Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21776

101 (2018) 283–290
January

A novel surfactant assisted dispersive liquid–liquid microextraction for the removal/recovery of beryllium from industrial effluents

Noorbasha N. Meeravali, K. Madhavi, Sunil Jai Kumar*

National Centre for Compositional Characterization of Materials (NCCCM), Bhabha Atomic Research Centre, ECIL Post, Hyderabad 500 062, India, Tel. +91 40 27123550; Fax: +91 40 27125463; emails: suniljaikumar@rediffmail.com (S.J. Kumar), nnmeeravali29@rediffmail.com (N.N. Meeravali), madhu_jonnavithula@yahoo.co.in (K. Madhavi)

Received 1 June 2017; Accepted 5 December 2017

ABSTRACT

In this work, a new surfactant assisted dispersive liquid–liquid microextraction procedure is developed for removal/recovery of potentially harmful trace and ultra-trace levels of beryllium from industrial effluents. An anionic hydrophobic double tailed surfactant, dioctyl sodium sulfosuccinate (AOT) is used as the dispersing solvent which disperses uniformly in aqueous as well as in extracting solution by forming vesicle aggregates. These vesicles entrap beryllium in its cavity in the presence of salicylic acid. Chloroform is used as extracting agent for the pre-concentration of the vesicles carrying beryllium salicylate from bulk aqueous phase into a small chloroform phase at room temperature providing an energy efficient extraction process. The recoveries are in the range 88%–99% at 0.05–1,000 ng mL^{-1} beryllium with relative standard deviation of 1%–10%. Several factors influencing the recovery were optimized for providing better recoveries. The formation of vesicles has been conformed in the transmission electron microscope analysis. Under the optimized conditions, the pre-concentration factor is 25. The accuracy of the procedure is verified by analyzing NIST standard reference materials such as 1640, 1640a and 1643e using electrothermal atomic absorption spectrometry. The procedure has been utilized for the recovery of beryllium from effluent samples collected from beryllium processing plant and also been applied to natural water samples.

Keywords: Surfactant assisted dispersive liquid–liquid microextraction; Beryllium; Recovery; Industrial effluents

1. Introduction

Beryllium (Be) is being used extensively in recent high-technology applications in aerospace and nuclear industries due to its unique properties of low-density, high-strength and rigidity; and also as a neutron source, multiplier, reflector and moderator [1,2]. Furthermore, the levels of this metallic element have increased in the environment through beryllium processing plants and waste generated in the high-technological applications. Hence, beryllium and its compounds that enter into the environment cause acute and chronic lung diseases known as berylliosis [3–6]. However, various international guidelines indicated a maximum Be contaminant level of 0.1 ng mL^{-1} in drinking water. In order to prevent water and environmental contamination, with its use in high-technology applications, recycling of Be can be a good option. This demands the development of a simple and fast analyte separation and selective pre-concentration procedure, which can provide lower detection limits to determine natural levels as well as to recover higher concentrations of Be from effluents.

Over the last several years, various extraction procedures have been developed for separation and pre-concentration of Be from various water samples. Solid phase extraction using either of chrome Azurol S and acetyl acetone as chelating agent and also co-precipitation with hafnium hydroxide have been used most frequently for the separation of Be [7–9]. Some researchers have used chrome Azurol S, cupferron and 1,8-dihydroxyanthrone as chelating agents and extracted

---

* Corresponding author.

1944-3994/1944-3986

using micelle and mixed micelle-based cloud point extraction [10–14]. Recently, hydroxybenzoquinoline, a fluorescent chelating agent, immobilized in silica nanopiller platform and silica gel loaded column has been used for extraction of Be [15,16]. Most of these procedures reported extraction of Be from natural waters using chelating agents to determine its concentration. Until now, no single procedure is reported for removal/recovery of beryllium from its natural level to higher levels without using any chelating agent.

Nowadays, dispersive liquid–liquid microextraction (DLLME) has emerged as an efficient microextraction procedure for the separation and pre-concentration of a variety of uncharged hydrophobic species [17–25]. One of its greatest limitations is the lower extraction efficiencies of hydrophilic inorganic/organic species and polar organic compounds. It is mainly due to lower partition coefficient of these species into the extracting solvent in the presence of conventional organic disperser [26]. These limitations can be alleviated by the introduction of a new version of DLLME named surfactant assisted dispersive liquid–liquid microextraction (SA-DLLME) using a surfactant as disperser. It uses small amounts of environmentally friendly surfactants for the extraction of toxic organic pollutants through their reactive solubilizing sites. Moradi et al. [27] reported the extraction of chlorophenols in water samples using a cationic cetyl trimethyl ammonium bromide (CTAB) as disperser and 1-octanol as extraction solvent. Cheng et al. [28] developed an ultra-sound assisted surfactant enhanced emulsification microextraction for the determination of fungicides in water using a non-ionic Tween-80 and carbon tetrachloride as extraction solvent. Behbahani et al. [29] reported the pre-concentration of antiepileptic drugs from urine using CTAB as disperser and 1-octanol as extraction solvent.

Recently, a few SA-DLLME procedures have been reported for the extraction of inorganic trace metals from water samples using chelating agents. Deng et al. [30] reported a pre-concentration procedure for the determination of nickel in water samples using a pyridylazo naphthol as chelating agent. Triton X-100 monomers are used as dispersers for the transfer of thus formed hydrophobic nickel chelate from aqueous phase into extracting carbon tetrachloride. Yousefi and Shemirani [26] reported the ion pair-based SA-DLLME for the extraction and pre-concentration of Cr(VI) from aqueous samples using diphenylcarbazide for chelation. Anionic sodium dodecyl sulfate (SDS) monomers have been used as ion-pairing and dispersive agents; and 1-octanal as an extracting solvent in the above procedure. Until now, utilizing the concept of surfactants aggregates (micelles or vesicles) for the extraction of metals has not yet received much attention in SA-DLLME. It is envisioned that the surfactant aggregates formed with ionic surfactants must have significantly high-reactive solubilizing sites with varying structures, which react/incorporate more selectively the hydrophilic analyte species. To our knowledge, the double tailed AOT anionic surfactant aggregates have never been utilized before for the removal/recovery of beryllium from natural waters and industrial effluents.

This paper describes, a new SA-DLLME procedure for the separation and pre-concentration of Be from drinking water, groundwater and industrial effluents samples. A double tailed surfactant, AOT, is used as a disperser, which forms vesicle aggregates above its critical micelle concentration. Beryllium forms hydrophilic anionic species with salicylic acid, which is trapped into the cavity of AOT vesicles. It is then extracted from a bulk aqueous phase into a small volume of extracting chloroform. The procedure has been applied on certified reference materials for accuracy and used for the analysis of effluent samples collected from beryllium processing plant.

2. Materials and methods

2.1. Instrumentation

Beryllium concentrations in the organic phases were determined by using continuum source electrothermal atomic absorption spectrometry (ETAAS; Contra AA 700, Analytik Jena AG, Jena, Germany). A transversely heated graphite tube, MPE 60 auto sampler and xenon short arc lamp (Analytik Jena AG, Jena, Germany) in hot-spot mode operated at 300 W as a continuum radiation source were used. A high-resolution double monochromator consisting of a prism and an echelle grating monochromator, providing a spectral bandwidth per pixel of ca. 2 pm at 200 nm were used. A linear charge coupled device array detector was used for measuring the integrated absorbance of beryllium at 234.8605 nm. Argon (Baba Agencies, Hyderabad, India) with a purity of 99.99% was used as the purge gas. The optimized temperature programme used for determination of beryllium is given in Table 1. A magnetic stirrer (Tarson, Chennai, India) was used for mixing the solutions.

2.2. Reagents and standard solutions

Ultra-pure water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all the solutions. Sub-boiled HNO_3 and HCl (Merck, Darmstadt, Germany) were prepared in our laboratory using quartz stills kept inside the clean bench. A stock standard solution (0.1 mg mL^{-1}) of beryllium was prepared using 1 mg mL^{-1} beryllium in 20% HCl (Merck, Darmstadt, Germany). Working standards were prepared daily by subsequent dilutions. The solutions of 10% m/v AOT, SDS, CTAB, Aliquat-336, salicylic acid and Triton X-114 (Sigma-Aldrich, Steinheim, Germany) were prepared in ultra-pure water except Aliquat-336 and AOT, which were prepared in methanol. A 1 mg mL^{-1} Pd in 2% HNO_3 prepared from the 10 mg mL^{-1} stock standard solution (Sigma-Aldrich,

Table 1
Optimized temperature program used for the determination of beryllium in the surfactant assisted dispersive liquid–liquid microextraction using ETAAS

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Ar flow (mL min^{-1})
Drying-1	60	6	10	250
Drying-2	90	5	10	250
Pyrolysis	1,500	300	10	250
Gas adaption	1,500	0	5	250
Atomization	2,300	2,000	4	0 (read)
Cleaning	2,400	1,500	3	250

Steinheim, Germany) was used as a conventional modifier. The Zr (5 mg mL^{-1}) solution, used as permanent chemical modifier, was prepared from ZrO_2 (Merck, Mumbai, India) by dissolving the appropriate amount in 5 mL HNO_3 and 5 mL HF (Merck, Darmstadt, Germany) and made up to 100 mL using ultra-pure water. The 50 µg Zr was coated on the integrated platform of standard pyrocoated tube as described in Lima et al. [31]. Sodium chloride (Merck, Darmstadt, Germany) was used without further purification. The dibasic acids such as salicylic acid and oxalic acid; and chloroform, carbon tetrachloride and trichloroethylene were procured from Merck (Mumbai, India) and have been used directly without any further purification. Interference study was carried out by using 1 mg mL^{-1} of Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Fe^{3+}, Cr^{6+}, SO_4^{2-} and PO_4^{3-}solutions.

Drinking water, groundwater and industrial effluent (Be processing industry) samples were collected at different stages and named as effluent stage-1 and stage-2. All the samples were acidified with salicylic acid and analyzed immediately.

2.3. Surfactant assisted dispersive liquid–liquid microextraction procedure

Aliquots of 1–5 mL certified reference materials, natural and industrial wastewater samples were taken in pre-cleaned sample vials containing a polytetrafluoroethylene (Teflon) coated stirrer bar. Then, 3.8 mL of 10% v/v salicylic acid, 1 mL of 10% m/v AOT and 1 mL v/v chloroform were added. These solutions were made up to 25 mL using Milli-Q water. A cloudy solution was formed by the uniform dispersion of chloroform in the aqueous phase in the presence of dispersive surfactant. The magnetic stirrer was turned on and the solution was mixed for 5 min at 400 rpm to enhance the rate of the reaction between beryllium salicylate and reactive solubilizing sites of surfactant. After stirring, the fine droplets of the chloroform were settled at the bottom of the sample vial. The chloroform layer was separated by removing the supernatant using micropipette and an aliquot of 10 µL was injected into the graphite tube for quantification of beryllium. Procedural blank was also prepared in the same manner.

3. Results and discussion

3.1. Optimization of surfactant assisted DLLME parameters

The effects of each variable parameter in the SA-DLLME process have been studied by spiking the 50 pg mL^{-1} beryllium to drinking and effluent samples.

3.1.1. Type and concentration of acids

Acid plays important role in stabilizing inorganic analytes. Beryllium forms stable negatively charged hydrophilic complexes with bidentate acids such as oxalic acid, salicylic acid; covalent and ionic compounds with hydrochloric and nitric acids, respectively. Hence, the effect of oxalic acid, salicylic acid along with common inorganic acids such as HCl and HNO_3 at 0.4% v/v concentration on the relative absorbance signal of beryllium from drinking water was studied in the presence of 0.5% v/v AOT and 1 mL chloroform for selecting the appropriate stabilizing acid. The results are given in Fig. 1. These results indicated that best recoveries were obtained with organic acids compared with inorganic acids. Hence, oxalic and salicylic acids were selected for further optimization of its concentration in various water matrices.

The effects of concentration of oxalic and salicylic acids on the recovery of beryllium in drinking and effluent stage-1 samples were studied in the range of 0.1% to 3% v/v. The results are shown in Figs. 2(a) and (b). In drinking water as shown in Fig. 2(a), quantitative recoveries (98%–100%) were

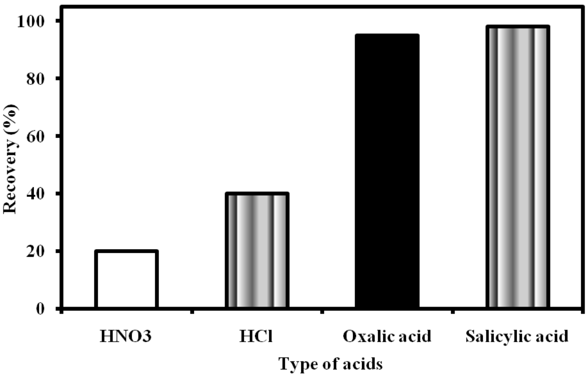

Fig. 1. Effect of type of acids such as HNO_3, HCl, oxalic acid and salycilic acids on the recovery of beryllium from drinking water using surfactant assisted dispersive liquid–liquid microextraction in the presence of 0.5% v/v AOT and 1 mL chloroform (n = 3).

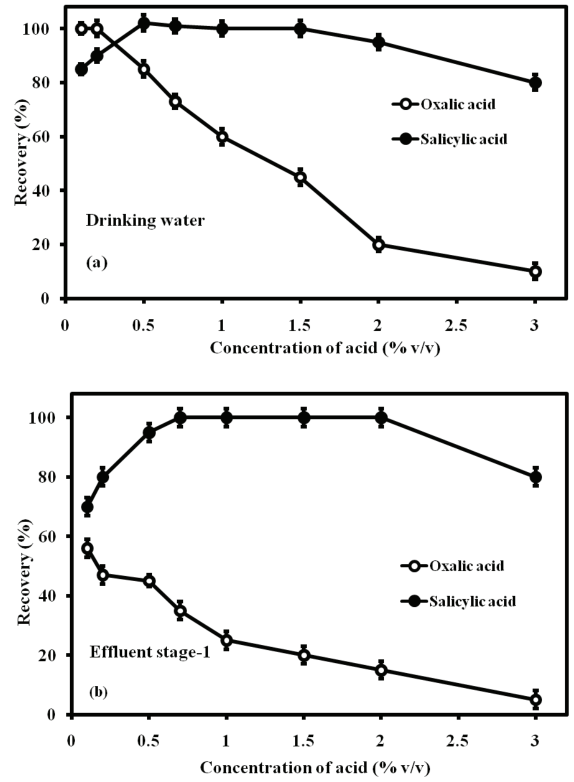

Fig. 2. Effect of oxalic and salicylic acid concentration on the recovery of beryllium spiked to (a) drinking water and (b) effluent stage-1 in the presence of 0.5% v/v AOT and 1 mL chloroform. The error bars indicate the relative standard deviation (%) of each measurement (n = 4).

observed in oxalic acid concentration range of 0.1%–0.2%, which decreased with further increase in the concentration of oxalic acid and reached 10% at an oxalic acid concentration of 3%. In case of salicylic acid, recoveries were increased gradually and reached 101% and remained consistent between 0.5% and 1.5% and the same was found to decrease to 80% at a salicylic acid concentration of 3%. In effluent stage-1 sample, as can be seen in Fig. 2(b), recoveries of beryllium were only 56% in the presence of 0.1% oxalic acid, which decreased to 5% with 3% oxalic acid. Under similar conditions with salicylic acid, the recovery of beryllium was 70% in the presence of 0.1% salicylic acid, which increased to almost 100% and remained consistent between 0.7% and 2% salicylic acid. A lower recovery of 80% was obtained at 3% salicylic acid. Hence, 1.5% salicylic acid was selected for the extraction of beryllium from the drinking and effluent samples.

3.1.2. Type and concentration of dispersive surfactants

Surfactants are amphiphilic molecules and form various aggregates that depends on volume and length of tail and size of head groups, these groups consist of various reactive hydrophobic, hydrophilic and amphiphilic solubilizing sites [32]. They quickly disperse in aqueous samples and interact effectively with targeted species using its reactive solubilizing sites. Therefore, various surfactants such as cationic CTAB and Aliquat-336, anionic SDS and AOT and a non-ionic Triton X-114 were prepared above critical micelles concentration (CMC) and their effect on the recovery of hydrophilic Be-salicylate in wastewater was studied. As shown in Fig. 3, the recovery of 95% was obtained using AOT. However, it is expected that the anionic Be-salicylate will be easily extracted with cationic surfactants, CTAB and Aliquat-336, but on the contrary this recovery is poor (20%–30%). Probably, this is due to steric hindrance caused by bulky salicylate that does not allow electrostatic interaction between cationic head group and anionic Be-salicylate. Better recoveries with anionic AOT could be obtained due to the fact that it has two hydrophobic tails with small sulfite head group that can form vesicle aggregates when compared with SDS which has only one tail and large sulfate head group that favor formation of micelle aggregates, therefore, interaction with Be-salicylate is more effective with AOT vesicle aggregates [33]. However, the recovery was only 15% in the case of non-ionic Triton X-114 micelles; it is mainly due to the absence of any active ionic solubilizing sites in the extracting micelles aggregates. Hence, anionic AOT surfactant was selected for the further optimization of its concentration.

The concentration of AOT was optimized in the range of 0.05%–0.6% v/v with drinking and effluent stage-1 samples. As shown in Fig. 4, good recovery was obtained in the aggregate region when compared with monomer region. In monomer interaction region of 0.05%–0.17% (CMC), the monomers were responsible for the extraction of Be, where a maximum recovery of 80% from drinking water and only 30%, from effluent was obtained. Above the CMC, in aggregates interaction region of 0.2%–0.6% AOT, the recovery of Be from drinking water was in the range of 95%–98% and from effluent it was 85%–90%. Hence, a concentration of 0.4% v/v AOT in the plateau region was selected.

3.1.3. Type and volume of extraction solvent

The extraction solvent plays an important role in the separation and pre-concentration of Be-salicylate, stabilized by vesicle aggregates, from aqueous phase. Therefore, the effect of 1 mL chloroform, carbon tetrachloride and trichloroethylene was studied to select the type of solvent. The results (Fig. 5) showed that chloroform has the highest extraction recovery compared with other studied solvents. Therefore, chloroform was selected and its volume was optimized in the range of 0.1–1.5 mL. These results showed that in the range of 0.1–0.3 mL, the recovery was found to increase from 40% to 80%, the recovery was 95% on further increase of volume to 1.5 mL. Hence, 1 mL of chloroform was selected as extracting solvent.

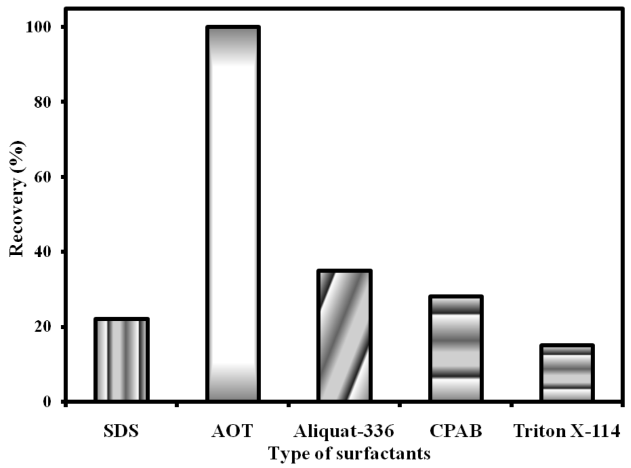

Fig. 3. Effect of surfactants such as SDS, AOT, Aliquat-336, CTAB and Triton X-114 on the recovery of beryllium using surfactant assisted dispersive liquid–liquid microextraction in the presence of 1.5% v/v salicylic acid and 1 mL chloroform ($n = 3$).

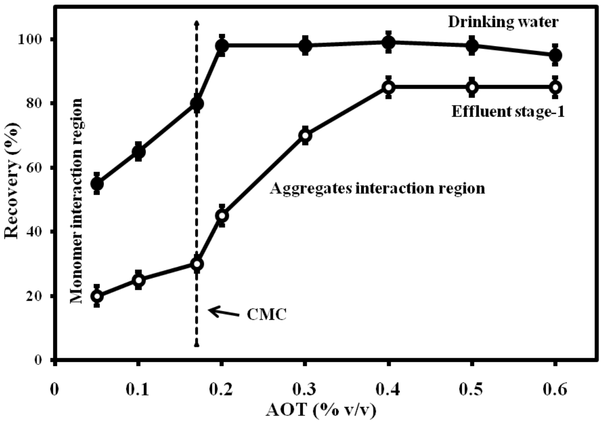

Fig. 4. Effect of AOT concentration below and above the critical micelles concentration (CMC) on the recovery of beryllium in drinking and effluent stage-1 samples in the presence of 1.5% v/v salicylic acid and 1 mL chloroform. The error bars indicate the standard deviation at each measurements ($n = 3$).

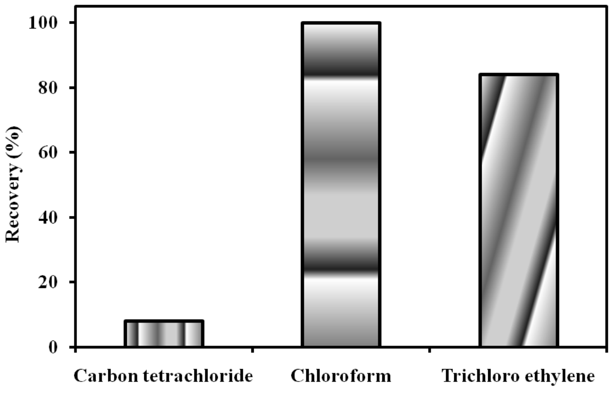

Fig. 5. Effect of various extraction solvents on the recovery of beryllium in the presence of 1.5% v/v salicylic acid, 0.4% v/v AOT ($n = 3$).

3.1.4. Mechanism of beryllium extraction

Beryllium reacts with salicylic acid and forms hydrophilic Be-salicylate, $Be(C_6H_4OCO_2)^{2-}$. The size of the Be-salicylate is sufficient to embed in the cavity of the vesicles aggregates formed by the dispersant AOT and hence was separated and pre-concentrated from aqueous phase into extracting chloroform phase. Various steps involved in the extraction of beryllium in the present procedure are given in Fig. 6. This mechanism is supported by the transmission electron microscopy (TEM) analysis and the results are shown in Figs. 7(a) and (b). The results from Fig. 7(a) indicated the formation of AOT vesicle aggregates alone without any beryllium salicylate and Fig. 7(b) indicated the trapping of the beryllium salicylate in their cavity. This result has been supported by earlier results of formation of AOT vesicles [34].

3.1.5. Effect of NaCl

The effect of electrolyte on the recovery of beryllium was briefly studied in the range of 1%–20% m/v NaCl from drinking water. No significant effect was observed on the recoveries of Be within the studied range of NaCl.

3.1.6. Effect of stirring rate and extraction time

Stirring rate plays important role on the rate of the formation of Be-salicylate and its subsequent transfer into an extracting solvent. Hence, the effect of stirring rates (0, 100, 200, 400 and 800 rpm), using a magnetic stirrer, on the recovery of Be was studied by keeping constant extraction time (5 min). These results indicated that the recovery was found to increase with increase in the stirring rate up to 200 rpm. There after it remained constant up to 800 rpm. Therefore, an optimum stirring rate of 400 rpm was selected.

The effect of the extraction time on the recovery of Be was studied in the range of 0–15 min by keeping other parameters constant. The results showed that there was no significant difference between the different extraction times above 5 min. It is mainly because of the fast dispersion of the fine droplets of the solvent, chloroform in the presence of the surfactant dispersant, AOT.

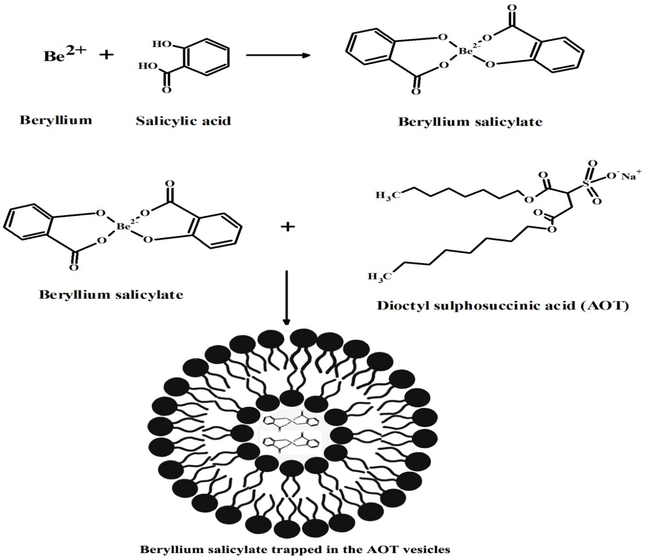

Fig. 6. The proposed reaction mechanism of beryllium extraction in the present procedure.

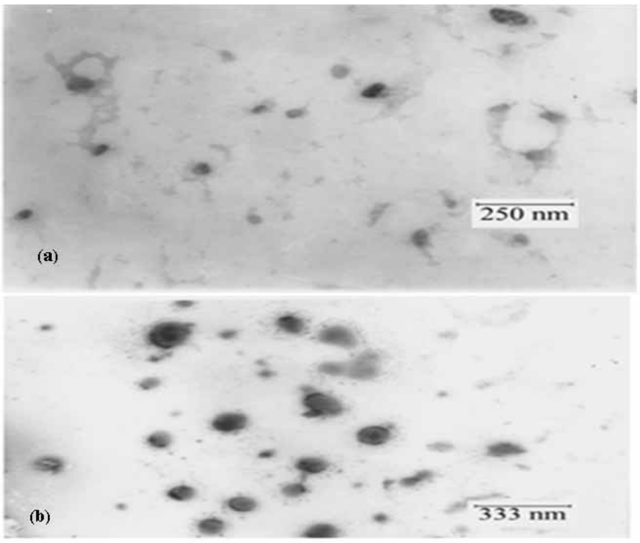

Fig. 7. TEM images of (a) AOT vesicles above CMC (0.4% v/v) at a magnification of 250 nm and (b) AOT vesicles with beryllium salicylate at a magnification of 333 nm support the extraction of beryllium salicylate by cavity mechanism of vesicles.

3.1.7. Interference studies

In order to evaluate the performance of the present optimized procedure to various natural environmental matrices, the highest tolerability of the various common interfering ions was studied. Interferences may occur because of the competition of other metal ions to form ion associates with the dispersing agent AOT and also with anionic Be-salicylates. The highest tolerability limits of various foreign ions spiked to 50 pg mL^{-1} of Be, by keeping the relative error between

±5% were found to be 100 mg L^{-1} of Mg^{2+}; 50 mg L^{-1} of Ca^{2+}; 10 mg L^{-1} of Cu^{2+}, Mn^{2+} and Pb^{2+}; 5 mg L^{-1} of Fe^{3+}; 1 mg L^{-1} of Cr^{6+} and 100 mg L^{-1} of SO_4^{2-} and PO_4^{3-} for proposed procedure. Therefore, these results demonstrated the applicability of the present procedure to the studied real water samples.

3.2. Optimization of furnace temperature program

The effect of pyrolysis and atomization temperature on the absorbance signal of 50 pg mL^{-1} of Be extracted into extracting chloroform was studied by using pyrocoated standard tube with conventional palladium and permanent Zr coated tube. The results shown in Fig. 8 indicated that permanent Zr coated tube improved absorbance signal compared with standard pyrocoated tube with palladium modifier. In both the tubes, the absorbance increased initially between 900°C and 1,100°C, and then reached a plateau region up to a pyrolysis temperature of 1,400°C and 1,500°C, respectively, for standard pyrocoated and permanent Zr coated tube. Beyond 1,400°C there is a loss of Be in case of standard coated tube. Hence, permanent Zr coated tube was selected with a pyrolysis temperature of 1,400°C. The optimizations of atomization temperatures were carried out in the range of 2,000°C–2,400°C for both the tubes. The atomization signal increased with increase in the atomization temperature from 2,000°C to 2,200°C and stabilized around 2,300°C in both cases. Hence, the Zr coated tube was selected with a 2,300°C atomization temperature.

3.3. Analytical figures of merit

Under the optimized experimental conditions, the calibration curve was obtained by pre-concentrating the successively spiked standards of Be in the range of 0.05–1,000 ng mL^{-1} to wastewater samples. The correlation coefficient obtained was 0.9986. Quantifications of Be in drinking water, groundwater and wastewater samples have been performed by using the aqueous calibration graph. Under the optimized conditions, the pre-concentration factor (PCF) was 25. The PCF is defined as the ratio of the analyte concentration in the final chloroform layer to that of the initial aqueous phase. The limit of detection (LOD) calculated based on the three times the standard deviation of 10 measurements of procedural blanks with 0.0045 ± 0.0015 absorbance was 1 pg mL^{-1}. A characteristic mass (m_o) of 0.25 pg was obtained by measuring the integrated absorbance signal on Zr coated tube, which is better than the reported value where tungsten platform kept in a pyrolytically coated tube with zirconium as a chemical modifier was used. The advantages of the proposed procedure were comparable with the recently published pre-concentration and procedures as given in Table 2 [10–14,16,35]. It clearly shows the utility of surfactant aggregates for the extraction of beryllium by acting as a chelating agent as well as dispersing agent. It also avoids the use of heating step commonly used in the cloud point extraction and provides fast extraction compared with reported micelle and mixed micelle cloud point extraction procedures.

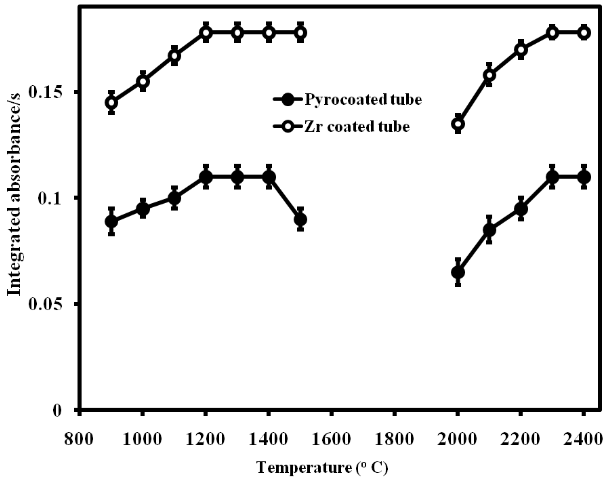

Fig. 8. Effect of pyrolysis and atomization temperature on the absorbance of 50 pg mL^{-1} of beryllium extracted into extracting chloroform in the present procedure with pyrocoated tube (standard tube with palladium conventional modifier) and Zr coated tubes (standard tube permanently coated with 50 µg Zr). The error bars indicate the standard deviation at each measurements ($n = 3$).

3.4. Applications

In order to evaluate the analytical applicability of the present optimized procedure to effluents and natural water samples, the recovery studies were performed by spiking the Be in the range of 0.05–1,000 ng mL^{-1}. The recoveries obtained are given in Table 3. The recoveries were in the range of 88%–99% in the studied concentration range with 1%–10% relative standard deviation. These results show that the proposed method can be applied successfully to the separation, recovery and determination of trace and ultra-trace levels of Be in real effluents and water samples.

The accuracy of the proposed procedure was verified by analyzing certified reference materials such as NIST 1640, 1640a and 1643e trace elements in natural water. As can be seen in Table 4, the values obtained are in good agreement with certified values based on Student's *t*-test at 95% confidence level. The Be concentration obtained by the present procedure in certified reference materials are compared with the results obtained by reported CPE procedure using the chelating agent [11]. These values show that there is a good agreement of results obtained by both procedures. After ensuring accuracy the proposed procedure was applied for the analysis of drinking water, groundwater and also industrial effluents of Be processing industry collected at different stages and named as effluent stage-1 and stage-2.

4. Conclusions

The described procedure provides a novel cost-effective SA-DLLME procedure for the simultaneous separation and recovery of Be prior to its determination by ETAAS. This procedure was carried out at room temperature by utilizing the solubilizing ability of the AOT vesicles formed spontaneously in the process. It does not use any special type of chelating agents and heating source; hence more cost-effective and energy efficient; and can be applied to water and effluents collected at Be industry. The procedure enables

Table 2
Comparison of analytical figures of merit of proposed surfactant assisted dispersive liquid–liquid microextraction procedure with various reported pre-concentration procedures

Pre-concentration scheme and instrument	Chelating agent/surfactants	Condition (temperature, °C and time, min)	LOD (pg mL^{-1})/PCF	Reference
CPE-SP	Chrome Azurol S/CTAB[e] + KI	RT/15	500/20	[10]
CPE-ETAAS	Cupferron/Triton X-114	60/35	20/20	[11]
MM-CPE-SP[a]	Chrome Azurol S/CPAC[f] + Triton X-114	50/20	50/25	[12]
MM-CPE-ICP-AES[b]	1,8-Dihydroxyanthrone/CPAC[f] + Triton X-114	50/20	1/16.7	[13]
MM-CPE-SP	Chrome Azurol S/CTAB[e] + Triton X-114	RT/5	980/20	[14]
SPE[c]-ICP-MS	Silica gel/EDTA	RT/90	0.0036/170	[16]
SPE[c]-ETAAS	Acetyl acetone/C_{18}	RT/60	2/–	[7]
SPE[c]-FAAS	Aluminon/octadecyl silica	80/30	100/–	[35]
SPE[c]-SP	Chrome Azurol S/hair	RT/100	28/50	[9]
SA-DLLME-ETAAS[d]	Salicylic acid/AOT + chloroform	RT/5	0.08/25	Present procedure

[a] Mixed micelle-cloud point extraction-spectrophotometer.
[b] Mixed micelle-cloud point extraction-inductively coupled plasma-atomic emission spectrometry.
[c] Solid phase extraction.
[d] Vesicle-mediated dispersive liquid–liquid microextraction–electrothermal atomic absorption spectrometry.
[e] Cetyl trimethyl ammonium bromide.
[f] Cetyl pyridyl ammonium chloride.

Table 3
Recovery of trace and ultra-trace levels of beryllium from various water and effluent samples using proposed surfactant assisted dispersive liquid–liquid microextraction procedure

Matrices	Spiked/ ng mL^{-1}	Found/ng mL^{-1} (mean ± SD)[a]	Recovery (%)
Drinking water	0	ND[b]	–
	50[c]	45 ± 3	90 ± 6
	50	48 ± 4	96 ± 8
	250	242 ± 7	97 ± 3
	1,000	990 ± 10	99 ± 1
Groundwater	0	ND[b]	–
	50[c]	44 ± 4	88 ± 8
	50	46 ± 5	92 ± 10
	1,000	980 ± 20	98 ± 2
Effluent stage-1	0	45 ± 1	–
	100	140 ± 8	95 ± 8
	250	285 ± 10	96 ± 4
	1,000	1,015 ± 20	97 ± 2
Effluent stage-2	0	9 ± 1	–
	50	56 ± 5	94 ± 10
	250	249 ± 10	96 ± 4
	1,000	979 ± 30	97 ± 3

[a] Mean of four determinations ± standard deviation.
[b] Not detected.
[c] Values are in pg mL^{-1}.

Table 4
Analytical results for the determination of beryllium in certified reference materials using the proposed surfactant assisted dispersive liquid–liquid microextraction and compared with reported micelle-based cloud point extraction procedure

Type of matrices	Measured value/ng g^{-1} (mean ± $ts(n)^{-1/2}$)[a]		
	Vesicle-mediated DLLME	Micelle-based CPE[b]	Certified value/ng g^{-1}
Trace elements in natural water NIST 1640	35.2 ± 0.4	34.9 ± 0.6	34.94 ± 0.41
Trace elements in natural water NIST 1640a	3.0 ± 0.1	3.0 ± 0.1	3.002 ± 0.027
Trace elements in water NIST 1643e	13.8 ± 0.1	13.5 ± 0.2	13.64 ± 0.16

[a] $t_{0.95} = 3.18$, $n = 4$ and s = standard deviation.
[b] Values are obtained from non-ionic-based CPE procedure with chelating agent [11].

pre-concentration of Be into smaller volumes of organic phase which can be transported easily to analytical laboratories. These features make the procedure more attractive to handle the thermally labile analytes easily. This procedure is more useful to establish the background levels of beryllium in and around the beryllium treatment plant and also to removal/recovery of high levels of beryllium from effluent samples to control its environmental contamination.

References

[1] T.A. Tomberlin, Beryllium – A Unique Material in Nuclear Applications, 36th International SAMPE Technical Conference, INEEL/Con-04-01869, 2004, Available at: http://citeseerx.ist.psu.edu/viewdoc/download;jsessionid=9622DD04578318D3090B7DFA7859EFA2?doi=10.1.1.543.4019&rep=rep1&type=pdf

[2] W. Speer, O.S.E. Said, Application of an Aluminium-Beryllium Composite for Structural Aerospace Components, 2003 Available at: http://materion.com/~/media/Files/PDFs/Beryllium/ApplicationsStructural-MAS/MAS-013SpeerReportAppsofanAlBeCompositeforStructuralAerospaceComponents.pdf

[3] R.G. Cooper, A.P. Harrison, The uses and adverse effects of beryllium on health, Indian J. Occup. Environ. Med., 13 (2009) 65–76.

[4] D.K. Verma, A.C. Ritchie, M.L. Shaw, Measurement of beryllium in lung tissue of a chronic beryllium disease case and cases with sarcoidosis, Occup. Med., 53 (2003) 223–227.

[5] W.T. Sanderson, E.M. Ward, K. Steenland, M.R. Petersen, Lung cancer case-control study of beryllium workers, Am. J. Ind. Med., 39 (2001) 133–144.

[6] M.K.S. Berigan, J.A. Deddens, J.R. Couch, M.R. Petersen, Risk of lung cancer associated with quantitative beryllium exposure metrics within an occupational cohort, Occup. Environ. Med., 68 (2011) 354–360.

[7] H.W. Peng, M.S. Kuo, Determination of trace amounts of beryllium(II) in drinking water and of beryllium vapour in air by graphite furnace atomic absorption spectrometry using acetyl acetone as a chelating agent, Anal. Sci., 16 (2000) 157–161.

[8] J. Ueda, T. Kitadani, Separation and concentration of beryllium by co-precipitation with hafnium hydroxide prior to determination by graphite furnace atomic absorption spectrometry, Analyst, 113 (1988) 581–583.

[9] N. Khan, T.G. Kazi, M. Tuzen, M. Soylak, A multivariate study of solid phase extraction of beryllium(II) using human hair as adsorbent prior to its spectrophotometric detection, Desal. Wat. Treat., 55 (2015) 1088–1095.

[10] A. Afkhami, T. Madrakian, E. Bozorgzadeh, M. Bahram, Spectrophotometric determination of beryllium in water samples after micelle-mediated extraction preconcentration, Talanta, 71 (2007) 1103–1109.

[11] L. Machackova, M. Zemberyova, Cloud point extraction for preconcentration of trace beryllium and chromium in water samples prior to electrothermal atomic absorption spectrometry, Anal. Methods, 4 (2012) 4042–4048.

[12] A. Beiraghi, A.R. Zarei, S. Babaee, Cloud point formation based on mixed micelles for the extraction, preconcentration and spectrophotometric determination of trace amounts of beryllium in water samples, Anal. Sci., 23 (2007) 527–531.

[13] A. Beiraghi, S. Babaee, Separation and preconcentration of ultra trace amounts of beryllium in water samples using mixed micelle-mediated extraction and determination by inductively coupled plasma-atomic emission spectrometry, Anal. Chim. Acta, 607 (2008) 183–190.

[14] M. Bahram, T. Madrakian, E. Bozorgzadeh, A. Afkhami, Micelle-mediated extraction for simultaneous spectrophotometric determination of aluminum and beryllium using mean centering of ratio spectra, Talanta, 72 (2007) 408–414.

[15] J.J. Charlton, N.C. Jones, R.A. Wallace, R.W. Smithwick, J.A. Bradshaw, I.I. Kravchenko, N.V. Lavrik, M.J. Sepaniak, Nanopillar-based enhanced-fluorescence detection of surface-immobilized beryllium, Anal. Chem., 87 (2015) 6814–6821.

[16] H. Tazoe, T. Yamagata, H. Obata, H. Nagai, Determination of picomolar beryllium levels in seawater with inductively coupled plasma mass spectrometry following silica-gel preconcentration, Anal. Chim. Acta, 852 (2014) 74–81.

[17] P.P. Francisco, I. Lavilla, C. Bendicho, Miniaturized preconcentration methods based on liquid-liquid extraction and their application in inorganic ultratrace analysis and speciation: a review, Spectrochim. Acta, Part B, 64 (2009) 1–15.

[18] H.M.A. Saidi, A.A.A. Emara, The recent developments in dispersive liquid–liquid microextraction for preconcentration and determination of inorganic analytes: a review, J. Saudi Chem. Soc., 18 (2014) 745–761.

[19] C. Ozdemir, S. Sacmaci, S. Kartal, M. Sacmaci, Determination of gold and palladium in environmental samples by FAAS after dispersive liquid–liquid microextraction pretreatment, J. Ind. Eng. Chem., 20 (2014) 4059–4065.

[20] S. Sacmaci, S. Kartal, S. Dural, Dispersive liquid-liquid microextraction procedure for the determination of palladium by flame atomic absorption spectroscopy, J. Braz. Chem. Soc., 23 (2012) 1033–1040.

[21] S. Sacmaci, S. Kartal, G. Kalkan, Determination of gold in various environment samples by flame atomic absorption spectrometry using dispersive liquid–liquid microextraction sampling, Croat. Chem. Acta, 88 (2015) 113–119.

[22] S. Sacmaci, M. Sacmaci, A new chelating reagent: its synthesis/characterization and application for the determination of Cd(II) and Ni(II) in various food and make-up product samples by FAAS using simultaneous microextraction sampling, J. AOAC Int., 99 (2016) 1058–1065.

[23] N. Khan, M. Tuzen, T.G. Kazi, D. Citak, M. Soylak, Pressure-assisted ionic liquid dispersive microextraction of vanadium coupled with electrothermal atomic absorption spectrometry, J. Anal. At. Spectrom., 28 (2013) 1441–1445.

[24] Z.A. Alothman, N.H. Al-Shaalan, M.A. Habila, Y.E. Unsal, M. Tuzen, M. Soylak, Dispersive liquid–liquid microextraction of lead(II) as 5-(4-dimethylaminobenzylidene) rhodanine chelates from food and water samples, Environ. Monit. Assess., 187 (2015) 1–8.

[25] M. Soylak, E. Kiranartligiller, A simple vortex-assisted dispersive liquid–liquid microextraction system for copper(II) to preconcentration and separation from natural water and table salt samples, Arabian J. Sci. Eng., 42 (2017) 175–181.

[26] S.M. Yousefi, F. Shemirani, Selective and sensitive speciation analysis of Cr(VI) and Cr(III) in water samples by fiber optic-linear array detection spectrophotometry after ion pair based-surfactant assisted dispersive liquid–liquid microextraction, J. Hazard. Mater., 254–255 (2013) 134–140.

[27] M. Moradi, Y. Yamini, A. Esrafili, S. Seidi, Application of surfactant assisted dispersive liquid–liquid microextraction for sample preparation of chlorophenols in water samples, Talanta, 82 (2010) 1864–1869.

[28] J. Cheng, Y. Xia, Y. Zhou, F. Guo, G. Chen, Application of an ultrasound-assisted surfactant-enhanced emulsification microextraction method for the analysis of diethofencarb and pyrimethanil fungicides in water and fruit juice samples, Anal. Chem. Acta, 701 (2011) 86–91.

[29] M. Behbahani, F. Najafi, S. Bagheri, M.K. Bojdi, M. Salarian, A. Bagheri, Application of surfactant assisted dispersive liquid–liquid microextraction as an efficient sample treatment technique for preconcentration and trace detection of zonisamide and carbamazepine in urine and plasma samples, J. Chromatogr., A, 1308 (2013) 25–31.

[30] Q. Deng, M. Chen, L. Kong, X. Zhao, J. Guo, X. Wen, Novel coupling of surfactant assisted emulsification dispersive liquid–liquid microextraction with spectrophotometric determination for ultra trace nickel, Spectrochim. Acta, Part A, 104 (2013) 64–69.

[31] E.C. Lima, F.J. Krug, K.W. Jackson, Evaluation of tungsten-rhodium coating on an integrated platform as a permanent chemical modifier for cadium, lead and selenium determination by electrothermal atomic absorption spectrometry, Spectrochim. Acta, Part B, 53 (1998) 1791–1804.

[32] S. Segota, D. Tezak, Spontaneous formation of vesicles, Adv. Colloid Interface Sci., 121 (2006) 51–75.

[33] R. Saha, P.K. Verma, R.K. Mitra, S.K. Pal, Structural and dynamical characterization of unilamellar AOT vesicles in aqueous solutions and their efficacy as potential drug delivery vehicle, Colloids Surf., B, 88 (2011) 345–353.

[34] J.I. Briz, M.M. Vel´azquez, Effect of water-soluble polymers on the morphology of aerosol OT vesicles, J. Colloid Interface Sci., 247 (2002) 437–446.

[35] A.R. Farahmand, S.R. Yousefi, N.S. Fumani, S. Mirza, M. Shamsipur, J. Hassan, Preconcentration of beryllium via octadecyl silica gel microparticles doped with aluminon, and its determination by flame atomic absorption spectrometry, Microchim. Acta, 166 (2009) 89–94.