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Cloud Point Extraction Based on Binary Surfactants for Separation, Preconcentration and Spectrophotometric Determination of Beryllium with 1,8-Dihydroxy Anthrone

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A new micelle-mediated phase separation of metal ions, using mixed micelles of the cationic surfactant cetyl pyridinium chloride (CPC) and non-ionic surfactant Triton-X-114, applied for preconcentrating trace levels of beryllium as a prior step to its determination by spectrophotometry has been developed. Beryllium was compelexed with 1,8-dihydroxy anthrone in an aqueous surfactant medium and it was concentrated in the surfactant rich phase after separation. The chemical variables affecting the cloud point extraction (*e.g.*, pH, surfactant and reagent concentrations, temperature, incubation and centrifuge times) were evaluated and optimized. Under the optimum experimental conditions, calibration graph was linear in the range of 2-120 ng mL^{-1} with detection limit of 0.2 ng mL^{-1} and the precision (% RSD) for 5 replicate determinations at 60 ng mL^{-1} of Be(II) was 0.16 %. In this manner the preconcentration and enrichment factors were 25 and 14.2, respectively. The interference effect of some cations and anions was also studied. Finally, the proposed method was successfully applied to the determination of beryllium in synthetic and real water samples.

Key Words: Cloud point extraction, Spectrophotometric determination, Beryllium, Anthralin, Mixed micelle.

INTRODUCTION

Demand for beryllium in industries has been increasing due to a great variety of its uses[1] and therefore beryllium containing waste waters from these industries can contaminate natural water sources. Beryllium is carcinogenic and exhibits latent toxicity, *i.e.* symptoms appear several years after exposure. It has been documented that occupational exposure to beryllium and its compounds, even at relatively low exposure levels, below 2 μg m^{-3} in air and 4 μg L^{-1} in waters, can cause many serious and sometimes fatal diseases[2]. This demands a need to develop reliable, selective and sensitive technique for the measurement of beryllium.

Some technologies and analysis methods have been developed to detect and monitor hazardous beryllium contamination in water samples[3-16]. In contrast to the majority of these expensive and sophisticated analysis systems, absorption spectrophotometric methods offer many appealing characteristics, including simple instrumentation, rapid response times and easy operation. These properties are highly desirable to the future design and development of portable analytical devices capable of quickly responding to trace levels of hazardous beryllium content in the field. Using these methods based on colorful complexation, usually an effective enrichment procedure prior to the determination are essential in order to increase the concentration of target and for suppression of interferences due to the complex matrix of the samples[17].

Beryllium enrichment based on various principles, including liquid-liquid extraction[18,19], coprecipitation[20], adsorption[21-23], liquid ion exchanger[24] and solid-phase extraction[10,25,26] have been reported. However, these techniques have important restrictions and drawbacks related to the use of excess amounts of toxic organic diluents and mass losses of the extractant.

Recently, cloud point extraction (CPE) based on the clouding phenomenon of surfactants over a certain temperature, has become more and more attractive[27-30]. As a new separation technique, CPE offers many advantages over traditional liquid-liquid extraction. It uses water and avoids the use of large amounts of toxic and flammable organic solvents[31]. In addition, CPE can lead to higher recovery efficiency and a large preconcentration factor because the presence of surfactant can minimize losses of analytes due to their adsorption onto the container. In this manner mixed micelle-mediated extraction (Mixed-MME) system is becoming an important and practical method for the use of different surfactants in analytical chemistry[32-34]. Mixed surfactants of different charge accomplish both ideal hydrophobic and non-ionic electrostatic interactions within the same extraction system[35,36].

1, 8-Dihydroxy anthrone (Anthralin) is a yellow amorphous solid which is readily soluble in water at alkaline pH. This reagent for the first time was used in spectrophotometric determination of beryllium by present research team[37].

In this paper, we report a rapid, simple, precise and accurate method based on mixed micelle-mediated extraction (mixed-MME) coupled with spectrophotometry for preconcentration and determination of ultra trace amounts of beryllium in water samples. To the best of our knowledge this extraction based on a mixture of cationic and non-ionic surfactants is the first report in the mixed-MME of beryllium using anthralin as a new reagent.

EXPERIMENTAL

A Philips model PU8750 UV-Vis spectrophotometer connected to an IBM PCS-3 computer with ASY-PU8700 (Version-3.1) software to convert absorbance data to ASCII format with a 0.5 mL quartz cells (light path length = 10 mm) was used for recording absorbance spectra. All spectral measurements were performed using the blank solution as a reference. A Metller pH meter (model E603) combined with a glass-colomel electrode was used for pH measurements. A Julabo model F12 water bath with ± 0.1 °C temperature control (Germany) and a centrifuge with calibrated centrifuge tubes (Superior, Germany), to accelerate the phase separation process, were used.

All the chemicals and reagents were of analytical grade from Merck (Germany) and solutions were prepared with triple-distilled water. The surfactants, Triton-X-114 and cetyl pyridinium chloride (CPC) received from Sigma and were used without further purification. Standard beryllium solutions were prepared by serial dilution of a 1000 μg mL^{-1} standard (Shimadzu Pure Chemical Co. Ltd.) with distilled water. A stock solution of anthralin (2×10^{-3} mol L^{-1}) was prepared by dissolving 46 mg anthralin (Sigma) in 5 mL NaOH (0.05 mol L^{-1}) and diluted to the mark with distilled water in a volumetric flask (100 mL). A buffer of pH 9.5 was prepared from sodium tetraborate and 0.1 M NaOH solutions[38]. A stock solution of EDTA (0.4 mol L^{-1}) was prepared by dissolving appropriate amount of Na_2EDTA (Merck) in water.

Procedure: An aliquot containing 0.02-1.2 μg of Be(II) was transferred to a 10 mL centrifuge tube, 1 mL anthralin (2.0×10^{-3} mol L^{-1}), 1 mL cetyl pyridinium chloride solution (1.2×10^{-3} mol L^{-1}) and 1 mL buffer solution (0.02 mol L^{-1}, pH 9.5) were added, respectively. After addition of 1 mL Triton-X-114 solution (1.5 %, v/v) the volume was made up to the mark with triply distilled water. The contents of tube was shaken and left to stand in a thermostated water bath for 10 min at 50 ºC before centrifugation. Separation of the aqueous and surfactant-rich phase was accelerated by centrifuging the solution at 3500 rpm for 10 min. After cooling in a salt-ice bath, the surfactant-rich phase became viscous.The aqueous phase was easily separated by inverting the tube. THF (0.2 mL) was added to the surfactant-rich phase and the absorbance of solution was measured at 540 nm, using a 0.5 mL quartz cell, against a blank reagent which was prepared in a similar way without beryllium.

Water samples: Tap, mineral and sea water samples were collected from Tehran, Rudbar (Guilan, Damash Co.) and Caspian Sea (Chalus) in Iran, respectively. Each sample was acidified to pH < 2 with concentrated HNO_3 and filtered through a 0.45 μm PTFE filter. After adjusted to *ca.* pH 5 by $NaOH/HNO_3$, 5 mL of each sample, along with 1 mL EDTA (0.4 mol L^{-1}), first directly and then spiked with appropriate amount of Be(II) and was subjected to the cloud point extraction methodology as described above. The results obtained were compared by those which was carried out by ICP-AES method (Table-4).

RESULTS AND DISCUSSION

According to our previous work[37], anthralin form coloured complex with Be(II) ion. The stoichiometry of Be(II)-anthralin was 1:2 and an anionic complex was formed. The presence of a cationic surfactant, such as CPC causes the formation of ternary complex Be(II)-anthralin-CPC, which have molar absorptivities greater than those of binary complexes (in the absence of surfactant). Molar-ratio method was showed that the stoichiometry of Be(II)-anthralin in CPC medium was 3:4 (M:L). It was observed that addition of Triton-X-114 as a non-ionic surfactant and heating makes the solution turbid, therefore the ternary complex of Be(II)-anthralin-CPC can be extracted by cloud point extraction (CPE) method. Fig. 1 shows the absorption spectrum of Anthralin-CPC (a) and a ternery complex of Be(II)-anthralin-CPC against a blank reagent (b) with a maximum absorbance at 540 nm.

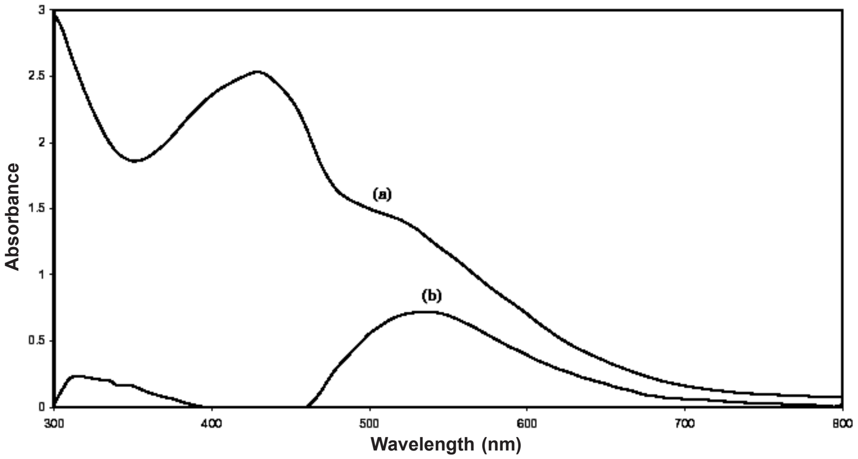

Fig. 1. Absorption spectra of anthralin-CPC (a) and net Be(II)-anthralin-CPC *vs.* anthralin-CPC (b) after cloud point extraction. Conditions: Be(II), 100 ng mL^{-1}; anthralin, 2.0×10^{-4} mol L^{-1}; CPC, 1.2×10^{-4} mol L^{-1}; Triton-X-114, 0.15 % (v/v); pH = 9.5; equilibrium temp. 50 ºC (for 10 min) and centrifugation time 10 min

Optimization of the system

Effect of pH: pH plays a unique role on metal-chelate formation and subsequent cloud point extraction. Fig. 2 shows the influence of pH on the extraction recovery. As shown extraction percentage reaches a maximum at pH 9.5. A decrease in metal extraction efficiency at pH < 9.5 is

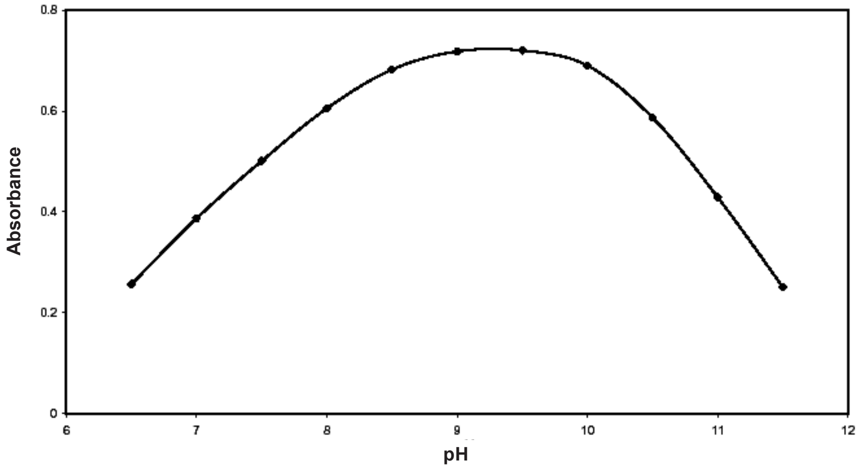

Fig. 2. Effect of pH on absorbance of extracted phase at 540 nm, Be(II), 100 ng mL^{-1}; anthralin, 2.0×10^{-4} mol L^{-1}; CPC, 1.2×10^{-4} mol L^{-1}; Triton-X-114, 0.15 % (v/v), experimental conditions as described in the text

explained by the low complex hydrophobicity, whereas, at pH > 9.5, hydrolysis of the metal takes place upon heating the solutions. Therefore, pH 9.5 was chosen for the subsequent experiments.

Effect of ligand concentration: The extraction efficiency as a function of the anthralin concentration is shown in Fig. 3. For this study, 10 mL of a solution containing 1μg Be ion with various amounts of anthralin

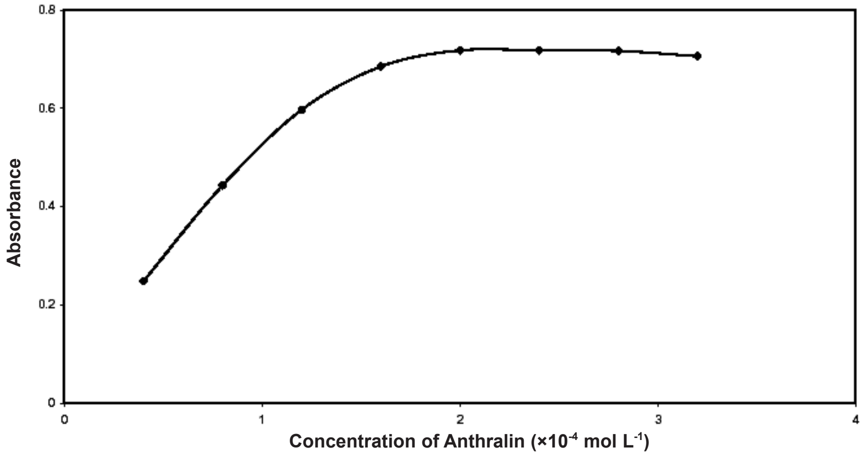

Fig. 3. Effect of anthralin concentration on absorbance of extracted phase at 540 nm. Be(II), 100 ng mL^{-1}; CPC, 1.2×10^{-4} mol L^{-1}; Triton-X-114, 0.15 % (v/v). Experimental conditions as described in the text

(4.0×10^{-5}–3.2×10^{-4} mol L^{-1}) was subjected to the cloud point preconcentration process. The results revealed that the extraction efficiency increased by increasing anthralin concentration up to 2.0×10^{-4} mol L^{-1} and remained nearly constant at higher concentration. Therefore, this concentration was selected as optimum value.

Effect of CPC concentration: Cloud point extraction of beryllium was studied in different CPC concentration range from 3.0×10^{-5} to 2.4×10^{-4} mol L^{-1} (Fig. 4). As seen that the per cent recovery is increased by increasing CPC concentration up to 1.2×10^{-4} mol L^{-1} and decreased at higher concentration. This is due to sufficient hydrophobicity of Be(II)-anthralin-CPC that can be extracted by Triton-X-114. At higher CPC concentration, the formed ternary complexes became hydrophilic and can not be extracted by Triton-X-114.

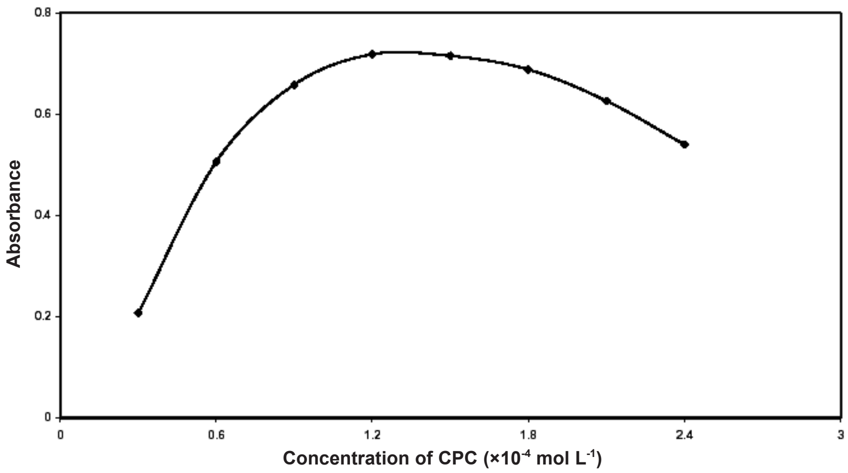

Fig. 4. Effect of CPC concentration on absorbance of extracted phase at 540 nm. Be(II), 100 ng mL^{-1}; anthralin, 2.0×10^{-4} mol L^{-1}; Triton-X-114, 0.15 % (v/v). Experimental conditions as described in the text

Effect of Triton-X-114 concentration: For low cloud point temperature and high density of Triton-X-114, this surfactant was chosen as the extraction solvent[39]. It was observed that Triton-X-114 concentration as a non-ionic surfactant can effect not only the extraction of complex but also the sensitivity of the method, therefore the effect of Triton-X-114 concentration on the absorbance intensity of the extracted phase was investigated in the range 0.02-0.30 % (v/v). The results are shown in Fig. 5. As seen the concentration of 0.15 % (v/v) was chosen as optimum concentration for the determination of the analyte. At lower concentrations, the extraction efficiency is low which is probably due to the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively.

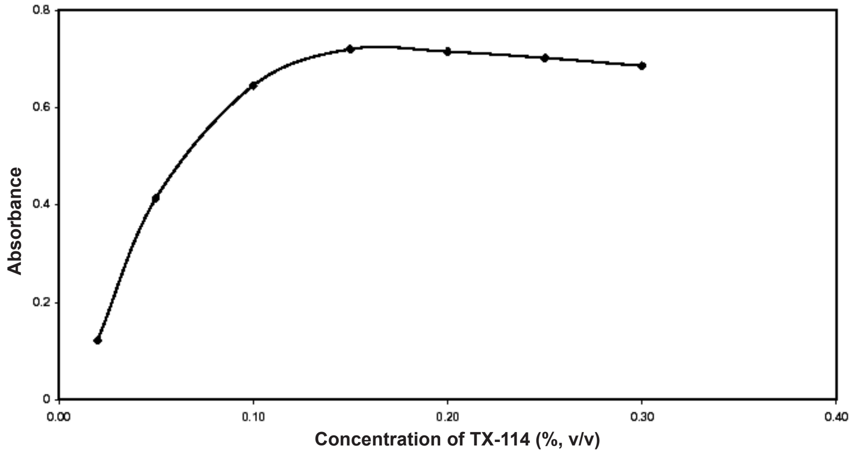

Fig. 5. Effect of Triton-X-114 concentration on absorbance of extracted phase at 540 nm. Be(II), 100 ng mL^{-1}; anthralin, 2.0 × 10^{-4} mol L^{-1}; CPC, 1.2 × 10^{-4} mol L^{-1}. Experimental conditions as described in the text

Effect of ionic strength: The influence of ionic strength was examined by studying the extraction efficiency for $NaNO_3$ concentration in the range 0-0.8 mol L^{-1}. It was revealed that ionic strength had no significant effect upon per cent recovery and sensitivity when the $NaNO_3$ concentration was up to 0.8 mol L^{-1}. This is in agreement with the results reported in the literature which demonstrate that increase in ionic strength in micellar media systems do not seriously alter the extraction efficiency of the analyte[29,40].

Effects of the equilibrium temperature and time: The effect of equilibrium temperature and incubation time was investigated. It is desirable to employ the shortest incubation time and the lowest possible equilibrium temperature, which comprise completion of the reaction and efficient separation of the phases. As mentioned above, after evaluation of incubation time in the range 5-30 min, incubation time was kept at 10 min, which is sufficient for the completion of the complex reaction and also for the clouding process. It was also observed that a temperature of 50 ºC is sufficient for maximum recovery of the beryllium.

In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same sense as in conventional separation of a precipitate from its original aqueous environment. Therefore, a centrifugation time of 10 min at 3500 rpm was selected as optimum, since complete separation occurred and no appreciable improvements were observed for longer time.

Because the surfactant-rich phase was viscous, THF was added to it, in order, to facilitate its transfer into spectrophotometric cell. The amount of 0.2

mL THF was chosen to have an appropriate amount of sample for transfer and measuring its absorbance.

Effect of EDTA concentration: The effect of EDTA concentration (as a masking agent for interfering cations) on the complexation reaction of 0.2 μg Be was studied in the range 0–7.0 × 10^{-2} mol L^{-1}. The results revealed that $EDTA^{2-}$ did not affected for beryllium determination in present method unless it was present in over 4.0 × 10^{-2} mol L^{-1}. Negative errors are caused by higher ratios because of its side reaction with the metal ion. The addition of 1 mL EDTA solution (0.4 mol L^{-1}) can effectively mask 0.4 mmol of binary and some ternary interfering cations, therefore the method could be made selective in this way.

Analytical characteristics: Table-1 summarize the analytical characteristics of the optimized method, including regression equation, linear range, limit of detection, reproducibility, (a) before and (b) after CPE. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration equation, respectively), was 0.2 ng mL^{-1}. Because the amount of beryllium in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of nearly 0.4 mL (0.2 mL surfactant-rich + 0.2 mL THF), the solution is concentrated by a factor of 25. In this manner, the improvement factor (the slope ratio of preconcentrated samples to that obtained without preconcentration) of 14.2 is resulted.

TABLE-1
ANALYTICAL CHARACTERISTICS OF THE METHODS (A) BEFORE CPE AND (B) AFTER CPE

Method	Before CPE	After CPE
Slope	0.0005	0.0071
Intercept	0.0075	0.0046
Correlation coefficient	0.9998	0.9998
Linear range (ng mL^{-1})	40-1040	2-120
Limit of detection[a] (ng mL^{-1})	12	0.2
Molar absorptivity (L mol^{-1} cm^{-1})	4.75 × 10^3	6.42 × 10^4
RSD (%)[b]	1.96	0.16
Preconcentration factor[c]	–	25
Improvement factor[d]	–	14.2

[a] For seven determination of blank (n = 7).
[b] For five determination of Be: 60 ng mL^{-1}.
[c] Ratio between Be concentation before and after the CPE method.
[d] The slope ratio of preconcentrated samples to that obtained without preconcentration.

Selectivity: To study the selectivity of the proposed method, the effect of various ions on the determination of beryllium was tested under the optimum condition. The results are summarized in Table-2. The tolerance limit was defined as the concentration of added ion causing less than ± 5 % relative error. The interfering ions studied were those relating to the preconcentration step, cations that may react with anthralin or species that may react with Be^{2+} and decrease the extraction efficiency. To perform this study, a berillium solution (10 mL, 36 ng mL^{-1}) containing interfering ion, in different interferent-to analyte ratios, was subjected to the complete procedure. Be^{2+} recovery was almost quantitative in the presence of other species with tolerance limits (error < ± 5 %) indicated in Table-2. As seen, some binary and ternary cations can interfere with the determination of Be^{2+}. The interference from these ions can be eliminated by the addition of EDTA solution (4.0×10^{-2} mol L^{-1}) and ascorbic acid (2.0×10^{-3} mol L^{-1}) as masking and reducing agents, in order to form strong hydrophilic complexes with bivalent and some trivalent cations and reduce Fe^{3+} to Fe^{2+} respectively.

TABLE-2
TOLERANCE RATIO OF DIVERSE IONS ON THE DETERMINATION OF Be^{2+} (36 ng mL^{-1})*

Diverse ion	Ratio [(Diverse ion):(M)]
Cations	
Na^+, K^+, Li^+ and NH_4^+	5000:1
Al^{3+}, Ga^{3+}, UO_2^{2+} and ZrO^{2+}	500:1
Ca^{2+}, Ba^{2+}, Sr^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+} and Pb^{2+}	50:1
Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}	5:1
Anions	
SO_4^{2-}, HPO_4^{2-}, NO_3^-, NO_2^-, BO_3^-, Cl^- and HCO_3^-	5000:1
F^-	20:1

*≤ 5.0 % Relative standard deviation (in the absence of masking agents).

Validation and application: In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of beryllium in both synthetic and real water samples. The results are shown in Tables 3 and 4. The mean recoveries for the addition of different concentration of beryllium to those samples were in the range 97-103 %. The results show that the proposed method could be successfully applied for determination of beryllium in different water samples.

TABLE-3
DETERMINATION OF BERYLLIUM IN SYNTHETIC SAMPLES*

Samples	Be^{2+} (ng mL^{-1})		
	Added	Found**	Recovery
1	2	1.95 ± 0.10	97.50 ± 5.00
2	10	10.24 ± 0.12	102.40 ± 1.20
3	20	19.85 ± 0.10	99.30 ± 0.50
4	40	39.60 ± 0.08	99.00 ± 0.60
5	60	60.57 ± 0.11	101.00 ± 0.20
6	80	78.95 ± 0.09	98.65 ± 0.10
7	100	100.90 ± 0.10	100.90 ± 0.10
8	120	120.00 ± 0.06	100.00 ± 0.05

*Synthetic samples from Mg^{2+} (300 µg mL^{-1}), Ca^{2+} (200 µg mL^{-1}) and equal amounts of Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} (0.5 µg mL^{-1}) in the presence of EDTA (4×10^{-2} mol L^{-1}).
**Mean value of three determination ± standard deviation.

TABLE-4
DETERMINATION OF Be^{2+} IN REAL SPIKED SAMPLES*

Samples	Be^{2+} (ng mL^{-1})		
	Added	Found	Recovery (%)
Tap water	0	ND[a]	–
	4	3.88 ± 0.06	97.2 ± 1.3
	10	10.20 ± 0.04	102.0 ± 0.2
	20	19.90 ± 0.05	99.5 ± 0.3
Mineral water	0	ND[b]	–
	2	1.96 ± 0.08	98.0 ± 4.0
	10	10.23 ± 0.07	102.3 ± 0.7
	20	20.18 ± 0.03	100.9 ± 0.2
Sea water	0	2.12[c] ± 0.18	–
	4	6.24 ± 0.16	103.0 ± 4.0
	10	12.36 ± 0.13	102.4 ± 1.3
	20	21.92 ± 0.12	99.0 ± 0.6
	30	32.42 ± 0.08	101.0 ± 0.3

*Average of three determinations ± standard deviation.
[a,b,c]ICP-AES resulted were ND, ND and 2.12 ± 0.18 ng mL^{-1}, respectively (n = 3). [d]Samples sources as described in the text.

Conclusion

The proposed method gives a simple, sensitive and low-cost procedure for determination of beryllium, that can be applied to real samples, based on mixed micelle-mediated extraction coupled with spectrophotometry.

This process is solvent-free extraction of the Be(II) from its initial matrix without previous treatment. The explained cloud point extraction method gives lower LOD (0.2 ng mL^{-1}) and also better RSD compared to the previous enrichment methods[19-21]. It is also possible to obtain a better detection limit by extraction of beryllium from large volumes of sample solution (for example with 50 mL centrifuge tube containing 0.02-1.20 μg Be^{2+} instead of 10 mL) or diluting the surfactant rich phase to a smaller volume.

In this work, EDTA and ascorbic acid can be used as a masking agents for various metal ions. Therefore, the method could be made selective in this way. Unlike other spectrophotometric methods[3-5,17] aluminum(III) does not interfere, when its concentration is up to 500-fold molar ratio of Be^{2+}, even without using EDTA.

The method can be successfully applied for ultra trace amounts of beryllium in different water samples with complex matrices. Finally this extraction procedure based on binary surfactants is the first report in the mixed-micelle-mediated extraction of beryllium using a new reagent.

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