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Surfactant Enhanced-Spectrophotometric Determination of Uranium (VI) at Trace Levels by Using Eriochrome Black T as a Chelating Agent

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A sensitive and relatively selective spectrophotometric method is proposed for the rapid determination of uranium using Eriochrome Black T (EBT) being a 2,2'-dihydroxy azo benzene derivative metal indicator in the presence of cationic surfactant of N-cetyl N,N,N-trimethylammonium bromide (CTAB). The complex formation reaction between EBT and uranyl ion, UO_2^{2+} is instantaneous in presence of NH_3/NH_4Cl buffer at pH 9.5 and the absorbance as analytical signal remains stable for over 6 h. CTAB as cationic surfactant and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether, octyl phenol ethoxylate (Triton X-100) as nonionic surfactant are used for improving the sensitivity and solubility of the analytical system, respectively. The proposed method allows the determination of uranium in the concentration range of 0.025-2 μg mL^{-1} with a molar absorption coefficient of 92440.60 L mol^{-1} cm^{-1} and Sandell's sensitivity of 2.92 μg cm^{2-} in micellar medium while it allows the determination of uranium in the concentration range of 0.25-2.5 μg mL^{-1} with a molar absorption coefficient of 57019.44 L mol^{-1} cm^{-1} and Sandell's sensitivity of 4.74 μg cm^{2-} at 565 nm in water. The method has a detection limit of 4.60 μg L^{-1} (C_{DL}: $3S_b/m$) at an analytical measurement wavelength of 637 nm with a bathochromic shift of 72 nm. The selectivity of chelating reagent was improved by the use of a mixture containing ethylenediaminetetraacetic acid (EDTA), sulfosalycylic acid and NaF as masking agent The proposed method has been successfully applied to the determination of uranium at trace levels in different environmental water samples such as tap-water, natural spring-water and river-water. The precision (with coefficient of variation of 1.85%) and the accuracy obtained were highly satisfactory. In order to test the accuracy and validation of the method, the certified reference material (TMDA-70; fortified lake water sample) was also analyzed. It was found that the found and the certified values were in good agreement for validating the surfactant enhanced-spectrophotometric method.

Keywords: Surfactants, CTAB, EBT, bathochromic shift, spectrophotometry, uranium determination

INTRODUCTION

Uranium metal in its pure form is chemically active, anisotropic and has poor mechanical properties. On the other hand, uranium alloys are useful in diluting enriched uranium liquid fuel meant for nuclear reactors and pure uranium coated with silicon and canned in aluminum tubes are used in production reactors. However, uranium and its compounds, like lead are highly toxic which cause progressive or irreversible renal injury and in acute cases may lead to kidney failure and death. The tolerable daily intake of uranium established by WHO based on Gilman's studies is 0.6 μg/kg of body weight per day [1-3]. The WHO, Health Canada and Australian drinking water guidelines fixed the maximum uranium concentration in drinking waters to be less than 9, 20 and 20 μg L^{-1} [1,2]. The inhalation of uranium compounds results in deposition of uranium in lungs and reaches kidneys through blood stream.

A similar methodology was developed for trace levels determination of uranium in tap and river waters [4]. Uranium (VI) was complexed with 1-(2-pyridylazo)-2-naphtol (PAN) to form the hydrophobic species which were readily concentrated in the surfactant–rich phase of a non-ionic surfactant (Triton X-114). In all the experiments the solutions were buffered at pH 9.2 and the analytical signal was a function of the initial volume (V_i) of preconcentrated sample and the final volume (V_f) chosen for the measurement. For a V_i/V_f ratio of 50, the limit of detection was of 1.4 μg L^{-1}. The samples analyzed were uranium free and the recovery test was carried out only to show the reliability of the procedure developed.

Uranium may be determined spectrophotometrically using various complexing

agents after extraction of its complexes in some organic solvents [5-7]. These methods lack sensitivity and selectivity. Although atomic absorption spectroscopy [8,9], neutron activation analysis [10], X-ray fluorescence [11], ICP-AES and ICP-MS [12,13] may be applied for the determination of uranium in complex samples, these instruments are expensive, day to day maintenance is high and they are not free from various types of inherent interference [8-13]. Especially, atomic spectrometry methods have found little application for the determination of uranium mainly due to its high spectral background and the low sensitivity attainable due to the high thermal stability of uranium oxides [14,15].

The azo- and thiazolylazo-compounds have attracted much more attention in analytical applications as they are sensitive and selective chromogenic reagents in addition to being important complexing agents. They have been used for spectrophotometric and extractive-photometric and/or spectrophotometric determination of many metal ions. These dyes have been useful in the spectrophotometric determinations due to its good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesize and purify[16-18].

Eriochrome Black T (1-(1-hydroxy-2-naphtylazo)-6-nitro-2-naphtol-4-sulphonic acid, EBT) is a well-known colorimetric reagent, which is also called as a 2, 2'-bis-dihydroxy azo compound.

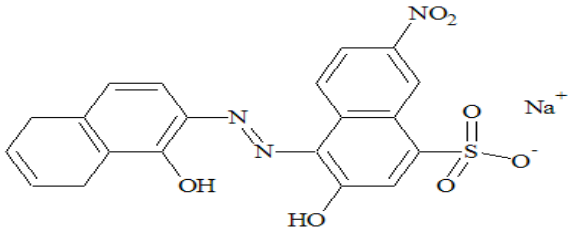

Figure 1: The structure of Eriochrome Black T.

This reagent, which is a metalochromic dye, is extensively used in chemical analysis, especially in the determination of hardness of waters. The reagent serves as active components in liquid-membrane electrodes, as equivalence point indicators in complexiметic titrimetry, and as ligands forming suitable complex species for the spectrophotometric and fluorometric determination of metal ions and anions [19-22]. However, it was not encountered that there is any study in literature regarding the determination of U(VI) at trace levels based on complex formation with EBT by means of spectrophotometric or surfactant modified-spectrophotometric method.

Due to being low of this element concentration for their simple and easy spectrophotometric determination in various biological and industrial samples an aggregation and solubilization is required, that can be achieved using surfactants [23]. Surfactant and/or micellar systems are convenient to use because they are optically transparent, readily available and stable [24]. In the field of metal ion complexation, at concentrations below or above the critical micelles concentration (CMC), micelles form a ternary complex with advantageous properties, such as hyperchromic and bathochromic displacements, that can be modify sensitivity of the method by affecting the interferences and matrix effects [25]. The ability of micellar system to solubilize slightly insoluble or even very insoluble complexes and/or ligands has been used to enhance the analytical merit of given methods [26-28]. The ability of micelles to solubilize metal-complexes in aqueous solution can eliminate the need for non-aqueous extraction step in a given analysis [26,29,30], which reduces the cost and toxicity of the method. Since organic ions and molecules can bind the surfactant assemblies by electrostatic and hydrophobic interaction, therefore the methods based on surfactants, lead to modification and improving sensitivity, which emerged from the fact that non-polar part of solute molecules has a strong interaction with the exposed hydrocarbon chains of the surfactant and lead to improvement in method characteristics performance. There are also several new studies concerning the use of surfactants in analytical aspect. They are based upon the surfactant effect on kinetic of reaction of some sulphonamides with p-dimethylaminobenzaldehyde [31], colorimetric microdetermination of bromhexine drug in aqueous solution [32] and micellar catalysis in reactions of some β-lactam antibiotics with p-dimethylaminobenzaldehyde, respectively [33].

In this study, a simple, sensitive, relatively selective, accurate and precise method for the determination of U(VI) in different water samples by spectrophotometry is described based on the formation of the U(VI)-EBT complex in the mixed surfactant medium. In order to improve the sensitivity and solubility of analytical system, CTAB as cationic surfactant and TritonX-100 as nonionic surfactant were used, respectively. The method was applied to the determination of uranium in real water samples. The results were evaluated by adding standard U(VI) solutions at known amounts into the samples under the

optimal conditions and it was concluded that the results found by using the purposed method was at acceptable recovery levels.

EXPERIMENTAL

Reagents and Solutions

All reagents used were of analytical grade and the doubly-distilled water was used throughout analysis.

Stock U(VI) solution of 1 mM was prepared by dissolving 0.1255 g $UO_2(NO_3)_2$ x $6H_2O$ (Merck) in water and diluting to volume with water in a 250 mL volumetric flask. The working solution of 0.1 mM was prepared by diluting the stock solution with water at 1:10 ratio.

EBT solution of 0.5% (w/v) (0.0108 M) was prepared by dissolving 0.5 g of indicator dye (Merck) in 100 mL of ethanol-water mixture (80+20, v/v).

Masking agent solution was prepared by suspending 5 g ethylenediaminetetraacetic acid sodium salt (NaEDTA, Merck), 0.5 g NaF (Merck) and 13 g sulfosalicylic acid (Sigma) in 50 mL of water, neutralizing to pH 9.5 with sodium hydroxide and diluting 100 mL.

CTAB solution of 0.5% (w/v) (13.2 mM) was prepared by dissolving 0.5 g of cationic surfactant, mixing properly and diluting in 100 mL of water.

Triton X-100 solution of 0.5% (v/v) (8.40 mM) was prepared by dissolving 0.5 mL of nonionic surfactant, mixing properly and diluting in 100 mL of water.

Sodium dodecyl sulphate (SDS) solution of 0.5% (w/v) (17 mM) was prepared by dissolving 0.5 g of anionic surfactant mixing properly and diluting in 100 mL of water. All of the surfactants were used without further purification.

NH_3/NH_4Cl buffer solution of 0.25 M, pH 9.5 was prepared by dissolving 0.4815 g solid NH_4Cl in approximately 50 mL of water, mixing with 4.95 ml conc. NH_3 solution and diluting to 100 mL with water.

Instrumentation

A Shimadzu Model UV-Visible 160 spectrophotometer equipped with a 1 cm quartz cell was used for absorbance measurements. This spectrophotometer has a wavelength accuracy of ±0.2 nm and a bandwidth of 2 nm in the wavelength range of 190–1100 nm. A Grant LTG-6G model thermostatic water bath with good temperature control was used. A stopwatch was used for recording the reaction time. A pH meter consisting of a glass-calomel electrode double with an accuracy of ±0.1 pH unit was used to determine pH values of solutions. Two standard buffer solutions of pH 7±0.01 and pH 4±0.01 were used for the calibration of pH meter. All solutions were preheated to a working temperature of 25±0.1°C before the initiation of the complex formation reaction in surfactant medium. The absorbance measurements were made at a working wavelength of 637 nm.

General procedure

Into a 10 mL standard flask, transfer a portion of the solution containing uranyl ion, U(VI) in the concentration range of 0.025–2 μg mL^{-1}, 1-2 mL of masking agent solution, 0.85 mL of 0.0108 M EBT solution, 0.6 mL of 13.2 mM CTAB solution, 0.5 mL of 8.40 mM Triton X–100 solution and 2 mL 0.25 M pH 9.5 NH_3/NH_4Cl buffer solutions. Dilute to the mark with bidistilled water and measure the absorbance at a fixed wavelength of 637 nm in a 1-cm quartz cell, against a reagent blank prepared in the similar way but without uranium.

RESULTS AND DISCUSSION

Spectral characteristics of U(VI)-EBT complex

Investigations on the effect of various surfactants on the absorbance of U(VI)-EBT complex were carried out. The surfactants used were CTAB as cationic surfactant, SDS as anionic surfactant and TritonX-100 as nonionic surfactant. The study was performed using uranium at known amounts in the optimum conditions. The absorbance values and corresponding molar absorptivities at absorption maxima of uranium complexes in these media are given in Table 1.

Table 1: Influences of some surfactants on the absorbance of U(VI)-EBT complex (Optimum conditions: 2 mL 0.25 M pH 9.5 NH3/NH4Cl buffer solution, 0.4 mL 0.75 mM Surfactant, 0.75 mL 0.0108 M EBT and 1.25 mL 10 μg mL–1 UO22+ ion).

Surfactant	Nature of surfactant	λ_{max} (nm)	$\Delta\lambda_{max}$** (nm)	Absorbance	ε_{max} (L mol^{-1} cm^{-1})	Stability (hour)
In water	-	565	-	0.264	57019.44	1
SDS	Anionic	572	7	0.317	68466.52	-
CTAB*	Cationic	637	72	0.428	92440.60	6
Triton X-100	Nonionic	581 and	16 and	0.275	59395.25	-

* The best surfactant increasing its sensitivity and selectivity according to those of complex in aqueous solution.
** It shows that the absorption maximum of the metal-complex shifted to longer wavelength.

As can be seen from Table 1, for same concentration CTAB media, spectra with high sensitivity and red shift could be constructed and its slope was about two times more than in the absence of it, whereas the anionic surfactant, SDS with a red shift of 7 nm also showed positive effect or increased it. This suggests that U(VI)-EBT complex was dissolved in surfactant phase due to both forming ion-pairing complex with CTAB and the hydrophobic interaction of metal chelate. Therefore, CTAB in presence of Triton X-100 was selected to improve the analytical performance of the present study. However, SDS was not considered for further studies. The maximum increase in the absorbance of the complexes occurred only in the presence of CTAB. The cationic surfactant, CTAB was used as a micellar forming surfactant throughout this work. The U(VI) ions and EBT form a red complex with an absorption maximum in micellar medium at 637 nm. The reaction between EBT and U(VI) is rapid and the metal complex formed is stable for at least 6 h. The use of CTAB as cationic surfactant leads to a maximum increase in the absorbance signal and as a result the analytical determination sensitivity is also increased. Addition of CTAB was accompanied by a bathochromic shift of the absorbance of the U(VI)-EBT complex and an increase in its molar absorptivities; 72 nm was selected as the wavelength to be measured. In the presence of CTAB, the U(VI)-EBT complex has a low solubility in water, which can be overcome by adding TritonX-100 as nonionic surfactant. Reagent blank was used thereafter as a reference because it showed absorption at this wavelength.

Effect of the pH

The effect of pH on the formation of the U(VI)-EBT complex in presence of CTAB was examined at 637 nm by using 0.1 M NaOH and 0.1 M HCl solutions and adjusting a suitable pH value with a pH meter in the pH range of 6.0-11.0, provided that the dilution factor from changing the pH of the solution is considered. The maximum absorbance was obtained at pH 9.5. The results are given in Figure 1.

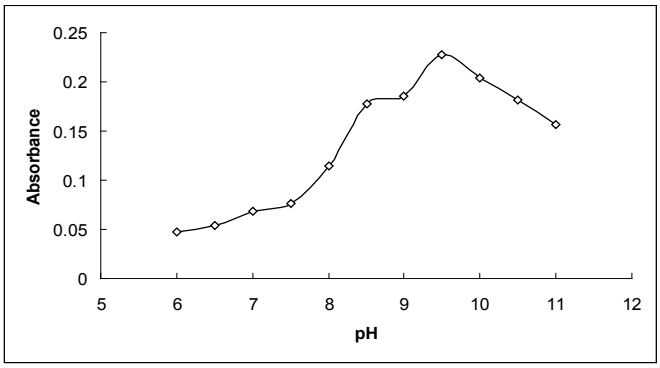

Figure 1: The effect of pH on the absorbance of U(VI)-EBT complex in the presence of cationic surfactant CTAB at 637 nm.

The U(VI)-EBT-CTAB ternary complex begins to form at approximately pH 6.0, with maximal and constant absorbance being reached at pH 9.5. At higher pH values, a precipitation and turbidity was formed under experimental conditions. In order to remain constant the pH of media at pH 9.5, the various buffer solutions such as ammonium acetate, ethanolamine-$HClO_4$, phosphate and borate buffer solutions at same concentrations were used and the most stable and highest sensitivity was obtained in presence of NH_3/NH_4Cl buffer pair. In the light of these findings, all subsequent studies were carried out at pH 9.5 using NH_3/NH_4Cl buffer. The effect of the buffer concentration on the U(VI)-EBT complex was studied within buffer concentration range from 0.05 to 0.35 M and according to the obtained results, a maximum increase was observed in the absorbance signal in the buffer concentration of 0.25 M. Thus, a concentration of 0.25 M was chosen for the further procedure (Figure 2).

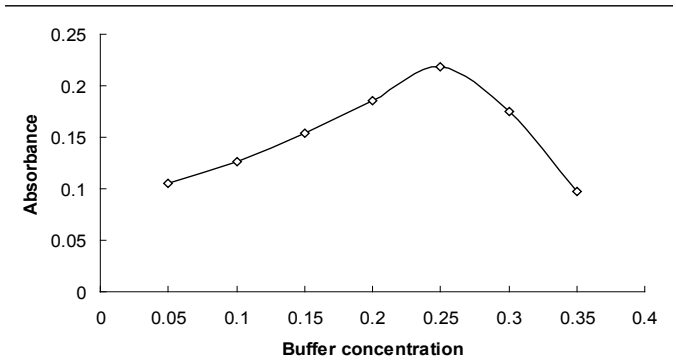

Figure 2: The effect of buffer concentration on the absorbance of U(VI)-EBT complex in the presence of cationic surfactant CTAB at 637 nm.

Effect of the chelating reagent concentration

The effect of EBT amount on U(VI)-EBT

complex formation in the range of 0.092-2.303 mM was studied both in water and cationic surfactant medium at optimum pH value. It was found that the absorbance signal also increased linearly with increasing EBT concentration in both reaction media in the concentration range of 0.553-1.843 mM. It can clearly be seen that the absorbance change is higher for the same reagent concentration in the cationic surfactant medium. A maximum, constant and stable absorbance value was obtained at least with ten fold-excess reagent concentrations from those of uranium in presence of CTAB. When CTAB/U(VI) concentration ratio is at least 5 fold, the maximum reproducible absorbance values were obtained with an EBT/U(VI) ratio of 10. In fact, higher CTAB/U(VI) concentration ratios didn't lead to a considerable decrease in absorbance as an opposition to other many micellar system. However, since the results are well-matched at this concentration level, a reagent concentration of 0.921 mM (approximately 1 mM reagent) was used as optimum for further studies.

Effect of nature and amount of surfactant

The desired complex and ligand has good water solubility in alkaline media, but the sensitivity of its complex in the absence of surfactants is low. In order to improve the sensitivity and selectivity of complex formation reaction, the effect of type and concentration of different surfactants on the reaction were examined. To ensure the effect of the types of surfactants, TritonX-100 as nonionic surfactant, SDS as anionic surfactant and CTAB as cationic surfactant on the absorbance of complex were studied. The effect of SDS concentration on the determination of uranium was not considered in the further studies due to giving a low analytical signal. The effect of CTAB concentration on the determination of uranium was studied in the concentration range of 0.264-1.98 mM. The results are shown in Figure 4.

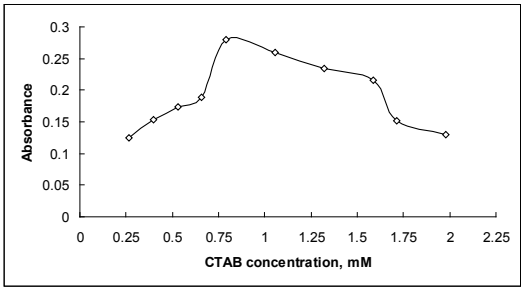

Figure 4: The effect of CTAB concentration the absorbance of U(VI)-EBT complex at pH 9.5 at 637 nm.

The absorbance has increased with increasing CTAB concentration up to approximately the range of 0.8-1.0 mM and has decreased at higher concentrations. However, the blank absorbance signal has also increased with increasing CTAB concentration. This is due to more much aggregation of EBT with increasing CTAB concentration. However, the difference between the absorbance signals with and without uranium increased with increasing CTAB concentration up to 0.792 mM, and decreased at higher concentrations. Therefore, the CTAB concentration of 0.792 mM was chosen as optimum value for the further study (Figure 4).

In order to stabilize the colored ternary complex formed and to increase the sensitivity, the effect of Triton X-100 concentration on the determination of uranium was studied in the concentration range of 0.084-0.84 mM. Results are shown in Figure 5.

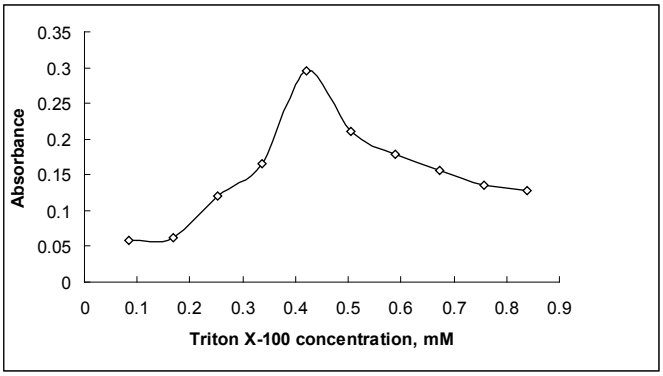

Figure 5: The effect of Triton X–100 concentration on the absorbance of U(VI)-EBT complex in the presence of CTAB at pH 9.5 at 637 nm.

As can be seen in Figure 5, the results showed that Triton X-100 must be present in analytical system in a minimum concentration of 0.42 mM in order to avoid precipitation and turbidity. When this surfactant is present in the concentration range of 0.4-0.5 mM, a pronounced increase of 0.015 in the absorbance signal was observed in presence of CTAB except for stability of the metal-complex. Thus, the concentration of 0.42 mM was chosen as optimum value for the procedure. Additionally, we have measured the CMC of CTAB in our research lab at 25°C and at the pH values of 4, 6 (natural pH), 9 and 11 and obtained the decreasing values of 0.974, 0.891, 0.867 and 0.738 mM respectively. At 25°C and buffered solution to pH 9.50, the effect of Triton X-100 on the CMC of CTAB was investigated in the absence and presence of 0.5 mM Triton X-100. It

has found that Triton X-100 at fixed concentration leads to a decrease of 0.028 in CMC of CTAB (ΔC_{CMC}: 0.845-0.817).

Effect of the order of addition of the reagents on the complex formation

The absorbance of U(VI)-EBT-CTAB ternary complex was a little dependent of the order of mixing the reactant components. The best sequence was uranyl cation, UO_2^{2+} being determined, chelating reagent EBT, pH 9.5 NH_3/NH_4Cl buffers, cationic surfactant CTAB as enhancing sensitivity and TritonX-100 as improving the solubility of ternary U(VI)-EBT-CTAB complex. When the other sequences were investigated, compared with the above-sequence, they had given the lower absorbance signals.

Composition of U(VI)-EBT complex

To study the composition of U(VI)-EBT-CTAB ternary complex, the molar ratio of U(VI) and EBT in U(VI)-EBT complex with and without CTAB was measured. The results are shown in Figure 6(a) and (b).

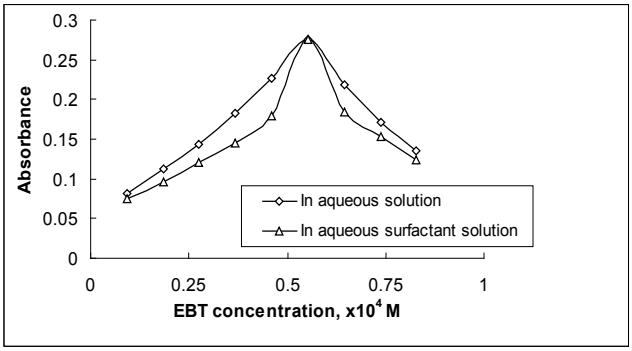

Figure 6 (a): The determination of composition of U(VI)-EBT complex in aqueous solution and surfactant medium at 565 nm and 637 nm at pH 9.5 by using Job's method, respectively.

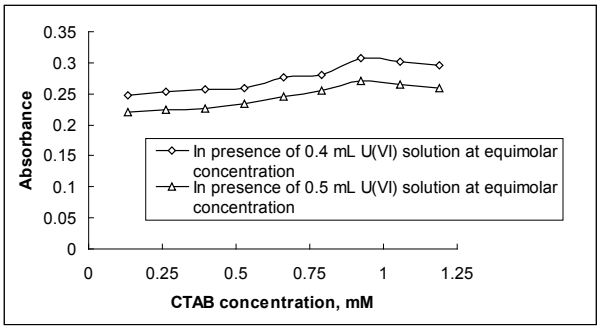

Figure 6 (b): The determination of composition of U(VI)-EBT-CTAB ternary complex in presence of CTAB at 637 nm at pH 9.5 by using Job's method

The molar ratio of U(VI) and EBT in the U(VI)-EBT complex was determined by using Job's method, which is also called as the continuous variation method [34] with measurement of the absorbance of each solution containing a different volume fraction of U(VI) and EBT of the same concentration. The molar composition of U (VI) to EBT was 1:2 in both the absence of CTAB and in the presence of CTAB. The stochiometric mole ratio of U(VI) to EBT of the U(VI)-EBT complex remained constant without a pronounced change in surfactant and/or premicellar medium. The molar ratio of U(VI) to CTAB in the U(VI)-EBT-CTAB complex was determined by means of the Job's method. It appeared that the molar ratio of U(VI) and CTAB in the ternary complex of U(VI)-EBT-CTAB was 1:2. As a result, a binary U(VI)-EBT complex/CTAB at 1:2 mole ratio was found. The positive charge of the cationic surfactant would attract the negatively charged complex or mixed ligand complex forming 1:2 (mole ratio) complex of CTAB and U(VI)-EBT. Thus, it could be concluded that the ternary complex was a U(VI)-EBT-CTAB complex having 1:2:2 mole ratio.

Effect of the reaction temperature and time

In order to make a surfactant-sensitized spectrophotometric measurement in a fast and easy way and to fulfill the complex formation reaction, the equilibrium temperature and time must be optimized. The dependency of the absorbance on equilibrium temperature was studied in the temperature range of 20-60°C, and it was found that the absorbance signal remained a maximum and constant value in the temperature range of 25-45°C. At the higher temperatures, it was observed that the absorbance distinctly decreased. Therefore, a temperature of 25°C was chosen as optimum value due to convenience of operation. Also, the dependency of absorbance on equilibrium time was studied in the time range of 0.5-30 min and it was found that the complex formation equilibrium or the color development of the complex is complete in approximately 10 min and the color is stable for at least 6 h in terms of good reproducibility of absorbance. An equilibrium time of 10 min was chosen as an optimum value for complex formation equilibrium.

Effect of interfering ions

EBT is not highly a selective reagent for the

spectrophotometric determination of uranium at trace levels. However, in order to mask the interfering ions, the use of a masking agent solution containing EDTA, sulfosalicylic acid and NaF highly increases the selectivity of reaction. Each of compositions of this masking solution independently leads to a change of ±%5 in absorbance when adding 1-2 mL masking solution for a final volume of 10 mL. A similar mixture was used previously in the uranium determination with TAR [18], PAR [35], PADAP [36] and Br-PADAP [37].

To study the effect of potential interfering metal cations on the determination of uranyl ion, UO_2^{2+} at optimum conditions, a series of solution containing both interfering cations and uranyl ion was treated according to the general method. The selectivity of the reaction was investigated by determining 0.5 μg mL^{-1} of uranium in the presence of interfering ions at different concentrations using the mixed EDTA, NaF and sulfosalysilic acid masking agent solution. The tolerance limit was accepted as a change of ±5.0 % in absorbance value in which the uranyl ion solution of 0.5 μg mL^{-1} gives at optimum conditions. It is clear that the best serious interference is insoluble metal hydroxide salts in higher alkaline pH values from 9.5 and metal cations which have formed the stable complexes with reagent. It was found that for these concentrations, NH_4^+, Na^+, Li^+, K^+, Ce^{3+}, Mn^{2+}, Hg^{2+}, Ag^+, Zn^{2+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Mg^{2+} and Cu^{2+} did not interfere, but Ni^{2+}, Bi^{3+}, Cr^{3+}, Al^{3+}, Fe^{3+}, Zr^{4+}, especially lanthanide-actinide serial elements such as Th^{4+} and La^{3+} ions caused a serious interference. The tolerable limits for these interfering species are given in Table 2 in both the presence and absence of masking agents.

Table 2: Tolerance limits of possible interfering ions in the surfactant-sensitized spectrophotometric determination of 0.5 μg mL–1 Uranyl ions in the optimum conditions.

Interfering ion	Tolerance ratio ([Interfering ion] / [U(VI)])
NH_4^+, Na^+, Li^+ and K^+	1000
Ce^{3+}, Mn^{2+}, Hg^{2+} and Ag^+	600
Zn^{2+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Mg^{2+} and Cu^{2+}	500
Ni^{2+}, Bi^{3+}, Th^{4+} and Zr^{4+}	7 (100)[a]
Cr^{3+}, Al^{3+}, Fe^{3+} and La^{3+}	10 (100)[a]
SO_4^{2-}, F^-, Br^-, I^-, HCO_3^- and Cl^-	7500
NO_3^-, CH_3COO^- and HPO_4^{2-}	12000

a After the addition of 1-2 mL masking agent solution

Also, it was found that Cl^-, Br^-, SO_4^{2-}, NO_2^-, NO_3^-, HCO_3^-, HPO_4^{2}, CH_3COO^- and F^- ions as anionic interfering species did not interfere in the determination of 0.5 μg mL^{-1} U(VI) in both the aqueous solution and surfactant medium.

Analytical characteristics and its applicability of the method into real samples

The calibration graph was constructed in the above-mentioned optimum conditions. The calibration curve was made as described in the experimental procedure and a good correlation coefficient (R^2: 0.9956) was found by using a EBT/U(VI) concentration ratio of 5.5. At the lower and higher EBT/U(VI) concentration ratios, the correlation coefficient (R^2) distinctly decreased. The results are shown in Figure 7.

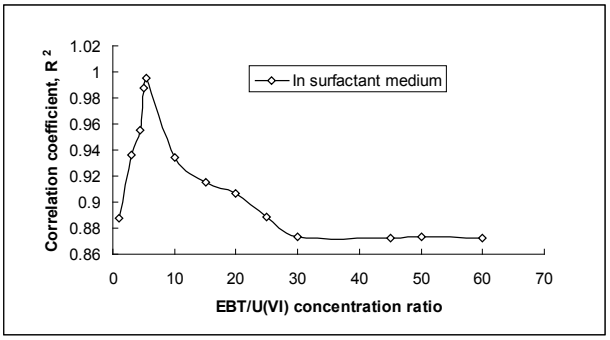

Figure 7: The change of the correlation coefficient (R2) with EBT/U(VI) concentration ratio in the construction of calibration curve in cationic surfactant medium at 637 nm at pH 9.5.

In the proposed method, Beer's law is obeyed from 0.025 to 2 μg mL^{-1}, with a detection limit of 4.60 μg L^{-1} and with a coefficient of variation of 1.80 % (for ten repetitive measurements at a confidence level of 95%). The molar absorption coefficient and Sandell's sensitivity as a measure of the method sensitivity was also calculated and a molar absorption coefficient of 92440.60 L $mol^{-1}cm^{-1}$and Sandell's sensitivity of 2.92 μg cm^{2-} were obtained in the concentration range of 0.025–2 μg mL^{-1} in the presence of CTAB at 637 nm while a molar absorption coefficient of 57019.44 L $mol^{-1}cm^{-1}$ and Sandell's sensitivity of 4.74 μg cm^{2-} are obtained in the concentration range of 0.25–2.5 μg mL^{-1} in the absence of CTAB at 565 nm.

In order to both demonstrate and control the applicability and also accuracy of the proposed surfactant-enhanced spectrophotometric method for the determination of U(VI) in aqueous samples, different matrixes were studied. At first, each sample

was analyzed in optimal conditions with and/or without masking agent solution after passing through the acetate cellulose filter to remove their particulates and then bringing their pH values to 9.5. The results showed that concentration of the analyte was lower than the limit of detections of our method. Then, for studying the matrix effect on the surfactant sensitized-analytical signal, the samples were spiked at 0.5, 1.0 and 1.5 μg mL^{-1} concentration levels of the analyte. Finally, for the spiked samples, the calibration curve was plotted against the aqueous standards submitted to the surfactant mediated spectrophotometric procedure. The summarized results in Table 3 are the average of three replicate measurements.

Table 3: Determination of uranium, U(VI) in three different water samples and synthetic mixture by using the proposed surfactant-sensitized spectrophotometric method.

Sample	Added U(VI), μg mL^{-1}	Found U(VI), μg mL^{-1}	RSD %	Recovery %
Tap-water[1]	-	nd[a]	-	-
	0.5	0.48±0.013[b]	2.71	96.00
	1.0	0.98±0.012	1.22	98.00
	1.5	1.50±0.010	0.67	100.00
Natural spring water[2]	-	nd[a]	-	-
	0.5	0.48±0.015	3.13	96.00
	1.0	0.98±0.013	1.33	98.00
	1.5	1.49±0.011	0.74	99.33
River water[3]	-	nd[a]	-	-
	0.5	0.47±0.014	2.98	94.00
	1.0	0.98±0.012	1.22	98.00
	1.5	1.51±0.010	0.66	100.67
Synthetic mixture[4]	1.5	1.48±0.012	0.81	98.67

a Below the method detection limit
b Mean of three replicates ±standard deviation (SD)
1 Tap water sample was collected from any tap coupled to City network drinking water (Sivas, Turkey)
2 Natural cold spring water sample was collected directly from the pool used with healthy purpose (Sivas, Turkey)
3 River water sample was collected from Kızılırmak River (Sivas, Turkey)
4 Synthetic mixture contains: 2 μg mL-1 of Uranyl ion with Na+, NH4+ (50 μg mL-1), Zn2+, Cu2+, Ca2+, Mg2+ (25 μg mL-1), Al3+, Fe3+ (0.5 μg mL-1), Ni2+, Th4+, Zr4+ (0.35 μg mL-1)

As can be seen in Table 3, there is a good agreement between the obtained results and the known values, indicating the successful applicability of this method for the determination of uranium (VI) in aqueous samples containing different interfering matrix components. Also, the accuracy of proposed method was tested by performing recovery experiments for a synthetically prepared mixture. The attractive feature of the method is its relative freedom from other metal ions present in the synthetic mixture sample. Although the recoveries are partly low, they are between quantitative acceptable limits. It can clearly be seen that the proposed method is useful for the determination of uranium in environmental water samples in analytical point of view.

Validation and analytical application of the surfactant enhanced-spectrophotometric method

In order to destruct the natural organic chelating species and the possible anionic uranyl carbonate complexes such as $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ existing in natural seawater, the sample was treated with HNO_3 solution after adjusting to a pH value of 3.0 and heated until the they completely were degraded. After cooling, filtrating and buffering to pH 9.50 with NH_3/NH_4Cl buffer solution, the accuracy of the proposed method was tested by performing recovery experiments through the standard addition method under optimum conditions. The recovery was evaluated either by dividing the intercept by the slope value of the line of linear regression of the standard addition method or by the extrapolation of the same line of best fit (Table 4). It is evident from Table 4 that the linearity of the regression line of the standard addition method was good. The uranium content of seawater sample was approximately near to the detection limit of surfactant enhanced spectrophotometric method. In order to test both the accuracy and validation of the method, the certified reference material (TMDA 70; fortified lake water sample) was analyzed, and the recovery studies were performed in which the analyte was added to the seawater sample at known amounts. The uranyl (VI) ions were added to seawater samples at concentrations of 5.0, 10.0 and 15.0 μg L^{-1}. The results of the analysis are given in Table 4.

Table 4: Results for tests of standard addition and recovery for uranium determinations in a seawater sample from Black Sea (for five replicate measurements).

Sample	Added, μg L^{-1}	Seawater from Black Sea	
		Found, μg L^{-1}	Recovery %
U(VI)	0	4.15±0.35	-
	5.0	9.32±0.30	103.4±2.5
	10.0	14.30±0.30	101.5±2.1
	15.0	19.40±0.25	101.7 ±1.5

A good agreement was obtained between the added and the found analyte contents. While the recovery values for the uranyl ion were 103.4, 101.5 and 101.7%, the relative standard deviation values for the samples were 5.80, 2.96 and 1.64%, respectively. Analyzing the CRM (included 55.8±0.8 μg L^{-1}) for the U(VI) ion gave a result of 53.8±1.3 μg L^{-1} with a relative error of -3.58% (n: 5, at 95% confidence interval). The found and the certified values were in good agreement for validating the surfactant enhanced-spectrophotometric method.

CONCLUSIONS

The use of surfactant/premicellar systems around CMC as an alternative to other methods of separation and preconcentration offers several advantages including experimental convenience, safety and being an inexpensive method. Further, in comparison to solvent extraction methods, it is much safer, since only a small amount of the surfactant, which has a low toxicity, is used. In the present study, we investigated the application of the surfactant-sensitized spectrophotometric method for the determination of U(VI) at trace levels. This method gives low limit of detection as well as good relative standard deviation, RSD and linearity for the uranyl ion as analyte. The method was verified by determination of the analyte concentration in the real samples and the satisfactory results were obtained. Our experimental findings showed that it is possible to obtain a better limit of detection in surfactant medium according to the limit of detection in aqueous medium. In order to evaluate the accuracy and validation of the proposed surfactant sensitized spectrophotometric method, the certified reference material (TMDA-70; fortified lake water sample) was also analyzed. It was found that the found and the certified values were in good agreement for validating the surfactant enhanced-spectrophotometric method. The comparison of the method with the spectrophotometric methods reported in literature has shown that the proposed surfactant-sensitized spectrophotometric method is a simple and rapid method as much as the present methods and gives a detection limit at a comparable size (Table.5). Also, the obtained detection limit is better than those obtained by some presented spectrophotometric methods [38,39,42,43] and higher than WHO and Health Canada and Australian drinking water quide-line levels [1-3]. So, the proposed method is very convenient for the direct determination of the concentration of uranium in environmental real water samples and can be used as a routine method for the environmental evaluation and analysis even in a small laboratory or firm.

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