



Sodium dodecyl sulfate coated alumina modified with a new Schiff's base as a uranyl ion selective adsorbent

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ABSTRACT

A simple and selective method was used for the preconcentration and determination of uranium(VI) by solid-phase extraction (SPE). In this method, a column of alumina modified with sodium dodecyl sulfate (SDS) and a new Schiff's base ligand was prepared for the preconcentration of trace uranyl(VI) from water samples. The uranium(VI) was completely eluted with HCl 2 M and determined by a spectrophotometric method with Arsenazo(III). The preconcentration steps were studied with regard to experimental parameters such as amount of extractant, type, volume and concentration of eluent, pH, flow rate of sample source and tolerance limit of diverse ions on the recovery of uranyl ion. A preconcentration factor more than 200 was achieved and the average recovery of uranyl(VI) was 99.5%. The relative standard deviation was 1.1% for 10 replicate determinations of uranyl(VI) ion in a solution with a concentration of $5 \mu\text{g mL}^{-1}$. This method was successfully used for the determination of spiked uranium in natural water samples.

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1. Introduction

Uranium is one of the emerging pollutants due to its high toxicity and radioactivity and most recently its persistence in environment [1]. The hexavalent uranyl ion (UO_2^{2+} , U(VI)) was found to be the most stable form in vivo and is complexed in the blood by chelating agents such as proteins and carbonates. Distribution of toxic species and retention in target organs such as kidneys, liver and marrow occurs after chelation, potentially inducing cancer and chemical intoxication, especially in the case of heavy contamination [2]. On the other hand uranium is one of the contaminants that can be found in natural waters at ultra-trace concentration as a result of anthropogenic activities, weathering effects and erosion of rocks and soil. With due attention to this instance preconcentration and determination of this element in environmental samples (such as drinking and wastewaters) is an important task. The techniques which can be used for trace analysis of uranium generally have high sensitivity but are complex and costly, require skilled technicians and large laboratory-based instrumentation such as inductively coupled plasma atomic emission spectrometry (ICPAES) [3], inductively coupled plasma-mass spectrometry (ICP-MS) [4], fluorimetry [5], spectrophotometric [6] and voltammetric methods [7].

Liquid-liquid extraction of uranium has attracted considerable attention [8–10]. However these classical extraction methods are usually time-consuming and labor-intensive and require large volumes of high-purity solvents. Solid-phase extraction (SPE) [11–13] technique has increasingly become popular in comparison with the more traditional liquid-liquid extraction methods because of its several major advantages such as, simplicity to operation; high preconcentration factor, rapid phase separation; and the ability of combination with different detection techniques. Among solid-phase adsorbents, sodium dodecyl sulfate (SDS) coated alumina are very useful for preconcentration and separation of metal complexes [14,15] because of their good physical properties such as their porosity, high surface area and good adsorbent properties for great amounts of uncharged compounds. Surfactant present in aqueous solution can form stable self aggregates (micelles) when the surfactant concentration is above the critical micelle concentration (CMC). The formed micelles can incorporate hydrophobic organic compounds (HOCs), which can increase the solubility of these compounds apparently. Surfactant can also form self-aggregates at the solid surface such as alumina, silica and ferric oxyhydroxides surface. Generally, the alumina surface is hydrophilic and has low adsorption affinity for organic compounds; however, when it is treated with sodium dodecyl sulfate (SDS), alumina will acquire high adsorption capability for neutral compound. Due to the hydrophobic interactions of micelles formed on alumina surface, the HOCs escape from aqueous phase and become concentrated in the microscopic hydrophobic phase.

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The purpose of this work is to investigate the feasibility of absorption of uranyl ion on SDS coated alumina modified with a new Schiff's base. For obtaining maximum accurate and precise signal for evaluation of this ion content, the effective parameters such as pH of sample, amount of ligand and solid phase, type and concentration of eluting agent and contact time and stirring rate were optimized.

2. Experimental

2.1. Apparatus and measurement procedures

The UV/vis spectra and absorbance measurements were obtained using a Carry 3E UV–vis spectrophotometer (Varian Co.). Absorbance measurements at fixed wavelength were performed using a 1-cm quartz cell (1.0 mL). The absorbance of each sample was measured at 1 nm intervals using light with wavelengths between 400 and 800 nm. A Denver pH meter (model 270) with a combined glass electrode was employed for measuring pH values in the aqueous phase. The operational column dimensions for SPE were 10 mm × 150 mm with a sintered glass plate at the bottom of the column.

2.2. Reagents

All chemicals used were of analytical reagent grade purity available from Merck, Darmstadt–Germany or Sigma–Aldrich. Doubly distilled deionized water was used throughout. The pH adjustment was done by the addition of dilute nitric acid or sodium hydroxide to prepare the desired pH solution. The γ -Al₂O₃ (particle size > 0.2 mm) and sodium dodecyl sulfate (SDS) were purchased from Merck, Darmstadt–Germany and used as received. Stock solution of uranyl ion at a concentration of 1000 $\mu\text{g mL}^{-1}$ was prepared by dissolving appropriate amount of uranium nitrate salt in double distilled water. Working solutions were prepared by appropriate dilution of the stock solution with double distilled water. Arsenazo(III), 3,6-bis[(2-arsenophenyl)-azo]-4,5-dihydroxy-2,7-naphthalen- disulfonic acid, was obtained from Sigma–Aldrich. Acetate buffer solutions were prepared by mixing of appropriate volumes of 0.1 mol L⁻¹ acetic acid and 0.1 mol L⁻¹ sodium acetate solutions for pH 6.

2.3. Synthesis of

bis(2-hydroxyacetophenone)-1,2-propanediimine (BHAPN)

A solution of 1,2-propanediimine (0.223 g, 3.0 mmol) in absolute EtOH (15.0 mL) was added to a solution of 2-hydroxyacetophenone (0.817 g, 6.0 mmol) in absolute EtOH (20.0 mL) and boiled under reflux for 7.0 h. The reaction mixture was kept in the refrigerator overnight. After several hours, the product was obtained as yellow crystals. The crystals were filtrated and washed twice with cooled ethanol and dried under air (85% yields). Elemental analysis, % C₁₉H₂₂N₂O₂: C, 73.52; H, 7.14; N, 9.03; found: C, 73.21; H, 7.18; N, 8.98. IR (KBr, cm⁻¹): 3434 (bs, ν OH), 3158 (w, CH– Aromatic), 2922 (w, CH– Aliphatic), 1612 (–C=N), 1571 (C=C), 1506 (m), 1446 (m, C=C), 1382 (m), 1373 (s, C–N), 1298 (m), 1257 (m), 1226 (m), 1157 (s), 1061 (m, C–O), 1029 (m, C–O), 916 (m), 829 (s), 750 (s), 644 (m), 508 (m). ¹H NMR (500 MHz, CDCl₃): 16.18 (s, 1H), 15.96 (s, 1H), 7.54 (t, 2H, *J* = 7.75 Hz), 7.31 (m, 2H), 6.95 (d, 2H, *J* = 8.25 Hz), 6.84 (d, 1H, *J* = 7.65 Hz), 6.83 (d, 1H, *J* = 7.14 Hz), 4.35 (sext, 1H, *J* = 6.35 Hz), 3.85 (dd, 1H, *J* = 14.20 Hz and *J* = 7.15 Hz), 3.81 (dd, 1H, *J* = 14.2 Hz and *J* = 5.80 Hz), 2.44 (s, 3H), 2.37 (s, 3H), 1.45 (d, *J* = 6.35).

MS (*m/z*, fragment): 310(M⁺, HOC₆H₄C(CH₃)=N(CH₂)₃N=C(CH₃)C₆H₄OH), 295(HOC₆H₄C(CH₃)=N(CH₂)₃–N=C(CH₃)–C₆H₄–), 278(C₆H₄C(CH₃)=N(CH₂)₃N=C(CH₃)C₆H₄–),

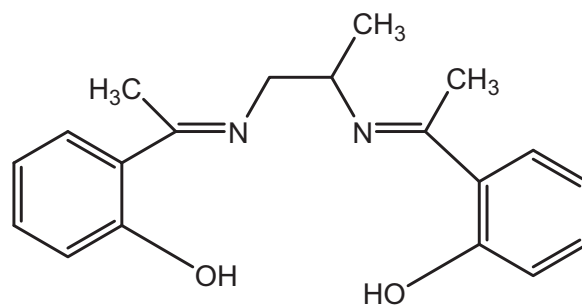


Fig. 1. Chemical structure of BHAPN.

176(HOC₆H₄C(CH₃)=N(CH₂)₃–), 160(HOC₆H₄C(CH₃)=N(CH₂)₂–),
148(HOC₆H₄C(CH₃)=N(CH₂–)), 134(HOC₆H₄C(CH₃)=N),
121(HOC₆H₄C(CH₃)C=), 108(HOC₆H₄CH=C=), 96(HOC₆H₄CH–),
83(HOC₆H₄–), 66(–C₆H₄–).

The structure of BHAPN is shown in Fig. 1.

2.4. Spectrophotometric titration

Standard stock solutions of BHAPN (1.0×10^{-4} mol L⁻¹) and the uranyl ions (1.0×10^{-3} mol L⁻¹) were prepared by dissolving appropriate and exactly weighed of pure solid compounds in pre-calibrated 25.0 volumetric flasks and diluted to the mark with MeCN. Working solutions were prepared by appropriate dilution of the stock solutions. Spectrophotometric titrations of the ligand were carried out by the addition of microliter amounts of a concentrated standard solution of the uranyl ion in MeCN using a precalibrated micropipette, followed by absorbance intensity reading at 25.0 °C at the $\lambda = 200$ –800 nm.

2.5. Preparation of solid phase

A BHAPN/SDS solution was prepared by dissolving 150 mg BHAPN and 250 mg SDS in 100 mL of double distilled water. A volume of 10 mL BHAPN/SDS solution was added to 40 mL of water solution containing 1.5 g of the γ -Al₂O₃ particles. While shaking the suspension with a stirrer, the pH was adjusted to 2 with 2 mol L⁻¹ nitric acid to form BHAPN -impregnated ad micelles on alumina particles. After mixing for 15 min, the supernatant solution was discarded and the remaining was used as modified solid phase. The solid phase was dried in room temperature and was used as adsorbent throughout the work. The SDS concentration was fixed below the CMC of SDS (8×10^{-3} mol L⁻¹) to avoid formation of micelles in the aqueous solution.

2.6. Recommended procedure

A glass column (10 mm × 150 mm) packed with 1.5 g BHAPN/SDS/ γ -Al₂O₃ was used as the operation column. Aliquot of 10 mL uranyl ion solution ($5 \mu\text{g mL}^{-1}$) in acetate buffer, pH = 6 was passed through the column at a flow rate of 0.5 mL min⁻¹. The adsorbed uranyl ion was eluted with 5.0 mL (2×2.5 mL) of HCl 2 M at an elution rate of 0.5 mL min⁻¹. Percent recovery of uranyl ion was calculated after analyzing uranyl ion in eluate by UV–vis spectrophotometer. The amount of U(VI) adsorbed was estimated by the difference between the initial concentration in aqueous solution and that found in the supernatant spectrophotometrically using Arsenazo(III) reagent [16]. After the addition of 4.0 mL HCl, then 0.5 mL of 0.01% Arsenazo (III) in a total volume of 10.0 mL the absorbance of Arsenazo(III) complex of U(VI) was measured at 654 nm against the reagent blank solution.

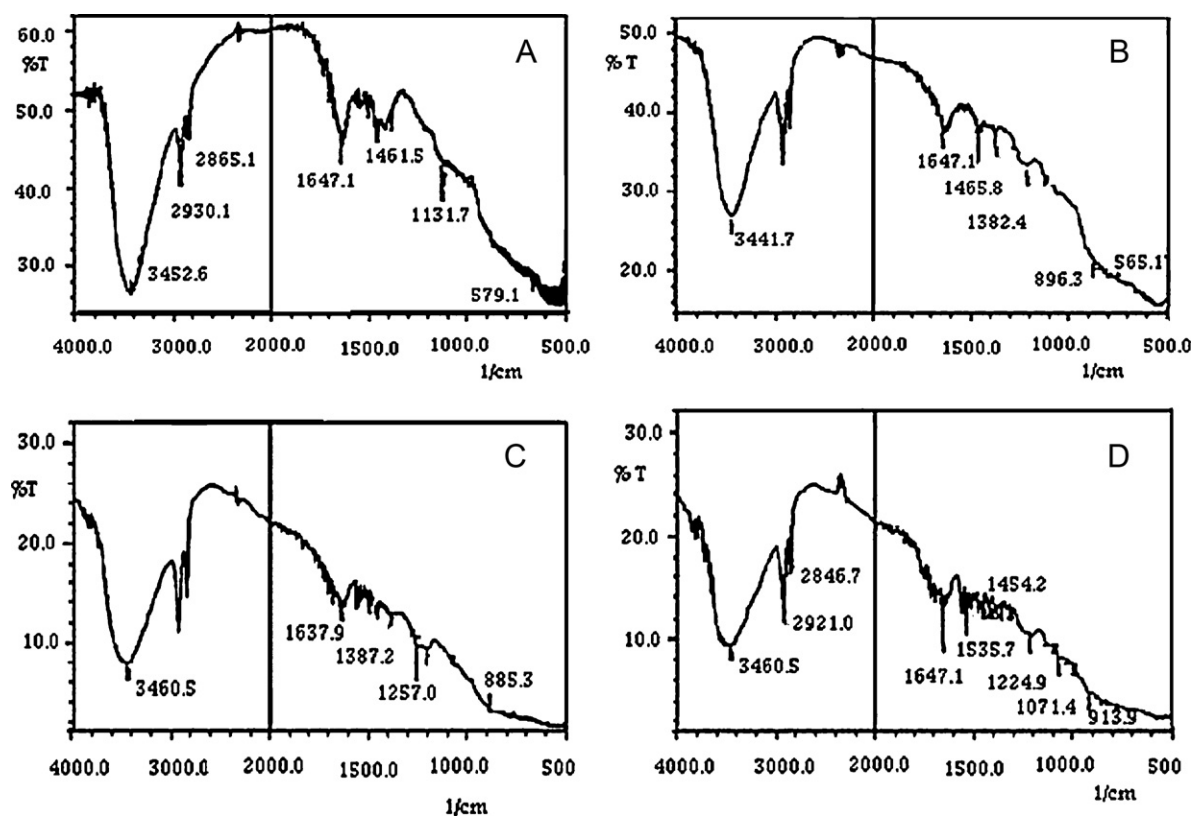


Fig. 2. FT-IR spectra of (A) Al_2O_3 , (B) Al_2O_3 modified with SDS, (C) $\text{Al}_2\text{O}_3/\text{SDS}$ modified with ligand and (D) $\text{Al}_2\text{O}_3/\text{SDS}$ –ligand uranium.

2.7. Analytical characterization of solid phase

In this experiment, the synthesized solid phase support was characterized using different analytical methods such as FT-IR spectrometry, thermogravimetric (TG) analysis and nitrogen adsorption isotherm. Fig. 2 shows the FT-IR spectra of solid support at different stages of modification and supporting processes. Compared with the FT-IR spectrum of alumina (Fig. 2A), the absorbance peak positioned at $\sim 1201 \text{ cm}^{-1}$ in Fig. 2B is related to the modification of alumina with SDS. Also, significant shift of this absorbance band to $\sim 1256 \text{ cm}^{-1}$ in Fig. 2C is correlated to the formation of covalent bond between ligand and alumina modified with SDS. Whereas compared with Fig. 2C, no significant differences were observed in Fig. 2D. The TG analysis of different forms of solid support is shown in Fig. 3. According to the thermograms, the small decrease in the weight percentage of the alumina to $\sim 0.4\%$ is related to the desorption of water from alumina. Also, the amount of SDS and ligand can be evaluated in accordance with the Fig. 3B and C. These values were estimated to $\sim 2.64\%$ and 0.52% , respectively. The nitrogen adsorption isotherms of solid supports are shown in Fig. 4 at 25°C . According to the nitrogen adsorption isotherm, the active surface areas of Al_2O_3 , $\text{Al}_2\text{O}_3/\text{SDS}$, $\text{Al}_2\text{O}_3/\text{SDS}/\text{ligand}$ and $\text{Al}_2\text{O}_3/\text{SDS}/\text{ligand}/\text{uranium}$ are evaluative to 213, 242, 311 and $351 \text{ m}^2 \text{ g}^{-1}$, respectively based on “Knudsen” equation [17]

3. Results and discussion

Activated alumina can function as either cation or anion preconcentrator depending on the pH. The adsorption of SDS on alumina is highly dependent on the solution pH. Negatively charged SDS was more effectively and nearly quantitatively adsorbed (about 99% even in 2 mol L^{-1} nitric acid) on the positively charged alumina surfaces at pH 1–4, so that organic compounds could be adsorbed on SDS-coated- γ -alumina which this phenomenon greatly increases

by decreasing the pH due to the higher charge density on the mineral oxide surface [18,19]. The anionic surfactant SDS is effectively adsorbed on positively charged γ -alumina surfaces via formation of self aggregates [16], over a wide pH range, whereas very little amount of SDS could be adsorbed on inert surface of α -alumina. Therefore, γ -alumina is essential for the preparation of surfactant-coated adsorbents. It was also confirmed that, while solid phase of alumina or alumina coated with SDS show no tendency for retention of metal ions, the solid phase of immobilized Schiff's base on surfactant coated alumina was capable of retaining metal ion from the sample solution quantitatively. Therefore, it was chosen as the adsorbent for subsequent work.

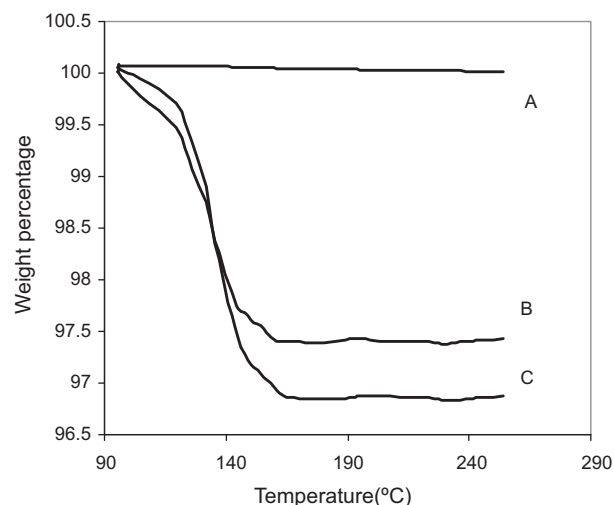


Fig. 3. Thermogravimetric analysis of (A) Al_2O_3 , (B) Al_2O_3 modified with SDS, and (C) $\text{Al}_2\text{O}_3/\text{SDS}$ modified with ligand.

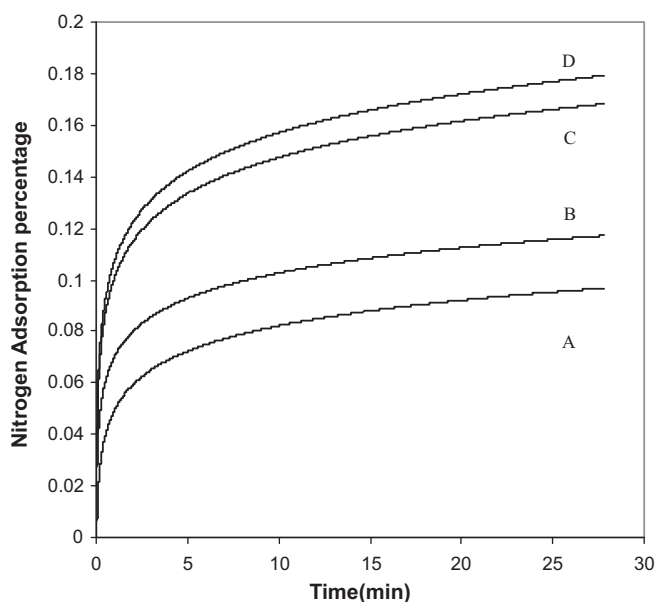


Fig. 4. Nitrogen adsorption isotherm of (A) Al_2O_3 , (B) Al_2O_3 modified with SDS, (C) $\text{Al}_2\text{O}_3/\text{SDS}$ modified with ligand and (D) $\text{Al}_2\text{O}_3/\text{SDS}$ -ligand uranium.

3.1. Investigation of complexation of ligand with uranyl ion

Bis(2-hydroxyacetophenone)-1,3-propanediimine (BHAPN) with two oxygens, two nitrogens donating Schiff base is insoluble in water at neutral pH. It is known that the Schiff bases ligands form very stable complexes with transition metal ions. The resulting complexes have attracted increasing attention, mainly due to their peculiar properties and their reactivity mainly in the area of binding small molecules.

The UV–vis spectra for the BHAPN were measured in acetonitrile to elucidate its uranyl complex behavior, which results a decrease in the ligand absorbance and produces a new absorbance peak at a longer wavelength (bathochromic shift). The spectra of a series of solutions containing a constant concentration of BHAPN at room temperature and varying amounts of the uranyl ion were obtained. The absorption of BHAPN in MeCN shows an absorption band at about 315. As is obvious from Fig. 5, a new absorption band at about 365 nm is observed upon addition of increasing quantities of uranyl ions to L, whereas the absorption intensity changes as a function of the $[\text{UO}_2^{2+}]/[\text{L}]$ molar ratio as shown in Fig. 5 (inset). High and obvious changes in the spectrum of ligand with the addition of uranyl ion indicate this ligand has strong interaction with this ion and is an efficient ionophore for trace metal enrichment. Therefore BHAPN was used as a suitable modifier for the selective concentration and extraction of uranyl ions on SDS-coated alumina. Some preliminary experiments were undertaken in order to investigate the quantitative retention of metal ions by the alumina in the absence and presence of BHAPN and/or SDS. It was observed that synergic effects of BHAPN in the presence of SDS lead to increase in recoveries, reproducibility and extraction efficiencies of this metal ion.

3.2. Effect of pH and flow rate of sample solution

The pH of sample solution plays an important role in metal–chelate formation and subsequent preconcentration. Therefore a series 10 mL of $5.0 \mu\text{g mL}^{-1}$ of uranyl ion sample solutions with different pH values from 1 to 10 were introduced into the packed column and uranyl ions were desorbed by eluent after adsorption. The initial pH of the solution was adjusted by the addition of concentrated solutions of HNO_3 or NaOH and measured by

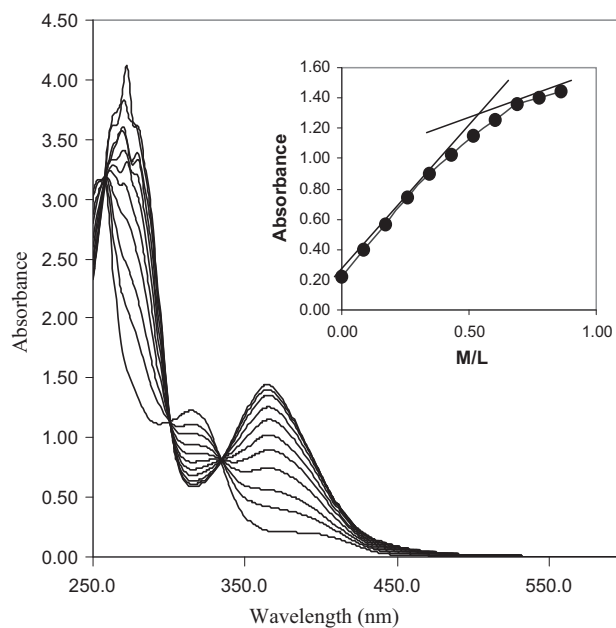


Fig. 5. UV-visible spectra of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ of (a) BHAPN in acetonitrile in the presence of various concentrations of uranyl ion $1.0 \times 10^{-3} \text{ mol L}^{-1}$, inset: mole ratio plot.

a calibrated pH meter. As shown in Fig. 6 maximum absorbance was obtained at pH 6. The progressive decrease in the retention of this metal ion at a low pH is due to the competition of the hydrogen ion with the metal ions for complexation and binding to Schiff's base. The decrease in absorption at $\text{pH} > 6$ is probably due to the precipitation of metal ions as insoluble $\text{M}(\text{OH})_2$ or $\text{M}(\text{OH})^+$. It is mentionable that at alkaline pH due to formation of a negative charge on the alumina surface the SDS adsorption on alumina will be reduced that causes a decrease in extraction efficiency. To achieve high efficiency and good selectivity, a pH of 6.0 was selected for subsequent work and in all experiments the pH of solution was fixed at $\text{pH} = 6$ with acetate buffer solution.

The effect of flow rate of the sample solution on the recoveries of uranyl on modified SDS coated alumina was examined in the range of $0.2\text{--}1.5 \text{ mL min}^{-1}$. It was found that, under optimum conditions,

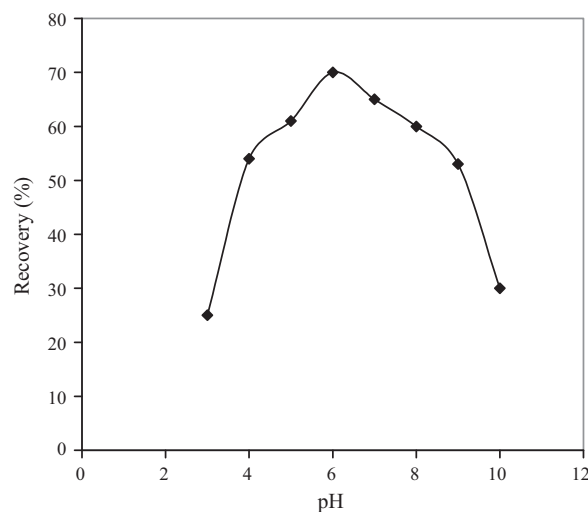


Fig. 6. Effect of pH of sample source on recovery of uranyl ions ($N = 3$). Experimental conditions: 10 mL of sample containing $5.0 \mu\text{g mL}^{-1}$ uranyl ion at various pHs, sorbent, 700 mg of BHAPN/SDS/ Al_2O_3 , eluent, 5 mL of 2.0 mol L^{-1} HCl.

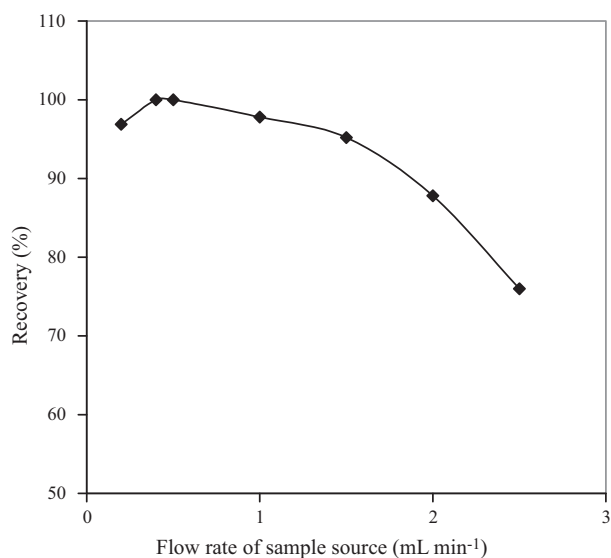


Fig. 7. Effect of flow rate of sample source on recovery of uranyl ions ($N=3$). Experimental conditions: 10 mL of sample at various flow rates, sorbent, 1.5 g of BHAPN/SDS/Al₂O₃, eluent, 5 mL of 2.0 mol L⁻¹ HCl.

the flow rate of the sample solution was lower than 0.7 mL min⁻¹ (Fig. 7).

3.3. Effect of ligand concentration

Since the amount of BHAPN is also an important factor in the preconcentration studies for the quantitative recoveries of analyte ion from the working media, the influences of the BHAPN amounts on the retention of uranyl ions on the SDS coated alumina was examined in the range of 0.0–25.0 mg and respective results are presented in Fig. 8. As it is obvious, maximum recovery at 10.0–15.0 mg of BHAPN could be achieved and further addition has not significant change on recovery of uranyl ion. Subsequent studies for further experiments were carried out with 15.0 mg of ligand.

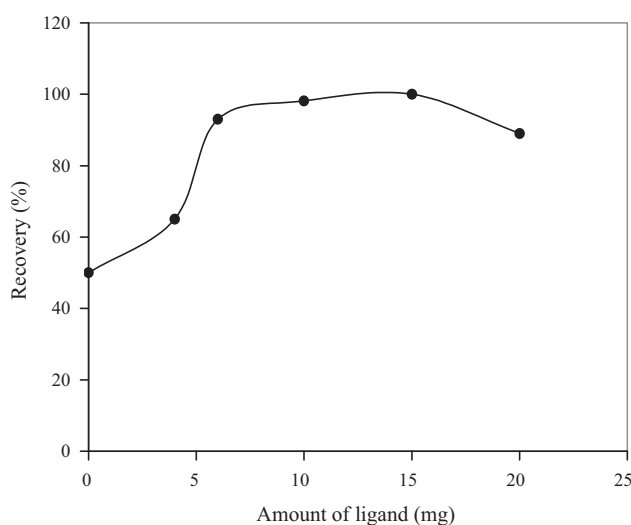


Fig. 8. Effect of amount of ligand on recovery of uranyl ions ($N=3$). Experimental conditions: 10 mL of 5 μ g mL⁻¹ uranyl ion at pH 6, solid phase, sorbent, 1.5 g of BHAPN/SDS/Al₂O₃ with different amounts of ligand, eluent: 5 mL of 2.0 mol L⁻¹ HCl.

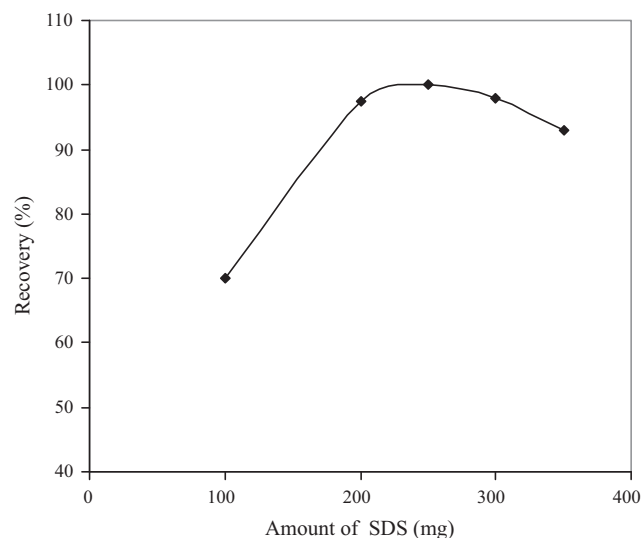


Fig. 9. Effect of amount of SDS on recovery of uranyl ions ($N=3$). Experimental conditions: 10 mL of 5 μ g mL⁻¹ uranyl ion at pH 6, sorbent, 1.5 g of BHAPN/SDS/Al₂O₃, different amounts of SDS, eluent, 5 mL of 2.0 mol L⁻¹ HCl.

3.4. Effect of sodium dodecyl sulfate concentration

The concentration (hemi-micelles, or ad-micelles) of surfactant aggregates on mineral oxides mainly depend on the surfactant/oxide weight ratio. In the absence of SDS, metal ions retained on alumina modified with BHAPN efficiency for uranyl ion were lower than 15%. The retention of metal ions on hemi-micelles which have a hydrophobic surface was clearly dependent on analyte complex polarity. Therefore, addition of SDS is necessary. The formation of minute amounts of ad-micelles was essential to achieve complete ad-solubilization of chelates of these ions. At surfactant concentrations higher than about 106 mg/g alumina, a decrease in the retention percentage of ions was observed, as a result of the formation of micelles. The adsorption amount began to decrease when the SDS added exceeded 106 mg for 1.0 g of alumina (Fig. 9). It can be explained by the fact that with more SDS added its molecules began to form micelles in the bulk aqueous solution; moreover, the micelles make distribute into the bulk solution again.

3.5. Amount of solid adsorbent

A series of different amounts of the solid adsorbent (250, 500, 750, 1000, 1250, 1500 and 1700 mg) were used for sorption of uranyl ions from 10 mL of 5 μ g mL⁻¹ uranyl ion solutions. The percent adsorption of uranyl ion using different amounts of the adsorbent showed that the appropriate amount of the solid adsorbent could be 1.5 g (Fig. 10). On the other hand, an excess amount of the adsorbent also prevents the quantitative elution of the retained metals by a small volume of eluent. Therefore in the proposed procedure, 1.5 g of solid phase is recommended.

3.6. Effect of elution condition on the recovery

For the elution of uranyl from the column, some parameters, i.e. type, volume, concentration and flow rate of eluent were investigated and optimized. The nature and concentration of eluting agents were found to have a significant effect on the elution process of the adsorbed ions from the solid phase. As could be seen from Fig. 6, the uptake of uranyl ions was negligible at pH < 3; therefore, the acidic eluents is the best solution for obtaining efficient extraction. Due to this point, various eluent solutions such as EDTA, nitric

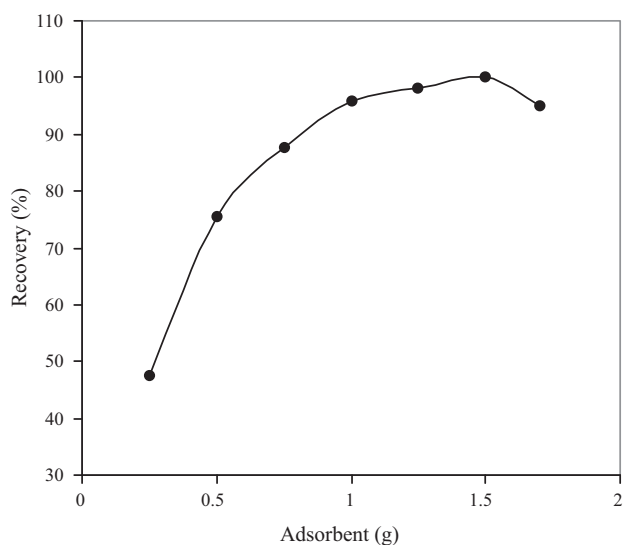


Fig. 10. Effect of amount of adsorbent on recovery of uranyl ions ($N=3$). Experimental conditions: 10 mL of $5 \mu\text{g mL}^{-1}$ uranyl ion at pH 6, different amounts of sorbent, eluent, 5 mL of 2.0 mol L^{-1} HCl.

acid, sulfuric acid and hydrochloric acid was used in order to find an appropriate eluent for desorbing of uranyl ion from adsorbent surfaces. Since the recovery was better in the presence of HCl as an eluent it was used as an appropriate eluent for desorbing of uranyl ion. Flow rate of HCl solution was the first parameter to be optimized. A volume of 10 mL of the sample containing 5 mg L^{-1} of uranyl ions was passed through the column at 0.5 mL min^{-1} . Elution of the SPE column was performed with 5.0 mL (2×2.5) of 2.0 M HCl at different flow rates between 0.2 and 1.0 mL min^{-1} . Fig. 11 shows the effect of eluent flow rate on the extraction recovery of uranyl. The quantitative recovery was observed at flow rates 0.5 mL min^{-1} . In order to find optimum volume of the elution solvent different volumes of HCl from 2 to 10 mL were investigated. The results are displayed in Fig. 12. As can be seen from the figure quantitative elution was attained using volume 5.0 mL. The influence of HCl concentration on the elution of uranyl ions from the adsorbent was also examined and the results are shown in Fig. 13

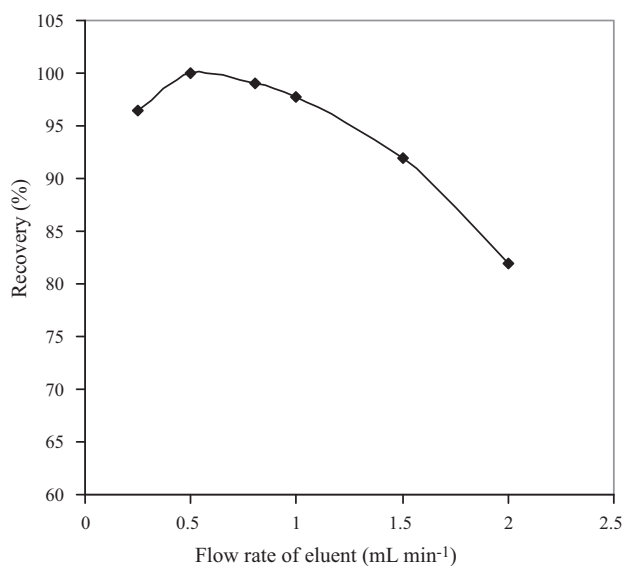


Fig. 11. Effect of flow rate of HCl on recovery of uranyl ions ($N=3$). Experimental conditions: 10 mL of $5 \mu\text{g mL}^{-1}$ uranyl ion at pH 6, sorbent, 1.5 g of BHAPN/SDS/ Al_2O_3 , eluent, 5 mL of 2.0 mol L^{-1} HCl; at different flow rates.

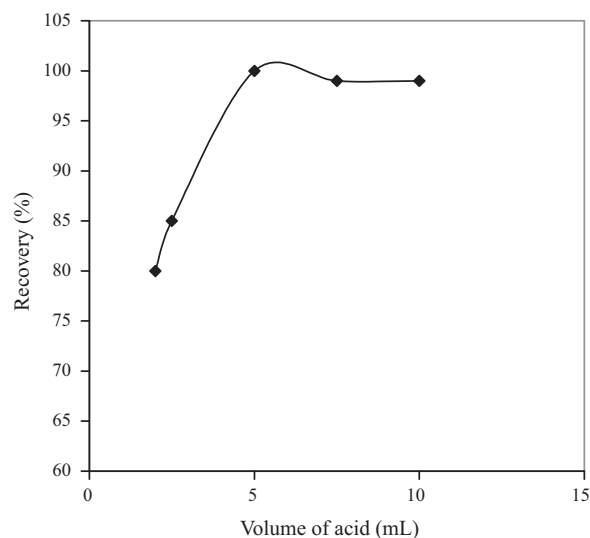


Fig. 12. Effect of volume of HCl on recovery of uranyl ions ($N=3$). Experimental conditions: 10 mL of $5 \mu\text{g mL}^{-1}$ uranyl ion at pH 6, sorbent, 1.5 g of BHAPN/SDS/ Al_2O_3 , eluent, various volumes of 2.0 mol L^{-1} of HCl; at flow rate 5.0 mL min^{-1} .

uranyl ions were quantitatively eluted from the column with 2.0 M HCl solution.

3.7. Repeatability and preconcentration factor

In order to find the relative error in the determination of uranyl ion, the recommended procedure was repeated ten times under optimum conditions. RSD was found to be 1.1% ($n=10$). Experiments to determine the sample loading volume were performed by passing increasing volumes between 10 and 1500 mL at increments of 50 mL until 1500 mL of aqueous solutions at pH 6 containing $5 \mu\text{g}$ of uranyl, through the solid phase column filled with 1.5 g of adsorbent. However, it should be pointed out that the larger amount of the sample solution, the more time (for passing it through solid phase) was required in the procedure. Uranyl ions were quantitatively recovered at the range of 10–1000 mL. At the higher volumes then 1000 mL, the recoveries for analytes were not quantitative.

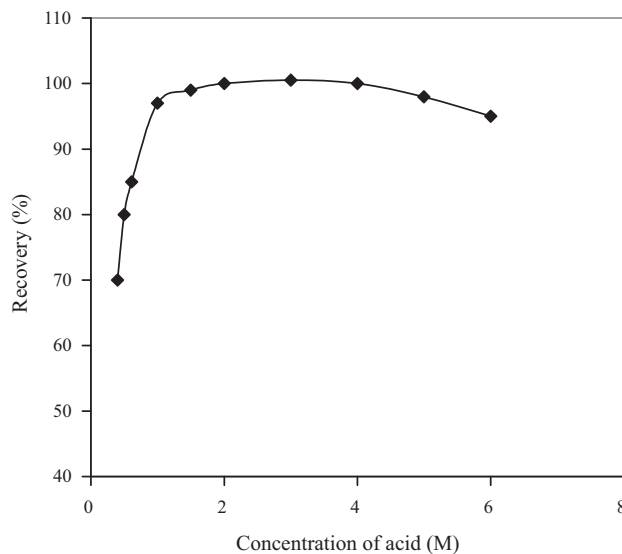


Fig. 13. Effect of concentration of HCl on recovery of uranyl ions ($N=3$). Experimental conditions: 10 mL of $5 \mu\text{g mL}^{-1}$ uranyl ion at pH 6, sorbent, 1.5 g of BHAPN/SDS/ Al_2O_3 , eluent, 5 mL various concentrations of HCl; at flow rate 5.0 mL min^{-1} .

Table 1
Percent recovery of uranyl ion in the presence of co-existing ions.

Co-existing ion	Concentration (mg L ⁻¹)	Recovery (%)
Al ³⁺	200	98.0 ± 0.7
Cl ⁻	1000	100.0 ± 0.3
NO ₃ ⁻	1000	97.0 ± 0.6
SO ₄ ²⁻	1000	100.0 ± 0.4
CO ₃ ²⁻	1000	97.8 ± 0.2
Mg ²⁺	1000	96.0 ± 0.5
Na ⁺	1000	98.0 ± 0.4
K ⁺	1000	98.1 ± 0.1
Ca ²⁺	1000	100.1 ± 0.7
Cd ²⁺	1000	96.2 ± 0.4
Co ²⁺	100	98.0 ± 0.3
Mn ²⁺	300	101.2 ± 0.8
Cu ²⁺	100	100.0 ± 0.3
Pb ²⁺	500	99.0 ± 0.6
Ni ²⁺	500	100.0 ± 0.4
Ba ²⁺	1000	97.8 ± 0.1
Fe ²⁺	20	100.2 ± 0.8
Fe ³⁺	50	100.0 ± 0.5
Cr ³⁺	100	100.0 ± 0.2
Hg ²⁺	1000	104.0 ± 0.7
Zn ²⁺	20	100.0 ± 0.3

To trade off the enrichment factor and analytical speed, 1000 mL of sample and 5.0 mL of HCl were used; therefore, an enrichment factor of 200 was obtained

3.8. Interference study and separation selectivity

To assess the possible analytical applications of the recommended procedure, the effect of some foreign ions which interfere with the determination of uranyl ion was examined with the optimized conditions. For these studies, a fixed amount of metal ion was taken with different amounts of foreign ions and recommended procedure was followed. The recoveries of metal ions in these studies were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions by the combination of the column solid phase extraction and spectrophotometric determination method. The results are summarized in Table 1. As it is seen, large numbers of ions used have no considerable effect on the determination of analyte ion.

3.9. Application

The procedure of SPE and determination of uranium was tested with some water samples such as tap water and well water. Various amounts of uranyl were spiked to these water samples and the recommended procedure was applied to the determination of uranyl in these samples. The results are given in Table 2. As it is obvious a good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method.

Table 2
Results of uranyl determination in natural waters according to the recommended procedure (N = 3).

	Sample	Added (mg L ⁻¹)	Found (mg L ⁻¹)	RSD (%)	Recovery (%)
1	Well water	1.00	0.98	0.56	98.0 ± 0.6
2	Well water	2.00	2.02	4.20	101.0 ± 0.2
3	Well water	2.50	2.47	4.50	98.8 ± 0.5
1	Tap water	1.00	0.96	3.4	96.3 ± 0.1
2	Tap water	1.70	1.65	5.5	97.0 ± 0.4
3	Tap water	2.00	1.99	2.5	99.5 ± 0.3

4. Conclusion

In the presented study, a new solid phase extraction technique was developed based on the preconcentration of UO₂⁺ ion in environmental samples on SDS coated alumina prior to the determination by spectrophotometric method. Under conditions given in this article, the determination of uranyl ion yields quantitative recoveries. The method is simple, accurate, and economical and can be applied for the determination of these ions in environmental samples. The system showed reproducibility and reliability in analytical data, with an R.S.D. value of lower than 5% on triplicate experiment.

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