



Development of an extractive spectrophotometric method for estimation of uranium in ore leach solutions using 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester (PC88A) and tri-*n*-octyl phosphine oxide (TOPO) mixture as extractant and 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol (Br-PADAP) as chromophore

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ABSTRACT

An extractive spectrophotometric analytical method has been developed for the determination of uranium in ore leach solution. This technique is based on the selective extraction of uranium from multi-element system using a synergistic mixture of 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester (PC88A) and tri-*n*-octyl phosphine oxide (TOPO) in cyclohexane and color development from the organic phase aliquot using 2-(5-Bromo-2-pyridylazo)-5-diethyl aminophenol (Br-PADAP) as chromogenic reagent. The absorption maximum (λ_{\max}) for UO_2^{2+} -Br-PADAP complex in organic phase samples, in 64% (v/v) ethanol containing buffer solution (pH 7.8) and 1,2-cyclohexylenedinitrotetraacetic acid (CyDTA) complexing agent, has been found to be at 576 nm (molar extinction coefficient, ϵ : $36,750 \pm 240 \text{ L mol}^{-1} \text{ cm}^{-1}$). Effects of various parameters like stability of complex, ethanol volume, ore matrix, interfering ions etc. on the determination of uranium have also been evaluated. Absorbance measurements as a function of time showed that colored complex is stable up to >24 h. Presence of increased amount of ethanol in colored solution suppresses the absorption of a standard UO_2^{2+} -Br-PADAP solution. Analyses of synthetic standard as well as ore leach a solution show that for 10 determination relative standard deviation (RSD) is <2%. The accuracy of the developed method has been checked by determining uranium using standard addition method and was found to be accurate with a 98–105% recovery rate. The developed method has been applied for the analysis of a number of uranium samples generated from uranium ore leach solutions and results were compared with standard methods like inductively coupled plasma emission spectrometry (ICPAES). The determined values of uranium concentrations by these methods are within $\pm 2\%$. This method can be used to determine 2.5–250 $\mu\text{g mL}^{-1}$ uranium in ore leach solutions with high accuracy and precision.

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1. Introduction

Uranium is an important element in the actinides series due to its wide applications in nuclear industry as a nuclear fuel. The primary source of uranium is naturally occurring uranium ore present in the earth crust. The recovery of uranium from ore is carried out via two step process viz. (a) acid, alkali or bio leaching, and (b) separation from the ore leach solution [1–7]. Monitoring of uranium concentration in ore leach solution is an important aspect for its effective and efficient recovery. A large number of

analytical techniques have been used for the determination of uranium in a wide variety of samples such as environmental, seawater, process streams, effluent/waste streams, ores and ore leach solutions. The increasing availability of power full instrumentals techniques such as neutron activation analysis (NAA), energy dispersive X-ray fluorescence (EDXRF), inductively coupled plasma emission spectrometry (ICPAES), inductively coupled plasma emission mass spectrometry (ICP-MS) has enabled the analysis of complex mixtures with high accuracy and precision [8–13]. However, these advanced techniques require sophisticated, high value instruments (including nuclear reactors). On the other hand, the low cost techniques (such as spectrophotometry) cannot be used successfully without prior chemical separations due to spectral interference of rare earths and transition elements [14,15].

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Table 1
Typical composition of an ore leach solution analyzed by ICPAES technique.

Elément	Concentration, $\mu\text{g mL}^{-1}$
U	193.9
Al	1214.6
B	2.1
Ce	43.7
Cr	19.8
Co	1.6
Dy	4.6
Er	2.1
Eu	0.6
Fe	330.4
Gd	5.1
Mg	1017.1
Mn	3440.9
Ni	6.0
Sm	6.7

Nevertheless, the association of spectrophotometric techniques employing chelating agents and chemometric methods, such as partial least squares (PLS), multivariate calibration procedures, offers outstanding advantages for the analysis of complex matrices [16,17]. In this context, 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol (Br-PADAP) as chelating agent has been extensively used for the spectrophotometric analysis of U(VI) in various matrices [18,19]. It is observed that Br-PADAP has been used to complex a variety of metal ions including cobalt, zinc, copper, rare-earths and U(VI). Das *et al.* demonstrated the determination of trace amounts of U(VI) in nitric acid medium by selective extraction of U(VI) from a mixture of U(VI), Pu(IV), Fe(III), Th(IV) in to organic phase comprising of tri-*n*-octyl phosphine oxide (TOPO)/cyclohexane and simultaneous color development using Br-PADAP [20]. Suresh *et al.* developed an analytical method for the determination of trace amount of U(VI) in presence of large excess of Th(VI) in nitric acid medium using excess amount of complexing agents [21].

In the present paper, a modified method has been developed for the measurement of trace amounts of U(VI) present in ore leach solutions containing a large number of other metal ions viz. rare earths, transition elements (Fe, Mn, Ni, Cr, etc.) in sulphate medium (Table 1). In view of non selective nature of Br-PADAP, U(VI) has been selectively extracted from ore leach solution in to organic medium containing a synergistic mixture of 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester and tri-*n*-octyl phosphine oxide (PC88A + TOPO) in cyclohexane and simultaneously color development in organic medium using Br-PADAP in presence of a buffer solution at pH 7.8. NaF and ascorbic acid were used as additive in the aqueous phase for masking of extraction of other elements. The complexation of Br-PADAP with U(VI) is pH dependent and is optimum at ~ 8 . Several common laboratory buffers such as phosphate, borate and *N*-cyclohexyl-3-aminopropanesulfonic acid (CAPS) are capable of maintaining the pH within the acceptable range. Because of limited water solubility of Br-PADAP, stock solution of Br-PADAP was prepared in absolute ethanol prior to addition to the reaction mixture. After addition of Br-PADAP, color development is very rapid in the presence of sufficient amount of U(VI). This results in a bathochromic shift of the absorbance maxima from 444 nm to 576 nm (Fig. 1). The wavelength shift can be detected with a visible-light spectrophotometer. PC88A in combination with TOPO shows quantitative extraction of uranium from 1 M HNO₃. Conditions have been optimized for extraction and spectrophotometric estimation of uranium in ore leach solution containing 2.5–250 $\mu\text{g mL}^{-1}$ uranium.

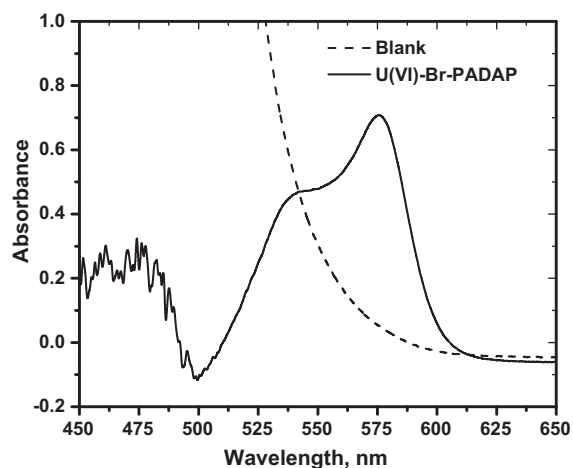


Fig. 1. Absorption spectra of U(VI)-Br-PADAP complexes in 0.1 M PC88A + 0.05 M TOPO/cyclohexane medium.

2. Experimental

2.1. Reagents

PC88A (Daihachi Chemical Industry Co. Ltd. Japan, 95% pure), TOPO (E-Merck) and cyclohexane (E-Merck), ascorbic acid (B.D.H, A.R Grade) were used without further purification. Nuclear grade pure U₃O₈ was obtained from uranium extraction division, BARC, India. 1,2-Cyclohexylenedinitrilotetraacetic acid (CyDTA), sodium fluoride (NaF), sulphosalicylic acid (SSA), triethanolamine (TEA) was procured from SIGMA, USA. The chromogenic reagent 2-(5-bromo-2-pyridylazo-5-diethylaminophenol) (Br-PADAP) was purchased from Fluka, Germany. All other reagents used in the experiment were of A.R. grade.

2.2. Preparation of standard uranyl sulphate solution

Nuclear grade pure U₃O₈ was first dissolved in 6–8 M HNO₃ by warming and then fumed with sulphuric acid to convert in to sulphate medium. The volume of the solution was made up to 100 mL by H₂SO₄ in such a way that the free acidity of the solution became 2 M and uranium concentration 1000 $\mu\text{g mL}^{-1}$. The standard solutions of various concentrations were prepared with proper dilution.

2.3. Preparation of complexing solution

To 40 mL of redistilled water, 1.25 g of CyDTA, 0.25 g NaF and 3.25 g of SSA were dissolved. The pH of the solution was adjusted to 7.8 using NaOH solution and the final volume was made up to 100 mL.

2.4. Buffer solution

To 80 mL of redistilled water 14.2 mL of TEA was dissolved and pH of this solution was adjusted to 7.8 by adding concentrated HClO₄. The solution was left to stand overnight and pH of the solution again readjusted to 7.8. The solution was further diluted to 100 mL using double distilled water.

2.5. Br-PADAP solution (0.05%, w/v)

0.05 g of Br-PADAP chromophore was dissolved in 100 mL absolute ethanol.

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