

COLUMN PRECONCENTRATION OF URANIUM BY 1-(2-PYRIDYLAZO)-2-NAPHTHOL SUPPORTED ON NAPHTHALENE USING DIFFERENTIAL PULSE POLAROGRAPHY

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Abstract

A solid chelating material, 1-(2-pyridylazo)-2-naphthol (PAN) supported on naphthalene provides a rapid and highly selective means of preconcentration of uranium from aqueous solution. Uranium is quantitatively retained on this adsorbent in the pH range 9.8-10.7 with a flow rate of 1 ml min⁻¹. The metal complex was desorbed with 10 ml of 2 M hydrochloric acid and uranium is determined by differential pulse polarography (DPP). The detection limit is 1.5 µg ml⁻¹ (Signal to noise ratio = 2). The linearity is maintained in the concentration range 3.0 - 310 µg ml⁻¹ with a correlation coefficient of 0.9994 (n=7) and relative standard deviation of ±1.1%(n=7). Characterization of the electroactive process included an examination of the degree of reversibility. Various parameters such as the effect of pH, volume of aqueous phase and interference of a number of metal ions on the determination of uranium have been studied in detail to optimize the conditions for determination of uranium.

Introduction

The possibility of using 1-(2-pyridylazo)-2-naphthol (PAN) for analytical purposes was investigated by Cheng and Bray [1]. This reagent reacts with many metal ions in the periodic table to form water insoluble, colored chelate complex and has been applied widely in the liquid extraction and spectrophotometric determination of metal ions in materials [2]. Although solvent extraction is a simple and convenient technique, it is unsuitable if an emulsion forms

in an aqueous-organic phase, solubility of the metal complex is poor or the metal complex is formed at a high temperature. These difficulties may be overcome by using molten naphthalene [3], molten paraffine [4], naphthalene adsorption [5] or benzophenone adsorption [6]. The main drawbacks of these methods are the filtration and drying operations that are required. Column methods have also been reported for the preconcentration of metals using various adsorbents such as activated carbon [7], thiol cotton [8], green tea leaves [9], chelating resins [10], cellulose [11] and polythioether [12]. Although some of them are fairly effective, their methods of preparation are lengthy and involve rigid conditions. The desorption of the metal complex is carried out by the slow process of elution, thus making the method more time consuming.

Earlier, much attention was given to the direct

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polarographic estimation of metals after extraction of their metal complexes into organic solvents [13-17]. Unfortunately, electrochemical methods for the direct determination of reducible substances require that the solvent should have a fairly high dielectric constant so a well defined polarogram can be obtained. In this regard, various researchers have mixed the organic phase after extraction with a solvent of high dielectric constant to obtain well defined polarograms [18-19]. The main disadvantage of this method is that the sensitivity and preconcentration factors are considerably lowered. Thus, the aim of the preconcentration and direct determination of a metal is not achieved. For the direct determination of metal ions after extraction of their metal complexes into molten naphthalene and dissolution of the product in an organic solvent such as dimethylformamide [20], an inert gas, normally N_2 or H_2 has to be passed for at least 10-15 minutes to remove dissolved oxygen, again making the method more time consuming and less reproducible owing to the partial evaporation of the organic solvent.

In the present communication, we have developed a simple, sensitive and economical method for the direct differential pulse polarographic determination of uranium after adsorption in the column and subsequent desorption by 8-10 ml of 2 M hydrochloric acid. The reagent PAN selected is very cheap, easily accessible and does not interfere in the polarographic estimation of uranium ion. Most of the problems with the above mentioned polarographic methods are solved in this way. The various parameters have been evaluated. This method is found to be highly selective, rapid, economical and fairly sensitive and the developed procedure has been used for the determination of trace amount of uranium in various samples.

Experimental Section

Apparatus

Polarograms were recorded with a three electrode Elico Model CL-90 polarographic analyser outfitted with an X-Y recorder (model LR-108). Cyclic voltammograms were recorded with a cyclic voltmeter (model CV-27 fitted out with a X-Y-T recorder. A funnel tipped glass tube (60×6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibers and then filled with a flat glass rod. All glassware and columns were washed with a mixture of concentrated sulfuric acid and concentrated nitric acid (1+1) before use. An Elico pH meter was used for pH measurements.

Reagents

All chemicals used were of analytical reagent grades, $UO_2(CH_3COO)_2 \cdot 2H_2O$ was dissolved in distilled water containing a few ml of concentrated hydrochloric acid and

then diluted to 1000 ml with distilled water in a standard flask and standardized by a known method [21]. A more diluted solution of uranium (5 ppm) can be prepared by diluting the standard solution. Sodium acetate-acetic acid (0.5 M) and aqueous ammonia - ammonium ion (0.5 M) buffers were used for pH adjustment. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used to study the interference of anions and cations, respectively. Twice distilled water was used whenever required.

Preparation of Loaded PAN-naphthalene Adsorbent

A mixture consisting of 1 g of PAN, 20 g of naphthalene, 10 ml of water and 100 ml of acetone was stirred on the stirrer hot plate arrangement at $\approx 40^\circ C$ for a few minutes to obtain a clear solution of the reagent and naphthalene. Then it was mixed with 1000-1500 ml of distilled water at room temperature. The coprecipitated mixture was further stirred for 3 hours and allowed to stand for 12 hours at room temperature. The supernatant solution was drained off with a siphon and the mixture was washed twice with double distilled water. The final adsorbent is slurry of PAN-naphthalene in water and stored in a bottle.

General Procedure

An aliquot of uranium solution containing 30-3100 μg of uranium was taken in a 25 ml beaker. The pH of this solution was adjusted ≈ 10.5 with 2 ml of a buffer solution and diluted to ≈ 5 ml with distilled water. The column loaded with the adsorbent PAN-naphthalene was conditioned to pH 10.5 with 2-3 ml of buffer and then the metal solution was passed through the column at a flow rate of 1 ml/min. The packing was washed with a small volume of water. Desorption of metal was carried out by passing 10 ml of 2.0 M of HCl at a flow rate of 1 ml/min and the solution was transferred to the polarographic cell. After the dissolved oxygen was removed by the passage of nitrogen gas, the differential pulse polarogram was recorded.

Results and Discussion

Reversibility of Uranium Reduction Process

In the present work, the differential pulse polarograms for uranium, 2.0-2.5 M HCl medium was used as the supporting electrolyte, showing a half peak width of 100 ± 2 mV, in both normal and reverse scan modes. The plot of applied potential versus $\log [i/(i_a - i)]$ from a d.c. polarogram has a slope of 62.0 ± 1 mV for two electron reduce ($r = 0.999$ and $n=5$, where is the correlation coefficient and n is the number of data points). The cyclic voltammetric study with a scan rate of 50 mV/sec, $X=Y=50$ mV/cm and gain 0.05 mA/V reveals that only a cathodic wave is obtained for uranium. Hence, all these studies clearly indicate that uranium is reduced irreversibly under these conditions.

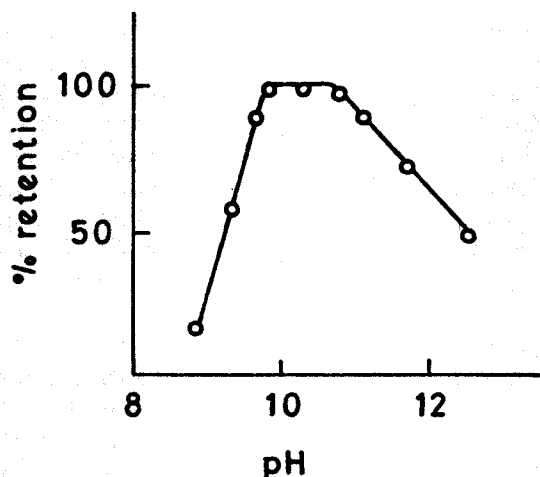


Figure 1. Effect of pH of adsorption of uranium complex Uranium, 50 μg in 10 ml of 2 M HCl of final solution; flow rate, 1 ml/min. Instrumental setting: scan rate, 12 mV/Sec; X=Y=100 mV/cm; sensitivity, 0.1 $\mu\text{A/V}$; drop time, 0.5 s

Retention Capacity of Chelating Agent Supported on Naphthalene

The retention capacity of the adsorbent was determined by a batch method. This experiment was carried out by taking 300 μg of uranium, 2 ml of buffer, and a suitable amount of the adsorbent material in a 100 ml separatory funnel. It was diluted to 30 ml, shaken with a mechanical shaker for 30 minutes and filtered through a filter paper. The amount of uranium in the filtrate was determined by the uranium remaining in the water solution after filtration. The retention capacity of uranium is found to be proportional to the amount of PAN naphthalene. The maximum capacity was found to be 0.2 mg of U/g of adsorbent (PAN-naphthalene).

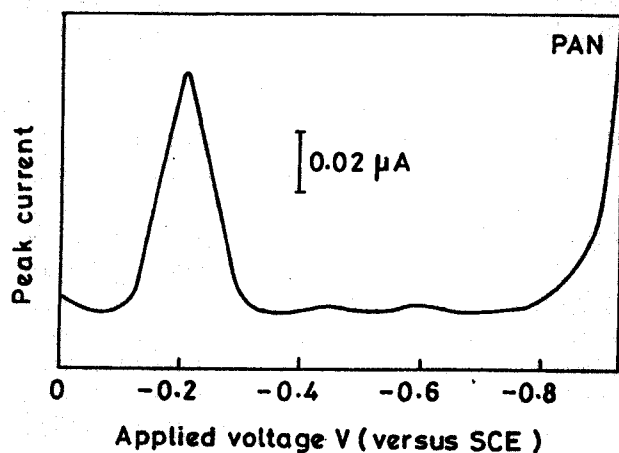


Figure 2. A typical differential pulse polarogram of uranium. Conditions and instrumental setting same as Figure 1

Reaction Conditions

The reaction conditions were investigated with 50 μg of uranium. Adsorption was carried out at different pH levels, keeping other variables constant. It was found that the uranium complex was quantitatively adsorbed on naphthalene in the pH range of 9.8-10.7 (Fig.1). The addition of 0.5-5 ml of buffer had no effect on the adsorption. Therefore, 2.0 ml of buffer was used in all the subsequent experiments. The flow rate was varied from 0.2 to 8 ml/min. It was found that a flow rate of 0.2-5.2 ml/min did not affect adsorption. A flow rate of 1 ml/min was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10-700 ml under optimum conditions, keeping other variables constant. It was observed that the signal height was almost constant up to 450 ml (preconcentration factor of 45). However, for convenience, all the experiments were carried out with 30 ml of the aqueous phase.

Preliminary observations indicated that uranium complex was desorbed completely with 8-10 ml of 1.5-2.5 M hydrochloric acid. Therefore, 10 ml of 2.0 M HCl was used in the present work.

Calibration

A typical polarogram for uranium is given in Figure 2. A calibration graph for the determination of uranium was prepared according to the general procedure under the optimum conditions developed above from its differential pulse polarogram with different concentrations. The detection limit was 1.5 $\mu\text{g ml}^{-1}$ (signal to noise ratio=2) and this was linear over the concentration range 3.0-310 $\mu\text{g ml}^{-1}$ (Fig.3) with a correlation coefficient of 0.9994 ($n=7$) and a relative standard deviation of $\pm 1.1\%$ ($n=7$) for 50 μg of uranium in 10 ml of 2 M HCl of final solution.

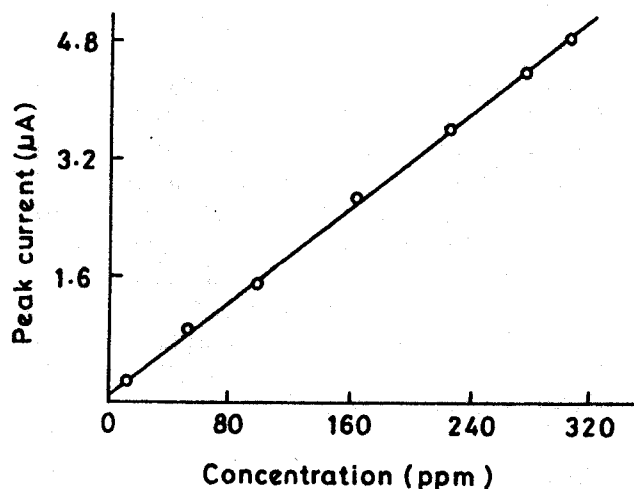


Figure 3. Calibration curve for uranium. Conditions and instrumental setting same as Figure 2

Effect of Foreign Ions

Various salts and metal ions were added individually to a solution containing 50 µg of uranium and the general procedure was applied. The tolerance limits (error<3%) are given in Table 1. Among the anions studied, only EDTA interfered seriously. Undoubtedly due to the higher formation constant of uranium-EDTA complex than its PAN complex. Among the metal ions studied, most did not interfere at the milligram level, except Fe (III). However, this could be easily masked by the addition of 2 ml of 5% triethanolamine solution. Thus, the method is highly selective and may safely be applied for the determination of uranium in synthetic samples.

Analysis of Synthetic Samples

A synthetic sample containing uranium was prepared in 10 ml of concentrated hydrochloric acid (1+1). The solution was filtered as needed and was made to 100 ml in a standard flask. An aliquot of the sample (40-100 ml) solution was analyzed by the general procedure and the results are given in Table 2.

Conclusion

An efficient adsorbent has been generated simply by mixing the solution of PAN and naphthalene and tried for the preconcentration of uranium from a large volume of the aqueous solution of its complex materials using

Table 1. Effect of foreign salts and metal ions

Salt or Ion	Tolerance limit
CH ₃ COONa. 3H ₂ O, KNO ₃	1g
(NH ₄) ₂ SO ₄	450 mg
NaCl	150 mg
NH ₄ Br	100 mg
K ₂ CO ₃ , KSCN	25 mg
Sodium potassium tartrate	20 mg
Trisodium citrate	15 mg
Sodium oxalate	10 mg
Disodium - EDTA	30 µg
Zn (II)	50 mg
Mn (II)	45 mg
Mo (VI)	40 mg
Ga (III)	20 mg
Al (III), Ti (IV)	19 mg
Se (VI), Cr (III)	15 mg
Bi (III), Te (IV)	5 mg
V (V), Ru (III), Th (IV)	2.5 mg
Rh (III), Pd (II), Cr (VI)	2 mg
Os (VIII), In (III), As (III)	1.5 mg
Pb (II), Cd (II), TI (I)	1 mg
Fe (III)	2 mg*
Ni (II), Sn (II), Co (II), Hg (I)	800 µg
Sb (III), Cu (II)	700 µg

*After masking with 2 ml of 5% triethanolamine solution

Table 2. Analysis of uranium in synthetic samples

Composition of synthetic sample (µg/g)	Expected value (µg/g)	Amount found by the present method* (µg/g)
As, 5.0; Cd, 0.60; Cu, 8.0 Ca, 60; Fe, 96; Ni, 25 Mn, 185; Hg, 0.11; Pb, 25; Zn, 218; Tl, 0.75; In, 10.5; In, 10.5; Bi, 27.0	2.4	2.37±0.07
Ni, 150; Fe, 110; V, 87 Zn, 315; Mn, 195; As, 4.0; Pd, 48; Se, 5.0; Th, 14; In, 17.8; Bi, 35.5; Cr, 118; Ca, 250	5.7	5.6±0.2
Pd, 4.7; Fe, 2.3; Co, 5.6; Mn, 28.5; Zn, 35.7; Ni, 45.5; In, 9.7; Bi, 8.5	3.4	3.3±0.1

*Average of five determinations and after masking with 2 ml of 5% triethanolamine solution ± standard deviation

differential pulse polarography.

It is difficult to obtain a well defined polarogram in the traditional analysis of metals after extraction of their complexes into an organic solvent owing to the low dielectric constant of the organic phase. Sensitivity is lost if it is mixed with another solvent of high dielectric constant. Sometimes a maximum suppressor is also required. Another major disadvantage is the removal of dissolved oxygen which is a tedious and time consuming process and affects the reproductibility of the method owing to partial evaporation of the organic solvent. The reported method had solved most of these problems and tested successfully for an estimation of uranium. Selectivity may be achieved by using AAS after the preconcentration step but AAS is expensive and its maintenance is high.

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