf powder prepared after drying Pomegranate leaf in air and grinded.

The Certificated Reference Material (CRM) of standard alloy sample (C36XCBC20E) and Reference Material (C36XCBC30A) was obtained from MBH (England).

Apparatus

Octadecyl silica cartridges containing 500 mg octadecyl silica (50 mm particle size, 60A° pore size) purchased from Waters Associates Co., MA. A 20 plus Varian atomic absorption spectrometer with a hallow cathode lamp at a wavelength of 234.9 nm and slit 1.0 nm using a N_2O–acetylene flame used for Be^{2+} determination. The pH was adjusted with a model 827 pH lab Metrohm pH meter with a combined glass–calomel electrode. Oil-less vacuum pump model Rocker 600 (Todays, Taiwan) was used for solution passing through cartridge.

General procedure for modified C18 cartridges

Prior to preconcentrating, octadecyl silica cartridge was conditioned with 5.0 mL methanol, 5.0 mL HNO3 (0.5 mol L^{-1}), 10.0 mL water and 5.0 mL methanol, respectively. Then 0.100 mL of 1000 mg L^{-1} Ellagic acid in DMSO was poured into the cartridge and allowed to completely penetrate inside the cartridge. The solvent was evaporated at 100 °C for 10 min and dry by passing air for 10 min. Each sample was transferred to a beaker and its pH was adjusted to pH = 6.1 by ammonium acetate buffer and was preconcentrated on modified cartridge. The Be^{2+} trapped on cartridge was then eluted with cartridge and eluate with 5.0 mL of 0.5 mol L^{-1} HNO_3.

RESULTS AND DISCUSSION

Preliminary experiments

Some primary experimental results show that only 7% of Be^{2+} can retained by the cartridge, but after cartridge modification with Ellagic acid, the tendency of solid phase increased towards Be^{2+}. This explained by complexation of Be^{2+} with Ellagic acid (Figure 1.). Recent report shows that Be^{2+} can form complex with ligand containing CO-C-CO unit [6,9]. For parameter optimizations, 50 mL of solution containing 50 µg L^{-1} of Be^{2+} and 0.1 mol L^{-1} ammonium acetate/acetic acid (pH = 6.7) passed through modified cartridge and eluate with 5 mL 0.5 mol L^{-1} HNO_3 (otherwise stated).

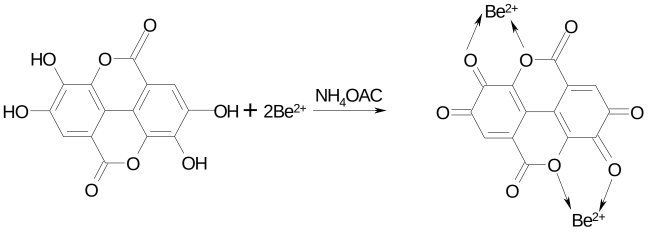


Figure 1 : Structure of Ellagic acid and its complex with Be^{2+}.

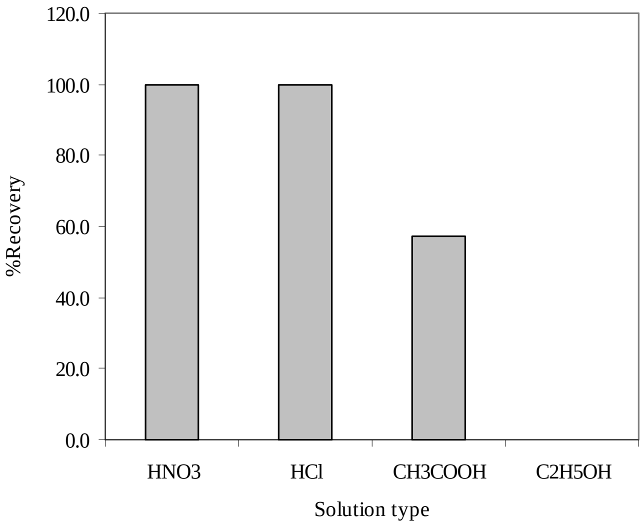


Figure 2 : Effect of eluant type on percent recovery of Be^{2+}. Conditions: Sample volume: 50 mL, the amount of Ellagic acid:100 µg, , pH of solution: 6.7, sample flow rate: 20 mL min^{-1}, eluant flow rate: 10 mL min^{-1}, concentration of eluant: 0.5 mol L^{-1}, eluant volume: 5 mL.

Eluant selection

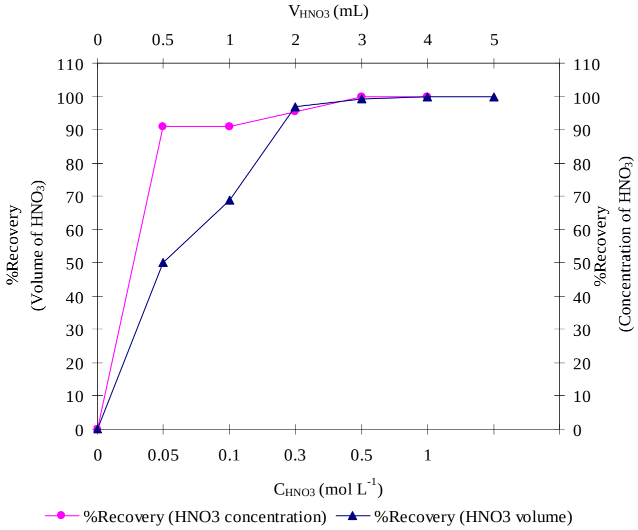
For elution of Be^{2+} from cartridge after extraction, 5.0 mL 1.0 mol $L^{-1}$of HCl, HNO_3, CH_3COOH and 5.0 mL ethanol were investigated, separately. The obtained results indicated that the recovery of Be^{2+} increased in order of HNO_3 > HCl > CH3COOH> C2H5OH.

Concentration and volume of eluant

The effect of concentration of HNO_3 in the range of 0.05-1.0 mol L^{-1} on desorption of Be^{2+}þ ions from the modified cartridge was investigated. As can be seen, the recovery of Be^{2+} is increased with acid increasing up 0.3 mol L^{-1}.

Effect of pH and ionic strength effect

The efficiency of Ellagic acid to react with Be^{2+} and form uncharged metal complex is largely dependent on pH. This is because Ellagic acid is protonated in acid solutions and form free acid structure and deprotonated in basic solutions. The effect of the pH (1.0–9.0) of on the extraction of Be^{2+} was tested. The pH of the solution was adjusted in a range of 1.0–9.0 using HCl (pH < 6) or NH_4OAC/axetic acid (6<pH< 7) or NaOH (pH > 7). According to the obtained experimental data given in Figure 3., it was found that acetate buffer at pH 6.5 is the most suitable, where the recovery of Be^{2+} is quantitative (~100%). The influence of the amount of NaCl on the recovery of Be^{2+} the 50 mL solutions containing 1.0 µg of beryllium ions was studied under these conditions established above. The recovery of Be^{2+} decreased with the increase in amount of NaCl above 1%(w/w).



Figur 3 : Effect of concentration and amount of HNO_3 0.5 mol L^{-1} on percent recovery of Be^{2+}. Conditions: Sample volume: 50 mL, the amount of Ellagic acid:100 µg, sample flow rate: 20 mL min^{-1}, eluant flow rate: 10 mL min^{-1}, concentration of eluant: 0.5 mol L^{-1} (for volume of HNO_3), eluant volume: 5 mL (for concentration of HNO_3), pH of solution: 6.7.

The solution and eluant flow rate

The flow rate of solution was changed within 5-25 mL min^{-1} and results show the flow rate has no effect on retention of Be^{2+} up to 10 mL min^{-1}

and in the higher flow rates (>10 mL min^{-1}) the recovery decreased at least 30%. The eluant flow rate has no effect on stripping of Be^{2+} up to 20 mL min^{-1} and recovery is quantitatively.

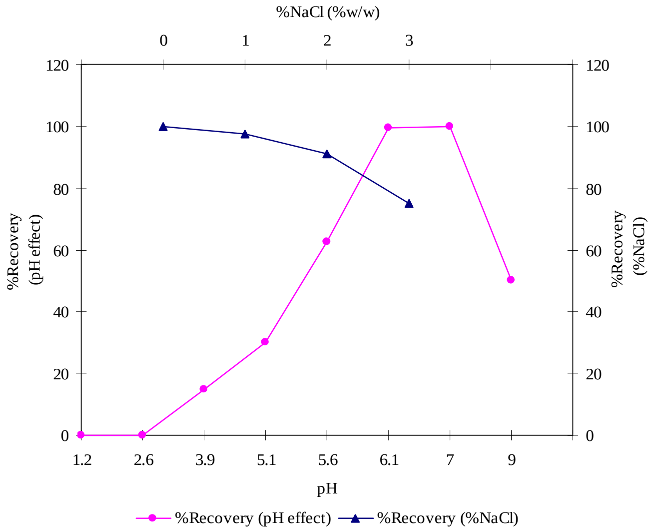


Figure 4 : Effect of pH of sample solution and the ionic strength on percent recovery of Be^{2+}. Conditions: Sample volume: 50 mL, the amount of Ellagic acid:100 µg (for effect of pH), sample flow rate: 20 mL min^{-1}, eluant flow rate: 10 mL min^{-1}, concentration of eluant: 0.5 mol L^{-1} (for volume of HNO_3), eluant volume: 5 mL (for concentration of HNO_3), pH of solution: 6.7 (effect of ionic strength).

Breakthrough volume and foreign ion effect

It is important to study dilution effect (breakthrough volume) on process kinetic and LOD calculation. For this purpose, 1.25 µg of Be^{2+} was added to solution volume of 25, 50, 100, 250, and 500 mL separately. These samples passed through cartridge according to general procedure in optimum conditions. The results show that recovery achieved above 90% in all case. The enrichment factor of 250 can be obtained for sample solution of 500 mL and 2.0 mL eluant.

The potential interference in the present system was investigated. The interference is due to the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with the Be^{2+}. To evaluate the selectivity of the proposed method, the effect of typical potential interfering ions were investigated. For this purpose according to general procedure separately 50 mL of solution containing 50 µg L^{-1} of Be^{2+} and 0.1 mol L^{-1} ammonium acetate (pH = 6.7) and foreign ion at desired ratio (w/w) passed through cartridge and finally eluate with 5 mL 0.3 mol L^{-1} HNO_3 separately. Aluminium ion can interfere on Be^{2+} recovery in ratio above 20 and other ions have no effect on Be^{2+} recovery (TABLE 1.)

TABLE 1 : Effect of foreign ion on recovery of beryllium.

Foreign ion	Ratio of foreign ion to Be^{2+} ion (w/w)	%Recovery
Al^{3+}	20	85 (±5)
Ba^{2+}	40	97 (±4)
Ca^{2+}	40	95 (±5)
Cd^{2+}	40	93 (±5)
Cl^{-}	40	95 (±7)
Co^{+2}	40	87 (±7)
Cr^{+6}	40	100 (±2)
Cu^{2+}	40	91 (±3)
F^{-}	40	93 (±5)
Fe^{3+}	8	92 (±6)
K^{+}	40	95 (±5)
Li^{+}	40	97 (±7)
Mg^{2+}	40	96 (±3)
Mn^{2+}	40	97 (±5)
Mo^{6+}	40	93 (±3)
Na^{+}	40	100 (±6)
Ni^{2+}	40	90 (±4)
Pb^{2+}	40	93 (±4)
SO_4^{2-}	40	99 (±6)
Sr^{2+}	40	91 (±8)
ZrO_2^{2+}	40	75 (±10)
Zn^{2+}	40	88 (±6)
NO_3^{-}	40	93 (±5)

Figures of merit and analytical performance

The figures of merits were calculated in the optimum condition obtained. The calibration curve was linear in the range of 1.0-200.0 µg L^{-1} with coefficient correction better than 0.99 and enhancement factor after preconcentration of 250 mL sample solution was 125. The detection limit 0.3 µg L^{-1} of Be^{2+} in the 500 mL sample solution after preconcentration into 2 mL was obtained. The precision of the method, evaluated by three replicate analyses of Certificated References Materials containing beryllium was in the range of 2.5-4.0 and relative error was less than 3%. In order to evaluate the analytical applicability of the proposed method, it was applied to beryllium in several water samples and alloy samples. The data were gathered and tabulated in TABLE 2. There is good agreement between the results obtained by proposed add-found method. The recoveries for the addition of different concentrations of beryllium to water and alloy samples were above 85% (except for ZrO_2^{2+}).

TABLE 2 : Determination of beryllium in water and certificated alloy samples by the proposed method.

Sample i.d.	Amount of Be^{2+} (µg)			Extraction (±%RSD)[b]
	Certificated amount (%)	Amount added	Amount found (±%RSD)[b]	
[a]Tap Water (Tehran)	-	-	<0.1	-
Tap Water (Tehran)	-	10.0	9.5(±0.3)	95 (±3)
C36XCBC20E	0.450	-	0.440(±0.011)	98 (±2.5)
C36XCBC30A	1.81	-	1.86(±0.08)	103 (±4)

[a] **Some 250 mL of each water sample was taken.**

[b] **Mean of triplicates with percent R.S.D.**

CONCLUSION

The present study shows that ellagic acid can be used for preconcentration/ removal of beryllium ions from aqueous solutions under optimum conditions. The enrichment factor of 250 can be obtained for sample solution of 500 mL and 2.0 mL eluant. This method is green, efficient, andselective for determination of in aqueous samples at µg L^{-1} level.

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