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Cloud point extraction of uranium using H_2DEH[MDP] in acidic conditions

Charles Labrecque, Sabrina Potvin, Laurence Whitty-Léveillé, Dominic Larivière*

Laboratoire de radioécologie, Département de chimie, Université Laval, 1045 Avenue de la Médecine, Québec, QC, Canada G1V 0A6

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ABSTRACT

A procedure has been developed for the cloud point extraction (CPE) of uranium (VI) using H_2DEH[MDP] (P,P-di(2-ethylhexyl) methanediphosphonic acid) with inductively coupled plasma coupled to mass spectrometry (ICP-MS). The method is based on the modification of the cloud point temperature using cetyl trimethyl ammonium bromide (CTAB) and KI. Optimal conditions of extraction were found using a cross-optimization of every parameter (non-ionic and ionic surfactant concentrations, chelating agent concentration, pH and the extraction, and phase separation temperatures). Furthermore, the figures of merit of the methodology were assessed (limit of detection, limit of quantification, recovery, sensibility, and linear range) and are reported. Quantitative extraction (99 ± 0.5%) was obtained in drinking water samples over a wide range of uranium concentrations. The approach was also validated using drinking (SCP EP-L-3 and SCP EP-H-3), and wastewater (SCP EU-L-3) certified materials. Interferences from most critical anions and cations were evaluated to determine the reliability of the method. The proposed method showed robustness since its performance is maintained over a wide range of pH and metal ion concentrations.

1. Introduction

Among the naturally-occurring actinides, thorium and uranium are the most abundant in the environment. Since uranium compounds are more soluble than their thorium counterparts, so they tend to be more widely distributed globally in the various compartments of the environment and the biota [1].

Uranium's chemical and radiological toxicity have already been clearly established [2]. The chemical toxicity of uranium originates essentially from soluble compounds, whereas radiotoxicity at regulatory levels arises from insoluble compounds [3]. However, the presence of anthropogenic uranium isotopes (e.g. $^{232,\ 233,\ 236}$U) originating from the use of uranium in the nuclear fuel cycle could modify the isotopic signature of uranium and therefore alter its radiological toxicity. In addition to toxicological assessments, the capacity to correctly and precisely measure isotopic composition provides valuable information on its biogeochemical cycle and enables "fingerprinting" capability regarding nuclear safeguards. For these reasons, analytical strategies oriented toward improving the detection of minor uranium isotopes and increasing precision regarding the isotopic ratios are welcomed.

Numerous analytical techniques are available to detect and quantify uranium. Because they are versatile, spectroscopic techniques such as UV–visible, inductively coupled plasma atomic emission spectroscopy (ICP-AES), and liquid scintillation counting (LSC) have been used extensively to evaluate uranium levels in the environment [4]. While they provide acceptable sensitivities and enable detection of U in the μg to mg L^{-1} range, these approaches lack the capacity to measure isotopic ratios. Mass and alpha spectrometry could provide such critical information. However, since natural abundances of ^{234}U (0.0055%) and ^{235}U (0.7202%) are low in comparison to ^{238}U (99.28%), and since anthropogenic isotopes are expected to be at the ultra-trace levels, except in fuel, their detection is challenging. Thus, preconcentration is mandatory to improve the detection limits of less abundant isotopes. If alpha spectrometry is used for the quantification of the isotopic ratio, preconcentration and separation from the matrix is required to provide the analytical performance required to obtain acceptable isotopic ratios.

Numerous methods have already been studied for the preconcentration and separation of uranium. One of the common techniques for uranium is liquid–liquid extraction (LLE). However, this approach generates significant amounts of waste and often requires large volumes of solvent, so it is not considered to be eco-friendly. One variation of LLE is liquid–liquid separation supported on a solid phase, also known as extraction chromatography (EXC). Although this approach is fairly selective towards

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* Correspondence to: Département de chimie, Faculté des sciences et de genie, Université Laval, 1045, avenue de la Médecine, Bureau 1250D, Pavillon Alexandre-Vachon, Québec, QC, Canada G1V 0A6.
Tel.: +1 418 656 7250; fax: +1 418 656 7916.
E-mail addresses: dominic.lariviere@chm.ulaval.ca, lariviere.dominic@gmail.com (D. Larivière).

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actinides, the lower retention capacity (k') observed for uranium using commercially available resins (TEVA/UTEVA/DGA) [5–7] makes it difficult to achieve a very high preconcentration factor (>200), as the breakthrough volume would be achieved before this level of preconcentration would be reached [8]. The limited reusability and potential cross-contamination of some EXC resins also translate into the production of a significant amount of contaminated waste [9].

One alternative to EXC is ion exchange chromatography (IEC). The main advantage of this technique over EXC is the stability of the stationary phase. Nevertheless, separation using IEC is less selective due to the type of interaction with the functional groups, which is essentially driven by the mass-to-charge ratio [10]. Over the last decade, hybrid phase extraction techniques such as dispersive liquid-liquid microextraction (DLLME) and cloud point extraction (CPE) have emerged. CPE is essentially a liquid-liquid extraction where the dispersed organic phase is composed of micelles. Following the modification of some of the system parameters, phase separation and aggregation of micelles, referred as coacervation, will occur. The most common system modification agent is temperature, however, addition of salt or solvents such as ethanol have been reported [11,12]. The use of CPE has shown great promise for metal extraction for several reasons [13,14]. Among them, one of the main advantages of CPE over traditional liquid-liquid extraction is that the extracting phase is dispersed throughout the aqueous phase in the form of micelles, enhancing interaction between the two phases with no need for an external force [15]. Furthermore, the CPE was recently demonstrated by Favre-Reguillon [16] to have a higher K_{ex} which is deem to be due to the higher concentration of ligand in the micellar phase which enhance the extraction efficiency. The demonstration of the higher extraction efficiency was done with an 8-hydroxyquinoline based extraction comparing CPE, using Triton X-114, and its equivalent in liquid–liquid extraction, using chloroform and water.

Organic solvents or inorganic salts can be added to enhance phase separation because they have higher surface excess and thus change the environment of the micelles [17]. Inorganic salts are regarded as more compatible with the usual atomic analytical techniques because they limit the formation of carbon-based interferences and deposits. Because this extraction method uses only millimolar amounts of surfactants, it is seen as a greener alternative to LLE [14]. Furthermore, coupling CPE with sensitive mass spectrometry can enhance the analysis because high preconcentration factors are achievable [18]. The selectivity of CPE system can be modulated by selecting a proper complexing agent and adequate extracting conditions to limit the extraction of interfering ions and to increase the elemental selectivity [19].

Several research groups have proposed CPE systems for the analysis of *U* (Table 1). Most of the systems are effective at neutral to basic pH values. However, at these conditions, the selectivity of the method is hindered by the precipitation of many transition metals as hydroxides from the aqueous solution (Table 2). Recently, Constatinou et al. [20] and Favre-Réguillon et al. [21], proposed new CPE methodologies enabling extraction to occur at $\text{pH}=4$ using tributylphosphonate (TBP) and 8-hydroxyquinoline (8-Hq) as extractants, respectively. In the TBP-based CPE system, while TBP's selectivity towards actinides is well-documented, [22] low efficiencies were achieved (Table 1) especially in comparison with 8-Hq CPE system, where excellent efficiencies were obtained. However, 8-Hq-based CPE systems have been used for metal extractions other than *U*, therefore, suggesting a lack of selectivity for this system [23,24].

Recently, Sanaa et al. [25] reported an extraction system with good recoveries around the D_2EHPA phosphonic-based extractant. The extraction pH was not disclosed, yet the addition of sodium acetate for the phase separation suggests a pH around 8–9. Although the D_2EHPA extraction of uranium offers good extraction efficiencies, the effect of possible interferences from the matrix was not assessed, nor any evaluation of the system on environmental samples. In addition, the extraction took 24 h to achieve phase separation, which strongly limits the sample throughput. However, this study demonstrated that the efficiency of the new CPE phosphonic-based ligand system is promising. If coupled to a CPE system operating in acidic conditions to limit transition metal hydroxide precipitation ($\text{pH} \leq 3.5$), this could improve on the deficiencies of previously designed systems for uranium.

In this article, we describe a new CPE system with an acidic extracting agent, $H_2DEH[MDP]$ (Fig. 1), that has a demonstrated selectivity towards actinides [33]. Cloud point conditions, extracting agent concentrations, and temperature are optimized. Finally, analytical figures of merit and interfering ions tolerance are presented.

2. Experimental

2.1. Instrumentation

Natural uranium and ^{233}U solutions were measured using an ICP-MS (Varian 800-MS, Mississauga, ON, Canada). Measurements for natural uranium were done in normal sensitivity whereas measurements for ^{233}U solution were done in high sensitivity (Table 3). A centrifuge (Beckman Allegra 64R, Mississauga, ON, Canada with the C1015 rotor) was used to accelerate the phase separation process. The pH values were measured with a pH meter (Sartorius PT-15, Mississauga, ON, Canada). Extraction experiments were performed as a set of four replicates.

2.2. Reagents

High purity water with a resistivity of 18.2 $M\Omega\,cm^{-1}$ provided by a Milli-Q water purification system (Millipore, Etobicoke, ON, Canada) was used for the trace metal analysis. A stock solution of natural uranium was purchased from SCP Science (Baie D'Urfé, QC, Canada). A solution of ^{233}U was obtained from the National Institute of Standards and Technologies (NIST, Gaithersburg, MD). Rhodium (SCP Science, Baie D'Urfé, QC, Canada) was used as an internal standard for the development of the method and for the analysis of natural samples. Certified reference materials (EP-L-3, low level drinking water, EP-H-3, high level drinking water, and EU-L-3, low level waste water) were also bought from SCP Science (Baie D'Urfé, QC, Canada). A stock solution of reagent-grade Triton X-114 (Sigma-Aldrich Canada, Oakville, ON, Canada) was used as a surfactant in the CPE system for the measurements of natural uranium. Other reagents used in the development of the CPE system were: NaOH (Fisher Scientific, Ottawa, ON, Canada), HNO_3 (Anachemia Chemical, Montreal, QC, Canada), KI and KNO_3 (EMD chemicals, Mississauga, ON, Canada), and cetyl trimethyl ammonium bromide (CTAB) (Acros Chemicals, Ottawa, ON, Canada). These reagents were used without any purification. P,P di(2-ethylhexyl) methanediphosphonic acid ($H_2DEH[MDP]$) was synthesized using the procedure proposed by Stepinski et al. [34] using Sigma-Aldrich reagents (Sigma–Aldrich Canada, Oakville, ON, Canada). Purity was assessed via NMR spectroscopy using a Bruker AC 300 MHz NMR ^{31}P and ^{1}H. $H_2DEH[MDP]$ was dissolved in a solution of Triton X-114 to enhance its solubility. Dasani (Coca Cola, Toronto, Ontario), Aquafina (Pepsico, Mississauga, Ontario), and Eska (Eska, Toronto, Ontario) water samples were purchase at a local grocery store.

Table 1
Comparison of reported CPE of uranium methodologies.

Surfactant	pH	Efficiency (%)	Extractants	Instruments	Reference
TTX-114	9.2	98	PAN	UV–Vis	Laespada et al. [26]
TTX-114	9	Quantitative	DBM	UV–Vis	Shemirani et al. [27]
TTX-114	8	98	Br-PADAP	UV–Vis	Ferreira et al. [28]
TTX-114	6.5	Quantitative	PCV	UV–Vis	Madrakian et al. [29]
TTX-114	5.2	Quantitative	ARS	UV–Vis	Ghasemi et al. [30]
TTX-100	N.P.	Quantitative	D_2EHPA	UV–Vis	Sanaa et al. [25]
TTX-114	4	55	TBP	LSC	Constantinou et al. [20]
TTX-114	4	95	8-Hq	ICP-AES	Favre-Reguillon et al. [21]
TTX-114	6	Quantitative	DBM	ICP-AES	Shariati et al. [31]

TTX-114=Triton X-114; TTX-100=Triton X-100; PAN=1-(2-Pyridylazo)-2-Naphthol; DBM=Dibenzoylmethane; Br-PADAP=2-(5-Bromo-2-Pyridylazo)-5-(Diethylamino)Phenol; PCV=Pyrocatechol Violet; ARS=Red arsenazo S; D_2EHPA=2-(2-ethylhexyl) phosphoric acid; TBP=Tributyl Phosphate; 8-Hq=8-Hydroxyquinoline; N.P.=not provided.

Table 2
Precipitation pH of selected metals at various concentrations, based on data published in reference [32].

Metals, M	$[M]=10^{-5}$ M	$[M]=10^{-4}$ M	$[M]=10^{-3}$ M	$[M]=10^{-2}$ M
Ti(IV)	1.9	1.4	0.9	0.4
V(II)	5.0	4.5	4.0	3.5
Cr(III)	5.2	4.9	4.5	4.2
Mn(II)	10.2	9.7	9.2	8.7
Fe(III)	6.5	5.5	4.5	3.5
Co(II)	11.0	10.0	9.0	8.0
Ni(II)	8.9	8.4	7.9	7.4
Cu(II)	6.9	6.4	5.9	5.4
Zn(II)	8.4	7.9	7.4	6.9
Pb(II)	9.4	8.9	8.4	7.9
U(VI)	6.4	5.9	5.4	4.9

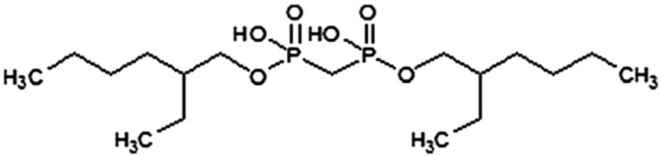

Fig. 1. Structure of the H_2DEH[MDP] ligand.

2.3. CPE system

An aliquot sample of 6.5 mL was spiked with a known concentration of uranium, and the pH of the solution was adjusted to approximately 3.5 with dilute HNO_3 or NaOH solution in a falcon tube. Afterwards, 100 μL of a solution of 0.01 M of CTAB was added, followed by 400 μL of an aqueous solution composed of 0.25 mM of H_2DEH[MDP] dissolved in 0.2 mM of TTX-114. 1 mL of 0.1 M KNO_3 and 0.5 ml of 0.1 M KI was added to complete the CPE system. Following the addition of the reagents, the volume of the solution was adjusted to 10 mL. The solution was then stirred for 1 h in an ice bath until equilibrium was reached. Subsequently the solution was left to settle for 30 min at room temperature. Finally, the solution was centrifuged at 4700 g for 10 min at a temperature of 20 °C. The surfactant-rich phase was isolated by removing the supernatant. A summary of the optimal CPE system conditions is presented in Table 4. These conditions were obtained through a cross-optimization process of all parameters. However, to provide a deeper understanding of the impact of each parameter, ranges of concentrations near the optimal value were assessed and are presented in the results and discussion section.

To enable the complexation of some of the interfering ions and to enhance the selectivity of the method, the aqueous phase containing the reagents and sample was spiked to 0.001 M of nitroacetic acid (NTA).

Table 3
ICP-MS conditions for the measurement of uranium.

Parameters	Value	
	High sensitivity	Normal sensitivity
Flow parameters (L/min)		
Plasma flow	18.0	18.0
Auxiliary flow	1.80	1.80
Sheath gas	0.22	0.21
Nebulizer flow	0.94	1.00
Torch alignment (mm)		
Sampling depth	5.0	5.0
Other		
RF power (kW)	1.40	1.40
Pump rate (rpm)	17	2
Stabilization delay (s)	15	15
Ion optics (volts)		
First extraction lens	−518	−5
Second extraction lens	−871	−171
Third extraction lens	−626	−205
Corner lens	−731	−218
Mirror lens left	52	35
Mirror lens right	53	20
Mirror lens bottom	11	25
Entrance lens	−4	−4
Fringe bias	−2.5	−2.5
Entrance plate	−34	−31
Pole bias	−0.5	−0.5

Table 4
Optimized CPE system conditions.

Parameters	Conditions[a]	Units
Sample	6.5	(mL)
pH	3.5	–
[TTX-114]	0.8	(mmol L^{-1})
[H_2DEH[MDP]]	9	(μmol L^{-1})
[CTAB]	100	(μmol L^{-1})
[KI]	5	(mmol L^{-1})
[KNO_3]	10	(mmol L^{-1})
$T_{extraction}$	4	(°C)
$T_{phase\ separation}$	20	(°C)
$RCF_{average}$	4 700	(G)

[a] Concentrations presented are for the total volume (aqueous phase prior to coacervation).

2.4. Figures of merit

The following figures were assessed using optimal conditions for the following factors: linear range, preconcentration factor, detection limits, and quantification limits. Extraction efficiency (EE,%), chemical recovery (CR,%) and preconcentration factor (PF) were determined using the following equations, which are based on those presented elsewhere [35,36] but modified to reflect the fact that analyte were measured in the surfactant rich and supernatant phases to ensure that mass balance is preserved:

$$EE = \frac{C_{SRP}}{C_{SRP} + C_{supernatant}} \times \frac{V_{supernatant}}{V_{SRP}} \times 100 \quad (1)$$

$$CR = \frac{c_{SRP} \times V_{SRP}}{c_{spiked} \times V_{initial}} \times 100 \quad (2)$$

$$PF = \frac{C_{initial} V_{initial} - C_{supernatant} V_{supernatant}}{C_{supernatant} V_{supernatant}} \quad (3)$$

where C_{SRP} is defined as the concentration in the surfactant rich phase, $C_{supernatant}$ is defined as the concentration in the supernatant after the phase separation, and $V_{supernatant}$ and V_{SRP} are the volume of the supernatant phase after the phase separation and the redispersed surfactant rich phase, respectively. In the recovery equation, the c_{spiked} is the concentration of the analyte that has been added to the solution. [37] Finally, $C_{initial}$ and $V_{initial}$ represent the uranium concentration initially present in the sample/standard and the initial volume of the solution (10 mL), respectively. Extraction efficiency was calculated to determine the level of extraction from the aqueous phase toward the surfactant rich phase whereas the chemical recovery was used to determine if uranium mass balance was near quantitative.

3. Results and discussion

3.1. Complexing agent

H_2DEH[MDP] is a widely used ligand for the extraction of various actinides in environmental samples that have a great affinity for uranium. Horwitz et al. [33] demonstrated that uranium extraction using H_2DEH[MDP] decreased by over 4000-fold when the HCl concentration increased from 0.03 M (pH = 1.52) to 4 M (pH = −0.60). This observation supports the fact that this extracting agent should be applicable at pH values typical for use in CPE systems (Table 1).

However, from a practical point of view, since H_2DEH[MDP] has low solubility in water near neutral pH, the complexing agent had to be dispersed in a hydrophobic media (Triton X-114, see Sections 3,2), similar to the approach used in extraction chromatography. By varying the H_2DEH[MDP] concentration from 0 to 10 μM/L, extraction efficiencies ranging from 10–99% were obtained (Fig. 2). Considering the small excess of complexing agent in comparison to U concentration, this demonstrates the strong affinity of the ligand toward uranium. In our experiment, a ratio of 2.43:1 (ligand:uranium) is sufficient to get a quantitative extraction of uranium. As it has been demonstrated that the stoichiometric ratio for the formation of the H_2DEH[MDP]:U complex is 1.5:1 [38], the calculated ratio in our CPE system highlight that nearly all the molecules of ligand added are involved in the extraction process. Maximal extraction efficiency was achieved at a concentration of 9 μM/L of H_2DEH[MDP]. At this concentration, recoveries of uranium were found to be optimal throughout a wide range of concentrations (45–1,000,000 ng/L) (results not shown).

Compared to other CPE systems, the extraction efficiency of the proposed methodology is essentially driven by the extracting agent because in its absence, the extraction is minimal (approximately 10%). In comparison, the method developed by Favre-Reguillon et al. [21] has an extraction of approximately 50% without their extractant, 8-HQ. Hence, this approach for extraction has a selectivity mostly driven by our extractant, H_2DEH[MDP], and not by the other constituents of the CPE system (e.g. non-ionic and ionic surfactant).

3.2. Non-Ionic surfactant

The choice of Triton X-114 (TTX-114) as a surfactant for this CPE system was driven by its theoretical cloud point temperature (CPT) near room temperature (25 °C) and its low toxicological impact at concentrations such as those used in this experiment [39]. However, biodegradation products of TTX-114, such as alkylphenols, have been reported to have demonstrated estrogenic effects [40]. Therefore, implementation of this methodology to large scale uranium treatment strategies should be evaluated thoroughly from an environmental point-of-view. The higher density of the TTX-114 surfactant-rich phase [39] (compared to water) facilitates the phase separation process. For these reasons, most CPE systems developed for uranium are designed around this non-ionic surfactant (Table 1). TTX-114 concentrations ranging from 0.8–12 mM were tested to determine the most efficient concentration of this non-ionic surfactant under the various pH conditions (Fig. 3). Typically, cloud point extractions are generally performed at concentrations near the determined critical micelle concentration (cmc) as the cloud point temperature increases with the concentration of NIS [41]. However, in the case of a ternary micellar system, Triton X-114, CTAB, and water, the cmc value decreases due the presence of CTAB. A concentration of 0.8 mM was found to be sufficient to enable the most efficient and

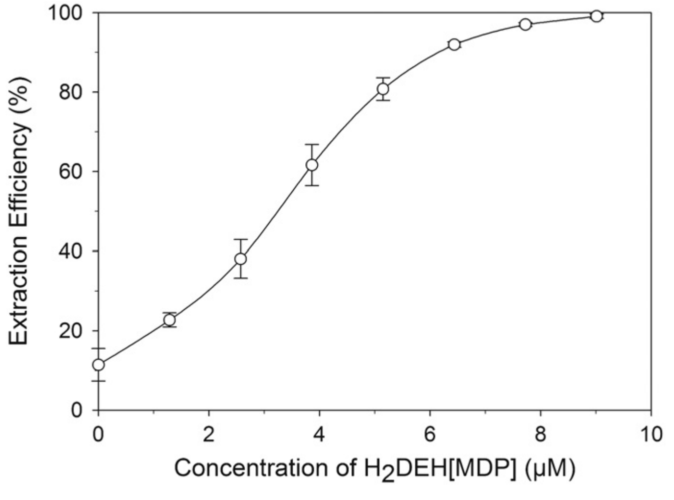

Fig. 2. Effect of the complexing agent on the extraction efficiency of 800 μg/L of uranium. Other parameters were kept constant at concentrations presented in Table 4.

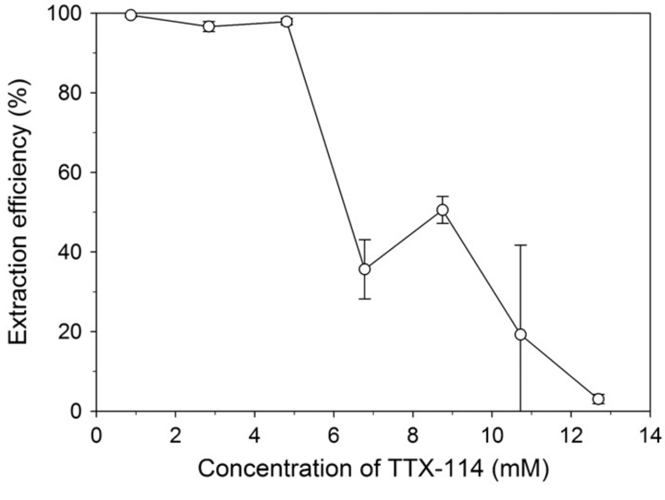

Fig. 3. Impact of the TTX-114 concentration on the extraction efficiency. Other parameters were kept constant at concentrations presented in Table 4.

reproducible extraction. However, the extraction efficiency was found to be stable through a relatively wide range of non-ionic surfactant concentrations (0.8–4 mM). At higher concentration of Triton X-114, yields were found to decrease below 40% due to the increase of the CPT as a result of higher concentration of non-ionic surfactant, which would reduce extraction efficiency with the parameters used, as demonstrated by Gu et al. [41].

The lowest concentration of TTX-114 possible was chosen in this experiment since it was believed that lower concentrations of organic surfactant would minimize the process of carbon deposition on the ICP-MS cones interface. However, it has been determined experimentally that at concentrations of TTX-114 as high as 10 mM, carbon deposit on the surface of the cones and nebulization issues were not noticed for an 8 h run. Yet, one of the advantages to using the lowest concentration of TTX-114 possible is that it minimizes the volume of the SRP, which should positively impact the preconcentration factor.

3.3. Effect of the Ionic surfactant

Cetyl trimethyl ammonium bromide (CTAB) was added to our system to tune the CPT of TTX-114, which is higher than room temperature (e.g. 28 °C) and to decrease the cmc of TTX-114. In fact, Koshy et al. [42] have demonstrated that the addition of foreign substances, such as CTAB, can change the cloud point temperature of a solution of Triton X-114. Using this approach, the $CPT_{TTX-114}$ can be decreased from 28 °C to below room temperature (20 °C), then phase separation can be achieved simply by warming up the sample. This would minimize the possibility of resolubilisation of the SRP during the centrifugation process. Furthermore, the addition of a cationic surfactant is recognized to enhance the extraction efficiency of polar organic compound [29] like the complex formed by uranium and H_2DEH[MDP]. This was demonstrated by Madrakian et al. [29] where CTAB was used to enhance the uranium extraction efficiency. In the developed system, we effectively observed that the extraction efficiency increased from 20% to 99% with the addition of CTAB (Fig. 4). It was determined that a concentration of 100 μM of CTAB was optimal for this CPE system.

3.4. Effect of addition of KI and KNO_3

Madrakian et al. [29] and Afkhami et al. [43] extensively studied the use of iodide as a phase separation agent in tandem with CTAB. Since iodide is polarizable, it enhances the interaction between the micelles and the ion in the aqueous phase. Thus, the interaction between iodide and micelles will decrease the cloud point temperature. KNO_3 was used in this system to maintain uranium as UO_2^{2+} and ensure that it is not reduced by any matrix constituent to its +4 oxidation state for which complexation with H_2DEH[MDP] could be limited. Furthermore, KNO_3 was used as a salting out agent to force the uranium–H_2DEH[MDP] complex formed inside the micelles. Concentrations of 5 and 10 mM for KI and KNO_3, respectively, were used in the optimal CPE system development.

3.5. Effect of pH

The pH is a very critical parameter for both the coacervation of the micelles and the complexation of the H_2DEH[MDP] with the uranium species. First of all, pH has an effect on the uranium species in solution and will therefore have a direct an impact on the complexation of uranium with H_2DEH[MDP]. For example, the complexation of U with HCO_3^-/CO_3^{2-} occurs essentially at pH values greater than 6 [44], so the presence of carbonated species of *U* would hamper the complexation with H_2DEH[MDP], and this would translate into lower extraction efficiency. Carbonated species will also indirectly impact the overall selectivity of the methodology as many metal carbonates are insoluble and will be precipitated in the SRP after centrifugation. The U:H_2DEH[MDP] complex formed must also be in its neutral form to transfer into the hydrophobic environment encountered inside the micellar structure. At more acidic pH values (i.e. $pH < 2.5$), the stability of iodine in its iodide form considerably decreases in favor of iodate and elemental iodine, species that will modify the hydration sphere of the micelles. This would, in return, affect the cloud point temperature and preclude phase separation from happening (Fig. 5).

The effect of the pH on uranium extraction was assessed by varying the pH from 3 to 7 with HNO_3 and NaOH (Fig. 5). The optimal extraction efficiency was observed for pH values ranging from 3.3 to 7, which is lower than the precipitation of the hydroxide of most transition metals (Table 2). The optimal extraction is probably due to the formation of a U:H_2DEH[MDP] neutral complex species at this pH range, although no spectrometric characterization was performed to confirm this hypothesis. For the rest of the optimization process, a pH of 3.5 was used to insure proper extraction and avoid rapid change in pH as it is a non-buffered environment.

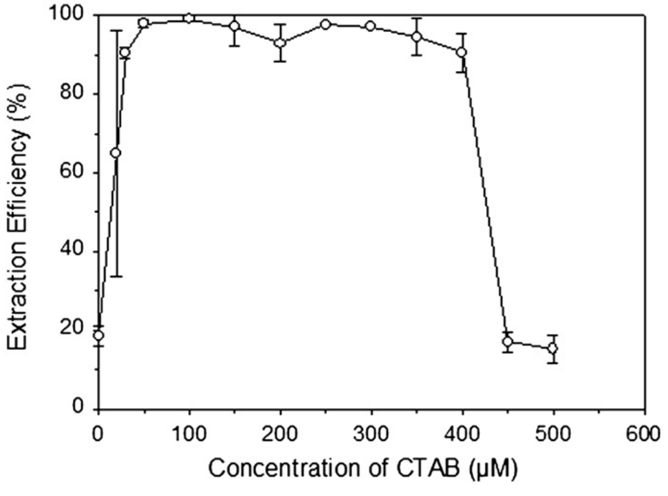

Fig. 4. Impact of the CTAB concentration on the extraction efficiency. Other parameters were kept constant at concentrations presented in Table 4.

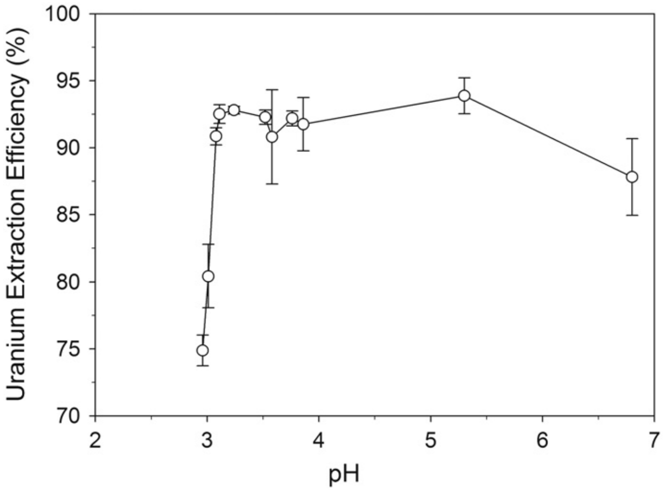

Fig. 5. Impact of the pH on the extraction efficiency. Other parameters were kept constant at concentrations presented in Table 4.

3.6. *Effect of the extraction and phase separation temperature*

Since the non-ionic surfactant (NIS) chosen for the extraction (TTX-114) has a cloud point temperature (CPT) of 25 °C, a CPE system was expected to be observed near room temperature. However, since the theoretical CPT are determined for a binary system composed of demineralized water and NIS, the addition of various salts and organic substances can alter the CPT [12]. Based on other studies using TTX-114 [45], it was expected that the phase separation process would occur at a temperature near the theoretical CPT, even in high ionic strength solutions [12]. For the developed system, a CPT of 8 °C was obtained, or 6 °C for a solution containing 1000 ppm of Na^+.

Two steps of the CPE process are proven to be critical with respect to temperature: (1) analyte extraction and (2) phase separation via centrifugation. Therefore, the optimal temperature was evaluated for both processes.

Fig. 6 illustrates that the extraction efficiency is significantly higher at lower temperature. We believe that the incorporation of the neutral complex of uranium is improved because of the equilibrium between the free surfactant and the surfactant forming the micelles. Because of the dynamic nature of the formation of micelles, this would facilitate the incorporation of the U:H_2DEH[MDP] complex. Similar temperature-related behaviors were obtained by Okada [17] for complexation and extraction of metal thiocyanate. Furthermore, when extraction occurs in the presence of micelles, the surface area in contact between the solution and the micelles is greater than the formation of coacervates. Hence, temperature greatly affects the extraction efficiency and the performances of the CPE system. Similarly, the temperature was optimized for the phase separation by centrifugation. The optimal phase separation was achieved at a temperature of 20 °C. It is assumed that at higher temperature, CTAB resolubilisation occurs. These findings are consistent with the temperature reported by Favre-Réguillon et al. [21] which also reported a more favorable phase separation when it occurs near room temperature. Multiple factors, including TTX-114 and CTAB concentrations, are known to change the cloud point temperature. Therefore, as temperature of extraction and phase separation used here were reached through cross-optimization, they are deemed optimal for the system presented and its cloud point temperature neighboring 6–8 °C. Yet, for a system with a different ratio of CTAB and TTX-114 both temperature are expected to change.

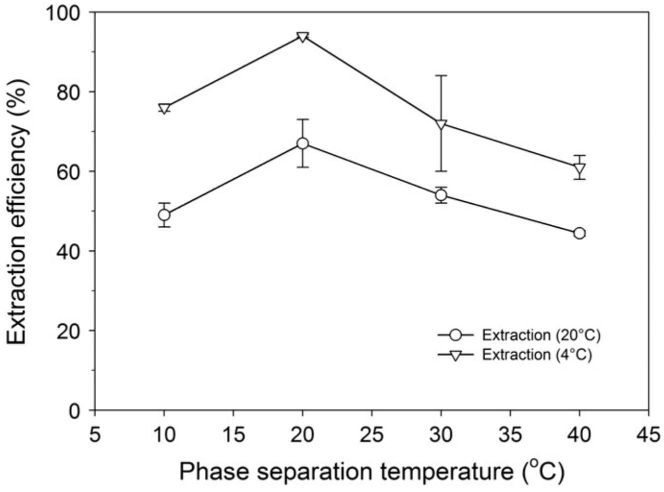

Fig. 6. Impact of the stirring and centrifugation temperature on extraction efficiency. Other parameters were kept constant at concentrations presented in Table 4.

3.7. *Analytical figures of merit*

To determine the applicability of the CPE method we developed, figures of merit were evaluated (Table 5). Detection limit and linear range of the methodology were determined using ^{238}U whereas extraction efficiency and recovery were determined using ^{233}U instead of naturally occurring uranium isotopes (234, 235, 238), as it became clear that some of the reagents used in the CPE systems contained some level of uranium that would artificially alter the figure of merit of the methodology. Experimentally, it was determined that TTX-114 was the main contributor to uranium contamination. This contamination could be overcome by using trace metal reagents; however, reagents with a sufficient level of purity were not available during the developmental stages of this system.

Using our approach, a LOD of 3 ng L^{-1} was determined. The proposed method also leads to exceptional extraction yield (99.0%) and recovery (99%). Because of the enhancement in the nebulisation resulting from the minimization of the surface tension by the surfactant in the SRP, recovery rates of over 100% were initially calculated using Eq. (2). This was subsequently corrected using the internal standardization approach. As nearly quantitative extraction efficiencies were measured in the SRP, minimal amounts of uranium are left in the supernatant after phase separation, demonstrating the efficiency of this approach for uranium decontamination of water source or uranium-mining wastewater.

The proposed methodology shows significant improvement regarding the limit of detection (LOD), limit of quantification (LOQ), and recoveries, compared to the methods already published (Table 5). This was expected, since other CPE methodologies used UV–visible or ICP-AES for detection, which are less sensitive than ICP-MS.

With respect to linear range and preconcentration factor (PF), our approach also provides values which are comparable to other studies. LOD and LOQ for the proposed method were determined using the standard deviation measured at m/z=238 of 10 method

Table 5
Analytical performance of the proposed method.

	Linear range (μg/L)	PF	LOD (ng/L)	LOQ (ng/L)	Recovery (%) (n=4)	Extraction efficiency (%) (n=4)
Proposed method	1 000	92	3	10	99 ± 4	99.0 ± 0.5
Laespada et al. [26]	N.P.	100	1100	4000	98	Quantitative
Shemirani et al. [27]	300	62	11,000	15,000	98	Quantitative
Ferreira et al. [28]	N.P.	122	N.P.	N.P.	N.P.	98
Madrakian et al. [29]	10	14.3	60	180	N.P.	Quantitative
Ghasemi et al. [30]	10	N.P.	2000	6000	105 ± 9	Quantitative
Sanaa et al. [25]	100,000	N.P.	N.P.	N.P.	98	97
Constantinou et al. [20]	N.P.	100	1.42×10^8	3×10^8	55	55
Favre-Reguillon et al. [21]	N.P.	122	N.P.	2400	98	95
Shariati et al. [31]	1240	50	1000	2500	N.P.	Quantitative

LOQ=limit of quantification; LOD=limit of detection; PF=preconcentration factor; N.P.=not provided.

blanks. These values could however be enhanced using TTX-114 trace metal reagents. With the use of this reagent, LOD and LOQ at pg L^{-1} level could potentially be achieved.

3.8. *CPE system resilience to competitive ions*

With a view to applying the developed methodology to environmentally relevant issues, the impact of other relevant ions on the extraction performances of the CPE system had to be assessed. Potential interfering ions (Table 6) were selected based on the work of Horwitz et al. [46] which investigated the affinity and selectivity of ions on a H_2DEH[MDP]-related chelating agent, HDEHP, also referred as D_2EHPA. This chelating agent should be more prone to interference because it lacks methylene bridges, which force the geometry for the targeted ions and thus enhance the selectivity.

Chiarizia et al. [47] also demonstrated that rare earth elements have a high affinity with the complexing agent and could compete with U extraction. However, as they are not abundant in the nature, the interference was studied for only one of the more abundant rare earth elements, lanthanum. It is to be expected that other rare earth elements should have a similar behavior. Furthermore, because of their abundance in nature, alkaline elements (e.g. Na^+, K^+, Li^+) were studied even though no impact on the complexing agent was expected. There was a chance that they could affect the clouding behavior or the micelle formation in solutions, thus impacting extraction efficiency.

Our results (Table 6) showed that even at high concentrations, alkaline elements had little impact during the extraction. In fact, the proposed system shows better resistance to high alkaline element concentrations than other cloud point extraction systems published. As well, alkaline metals can have a positive impact on the extraction through the salting out effect, as already demonstrated for extraction chromatography [48]. The tolerance of the CPE system was deemed acceptable when extraction efficiencies were above 90% of the original extraction efficiencies without the addition of the interfering ions. Maximal tolerable concentrations for various ions are presented in Table 6. The method was found to have a high resistance to alkaline metals and to halides. To enhance the tolerance to alkaline earth, nitrilotriacetic acid (NTA) was added to complex Mg, Ca, Sr, and Ba, to minimize their impact on our CPE system. An optimal NTA concentration of 1 mM was found to be best suited (results not shown) for the complexation of alkaline earth metals. The method was also found to be tolerant to the presence of ppm levels of BO_2^-. Although borate ions are not abundant in natural matrices, the tolerance of the system paves the way for the use of cloud point extraction with borate fusion of environmental samples, a strategy frequently used for the dissolution of refractory samples [49].

Table 6
Tolerance of the method to selected anions and cations.

Ion[b,c]	Concentration (mg/L)
Na^+, K^+	2000
Li^+	1100
Ba^{2+}, Sr^{2+}, Mg^{2+}	100[a]
Ca^{2+}	500[a]
Zn^{2+}	120[a]
Al^{3+}	15[a]
Fe^{3+},	24[a]
Pb^{2+}	10[a]
Ni^{2+}	10[a]
NO_3^-	4000
Cl^-	3000
CO_3^{2-}, PO_4^{3-}, Br^-, SO_4^{2-}	1000
BO_2^-	> 6500

[a] Solution spiked to 1 mM nitroacetic acid to complex alkaline earth metals and some transition metals.

[b] Cations were prepared using their chloride salts. Anions were prepared using their sodium salts.

[c] Tolerance of the method to anions and cations was assessed using analyte individually.

3.9. *Preconcentration/determination of uranium in drinking water and wastewaters*

The method developed was tested on natural source water and performances were assessed according to the phase partition of the uranium in natural samples (Table 7). Recovery was determined through a 225 ng L^{-1} spike of ^{233}U. Three bottled drinking water samples (Aquafina, Dasani, and Eska), two drinking water (EP-L-3 and EP-H-3), and one wastewater (EU-L-3) reference materials were used without dilution. Extraction efficiencies of over 98% were found for all samples tested and recoveries of over 95% of the ^{233}U were found in the SRP. This demonstrates that the determination of uranium in environmental matrices is possible when using the developed method. The method proposed performed surprisingly well with reference materials EP-H-3 and EU-L-3 even if the uranium concentration in these samples were above the linear range determined during the developmental stage of the methodology, which could be the result of interactions with complexing anions.

4. Conclusion

The proposed approach is a sensitive method for uranium preconcentration. It has low variation and leads to excellent extraction efficiencies. The method works in slightly acidic (pH=3.5) conditions, avoiding the interferences caused by the precipitation of transition metal hydroxides in the uranium extraction process. Cloud point extraction also has an edge over traditional solvent extraction because toxic solvents are replaced by minimal quantities of surfactant, leading to a high preconcentration factor.

Table 7
Determination of uranium in natural water and wastewater.

Source	Extraction efficiency (%)	Recovery (%)	Natural uranium found (ng/L)	Expected (tolerance interval)
Eska	99.08 ± 0.06	107 ± 3	N.D.	N.A.
Dasani	98 ± 1	98 ± 5	N.D.	N.A.
Aquafina	97.2 ± 0.4	99 ± 4	10 ± 4	N.A.
SCP EP-L-3	99.2 ± 0.2	95 ± 2	N.D.	N.A.
SCP EP-H-3	95.9 ± 0.9	104 ± 15	1,500,000 ± 200,000	1,500,000–2,340,000
SCP EU-L-3	98.6 ± 0.2	101 ± 17	11,600,000 ± 700,000	8,970,000–11,500,000

N.A.=not available; N.D.=not detected (below 3 ng/L)

The new CPE methodology is a significant improvement over existing approaches because extractions take place in more acidic and highly saline media; the previous CPE methods showing extractions at pH values higher than 7 and limited salinity. The cloud point extraction method could also be used with UV-visible spectroscopy or ICP-OES. Indeed, with the high preconcentration factor developed, the method could be coupled with ICP-OES to provide a rapid screening technique with a less expensive instrument. UV-visible spectroscopy could also be used after a ligand exchange step where H_2DEH[MDP] is displaced by another complexing agent active in UV–visible spectroscopy, like Sanaa et al. [25] proposed for D_2EHPA.

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