

# Extraction and Spectrophotometric Investigations on the Pollution in Depleted Uranium of Southern Iraq

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## Abstract

The reagent 2-(2-Pyridylazo)-5-diethylamine phenol (BPADAP), was used to investigate the pollution of southern Iraq by a collection of some damaged troops, the tanks metal and soil samples from this area. These samples were collected from certain military operation of the war against Iraq about 80 km away from Basra city. The pollution in depleted uranium of damaged troops and the tanks metal samples was found in the range of 0.56 – 9.6 %, whereas in the soil samples the pollution was found not to be by depleted uranium but by some other metal ions.

The study has involved the interpretation of electronic spectrum of BPADAP - uranyl complex (2:1 ratio) which absorbs light at 544 and 571 nm. From the calibration curves, it was found that the reagent can detect from 1 up to more than 25 micrograms of uranyl ion in water and ethanol solutions. The interference of twenty-three metal ions with the detection of uranyl ion was also investigated and was found that only  $Pb^{2-}$  and  $Th^{1-}$  have interfered in pure ethanolic solutions.

**Keywords:** Extraction of uranium, the pollution of southern Iraq, uranyl pollution, depleted uranium, Basra city pollution.

## Introduction

Previously many reagents were used for the detection of uranyl ion in ethanol and water solutions<sup>1-6</sup>. The reagent 2-(2- pyridylazo)-5- diethylaminophenol was found to be sensitive to uranium<sup>7,8</sup>, but Gusev and Shalarnova<sup>9</sup> found the derivative 2-(5- bromo -2- pyridylazo) -5- diethylaminophenol (BPADAP) is more sensitive to uranyl ion owing to its greater iron tolerance, and easier to prepare in a pure state. The reagent was used to determine micro-amount quantities of uranyl ion in the ores<sup>10,11</sup>. It was also found that the ions  $Li^{+}$ ,  $NH_4^{+}$ ,  $Cs^{+}$ ,  $Sn^{+2}$ ,  $Cd^{+2}$ ,  $Hg^{+2}$ ,  $Pb^{-2}$ ,  $Be^{-2}$ ,  $Mg^{-2}$ ,  $Ca^{+2}$ ,  $Mn^{+2}$ ,  $Al^{-3}$ ,  $Bi^{+3}$ ,  $Nd^{+3}$ ,  $Cr^{+3}$ ,  $Th^{+4}$ ,  $Mo^{-6}$ , and  $W^{-6}$  interfere with the determination of uranyl ion by 2% in the level of five milligrams in the detection of 50 micrograms of uranyl ion.

For the ions  $Cu^{+2}$ ,  $Ni^{+2}$  and  $Cr^{+6}$  the maximum interference allowed is 3 mg, and for the ions  $As^{+5}$  and  $Zr^{+4}$  it is 0.5 mg and for the ions  $Co^{+2}$ ,  $V^{+4}$  and  $V^{+5}$  the interference

allowed is 4, 0.2 and 0.01 mg respectively. In a recent study<sup>12</sup>, bis (salicylidene - 2 - amino pyridine) methane was prepared and it is selective for uranyl ion in ethanolic solutions only. All the above-mentioned metal ions and the ions  $Tl^{+2}$ ,  $Sr^{+2}$ ,  $Ba^{+2}$ ,  $In^{-3}$ ,  $Ir^{+3}$  and  $Ru^{+3}$  do not interfere with the detection of uranyl ion by this new reagent.

Presently, the work of BPADAP on uranyl ion is extended in neutral aqueous ethanolic solutions to involve measuring of the electronic spectra of complexes, determination of the reagent: metal ion by the molar ratio method, interference of other metal ions, determination of micro-amount quantities of uranyl ion, and to identify and detect the depleted uranium in some samples collected from certain militaries operation territories of the Gulf war in southern Iraq.

## Material and Methods

**Materials:** All metal ions used throughout this work were of "Fluka" as nitrates or chlorides of purity greater than 98%. Ethanol was absolute, and BPADAP (Scheme1) was of "Fluka" of purity greater than 95%. Varian DMS 100 UV - Visible Spectrophotometer was used to measure the electronic spectra and optical densities at  $\lambda_{max}$  using quartz cell.

**Method:** A series of solutions in aqueous ethanol was prepared once in which the concentration of uranyl ion was kept constant  $1.3 \times 10^{-5}$  mol.  $dm^{-3}$  and the concentration of BPADAP was variable  $0.4- 10.6 \times 10^{-5}$  mol.  $dm^{-3}$ , another series was prepared in which the concentration of BPADAP was kept constant,  $4.2 \times 10^{-6}$  mol.  $dm^{-3}$  and the concentration of uranyl ion was variable  $(1.26-13.0) \times 10^{-6}$  mol  $dm^{-3}$ . In every case, the electronic spectrum was measured.

**Samples Treatment:** Soil and metal samples were collected from areas around the damaged troops and the tanks in the military's operation about 80 km away from Basra City center.

A weighed quantity of metal sample was dissolved in hot concentrated nitric acid, after cooling the desired volume was diluted with distilled water. The optical density of 2 ml of the diluted acidic solution after adding 0.1-0.2 ml of  $0.001 \text{ mol.}dm^{-3}$  of BPADAP in ethanol solution was measured at  $\lambda_{max}$  of the complex. From these optical densities and the calibration curves (Figure5), the micro-amount quantity can be evaluated. The reference cell contained 2 ml of distilled water and the same volume of the reagent solution.

The metal samples which were investigated in this work are as follows:

**Sample 1:** Metal ash was collected from a cabinet of the damaged tank located at northern Rumaila oil field 15 km away from Basra city.

**Sample 2:** A small piece of metal collected from a place near the damaged tank of sample 1.

**Sample 3:** A small piece of metal from damaged troop collected from the midway between northern Rumaila oil field and Zubair City.

**Sample 4:** A small metal piece was cut from the edge of a hole in a damaged troop which was made by the action of projectile in the region of northern Rumaila oil field.

All soil samples were washed first by boiling distilled water to remove the water-soluble components. After drying a weighed quantity, each sample was treated with hot concentrated nitric acid, after cooling and filtration the desired volume was diluted with distilled water, then the same procedure of the metal samples was applied for analysis. The dry residue was weighed again to calculate the amount dissolved metals in nitric acid.

**Sample 5:** The metal ash sample washed with boiling distilled water.

**Sample 6:** Soil sample collected from northern Rumaila field region.

**Sample 7:** Soil sample was collected from a region 15 km away from the region of sample 2.

## Results and Discussion

### The Electronic Spectra of BPADAP and Uranyl Ion:

Figures 1 and 2 represent the electronic spectra of uranyl nitrate in water and BPADAP in ethanol. Uranyl nitrate absorbs light at 202 nm with extinction coefficient  $\epsilon = 2620 \pm 120 \text{ m}^2 \text{ mol}^{-1}$ . The longer wavelength absorption bands in the electronic spectrum of BPADAP in ethanol are at 446 nm ( $\epsilon = 3:340 \pm 240 \text{ m}^2 \text{ mol}^{-1}$ ) and 556 nm ( $\epsilon = 730 \pm 130 \text{ m}^2 \text{ mol}^{-1}$ ). The first transition was identified previously<sup>(11,13)</sup>, but the second one was not observed<sup>11,13</sup>. The reason may be attributed to  $n \rightarrow n^*$  transition of the quinoid structure of BPADAP as shown in scheme 1 owing to the following reasons: First, the intensity of the transition is relatively weak; Secondly, the band is located in the mid of the visible region and thirdly, the deep reddish - violet color of the reagent is characteristic of the quinoid compounds.

Uranyl ion forms reddish-violet complex with BPADAP in ethanol-water mixtures, the electronic spectrum is shown in figure 3. The complex absorbs light at 544 and 571 nm in the presence of high concentrations of BPADAP; its band at 446 nm appears in the spectrum, therefore the band at 571

nm is used in the analysis experiments.

Figure 4 illustrates the variation of optical densities at 571 nm with the molar ratios of [BPADAP]: [ $\text{UO}_2^{+2}$ ] when the concentration of uranyl ion was kept constant,  $1.3 \times 10^{-5} \text{ mol dm}^{-3}$ , and the concentration of BPADAP was variable,  $(0.4 - 10.6) \times 10^{-5} \text{ mol dm}^{-3}$ .

Figure 4 indicates that the complex of  $\text{UO}_2^{+2}$  ion with BPADAP which absorbs light at 544 and 571 nm is of molar ratio 2: 1 reagent to a metal ion. It was found that the presence of five micrograms of uranyl ion in absorption cell gives optical densities 0.21 and 0.26 at 544 and 571 nm respectively. And 25 micrograms give optical densities 1.06 and 1.54 at 544 and 571 nm respectively. Figure 5 shows the calibration curves for the determination of micro-amount quantities of uranyl ion by BPADAP in aqueous and ethanolic solutions.

Table 1 represents the interferences of some metal ions with the detection of uranyl ion with BPADAP in aqueous and ethanolic solutions. It seems from the data of table 1 that  $\text{Th}^{+4}$ ,  $\text{Pd}^{+2}$  and  $\text{Pb}^{-2}$  interfere with the detection, but under exact controlled concentrations and the ratios of water in ethanol, it was found possible to avoid such interferences.

It is clearly known that the alloy of the shells of depleted uranium projectiles of rockets, guns of tanks and troops etc. consists of 99.25% depleted uranium (very pure  $\text{U}^{-238}$ ) + 0.75% titanium, or 98% of depleted uranium + 2% molybdenum<sup>14,15</sup>. So the presence of metals such as lead, palladium, mercury and others in the shells of depleted uranium projectiles and in the alloy of the bodies of tanks and troops is unlikely. In the case of thorium metal, it may be present in a trace amount since  $\text{U}^{-238}$  decays by emission of alpha - particles forming  $\text{Th}^{-234}$  ( $t_{1/2}$  for  $\text{U}^{-238} = 4.47 \times 10^9$  y), and the  $\text{Th}^{-234}$  decays very fast by emission of beta-particles ( $t_{1/2} = 24.1$  d).

Figure 6 and 7 illustrate the electronic spectra of the complexes of BP ADAP with the solutions of metal samples 3 and 4 which were treated with hot .concentrated nitric acid and figures 8 and 9 show the electronic spectra of the complexes of BP ADAP with the solutions of soil samples 6 and 7 which were treated with hot distilled water. Table 2 summarizes the results of analyses of metal and soil samples that were collected from the military operation territories about 80 km away from Basra city centre. According to the data of table 2, it can be concluded that the pollution with depleted uranium is still after about eleven years from the Golf war against Iraq since 1991 and till now.

## Conclusion

The pollution of the metal contents of the damaged tanks, troops, guns and others in the region of southern Iraq ranged between 0.56 - 9.6.

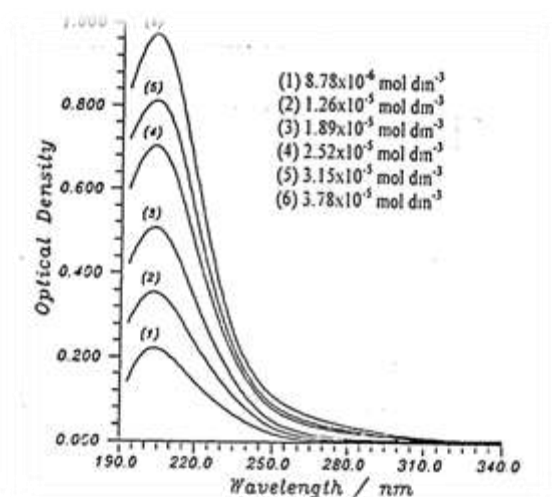
**Table 1**  
**The interference of some metal ions in the detection of uranyl ion by BPADAP in ethanol- water mixtures**

Metal ion	$\lambda_{\max}$ of the complex with BPADAP	Interference
Na <sup>+</sup> , K <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	-----	Do not form coloured complexes
Be <sup>+2</sup> , Ca <sup>+2</sup> , Sr <sup>+2</sup> , Ba <sup>+2</sup>	-----	Do not form coloured complexes
Cr <sup>+3</sup>	544	Forms complex after 24h
Zn <sup>+2</sup>	564	Forms complex only at very high concentrations
Fe <sup>+3</sup>	522.580	Interferes at higher concentrations
Cd <sup>+2</sup>	542.574	Interferes at higher concentrations
Hg <sup>+2</sup>	550.571	Interferes at higher concentrations
Bi <sup>+3</sup>	550.577	Interferes at higher concentrations
Co <sup>+2</sup>	534	Dose not interfere with the 571 nm of UO <sub>2</sub> <sup>+2</sup>
Cu <sup>+2</sup>	545	Dose not interfere with the 571 nm of UO <sub>2</sub> <sup>+2</sup>
Ni <sup>+2</sup>	517.549	Dose not interfere with the 571 nm of UO <sub>2</sub> <sup>+2</sup>
Al <sup>+3</sup>	548	Dose not interfere with the 571 nm of UO <sub>2</sub> <sup>+2</sup>
Sm <sup>+3</sup>	530.559	Dose not interfere with the 571 nm of UO <sub>2</sub> <sup>+2</sup>
Mg <sup>+2</sup>	510.540	Dose not interfere with the 571 nm of UO <sub>2</sub> <sup>+2</sup>
Pb <sup>+2</sup>	540.568	Interferes in ethanolic solutions only
Th <sup>+4</sup>	526.562	Interferes
Pd <sup>+2</sup>	540.575.618	Interferes in ethanolic solutions only

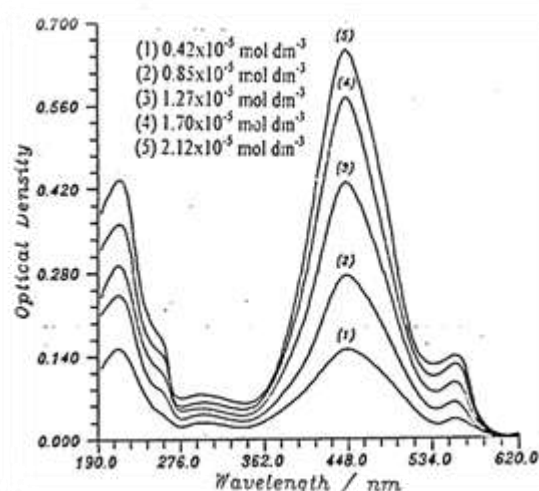
**Table 2**  
**The results of the analyses of metal and soil samples which were collected from northern ramaila oil field 80 km away from Basra city**

Sample No.	Weight /g	OD/2ml	$\lambda_{\max}$ /nm of complex	No. $\mu$ g/2ml	No. $\mu$ g/total weight	% of pollution by depleted uranium
1	0.053	0.18	571	3	636	1.15
2	0.7667	Trace	571	-----	-----	-----
4	0.8777	0.06	583	1	5000	0.56
5 <sup>(*)</sup>	0.1800	0.21	580	4.1	36	9.6
6 <sup>(*)</sup>	0.0238	0.17	580	2.8	15.4	0.065
7 <sup>(*)</sup>	0.2215	0.40	580	6.6	148.5	0.065

(\*)The analyses of these samples were carried out on their water-soluble components; their solutions in hot concentrated nitric acid do not give positive results about the presence of depleted uranium in these samples.



**Figure 1: The electronic spectrum of UO<sub>2</sub> (NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O in water**



**Figure 2: The electronic spectrum of BPADAP ethanol**

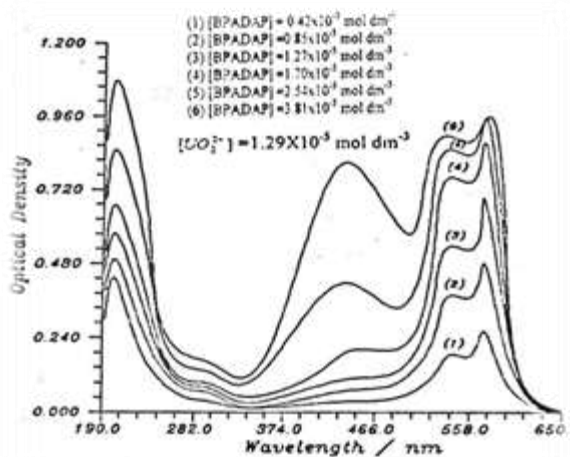


Figure 3: The electronic spectrum of  $UO_2^{+2}$  complex with BPADAP in ethanol

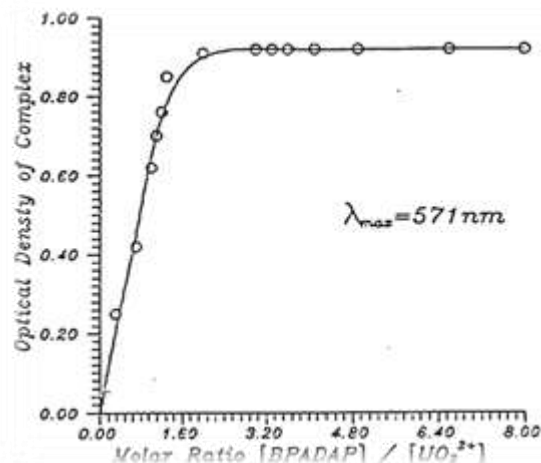


Figure 4: The variation of optical densities with molar ratios  $[BPADAP]:[UO_2^{+2}]$

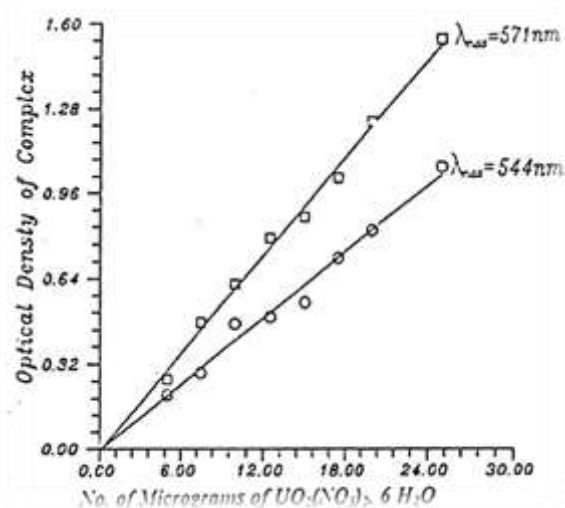


Figure 5: The calibration curves for determination of microamount quantities of  $UO_2^{+2}$  by BPADAP in aqueous ethanol solutions

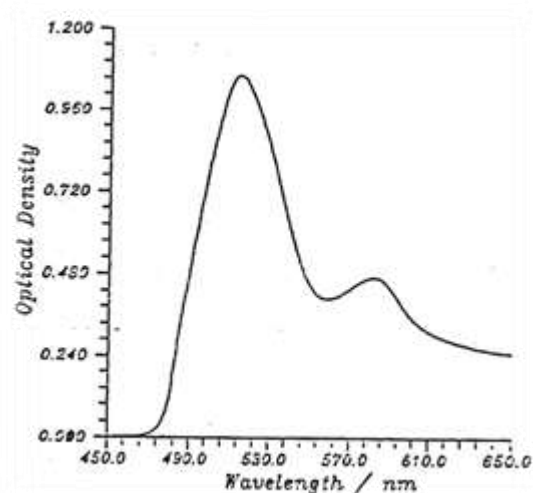


Figure 6: The electronic spectrum of the complex of solution sample 3 with BPADAP,  $\lambda_{max}$  at 516 and 583nm. The reference cell is contained the same amount of BPADAP

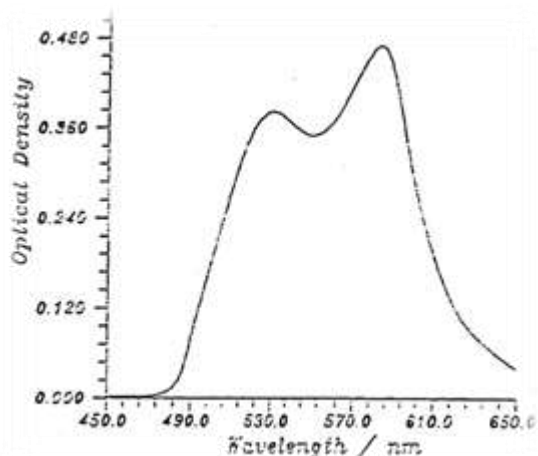


Figure 7: The electronic spectrum of the complex of solution sample 4 with BPADAP,  $\lambda_{max}$  at 534 and 583nm. The reference cell is contained the same amount of BPADAP

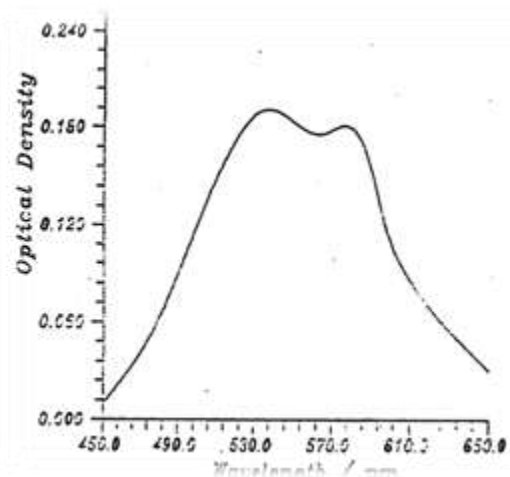
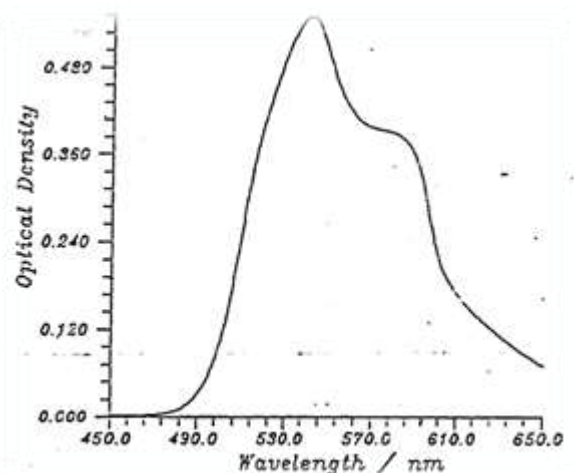


Figure 8: The electronic spectrum of the complex of solution sample 6 with BPADAP,  $\lambda_{max}$  at 538 and 578nm. The reference cell is contained the same amount of BPADAP





**Figure 9: The electronic spectrum of the complex of solution sample 7 with BPADAP,  $\lambda_{\max}$  at 546 and 586 nm. The reference cell is contained the same amount of BPADAP**

Since the contents of depleted uranium, after expulsion, consist mainly of water insoluble oxides, and the electronic spectra of water soluble components of soil samples with BPADAP, so it is reasonable to suppose that soil of the Basra city is polluted by some other metal ions other than depleted uranium which form complexes with BPADAP and absorb light in the same region. This suggestion is confirmed when solid samples were treated after washing with hot distilled water and with hot concentrated nitric acid did not give positive results with BPADAP.

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