Photometric Estimation of Uranium in Sea Water Based on Extraction

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Uranium forms an intensely red coloured ($\lambda_{max} = 560$ nm) complex with PAN, 1-(2-pyridylazo)-2-naphthol, at pH 8-10 which can be extracted quantitatively into 1,2-dichloroethane in a single extraction step. The interference of several metal ions present in sea water such as Be(II), Mn(II), Fe(II), Ni(II), Cu(II), Zn(II), Mo(VI), Hg(II), Th(IV), Y(III) and lanthanides can be effectively masked by the addition of 1,2-diamino cyclohexane tetraacetic acid (CDTA). The red colour of the complex in the organic phase is fairly stable and obeys Beer's law up to 10 $\mu$g of uranium/litre, the molar extinction coefficient and sensitivity of the colour reaction being 24,000 and 0.01 $\mu$g cm$^{-2}$ respectively. The method has been applied for the estimation of uranium in coastal waters of Bay of Bengal around Visakhapatnam and the average concentration is found to be 3.6 $\mu$g/litre with a standard deviation of 0.03. The composition of the extracted species, and the conditional stability constants of the uranium-PAN complex are evaluated. The proposed method is simple, sensitive, selective and fairly reproducible for the estimation of uranium in sea water.

The oceans are potential reservoirs of many chemicals and efforts are made to tap these sources for the recovery of some of the chemicals of industrial importance. The recovery of uranium from sea water is gaining much attention in recent years because of the fast depletion of its resources on the earth and its ever increasing demand in nuclear technology. Most of the procedures which have been used so far for the pre-concentration of uranium from sea water involve coprecipitation$^{1-3}$, co-crystallisation$^{4}$, flotation$^{5}$, ion-exchange$^{6,7}$ and solvent extraction$^{8,9}$. Among them solvent extraction appears to be the most convenient method of pre-concentration and estimation of uranium because of its simplicity and rapidity. Many metals including uranium$^{10,11}$ form intensely coloured and sparingly soluble complexes with 1-(2-pyridylazo)-2-naphthol(PAN) which can be extracted with a number of organic solvents. The extremely low solubility of PAN in water enables the reagent to act both as a precipitant for metal ions in microgram amounts and a collector of metal-PAN chelates$^{12}$. This has been taken advantage of in the pre-concentration and subsequent photometric estimation of uranium in sea water and the results of these investigations are presented in this paper.

Materials and Methods

Absorbance measurements were made with CZ spectrophotometer using 5 cm corex cells. A Toshniwal Digital (Model CL 46) pH meter with a combined calomel-glass electrode was used for pH adjustments.

Uranium stock solution (A)—Uranium trioxide (0.6008 g; BDH) was dissolved in 5 ml of 1:1 HCl, heated gently if necessary and made up to 250 ml with deionised water. The solution was standardised by reducing uranium(VI) to uranium(IV) in Jones reductor and titrating with standard solution of potassium dichromate using Barium diphenylamine sulphonate as indicator$^{13}$. This stock solution contain 2 mg uranium/ml.

Solution (B)—Five ml of stock solution (A) was diluted and made up to 500 ml with deionised water.

Working solution (C)—Ten ml of solution B was diluted and made up to 100 ml with deionised water. This working solution contain 2 $\mu$g uranium/ml.

1-(2-pyridylazo)-2-naphthol(PAN) (0.1%)—PAN (Riedel) was purified by recrystallisation from ethanol. A 0.1% PAN was prepared by dissolving 100 mg of recrystallised dye in 100 ml of methanol.

1,2-diamino cyclohexane tetraacetic acid (CDTA) (0.1 M)—CDTA (3.46 g; Sigma) and 0.8 g of NaOH were mixed and dissolved in deionised water and the solution was made to 100 ml.

Buffer solution (pH 9.0)—Ammonium chloride (60 g) was dissolved in about 300 ml of distilled water containing 75 ml of concentrated ammonium hydroxide and the solution diluted to 1 litre with deionised water.

Artificial sea water was prepared according to Martin.$^{14}$ Reagents used were of analytical reagent grade. Freshly distilled solvents were employed in the experiments.

Sea water samples were collected at 2 stations, one near the entrance channel of Visakhapatnam harbour and the other 3 km away from the coast using 5 litre Niskin bottles. They were transferred to polythene
carboys which had been pre-treated with acid and washed with water and deionised water. The samples were filtered through a 0.45 μm Millipore filter and acidified with 2 ml HCl/litre sea water.

Recommended procedure—An aliquot (1000 ml) of acidified sea water sample is taken in a beaker and treated with 15 ml of 0.1 M CDTA, 0.5 ml of PAN. pH of the solution was adjusted to 9 by adding dilute (1:2) solution of NH₄OH. Alternatively the pH of the solution can be adjusted by treating with 4 ml of (1:2) ammonia followed by the addition of 20 ml of NH₄Cl-NH₄OH buffer of pH 9. The contents were transferred to a separatory funnel, allowed to stand for 15 min and then equilibrated with 20 ml of 1,2-dichloroethane for 2 min. The absorbance of the organic extract after separation was measured with a spectrophotometer at 560 nm using 5 cm corex cells against reagent blank. A calibration curve was constructed by taking different amounts of uranium working solution (1-5 ml) in 1000 ml artificial sea water, and measuring the absorbance of the organic extract as described above. The amount of uranium present in the sample was computed from the calibration curve.

Results and Discussion

Preliminary experiments indicated that the system attains maximum absorbance on allowing 15 min from the time of mixing the reagents at pH 8-10. The intensity of the red colour of the complex is perfectly stable for 2 hr. Of the various solvents studied 1,2-dichloroethane was found to be the best because of the high absorbance of the complex in this solvent. The optimum time of equilibration was 2 min.

Absorption spectra—Typical absorption spectra of uranium-PAN complex and the reagent recorded at pH 9 are shown in Fig. 1. The absorption spectra indicate that there is a well defined maximum at 560 nm for the complex whereas the reagent has no appreciable absorbance at this wavelength.

Effect of pH—The effect of pH on the extraction of uranium-PAN complex into 1,2-dichloroethane was studied in the pH range 2-12 by adding dilute solutions of either hydrochloric acid or ammonium hydroxide. The optimum pH range for maximum colour development in the organic phase was 8-10. NH₄Cl-NH₄OH buffer of pH 9 was found to be suitable and convenient to use in this pH range.

Effect of PAN concentration—Quantitative recovery of uranium into 1,2-dichloroethane was obtained when the PAN to uranium ratio was 8 to 10. However, for preconcentration of uranium from aqueous solutions PAN concentration was kept at a large excess.

Beer's law—A plot of absorbance against the amount of uranium indicated that the system obeys Beer's law up to 10 μg uranium/litre. The molar absorption coefficient and sensitivity of the colour reaction (as defined by Sandell) obtained from Beer's law were 24,000 and 0.01 μg cm⁻² respectively.

Interferences—The interference of various substances on the photometric estimation of uranium in sea water is shown in Table 1. Anions like fluoride, chloride, bromide, iodide, sulphate, nitrate, oxalate, thiosulphate, thiocyanate and perchlorate do not interfere even when present in 1000 fold excess relative to uranium. Acetate, carbonate, EDTA and cyanide do not interfere at 100 fold excess.

Ca(II), Mg(II) do not interfere at 100 fold excess to that of uranium. Al(III), Ag(I), V(V), W(VI) and Pb(II) do not interfere at 10 fold excess. Cu(II), Ni(II), Fe(III), Mn(II), Cr(III), Zn(II), Co(II), Be(II), Mo(VI), Hg(II), Th(IV), Y(III), La(III), Ce(III) and Yb(III) interfere seriously even at less than 5 fold concentration. However, the interference of these ions can be masked completely by adding sufficient excess of CDTA as prescribed in the recommended procedure.

Table 2 gives the results obtained for analysis of sea water samples at 2 stations by the recommended procedure. To check the recovery of uranium, some samples were spiked with different amounts of uranium. From the Table it is evident that the uranium concentration found is practically independent of the volume taken for analysis. The precision of the procedure was checked up by carrying 5 replicate determinations with 1 litre samples of sea water, and the standard deviation was found to be 0.03 indicating that this procedure is fairly reproducible for the

![Fig. 1](https://example.com/absorption_spectra.png)

Fig. 1—Absorption spectra of (A) uranium-PAN complex extracted into 1,2-dichloroethane and (B) reagent blank
photometric estimation of uranium. The average concentration of uranium at the 2 stations was 3.6 and 4.5 μg/litre respectively. Though the uranium concentration level in the coastal waters is in agreement with the general oceanic value, the concentration of uranium in harbour entrance channel is high. This may be attributed to the pollution of Visakhapatnam harbour waters with metals such as Cu, Fe, Cr, V, Zn, U etc., because of the discharge of domestic sewage and industrial effluents and the atmospheric fall out of fine iron and manganese ore dust due to the continuous ore handling operation through the conveyer belt.

**Composition and the stability constant of the complex**—The Coleman, Varga and Mastin\(^1\) plots for uranium-PAN complex (Fig. 2) indicated the existence of only single absorbing species under the experimental conditions. The composition of uranium-PAN complex extracted into 1,2-dichloroethane obtained by Job’s method of continuous variations\(^1\) and mole ratio\(^1\) methods applied to 2 phase systems\(^1\) gave an uranium-PAN-Ratio of 1:2 (Fig. 3).

The conditional extraction constant \((K_e)\) for uranium-PAN complex was calculated by Likussar and Boltz method\(^1\) using the equation

\[
\log K_e = 0.3522 - 2 \log k + \log Y_{\text{max}} - 3 \log (1 - Y_{\text{max}})
\]

where \(k = C_M + C_R\), \(C_M\) and \(C_R\) are the total concentrations of the metal and the ligand respectively, and \(Y_{\text{max}}\) is the maximum obtained on the ordinate of the Job’s normalised curve (Fig. 3C). For comparison, the conditional extraction constants were also evaluated from Job’s method of continuous variations and the mole ratio methods and the values were found to be in good agreement with those obtained by Likussar and Boltz method. The average value of \(K_e\) from these 3 methods was found to be 12.4.

### Table 2—Determination of Uranium in Sea Water Samples

<table>
<thead>
<tr>
<th>SI No.</th>
<th>Volume taken for analysis (ml)</th>
<th>Coastal water (Uranium/μg)</th>
<th>Harbour entrance channel water (Uranium/μg)</th>
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<tr>
<td></td>
<td>Added</td>
<td>Found</td>
<td>Recovered</td>
</tr>
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<td>2</td>
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<tr>
<td>4</td>
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<td>—</td>
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<tr>
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<td>500</td>
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<tr>
<td>9</td>
<td>500</td>
<td>5</td>
<td>6.78</td>
</tr>
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</table>
PH VARIATION

PAN VARIATION

URANIUM VARIATION

Fig. 2—Coleman Varga plots for the determination of number of absorbing species: Uranium-PAN complex extracted into 1,2-dichloroethane.

A

B

C

\[
\frac{[\text{PAN}]}{[\text{UO}_2^{2+}]} \quad \text{or} \quad \frac{[\text{UO}_2^{2+}]}{[\text{PAN}]}
\]

\[\lambda = 560 \text{ nm}\]

\[\text{Absorbance} \quad \text{or} \quad \frac{A_{\text{max}}}{A_{\text{max}}}
\]

\[y_{\text{max}}\]

Fig. 3—Nature of the extracting species [A, Job's method; B, Mole ratio method; C, Likussar and Boltz method]

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References