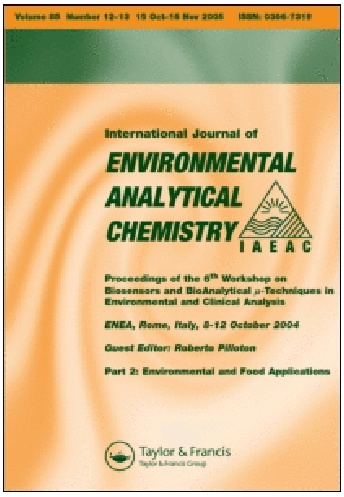

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Spectrophotometric determination of ultra trace uranium(VI) in seawater after extractive preconcentration with ionic liquid and dimethylphenylazosalicylfluorone

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A simple and effective method is presented for extractive preconcentration of uranium(VI) in water, in which the ionic liquid, 1-octyl-3-methylimidazolium hexafluorophosphate, abbreviated as [C_8mim][PF_6], was used as novel medium for liquid/liquid extraction of uranium(VI) and new reagent, dimethylphenylazosalicylfluorone, abbreviated as DMPASF, was employed to form neutral uranium(VI)-DMPASF complex. DMPASF reacted with uranium(VI) rapidly to form a stable red complex, the complex was then extracted into [C_8mim][PF_6] phase, and the uranium(VI) in [C_8mim][PF_6] was back-extracted into aqueous phase again with $3.0\,\mathrm{mol\,L^{-1}}$ hydrochloric acid. The extraction efficiency, back-extraction efficiency and preconcentration factor were 98.9%, 96.5% and 200 times for 100 µg of standard uranium(VI) in 1000 mL of water samples, respectively. The preconcentration coupled with spectrophotometry with chlorophosphonazo III, abbreviated as CPAIII, was developed for determination of ultra trace uranium(VI) in natural water. The apparent molar absorptivity of the uranium(VI)-CPAIII complex and the detection limit which was calculated using three times the standard error of estimate of the calibration graph was found to be $3.17 \times 10^6\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ and $0.22\,\mathrm{ng\,mL^{-1}}$ of uranium(VI), respectively. The absorbance of the uranium(VI)-CPAIII complex at 670 nm increase linearly with the concentration of uranium(VI) up to 45 µg of uranium(VI) in 1000 mL of aqueous solution. The interference study show that the determination of uranium(VI) is free from interferences of almost all positive and negative ions found in water samples. The relative standard deviation ($N = 10$) was 1.3% for uranium for 10 replicate determinations in the solution containing $1.0\,\mathrm{\mu g\,L^{-1}}$ of uranium(VI). The proposed method has been successively applied to determination of ultra traces of uranium(VI) in seawater samples.

Keywords: ionic liquid; uranium(VI); solvent extraction; dimethylphenylazosalicylfluorone; spectrophotometry

1. Introduction

Uranium and its compounds, like lead are highly toxic and cause progressive or irreversible renal injury and in acute cases may lead to kidney failure and death. The inhalation of uranium compounds results in deposition of uranium in the lungs and

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reaches the kidneys through the blood stream. Moreover, uranium behaves differently from many other metals due to its variable oxidation state. Unlike many other radioactive elements, its half life is commensurate with the age of the earth and, because of this, small amounts of uranium are found almost everywhere in the soil, rocks and water. In view of the extensive usage of uranium for various industrial purposes and their toxicity, precise determination of these metals in environmental, metallurgical and geological materials is of utmost importance prior to pollution control measures or its use as alloys or in understanding the correlation between diseases of animals and aquatic organisms and soil chemistry and to prepare soil maps. At present, many modern technologies have been applied for the determination of uranium concentration such as spectrophotometry using different chromogenic reagent [1], mass spectrometry [2], electrochemical method [3], radiochemical method [4], X-ray fluorescence spectrophotometry [5], laser-induced fluorimetry [6], reversed phase high performance liquid chromatography [7] and the optical sensor [8], but these are not sensitive enough to directly determine ultra trace uranium(VI). Therefore, in order to obtain a precise and accurate result, a suitable enrichment step was an important requirement [9,10]. To improve the sensitivity and selectivity, some new solvent extraction systems were reported to enrich trace uranium in various complex samples [11,12]. However, conventional solvent extraction needs to use organic solvents, which may result in some serious health and environmental problems due to the volatilisation of these organic solvents.

Ionic liquids have no detectable vapor pressure and are relatively thermal stable. Therefore, there is no loss of solvent through evaporation with ionic liquids, thus avoiding many of the environmental and safety problems associated with organic solvents. But, ionic liquids cannot extract simple metal ion from aqueous phase, it must be changed into neutral complex prior to extraction [12–15]. In previous work, two widely used chelating agent for actinide elements tributyl phosphate and chlorophosphonazo III (CPAIII) were investigated as the chelating agent to form neutral complex for extraction of uranium(VI) from aqueous solution using ionic liquid as novel medium. It was found that the above extraction systems offered very low extraction efficiency due to poor stability and hydrophobic property of the complex when the concentration of uranium(VI) is less than $1.0\,\mathrm{mg\,L^{-1}}$. In this work, we investigated the extractive preconcentration of uranium(VI) in a relatively large volume of water sample, in which ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim][PF_6]$) and new reagent dimethylphenylazosalicylfluorone (DMPASF) (see Figure 1) were used as medium and chelating agent to form neutral complex, respectively. Furthermore, the preconcentration coupled with spectrophotometry with CPAIII was also developed for determination of ultra trace uranium(VI) in seawater. The proposed method offers the advantages of rapidity, selectivity and sensitivity without the need for toxic organic solvent.

2. Experimental

2.1 *Apparatus and reagents*

A UV-240 spectrophotometer (Shimadzu, Japan) was used for recording the UV spectra using a 1-cm glass cell. All pH values were measured on a pHs-3C meter (Shanghai Leici Instrument Factory, China).

A stock standard uranium solution ($1.0\,\mathrm{mg\,L^{-1}}$) was prepared by dissolving appropriate amounts $UO_2(NO_3)_2 \cdot 6H_2O$ (spec pure) in water. The working standard

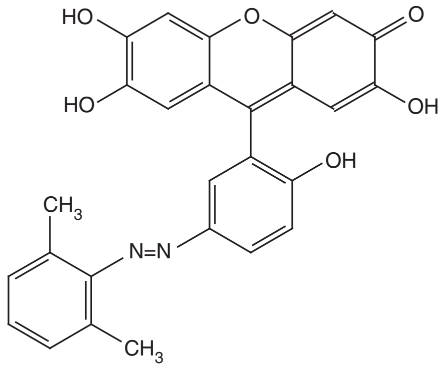

Figure 1. The molecule structure of dimethylphenylazosalicylfluorone (DMPASF).

solution (2.0 μg mL^{-1}) was prepared by diluting the stock standard uranium solution with water. DMPASF solution (3.0 g l^{-1}) was prepared by dissolving 0.3 g of DMPASF in 95% ethanol. The mixture solution used to form neutral complex was prepared by 50 g of ammonium acetate and 2.0 g of cetyltrimethyl ammonium bromide abbreviated as CTMAB in 250 mL of water. Unless above stated, other reagents used were of analytical grade and purchased from Shanghai chemical company (Shanghai, China), ultra pure water was used throughout the experiment and all glassware used was soaked with 10% nitric acid for one day and rinsed with ultra pure water before use.

2.2 *Synthesis of dimethylphenylazosalicylfluorone*

Fourty millilitres of acetic anhydride and 2.0 mL of concentrated H_2SO_4 were transferred to a 500 mL beaker, 11 g of benzol-1,4-diquinone was slowly added, stirring well, and the reaction temperature between 40 and 50°C. After that, a 200 mL of cool water was added into the beaker to precipitate 1,2,4-trihydroxylbenzene acetic ester. The precipitation was filtered, washed with cool water and dried at 70°C, 22 g of pure 1,2,4-trihydroxylbenzene acetic ester was obtained. In a 500 mL flask, 12.6 g of 1,2,4-trihydroxylbenzene acetic ester, 90 mL of ethanol, 8.0 mL of concentrated H_2SO_4 and 6 g of dimethylphenylazosalicylaldehyde were added, respectively. The above mixture was warmed at 50°C on a water-bath for 30 min to dissolve the mixture, then the flask was filled with nitrogen gas, sealed up and stood for one week under room temperature to form crystal DMPASF solid. The solid was filtered and dried at 80°C in a vacuum system, crude product of 4.43 g was obtained. Crude product of 1.0 g was dissolved in 20 mL of 50% (v/v) ethanol containing 1.0 mL of concentrated H_2SO_4. The precipitation was filtered and washed with hot water three times, and 0.7 g of pure product was obtained. Its structure was verified by IR, ^{1}H and ^{13}C NMR spectrometry and the elemental analysis results confirmed its purity. DMPASF is a yellow solid with melting point at 55°C, it is easy to dissolve in organic solvent such as acetone, ethanol and chloroform and difficult to dissolve in water.

2.3 *Preparation of ionic liquid*

An equal amount (0.5 mol) of 1-bromooctane and 1-methylimidazole distilled freshly were added to a 500 mL round bottom flask which is fitted with reflux condenser and nitrogen protecting facilities. After the mixture was stirred at 70°C for 12 h, a transparent viscous liquid, 1-octyl-3-methylimidazolium bromide was formed. The liquid was cooled to room temperature and then transferred to a 2000 mL beaker. Then 500 mL of water and 0.5 mol of potassium hexafluorophosphate were added to the well-stirred mixture. The mixture was continuously stirred for 4 h. Then the water phase was discarded and the ionic liquid formed [C_8mim][PF_6] was washed with water until bromide ion was wiped off completely using a silver nitrate test and heated to 80°C under vacuum to remove water and unreacted reagents, total yield was about 90%. Other 1-alkyl-3-methylimidazolium hexafluorophosphate was prepared by using a similar procedure [16].

2.4 *Determination of the uranium(VI) extraction efficiency*

To measure extraction efficiency, an aliquot of 3.0 mL of the mixture solution of ammonium acetate and CTMAB and 1.0 mL of DMPASF solution were added to 1000 mL of synthesised water sample containing 100 µg of standard uranium(VI). The solution was mixed well and DMPSF reacts with uranium(VI) to rapidly form red uranium(VI)-DMPASF complex. After 5.0 mL of the [C_8mim][PF_6] was added to the above solution, the biphasic system was shaken to ensure it was fully mixed and then deposited for 5 min. The absorbance at 555 nm of the complex in aqueous solution was measured on the spectrophotometer against a reagent blank solution. The extraction efficiency of the complex abbreviated as E was calculated by $E\ (\%) = (A_0 - A_1)/A_0 \times 100$, where A_1 and A_0 are the absorbances of the complex in aqueous phase after or before extraction.

2.5 *General procedure for determination of uranium(VI)*

An aliquot of 1000 mL of real water or synthesised water sample was transferred to a 2000 mL segregator, then 3.0 mL of the mixture solution of ammonium acetate and CTMAB and 1.0 mL of DMPASF solution were added. After the solution was mixed well, 5.0 mL of the ionic liquid [C_8mim][PF_6] was added to the solution. The biphasic system was shaken to ensure it was fully mixed and then deposited for 5 min, the aqueous solution discarded and the ionic liquid collected. The uranium(VI) in the ionic liquid [C_8mim][PF_6] was back-extracted into aqueous phase again by the addition of 5.0 mL of 3.0 mol L^{-1} hydrochloric acid, the aqueous solution was transferred into a 25 mL calibrated flask, 5.0 mL of 0.05% CPAIII solution added and then diluted to the mark in water. Then absorbance of the uranium(VI)-CPAIII complex at 670 nm was measured on the spectrophotometer against a reagent blank solution.

3. Results and discussion

3.1 *Formation condition and characteristics of the complex*

To optimise the formation conditions of the complex, various factors including the acidity, surfactant and amounts of reagents were tested in detail. As the uranium(VI)-DMPASF complex has a very sensitive absorption peak at 555 nm (shown in Figure 2), the complex can be easily determined by monitoring change of the absorbance of the complex at 555 nm on the spectrophotometer. It was found colour reaction of uranium(VI) with DMPASF gives a biggest and almost constant absorbance of the complex in the presence

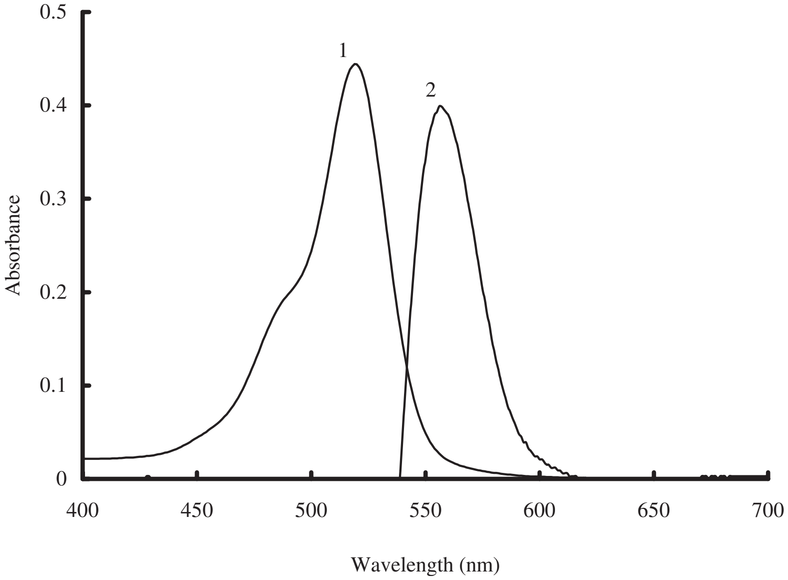

Figure 2. Absorption spectrum of DMPASF against water (1) and the complex against reagent blank (2).

of ammonium acetate medium of pH value between 7 and 9 and cationic surfactant CTMAB. For 100 µg of uranium(VI) in a 1000 mL water sample, the optimal amount of reagent was 3.0 mL of the mixture solution of ammonium acetate and CTMAB and 1.0 mL of DMPASF solution.

Under optimal formation condition, the reaction of uranium(VI) with DMPASF completes immediately at room temperature. The complex remain stable for at least 12 h, its composition ratio obtained using Job's method of continuous variation and the slope-ratio method is 1 : 3 (Uranium: DMPASF). Absorbance of the complex at 555 nm increase linearly with increasing uranium(VI) concentration up to 800 µg of uranium(VI) in 1000 mL of water solution. The apparent molar absorptivity of the complex was $1.25 \times 10^5 \, \mathrm{l\,mol^{-1}\,cm^{-1}}$. The interference study show the colour reaction has good selectivity, all foreign ions studied, apart from iron(III), aluminum(III) germanium(IV), molybdenum(VI) and tungsten(VI), can be tolerated in considerably amounts and do not interfere with the reaction.

3.2 *Effect of ionic liquid on the extraction of uranium(VI)*

Three 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids including the $[C_4mim][PF_6]$, $[C_8mim][PF_6]$ and $[C_{12}mim][PF_6]$ were investigated as solvent for liquid/liquid extraction of uranium(VI) in a relatively large volume of water samples such as 1000 mL, respectively. The results indicated that the uranium(VI) extraction efficiency using ionic liquid $[C_4mim][PF_6]$ as the medium is noticeably lower than that of the ionic liquid $[C_8mim][PF_6]$ and $[C_{12}mim][PF_6]$ when its amounts is less than 20 mL. This is due to the relatively high water-solubility of the ionic liquid $[C_4mim][PF_6]$. High water-solubility results in the loss of the ionic liquid during the extraction process and decreases the extraction efficiencies of the complex. Although both the ionic liquid [C_8mim][PF_6] and the [C_{12}mim][PF_6] showed excellent performance for liquid/liquid extraction of trace uranium(VI) due to good hydrophobic property and give a more than 98% extraction efficiency, the ionic liquid [C_{12}mim][PF_6] is solid state at room temperature and needs to be dissolved with and organic solvent such as acetone and ethanol or heat during whole extraction when the temperature is less than 25°C, which is very inconvenient. Thus, the ionic liquid [C_8mim][PF_6] was selected as medium for liquid/liquid extraction of uranium(VI) in the following experiment.

Once the solution of uranium(VI)-DMPASF complex was mixed with the ionic liquid [C_8mim][PF_6], the complex was rapidly removed from aqueous phase and the characteristic absorption peak of the complex in aqueous phase disappeared. It was found that the extraction efficiency of the complex varied greatly with the amounts of the ionic liquid used. With an increase in the volume of the ionic liquid [C_8mim][PF_6] used, the uranium(VI) extraction efficiency increased rapidly at first and then leveled off after the volume of the ionic liquid [C_8mim][PF_6] was greater than 4.0 mL. Thus, the recommended volume of the ionic liquid [C_8mim][PF_6] is 5.0 mL.

3.3 *Back-extraction of uranium(VI) from the ionic liquid*

Since the uranium(VI)-DMPASF was formed at a neutral medium, the complex may be decomposed to uranium(VI) ion and enter aqueous phase by using a strong acid solution. With this in mind, various mineral acids were used to strip uranium(VI) from the ionic liquid [C_8mim][PF_6] including nitric acid, sulfuric acid, hydrochloric acid and phosphoric acid. The experiments indicated these can decompose the complex into uranium(VI) ion rapidly and result in the uranium in the ionic liquid [C_8mim][PF_6] enter aqueous phase. The aqueous solution was directly used for determination of uranium in water samples by spectrophotometry with CPAIII without any pretreatment process in the following work. As the color reaction of uranium(VI) with CPAIII in the hydrochloric acid medium has a higher sensitivity than that in other acids, a hydrochloric acid solution was selected to strip uranium(VI) from the ionic liquid [C_8mim][PF_6]. When 3.0 mol L^{-1} hydrochloric acid exceeds 3.0 mL, almost all uranium(VI) was back-extracted to aqueous phase from the ionic liquid. Thus, an addition of 5.0 mL of 3.0 mol L^{-1} hydrochloric acid solution was recommended.

3.4 *Calibration graphs, sensitivity and precision*

The calibration graph was constructed according to the usual procedure (see Section 2.5). Beer's law was obeyed over the range 0–45 µg of uranium(VI) in 1000 mL aqueous solution. The apparent molar absorptivity was calculated from the slope of the calibration graph to be 3.17×10^6 L mol^{-1} cm^{-1}. The linear regression equation was calculated using the least squares method, which was found to be $A = 0.133 \times C + 0.00014$, where A is the absorbency at 670 nm, C the amount of aluminum (µg) in 1000 mL of aqueous solution. According to the procedure, another calibration graph, constructed on various uranium(VI) concentrations plus 10 g of sodium chloride were almost the same as that discussed. This indicates that the high concentrated sodium chloride in seawater samples has no effect on the results. The 3σ limit of detection for uranium(VI) in real sample was

Table 1. Tolerated limits of foreign ions and compounds.

Foreign ions	Tolerated limit ($g\,L^{-1}$)
Sodium chloride, potassium chloride, ammonium(I)	40
F^-, Br^-, SO_4^{2-}, CO_3^{2-}, NO_3^-, PO_4^{3-}	20
Lanthanum(III), cerium(III), ytterbium(III), calcium(II), magnesium(II), lithium(I)	5
Barium(II), zinc(II), manganese(II)	2
Cobalt(II), nickel(II), strontium(II), cadmium(II), Iron(III),	1
Chromium(III), aurum(III), silver(I),	0.5
Mercury(II), lead(II), thorium(VI),	0.04
Gallium(III), indium(III)	0.02
Tin(IV), molybdenum(VI), tungsten(VI),	0.01

0.22 ng mL^{-1} with a 1.3% of the relative standard deviation for 10 replicate determinations at the 1.0 µg of uranium(VI) per 1000 mL of sample solution.

3.5 *Interference study*

In order to test selectivity for determination of uranium, the effect of various foreign ions and compounds on the extraction of uranium(VI) and colour reaction of uranium(VI) with CPAIII were investigated, in turn. It was found that apart from aluminum(III), iron(III), molybdenum(VI), tungsten(VI) and germanium(IV) all metal ions and anions studied can be tolerated in considerabe amounts and do not interfere with the reactions of uranium(VI) with DMPASF. Although aluminum(III), iron(III), molybdenum(VI), tungsten(VI) and germanium(IV) also extract into the ionic liquid because these react with DMPASF to form neutral complex under the same reaction conditions, the molybdenum(VI), tungsten(VI) and germanium(IV) in the ionic liquid can be back-extracted by hydrochloric acid, only aluminum(III) and iron(III) enter aqueous phase from the ionic liquid. However, aluminum(III) and iron(III) do not interfere with the colour reaction of uranium(VI) with CPAIII. The tolerated limit of foreign ions were the concentration that caused an absorbance error less than ±5% in the determination of 5.0 µg of uranium(VI) in 1000 mL aqueous solution are given in Table 1. Table 1 indicates that the proposed analytical method for uranium is of excellent selectivity, it can be applied to determination of ultra trace uranium(VI) in seawater samples.

3.6 *Analytical application*

The proposed method was applied to the determination of uranium(VI) in a seawater sample, which was collected from the East China Sea, the mean value of five measurement is 1.5 µg L^{-1}. The percentage recovery was also employed for calculation of the method accuracy, since there is no certified reference material for seawater. To sample solutions having the initial uranium concentration, a known amount of standard uranium(VI) was added and the total content determined by the standard addition method. The recovery results between 97.2 and 104.2% showed that the method can be used to assay uranium in seawater with a good accuracy.

3.7 *Reuse of ionic liquid*

The reuse of $[C_8min][PF_6]$ and DMPASF was tested. They were used, respectively, as medium and chelating reagent for liquid/liquid extraction of uranium(VI). Then, the ionic liquid containing DMPASF was reused, with no DMPASF added to the sample solution, and the extraction efficiency for each reuse of the ionic liquid was measured. The results showed that the uranium(VI) extraction efficiency remained almost constant when the ionic liquid was not used more than three times. Why does increasing the times of reuse of the ionic liquid result in decreasing uranium(VI)extraction efficiency? In order to answer this question, the whole extraction process was investigated in detail. It was found that DMPASF in the ionic liquid can also react with uranium(VI) in sample solution when two phases were mixed well, but DMPASF concentration in the ionic liquid will noticeably decrease due to its loss partly during extraction and back-extraction of uranium(VI) with increasing times of reuse of the ionic liquid. Thus, the $[C_8min][PF_6]$ can be recycled for liquid/liquid extraction of uranium

4. Conclusions

The extraction system is very safe, simple, selective and effective, it can be widely applied to enrichment of uranium(VI) in industry or analytical chemistry. The enrichment combined with colour reaction of uranium(VI) with chlorophosphonazo III or other analytical reagents has high selectivity and sensitivity, it can be used for determination of ultra trace uranium(VI) in various complex samples such as water, ore and soil.

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