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Spectrophotometric determination of uranium in water samples after cloud point extraction using nonionic surfactant Triton X-114

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Abstract

A cloud point extraction process using the nonionic surfactant Triton X-114 to extract uranium from aqueous solutions was investigated. The method is based on the complexation reaction of uranium with Arsenazo III and micelle-mediated extraction of the complex. The optimal extraction and reaction conditions (e.g., pH, reagent concentration, effect of time) were studied, and the analytical characteristics of the method (e.g., limit of detection, linear range) were obtained. Linearity was obeyed in the range of 1.0-150.0 ng mL^{-1} of U(IV) ion. The detection limit of the method was 0.3 ng mL^{-1} of uranium ion. The interference effect of some anions and cations was also tested. The method was applied to the determination of uranium in water samples.

Keywords: Uranium; Cloud point extraction; Spectrophotometric; Determination; Triton X-114.

1. Introduction

Uranium is important element in industry especially as energy sources. Many methods have already been developed for the determination of uranium. These days, the methods include inductively coupled plasma atomic emission spectrometry (ICP-AES) [1], inductively coupled plasma-mass spectrometry (ICP-MS) [2, 3], ion chromatography (IC) [4], capillary zone electrophoresis (CZE) [5], and flow injection analysis (FIA) [6]. However, because these instrumental analyses require rather expensive equipment and higher running costs, they offer limited availability. Spectrophotometry is a relatively easy alternative method, which has been applied to determination of uranium [7, 8]. Arsenazo III is one of the most widely used chromogenic reagents because of its high sensitivity for uranium [9, 10]. Usually a pre-concentration step has been needed for uranium determination in several environmental samples. A scheme of pre-concentration can thus be proposed mediated by surfactants instead of liquid-liquid extraction mediated by organic solvents.

Micellar extraction with nonionic surfactants at cloud point is a highly effective method for microcomponents preconcentration, which has been developed, intensively in recent years. The aqueous solutions of some nonionic surfactants exhibit cloud point or turbidity above a certain temperature. The temperature at which this phenomenon occurs is called cloud point temperature and the methodology is known as cloud point extraction [11, 12]. When solutions containing

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nonionic surfactants are heated above the clod point temperature, two phases are formed. The first one is a surfactant-rich phase containing high concentration of surfactant and the analyte, the other one is the aqueous phase containing low concentration of surfactant. The surfactant-rich phase containing the analyte is separated, diluted with small volume of a solvent and the analyte is determined by suitable techniques. Cloud point extraction procedure is an easy, safe rapid and inexpensive methodology which has been designed for the separation, purification and preconcentration of a variety of substances including metal ions and organic compounds [13-16].

This paper describes a novel, simple and sensitive cloud point extraction method for the determination of uranium in water samples. The method is based on the micelle-mediated extraction of the complex of U^{4+} with Arsenazo III. A nonionic surfactant, Triton X-114, was chosen as the extraction agent.

2. Experimental

2.1. Apparatus

A Hewlett-Packard 8453 diode array spectrometer controlled by a Hewllet-Packard computer and equipped with a 1-cm path length quartz cell. A Horiba M-12 pH meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 3.00 and 9.00. A centrifuge (Sigma 3K30) was used to accelerate the phase separation process. A thermostated bath maintained at the desired temperature was used for the cloud point temperature experiments.

2.2. Reagents

All reagents were of analytical reagent grade. The water utilized in all studies was double-distilled and deionized. Stock solution of uranium (1000 µg mL^{-1}) was prepared by dissolving appropriate amounts of their corresponding salts in deionized water. Triton X-114 (Merck) was used without further purification. Stock solution 4×10^{-4} mol L^{-1} of Arsenazo III was prepared by dissolving the reagent in acetone. Aqueous 5% (w/v) solution of Triton X-114 was prepared by dissolving 5 g in 100 mL of distilled water. A universal buffer solution (pH 1.5) was prepared according to Lurie [17].

2.3. Procedure

For the cloud point extraction, an aliquot of 50 mL of a solution containing uranium, Triton X-114 5% (w/v), Arsenazo III 4×10^{-4} mol L^{-1} and 5 mL of universal buffer (pH = 1.5), were kept for 25 min in the thermostatic bath at 40 °C. Subsequently, separation of the phases was achieved by centrifugation for 12 min at 4000 rpm. The phases were cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted by simply inverting the tube. The surfactant-rich phase in the tube was made up to 1.5 mL by adding DMF. The absorbance was measured at the wavelength of maximum absorbance of the complex, 543 nm.

2.4. Analysis of water samples

Prior to the preconcentration procedure, all the water samples were filtered through a 0.45 µm pore size membrane filter to remove suspended particulate matter and then were stored at 4 °C in the dark.

3. Results and discussion

Fig. 1 shows the absorption spectra for the individual metal complex in surfactant-rich phase against reagent blank. The uranium complex of Arsenazo III is rarely soluble in water but easily dissolved in micelles such as Triton X-114. Cloud point extraction conditions were studied and suitably adjusted as follows (Table 1).

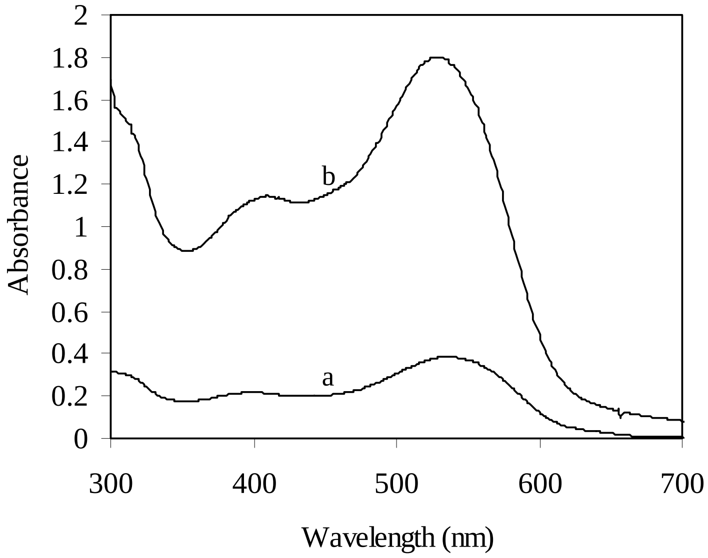

Fig. 1. Absorption spectra of (a) 0.16 mmol L^{-1} of Arsenazo III and (b) its complex with 110 ng mL^{-1} of uranium at pH 1.5 after clod point extraction.

Table 1
Optimum condition in determination of uranium by cloud point extraction

Parameter	Range study	Optimum
pH	1.0-4.5	1.5
$C_{\text{Arsenaso III}}$ (mM)	0.02-0.24	0.16 mM
C_{TX114} (%)	0.05-2.5	1.25 %
Temperature of bath (°C)	30-60	40 °C
Time of bath (min)	10-30	25 min
Time of centrifugation (min)	5-25	12 min

3.1. Effect of pH

The separation of uranium ion by cloud point method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase; thus obtaining the desired preconcentration. pH plays a unique role on metal-chelate formation and subsequent extraction. Fig. 2 shows the influence of pH on the absorbance of the uranium complex at 543 nm. As can be seen, at pH 1.5 maximum extractions efficiency was obtained. Hence, pH 1.5 was chosen as the working pH.

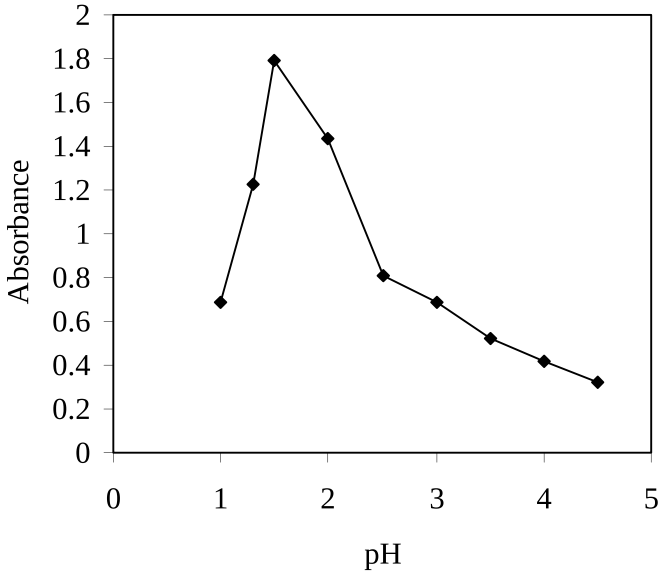

Fig. 2. Effect of pH on the absorbance of the complex. Conditions: 1.25% (w/v) Triton X-114, 0.16 mmol L^{-1} Arsenazo III and 110 ng mL^{-1} of uranium.

3.2. Effect of Arsenazo III concentration

The effect of concentration of Arsenazo III on analytical response is shown in Fig. 3. As it is seen for uranium complex, the signal increases up to a known concentration of Arsenazo III, reaching a plateau, which is considered as complete extraction. A concentration of 0.16 mmol L^{-1} of Arsenazo III was chosen as the optimum.

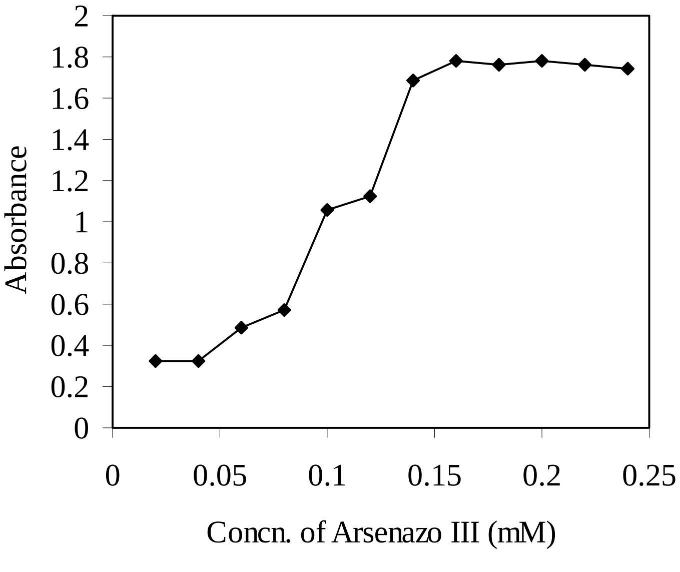

Fig. 3. Effect of Arsenazo III concentration on the absorbance of the complex. Conditions: 1.25% (w/v) Triton X-114 and 110 ng mL^{-1} of uranium at pH 1.5.

3.3. Effect of Triton X-114 concentration

The non-ionic surfactant Triton X-114 was chosen because of its commercial availability in a high purified homogenous form, low toxicological properties and cost. Also, the high density of the surfactant-rich phase, facilitates phase separation by centrifugation. Additionally the cloud point (~25-30 °C) of Triton X-114 permits its use in the extraction and/or pre-concentration of a large number of molecules and chelate. The variation of absorbance at λ_{max} of complex U(IV)-Arsenazo III as a function of the concentration of Triton X-114 is shown in Fig. 4. A concentration of 1.25% (w/v) was chosen as optimum concentration for the determination of uranium. At lower concentrations, the extraction efficiency of complex is low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively.

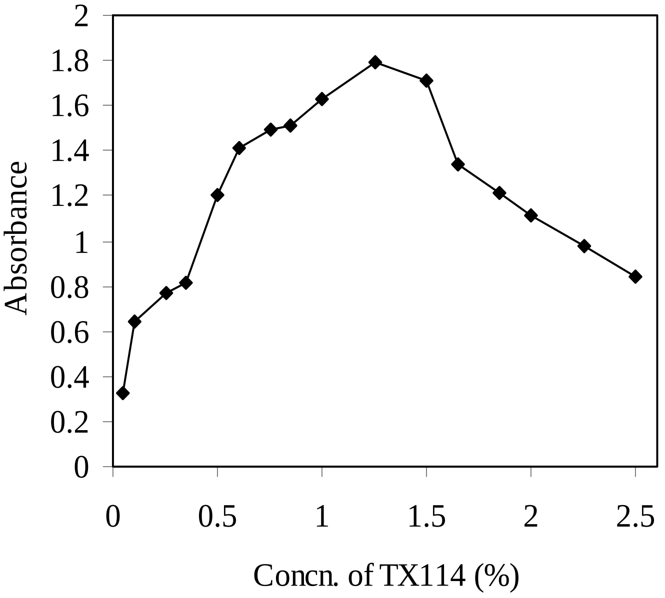

Fig. 4. Effect of Triton X-114 concentration on absorbance of the complex. Conditions: 0.16 mmol L^{-1} Arsenazo III and 110 ng mL^{-1} of uranium at pH 1.5.

3.4. Effect of the equilibrium temperature and time

It was desirable to employ the shortest equilibrium time and the lowest possible equilibrium temperature, as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction efficiency upon equilibrium temperature and time was studied over ranges of 30-60 °C and 10-30 min, respectively. The results showed that an equilibrium temperature of 40 °C and an equilibrium time of 25 min were adequate to achieve quantitative extraction.

3.5. Effect of centrifugation time

A centrifugation time of 12 min at 4000 rpm was selected as the optimum, since complete separation occurred at this time, and no considerable improvement was observed for longer periods of time.

3.6. Effects of added electrolyte

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. An increase in the ionic strength in the cloud point extraction does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant system, since it alters the density of the bulk aqueous phase [18]. It was observed that the addition of $NaNO_3$ within the interval of 0.1-1.0 mol L^{-1} had no significant effect on the cloud point extraction efficiency.

3.7. Selectivity studies

Arsenazo III is known to be fairly selective for uranium at pH 1.5, and only thorium can be extracted with uranium [19]. And interferences by thorium only affect the Arsenazo III concentration. The concentration of thorium is usually very low in most water samples and thus they have no interference in the extraction and determination uranium.

3.8. Analytical characteristics

Table 2, 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 the slope of calibration graph, respectively), was 0.3 ng mL^{-1}. Because the amount of uranium in 50 mL of sample solution is measured after preconcentration by cloud point extraction in a final volume of 1.5 mL (0.5 mL surfactant-rich phase and 1.0 mL DMF), the solution is concentrated by a factor of 33.3. The improvement factor defined as the ratio of the slope of the calibration graph for CPE method to that the calibration graph in Micellar media without preconcentration, was 375. The relative standard deviation (R.S.D.) for three replicate measurements of 10 ng mL^{-1} of uranium was 1.4%.

Table 2
Analytical features of the proposed method

Parameter	Result
Regression equation (n = 15) [a]	$\Delta A = 0.0146 \times C + 0.1293$, r = 0.9988 [b]
Linear range (ng mL^{-1})	10-150
Limit of detection (n = 5)	0.3 ng mL^{-1}
Repeatability (RSD, %) (n = 6)	1.23 (for 20 ng mL^{-1})
Maximum preconcentration factor	33.3

[a] Concentration of uranium in ng mL^{-1}
[b] Regression coefficient

3.9. Determination of uranium in water samples

In order to validate the proposed methodology, the developed procedure was applied to the determination of uranium in tap water, river water, and waste water samples. For this purpose, 10 mL of each of the samples were pre-concentrated with 1.25% (w/v) Triton X-114 and an Arsenazo III concentration of 0.16 mmol L^{-1}, following the proposed procedure. The results are shown in Table 3.

Table 3
Determination of uranium in water samples by proposed method.

Sample	Uranium added (ng mL^{-1})	Uranium found (ng mL^{-1})	Recovery (%)
Tap water	-	n.d. [a]	-
	10.0	9.7 ± 0.1 [b]	97.0
	20.0	19.8 ± 0.2	99.0
River water	-	n.d.	-
	20.0	20.6 ± 0.2	103.0
Waste water	-	n.d.	-
	50.0	50.6 ± 0.4	101.2
	100.0	101.4 ± 0.4	101.4

[a] No detected.
[b] mean ± S.D. (n=3).

4. Conclusion

The combined advantages of the cloud point methodology (easy, safe, rapid and inexpensive) and the use of Arsenazo III as a selective and sensitive chromogenic reagent for uranium was utilized for their determination in water samples. The method gives a very low limit of detection and good R.S.D. values. The results of this study clearly show the potential and versatility of this method, which could be applied to monitoring uranium spectrophotometrically in various water samples.

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