Spectrophotometric determination of trace amounts of uranium(VI) in water samples after mixed micelle-mediated extraction

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Abstract

A cloud point extraction process using mixed micelle of the cationic surfactant CTAB and non-ionic surfactant TritonX-114 to extract uranium(VI) from aqueous solutions was investigated. The method is based on the color reaction of uranium with pyrocatechol violet in the presence of potassium iodide in hexamethylenetetramine buffer media and mixed micelle-mediated extraction of complex. The optimal extraction and reaction conditions (e.g. surfactant concentration, reagent concentration, effect of time) were studied and the analytical characteristics of the method (e.g. limit of detection, linear range, preconcentration, and improvement factors) were obtained. Linearity was obeyed in the range of 0.20–10.00 ng mL\(^{-1}\) of uranium(VI) ion and the detection limit of the method is 0.06 ng mL\(^{-1}\). The interference effect of some anions and cations was also tested. The method was applied to the determination of uranium(VI) in tap water, waste-water and well water samples.

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1. Introduction

It is well known that uranium is toxic as well as being radioactive; the safety profiles for uranium compounds are well established [1,2]. Because uranium is a relatively mobile element in many surface or near-surface environments, its geochemical exploration methods require the measurement of the trace quantities of the metal ion in water samples [3,4], along with that in plants, soils, and rocks. The uranium concentration of seawaters is about 3.3 \(\mu\)g L\(^{-1}\) [4,5] in freshwater or even lower. Thus, highly sensitive methods are required for preconcentration and determination of uranium in water samples collected for prospecting purposes.

Several methods for determination of uranium based on the preconcentration techniques have been reported. Solid sorbents such as neutral polymer-Amberlite XAD series [6–8], silica [9], octadecyl silica membrane discs [10], activated silica gel [11], controlled pore glass [12], polyurethane foam [13] and cationic or anionic exchange resins [14–16] have been reported for the enrichment of uranium(VI) from dilute solutions prior to determination by a variety of analytical techniques.

To carry out the separation and preconcentration of the analyte, mixed micelle-mediated extraction (mixed-MME) system was used in this study. MME is becoming an important and practical application of the use of surfactants in analytical chemistry [17–19]. Such an extraction offers a convenient alternative to more conventional extraction systems. Cloud point (CP) phenomenon is generally observed in non-ionic surfactant micellar solutions when the temperature of the system is raised to a certain value. It was reported that the CP of Triton X-114 increased on adding small amounts of either cationic surfactant cetyl trimethylammonium bromide (CTAB) or anionic surfactant sodium dodecyl sulfate (SDS) [20]. Mixed surfactants of different charges in order to accomplish both ideal hydrophobic and non-ideal electrostatic interactions within the same extraction system. The use of cationic surfactants in combination with non-ionic surfactants has been documented with an increase in the extraction efficiency of polar organic compounds [21,22]. Moreover, the CP of a mixed solution of Triton X-114 and ionic surfactants decreased when small amounts of inorganic salts were added. The decreasing effect depended on the nature and concentration of the salt and salting out effect [23,24]. Mixed-MME was used...
to the preconcentration of organic compounds [23,25] and metal cations [26,27].

Although, there are several reports on the MME of uranium, to our knowledge, there is no report on the preconcentration of uranium using mixed-MME.

Pyrocatechol violet (PCV) or pyrocatechol sulfonaphthalein, a dye in the triphenylmethane series has been used for spectrophotometric determination of aluminum(III) and others [28,29]. The complexation of U(VI)–PCV–CTAB ternary complex has been studied [30]. The utility of pyrocatechol violet for spectrophotometric determination of uranium(VI) is reported rarely. The reaction of uranium(VI) with pyrocatechol violet in surfactant media has been studied [31]. This paper proposes a method to preconcentration and determination of uranium by spectrophotometry based on cloud point extraction (CPE) of the complex of uranium(VI) with pyrocatechol violet complex in mixed surfactant media.

2. Experimental

2.1. Apparatus

A Perkin-Elmer Lambda 45 UV/vis spectrometer was used for recording absorbance spectra. Absorption measurements at fixed wavelength were performed using a Shimadzu UV-mini-1240 V spectrophotometer with 1-cm quartz cell (0.5 mL). A Metrohm pH meter (model 713) with a combined glass electrode was used for pH measurements. A water bath with good temperature control and a centrifuge with 10-ml calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process.

2.2. Reagents

The surfactants, TritonX-114 and cethyl trimethylammonium bromide (CTAB) (obtained from Sigma company) were used without further purification. Stock solution of uranium(VI) was prepared by dissolving appropriate amount of uranium acetate salt in triply distilled water. Working standard solutions were obtained by appropriate dilution of the stock solution. A solution of 1.0 × 10^{-2} mol L^{-1} of pyrocatechol violet (PCV) (obtained from Merck) was prepared by dissolving appropriate amounts of this reagent in triply distilled water. The solution pH 6.8 ± 0.2 was adjusted with hexamethylene tetramine (HTM)/hydrochloric acid buffer. N,N-dimethyl formamide (DMF) solvent and potassium iodide salt were purchased from Merck.

2.3. Procedure

An aliquot of a uranium(VI) standard solution was transferred to a 10 mL centrifuge tube, 1.5 mL of the 1.0 × 10^{-3} mol L^{-1} PCV solution and 1 mL HTM buffer solution were added. This was followed by the addition of 1.5 mL of 1.0 × 10^{-3} mol L^{-1} surfactant CTAB solution, 1.0 mL of 0.2% (v/v) of TritonX-114 solution and 0.5 mL of 0.1 mol L^{-1} of KI solution. The solution was taken up to the mark with triply distilled water. Separation makes the solution turbid. Therefore the ternary complex of the neutral surfactant TritonX-114 and iodide ion and heating makes the solution turbid. Therefore the ternary complex U(VI)–PCV–CTAB can be extracted by CPE method. The absorption spectrum of the ternary complex in surfactant-rich phase shows a maximum absorbance at 690 nm. After separation of surfactant-rich phase, the absorbance was measured in 690 nm against a reagent blank as the reference (Fig. 1).

3. Results and discussion

Complex of uranium with PCV shows an absorption spectrum with maximum absorbance at 605 nm but in the presence of CTAB the ternary complex U(VI)–PCV–CTAB shows a red shift of the absorption maximum to 650 nm, with considerable increase in absorbance [31]. We observed that addition of the neutral surfactant TritonX-114 and iodide ion and heating makes the solution turbid. Therefore the ternary complex of U(VI)–PCV–CTAB can be extracted by CPE method. The absorption spectrum of the ternary complex in surfactant-rich phase shows a maximum absorbance at 690 nm. After separation of surfactant-rich phase, the absorbance was measured in 690 nm against a reagent blank as the reference (Fig. 1).

3.1. Optimization of the system

The effect of pH on the absorbance of the U(VI)–PCV–CTAB system at 600 nm in aqueous media was studied against the reagent blank. Maximum absorbance was obtained at pH 6.5–7.2. In more acidic or more alkaline solutions, absorbance decreased because of incomplete complex formation and hydrolysis of the complex. From this we concluded that the optimum pH to carry out all experiments ranged from 6.6 to 7.0.

Effect of CTAB concentration on the extraction and determination of uranium was investigated in the range 0.05–3.00 × 10^{-4} mol L^{-1}. The results are shown in Fig. 2. The amount of the absorbance for sample increased by increasing CTAB concentration up to 1.5 × 10^{-4} mol L^{-1} and remained nearly constant at higher concentrations. The blank signal also increased by increasing CTAB concentration. This is due to more extraction of PCV by increasing CTAB concentration, but the difference between the sample and blank sig-

![Fig. 1. Absorption spectra of (a) 1.5 × 10^{-4} mol L^{-1} PCV, (b) U(VI)–PCV–CTAB complex at pH 6.8 in the presence of: 5.00 ng mL^{-1} of uranium(VI), 1.5 × 10^{-3} mol L^{-1}, 1.5 × 10^{-4} mol L^{-1} PCV, CTAB, 0.2% Triton X-114, 5.0 × 10^{-3} mol L^{-1} KI in DMF media.](image)
nals (ΔA) increased by increasing CTAB concentration up to 1.50 × 10⁻⁴ mol L⁻¹ and decreased at higher concentrations. Therefore, 1.50 × 10⁻⁴ mol L⁻¹ CTAB was chosen as the optimum.

We observed that Triton X-114 concentration as a non-ionic surfactant can be affect the extraction of complex and sensitivity of the method, therefore the effect of Triton X-114 concentration on the absorbance of the extracted phase was investigated. The absorbance of the surfactant-rich phase increased by increasing Triton X-114 concentration between 0.02% and 0.5% (v/v) and remained nearly constant at higher concentrations. Therefore, 0.2% (v/v) Triton X-114 was used as optimum concentration.

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency [32]. Several inorganic salts, including NaCl, NaF, KNO₃, KBr and KI, was tested and KI was found as the best. It was observed that the addition of KI within the interval of 3.0 × 10⁻¹ to 1.5 × 10⁻² mol L⁻¹ had a good effect on the cloud point extraction efficiency, therefore 5.0 × 10⁻³ mol L⁻¹ KI was used.

Optimal incubation time and equilibration temperature are necessary to complete reaction, and to achieve easy phase separation and preconcentration as efficient as possible. The greatest analyte preconcentration factors are thus expected under conditions where the CPE is conducted using equilibration temperatures that are well above the cloud point temperature of the surfactant. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. It was found that a temperature of 60 °C is adequate for nearly complete recovery of uranium. The dependence of absorbance upon equilibration was studied within the range of 5–35 min. Times of 10 min were chosen as optimal times for equilibration and incubation.

In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same sense as in conventional separations of a precipitate from its original aqueous environment [33]. Therefore, a centrifugation time of 10 min at 3800 rpm was selected as optimum, since complete separation occurred for this time and no appreciable improvements were observed for long time.

Because the surfactant-rich phase was very viscous, DMF was added to the surfactant-rich phase after CPE to facilitate its transfer into spectrophotometric cell. The amount of 0.5 mL DMF was chosen to have an appropriate amount of sample for transferring and measuring the sample absorbance.

### 3.2. Analytical characteristics

Table 1 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, and limit of detection, reproducibility, and preconcentration and improvement factors. 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 graph, respectively), was 0.06 ng mL⁻¹. Because the amount

![Fig. 2. Effect of CTAB concentration on the absorbance in (a) sample solution, (b) blank solution, and (c) difference of them.](image-url)
of uranium in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of 0.7 mL (0.2 mL surfactant-rich phase + 0.5 mL DMF), the solution is concentrated by a factor of 14.3. The improvement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that the calibration graph in micellar media without preconcentration, was 286.

The relative standard deviation (R.S.D.) for five replicate measurements of 5.0 ng mL$^{-1}$ of uranium was 3.0%.

3.3. Interference study

The effect of different cations and anions on the determination of 5.00 ng mL$^{-1}$ uranium ion by the proposed method was studied. An ion was considered to be an interferent when it caused a variation greater than ±5% in the absorbance of the sample.

For the determination of 5.00 ng mL$^{-1}$ U(VI) by this method, the foreign ions can be tolerated at the levels given in Table 2. PCV forms stable complexes with various metal ions, including transition metal ions. Most of the cations and anions examined do not interfere with the extraction and determination of uranium, and many of them are tolerated at very high levels. However, some of the species tried such as Al$^{3+}$, Fe$^{3+}$, and Zr$^{4+}$ interfered on the determination of uranyl ion at 35–50 ng mL$^{-1}$ levels. The interfering effect of these ions was completely removed up to 500 ng mL$^{-1}$ in the presence of 0.5 mL of 0.1% of EDTA as a proper masking agent.

3.4. Application

The proposed method was applied successfully to the determination of uranium ion in tap water, well water, and waste-water samples. The results are shown in Table 3. The recoveries are close to 100% and indicate that the proposed method was helpful for the determination of uranium in the real samples.

4. Conclusion

The proposed procedure gives a simple, very sensitive and low-cost spectrophotometric procedure for determination of uranium ion that can be applied to water samples. The surfactant has been used for preconcentration of uranium in water, and thus toxic solvent extraction, has been avoided. A comparison of the proposed method with the previously reported methods for preconcentration and spectrophotometric determination of uranium (Table 4) indicates that the proposed method is faster and simpler than the existing methods and that it provides a lower limit of detection. To the best of our knowledge this is the first report in the mixed-MME of uranium.

References