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Solvent extraction and spectrophotometric determination of Uranium (VI) using 2,2′-[1,2-phenylenebis(nitrilomethylidene)]bisphenol (BSOPD) as an analytical reagent

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ABSTRACT

2,2'-[1,2-phenylenebis(nitrilomethylidene)]bisphenol (BSOPD) is synthesized in the laboratory and characterized by NMR, IR and elemental analysis for its purity. This reagent forms a yellow complex with U(VI) which can be quantitatively extracted into chloroform at pH 10. This complex in chloroform shows an intense absorption peak at 413.0 nm. It is observed that Beer's law is obeyed in the range of 2.0-10.0 ppm of metal solution. It gives a linear and reproducible graph under appropriate conditions, the complex having a molar absorptivity of 3.69×10^4 L $mol^{-1} \cdot cm^{-1}$. Sandell's sensitivity calculated was found to be 4.4×10^{-3} $\mu g \cdot cm^{-2}$. Nature of the extracted complex, determined by Job's continuous variation method, Slope ratio method and Mole ratio method shows that the composition of U(VI) : BSOPD complex is 1:4. Interference by various ions is studied and masking agents used where required. The proposed method has been applied for the determination of U (VI) in monazite sand and synthetic samples. The results of the analysis are found to be comparable with those obtained by standard method.

***Keywords*:** Uranium (VI); solvent extraction-spectrophotometric determination; monazite sand; 2,2'-[1,2-phenylenebis(nitrilomethylidene)]bisphenol (BSOPD).

1. INTRODUCTION

Uranium (*yew-RAY-nee-əm*) is a rare earth element in the actinide series of the periodic table. Natural uranium consists of three major isotopes: ^{234}U, ^{235}U, and ^{238}U. All are radioactive and decay by emitting an alpha particle.

Uranium is of great importance as a fuel for nuclear power plants to generate electricity. Uranium and uranium compounds have other minor applications: mordant for textiles, in photography, bricks for protection against gamma radiation, ballast, catalysts, alloys, etc.

Uranyl acetate and uranyl formate are used as electron-dense "stains" in transmission electron microscopy. Significant concentrations of uranium have been found in monazite sand. The first metal to be recovered in significant quantities using solvent extraction was Uranium. Following the development of the nuclear industry during and immediately after World War II, attention was focussed on developing technologies, which could be used to upgrade and purify uranium from low-grade ores, and in 1957 the first commercial solvent extraction plant using amines was opened in the USA [1].

Today most of the world's uranium is recovered in hydrometallurgical circuits, which involve solvent extraction, and a significant proportion of this uranium is produced in circuits, which use solvent extraction as the only recovery system.

Several reagents have been reported in the literature for the spectrophotometric extraction of trace metals [2], but some of the methods suffer from limitations of interferences, incomplete extraction, longer period of extraction etc.

Spectrophotometric methods coupled with solvent extraction can be advantageously employed for the determination of metals [3-13]. Schiff bases have been widely used as analytical reagents.

They act as chelating agents by bonding through oxygen atom and azomethine nitrogen atom and produce highly coloured complexes and then used in the selective and sensitive determination of metal ions [14, 15].

The present paper deals with the development of a selective and sensitive method for the extractive spectrophotometric determination of U(VI), using the Schiff base, 2,2'-[1,2-phenylenebis(nitrilomethylidene)]bisphenol. This compound, also known as Bisalicylidene-o-phenylenediamine (BSOPD), shows high coordinating affinity towards metal ions.

2. MATERIALS AND METHODOLOGY

The stock solution of U(VI) was prepared by dissolving an appropriate amount of analytical-reagent grade Uranyl nitrate in double distilled water containing nitric acid and finally made up to the desired volume.

The solution was standardized by reducing U(VI) to U(IV) and then titrating against standard Ce(IV) sulphate solution [16]. Working standard solutions were prepared by suitable dilution of this stock solution. All other chemicals and reagents used were of analytical reagent quality.

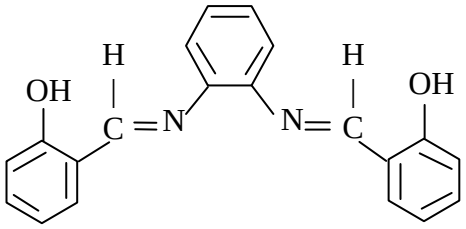
The absorbance measurements were carried out on a Shimadzu UV-Visible 2401 spectrophotometer with a 1cm quartz cell and pH measurements were carried out using appropriate buffer solution with an ELICO LI -120 pH meter.

2. 1. Reagent preparation

BSOPD was prepared by the slow addition of a solution of o-phenylene diamine (1.1 g in 20 mL of methanol) to a methanolic solution of salicylaldehyde (2.5 g in 20 mL). The product was formed as yellow-orange crystals.

These were recrystallized from methanol (M.P 164 °C). This reagent was characterized by NMR, IR and elemental analysis for its purity.

Structure of the Ligand



2, 2′-[1, 2-phenylenebis(nitrilomethylidene)]bisphenol

2. 2. Proposed analytical procedure

A working solution was obtained by diluting stock U(VI) solution. 1 mL of aqueous solution of U(VI) [containing 100 μg U(VI)] was taken in a separating funnel. The pH was adjusted using buffer (pH 10). To this 0.5 mL of 0.15 % reagent was added. Total volume of aqueous solution was made to 10 mL. The yellow coloured complex formed was extracted into 10 mL of chloroform by shaking for 1min. The phases were separated and absorbance of the organic layer was measured at 413.0 nm using a reagent blank.

3. RESULTS AND DISCUSSION

3. 1. Extraction as a function of pH

The extraction was found to be quantitative between pH 9.0 and 10.0. Hence pH 9.0 was selected for further studies **(Fig. 1)**.

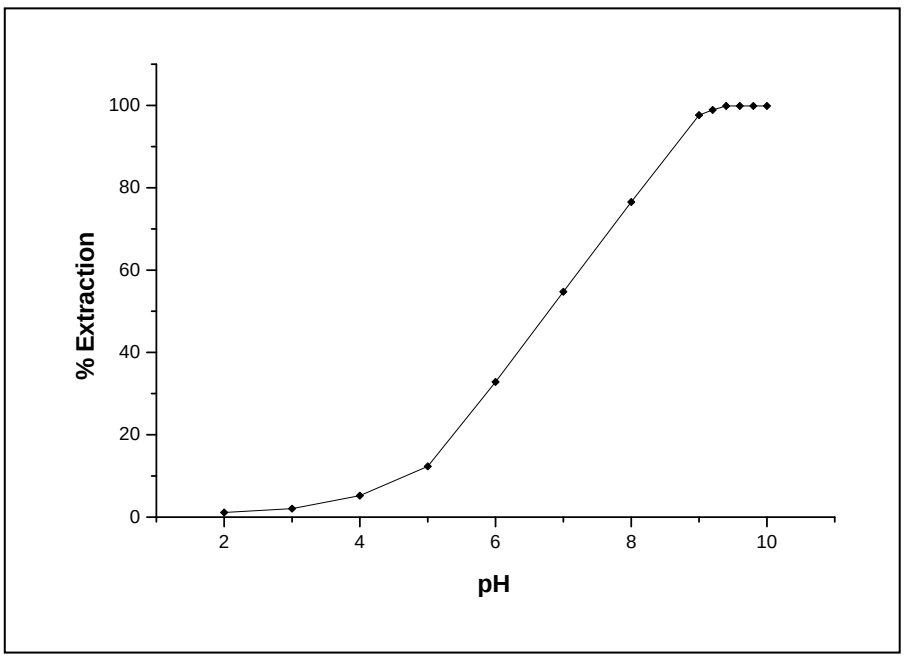


Fig. 1. Effect of pH on extraction of U(VI).

3. 2. Absorption spectrum

The spectrum of the complex extracted in chloroform (B) and that of the reagent blank in chloroform (A) are shown in **Fig. 2.** The spectrum of the U(VI) : complex in chloroform shows an intense absorption peak at 413 nm

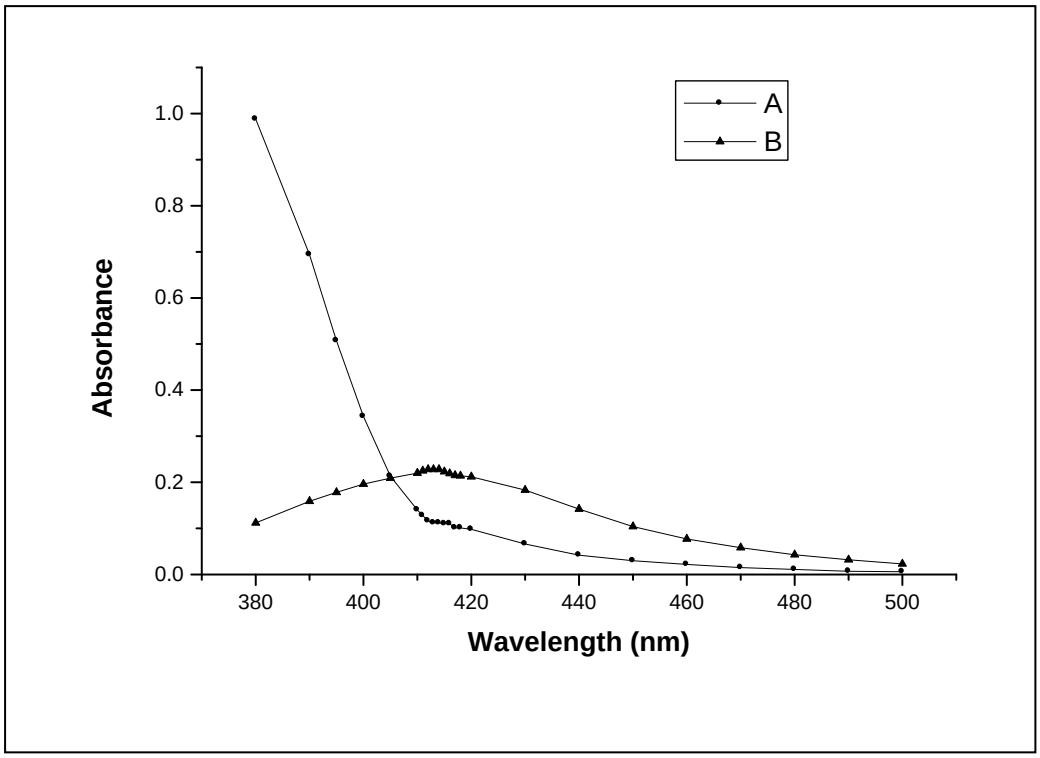


Fig. 2. Absorption spectrum of U(VI): BSOPD.

3. 3. Selection of Solvent

Many organic solvents were employed to determine the most suitable solvent for the extraction of U(VI) with BSOPD. The organic solvents can be arranged in the order of their extraction efficiency as follows, chloroform > n-butanol > isoamyl alcohol > toluene > xylene. Chloroform was chosen as the solvent as it gave clean and quick separation.

3. 4. Reagent concentration

Variation in concentration of reagent shows that 0.5 mL of 0.15 % BSOPD in acetone is sufficient for full colour development and extraction of 100 μg of U(VI).

3. 5. Effect of equilibration time

Equilibration time from 30 sec to 5 min was studied and it was found that 1 minute is sufficient for the quantitative extraction of U(VI).

3. 6. Stability of the complex with time

The extracted complex is found to be stable up to 48.0 hours.

3. 7. Calibration Plot

A calibration plot of absorbance against concentration of U(VI) gives a linear and reproducible graph in the concentration range of 2.0 ppm to 10.0 ppm of uranium indicating that the Beer's law is obeyed in this range **(Fig. 3)**. The molar absorptivity and Sandell's sensitivity were calculated to be 3.69 x 10^4 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ and 4.4 x 10^{-3} $\mu g \cdot cm^{-2}$ respectively.

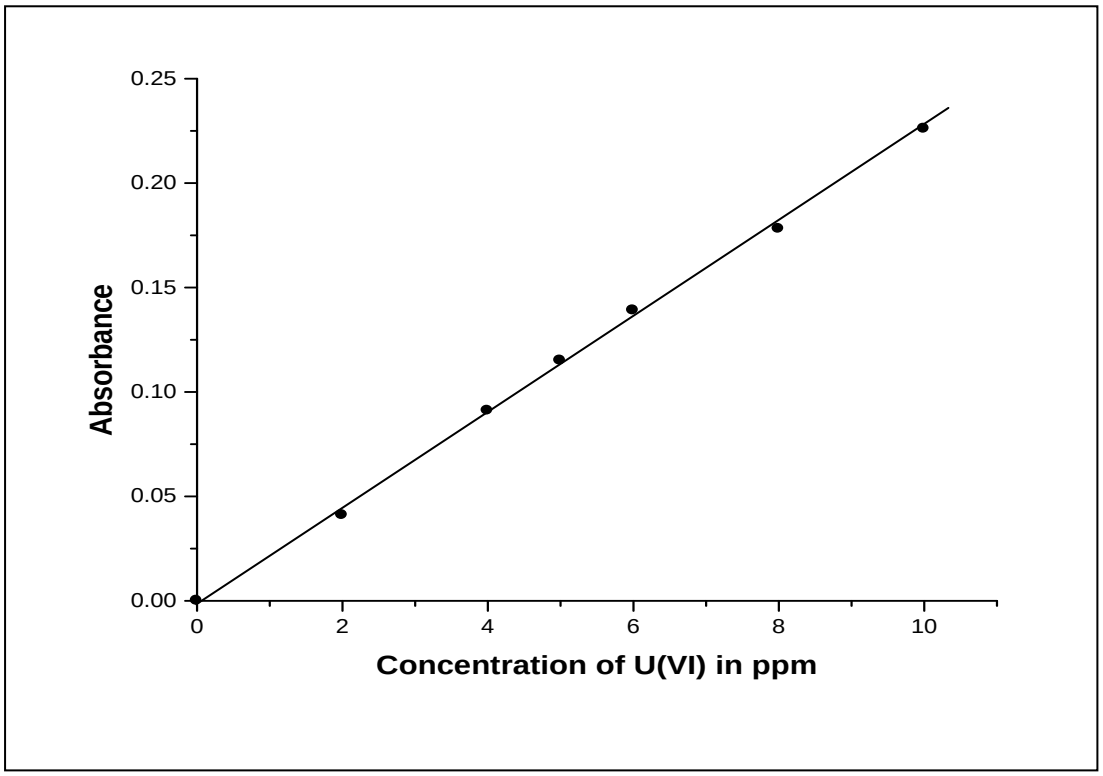


Fig. 3. Calibration Plot of U(VI) with BSOPD.

3. 8. Composition of extracted species

The composition of the extracted complex was studied by Job's continuous variation method, **(Fig. 4)**, Mole ratio method, and Slope ratio method, **(Fig. 5)**.

On the basis of results of these studies, it can be concluded that the composition of U(VI): BSOPD complex is 1:4.

3. 9. Effect of diverse ions

The effect of various ions at microgram levels on the determination of uranium was examined.

The tolerance limits of the interfering species were established for 100 µg of uranium. The ions which interfere in the determination of uranium were masked using appropriate masking agents **(Table 1).**

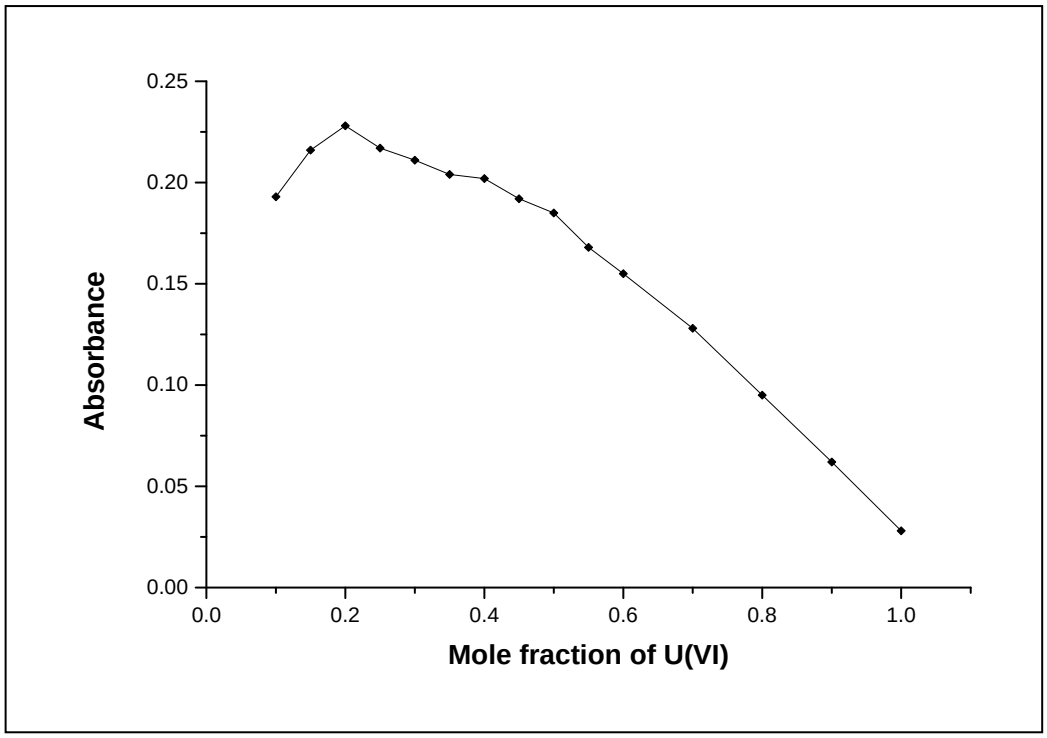


Fig. 4. Job's Continuous Variation Method.

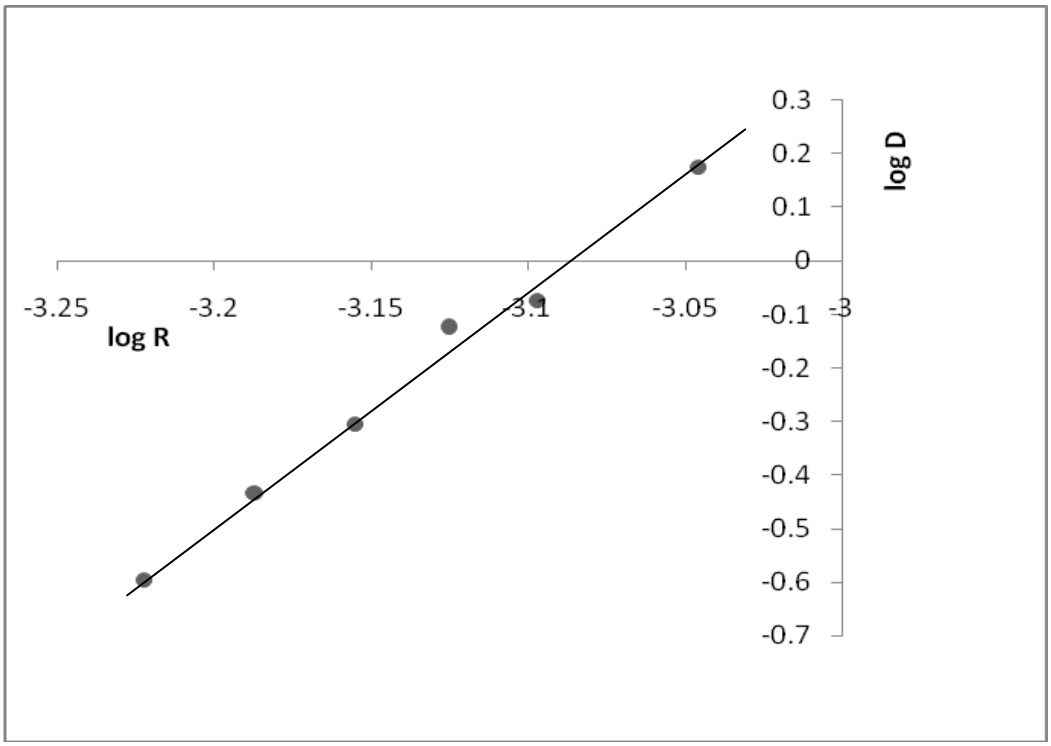


Fig. 5. Slope Ratio Method.

Table 1. Masking Agents Required To Suppress the Interference of Foreign Ions.

Sr. No.	Interfering Ion	Masking Agents Added
1	Zn(II)	Thioglycolic acid
2	Ni(II)	Sodium thiosulphate
3	Co(II)	Sodium cyanide
4	V(V)	Thiourea
5	EDTA	Sodium molybdate

3. 10. Precision and Accuracy of the method

The precision and accuracy of the method was tested by analyzing five solutions each containing 100 µg of uranium. The standard deviation and confidence limits were calculated accordingly **(Table 2).**

Table 2. Precision and Accuracy of the Method.

Sr. No.	Absorbance	Amt. of U(VI) in µg	$\bar{X}$	$D = \lvert X_i - \bar{X} \rvert$	$D^2 = (X_i - \bar{X})^2$
1	0.224	99.12	99.74	0.62	38.44×10^{-2}
2	0.225	99.56		0.18	3.24×10^{-2}
3	0.226	100.0		0.26	6.57×10^{-2}
4	0.226	100.0		0.26	6.57×10^{-2}
5	0.226	100.0		0.26	6.57×10^{-2}

Standard Deviation : ± 0.307
Confidence Limit (at 99%) : 99.74 ± 0.632

4. APPLICATIONS

A] Determination of uranium in synthetic samples:
Synthetic mixtures were prepared in the laboratory by mixing U (VI) and other metal ions in suitable proportions. An aliquot of 1.0 cm^3 of the mixture was taken for the determination of U (VI) by the proposed method.

B] Determination of uranium in real samples:

Monazite sand: One gram of monazite sand sample was taken in a round bottom flask to which aquaregia was added. This solution was heated under reflux for five hours. It was then evaporated almost to dryness. The dried mass was then mixed with 10 cm^3 of 5M HCl and again heated to boiling and allowed to cool. The solution was filtered and the filtrate was diluted to 100 cm^3 with distilled water.

A suitable aliquot of this solution was taken for the determination of U (VI) by the proposed method **(Table 3** and **4).**

Table 3. Determination of Uranium in Synthetic Mixtures and Monazite sand.

A] **Synthetic Mixtures:**

Composition of Sample (µg)	**U(VI) added (µg)**	**U(VI) found by proposed method (µg)**
Cd(100), Mg(100), V*(50)	100	99.93
Cu*(50), Al(50), Mo(100)	100	99.86
Be(100), Co*(100), Th(50)	100	99.95
Zn*(50), Fe(100), Ce(100)	100	100.07

* masked appropriately

Table 4. Determination of Uranium in Monazite sand.

B] **Real Samples:**

Sample	**Amount of U(VI)**	
	Standard Method#	**Proposed Method**
Monazite sand	0.640%	0.636%

*Average of three analysis #Vogel,1989

5. CONCLUSION

The results obtained indicate that the novel reagent, 2,2′-[1,2-phenylenebis (nitrilomethylidene)]bisphenol forms a stable complex with U(VI) which can be effectively extracted from aqueous media into chloroform. The newly developed method is simple, as well as precise. The extraction process is quick and requires less organic solvent. The method suffers from less interferences and can be successfully applied for the determination of

U(VI)) in synthetic and real samples. The results show good agreement with standard method (Vogel, 1989) and are accurate, reliable and reproducible.

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