Separation and Preconcentration of Trace Uranium(VI) by Solid Phase Extraction with 2,3-Dihydroxynaphthalene and Cetyltrimethylammonium Bromide on Molten Naphthalene and Its LED Fluorimetric Determination in Water Samples

Susanta Kumar PRADHAN*† and Balram AMBADE**

*Chemical Laboratory, Atomic Minerals Directorate for Exploration and Research, Department of Atomic Energy, Eastern Region, Khasmahal, Jamshedpur-831002, India

**Department of Chemistry, National Institute of Technology, Jamshedpur-831014, India

A simple and rapid solid phase extraction (SPE) procedure has been developed for the extraction and determination of uranium in water samples. The method is based upon the adsorption of uranium(VI)-2,3-dihydroxynaphthalene complex on microcrystalline naphthalene at the pH range 10 – 12 in the presence of a counter cation cetyltrimethylammonium ion. The solid mass consisting of uranium-2,3-dihydroxynaphthalene-CTA complex and naphthalene is ignited in the furnace at a temperature of 700°C for 1 h and then digested in dil. HNO₃ solution. Uranium is then determined by LED fluorimetry using fluorescence enhancing pyrophosphate buffer. The effects of different variables like pH of the solution, reagent concentrations, counter cations, stirring time, interfering ions *etc.* have been investigated thoroughly for the quantitative recovery of uranium. The accuracy of the developed method has been ascertained by standard addition method as well as conventional pellet fluorimetry method involving co-precipitation of uranium using aluminum phosphate as a carrier.

Keywords Uranium, solid phase extraction, 2,3-dihydroxynaphthalene, microcrystalline naphthalene, LED fluorimetry

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Introduction

Uranium is an important element in the nuclear industry especially as an energy source. U²³⁵, an isotope of uranium, is the only naturally occurring fissile element available in the earth's crust that can be directly used in a nuclear reactor to produce energy through nuclear fission. Low concentrations of uranium are normally present in various complex materials, like nuclear energy sights, alloys, plants, water, effluents, *etc.* Hydro-geochemical exploration is one of the methods of exploration to locate concealed uranium deposits. The application of water sampling in the geochemical exploration of uranium is based on its property of high solubility on the uranium(VI) oxidation state. U(VI) forms complexes with chloride, carbonate, sulfate, phosphate, fluorides, *etc.* present in natural water. As ground water flows, it tends to converge in lakes and streams. Therefore, systematic water sampling allows the detection of hydro-geochemical dispersion haloes of hidden uranium deposits.¹ Hence, it is very important from an analytical point of view to develop a sensitive, selective, rapid method for its quantitative determination present in trace and ultra-trace levels.

There are various methods available for the determination of uranium in geological samples. Mention may be made of a few such as gravimetry, volumetry, UV-visible spectrophotometry,

fluorimetry (pellet and LED/laser), X-ray fluorescence spectrometry (XRF), gamma-ray spectrometry, neutron activation analysis (NAA) as well as fission track method, *etc.*² Spectrophotometric determination of uranium using various complexing agents after extraction of its complexes in some organic solvents lacks sensitivity and selectivity.³⁻⁵ Although atomic absorption spectroscopy,⁶ neutron activation analysis,⁷ X-ray fluorescence,⁸ ICP-OES and ICP-MS^{9,10} may be applied for the determination of uranium in complex samples like rocks, minerals, concentrates *etc.*, these instruments are expensive, need day-to-day high maintenance costs and they are not free from various types of inherent interference.⁶⁻¹⁰ Determination of uranium in these samples by fluorimetry is a valuable tool in the uranium exploration. The most sensitive method for the determination of trace levels (ppm to ppb) of uranium is based upon the measurement of its fluorescence; either in sodium fluoride melts in the case of pellet fluorimetry, or in phosphate medium in the case of laser/LED fluorimetry. However, for the determination of uranium in water samples, where uranium is present in ppb to ppt levels, the energy of the excitation source (fluorescent lamp) in pellet fluorimetry is too weak to excite fluorescence. Therefore, instruments with high energy excitation sources like laser or LED are used for the determination of uranium at this ultra-trace level. This is because fluorescence intensity (F) is directly proportional to the intensity (I) of the excitation source ($F \propto I$), which leads the favorable detection limit of these instruments. However, an LED based fluorimeter is preferable due to higher stability of the excitation source,

† To whom correspondence should be addressed.
E-mail: skpradhan.amd@gov.in

wide linear working range up to 1000 ppb and longer life of LED.¹¹

However, direct determination of uranium in water samples is impossible when the concentration of the uranium is below the determination limit of the instrument used. Therefore, preconcentration methods are very much essential to bring the concentration of uranium to the desired level of an instrument like laser/LED fluorimetry. The widely used techniques for the separation and preconcentration of metal ion include solvent extraction, co-precipitation, ion-exchange, solid phase extraction, cloud point extraction, *etc.* All the techniques in their own have some advantages and disadvantages. However, recent publication on continuous liquid-liquid extraction of uranium from uranium containing wastewater using an organic phase refining type emulsion flow extractor has gained significant attention.¹² Almost all fluorimetry methods require separation of uranium from other elements that may interfere with the determination of uranium. Although liquid-liquid solvent extraction involving well known organic solvents like TBP, TOPO, D₂EHPA and ethyl acetate are used for extraction of uranium, they are not free from disadvantages, including consumption of time, high labor cost and need for a large volume of high purity solvent, *etc.* On the other hand, solid phase extraction (solid-liquid extraction) offers several advantages over liquid-liquid extraction, such as high enrichment factor, absence of emulsion, minimal costs due to low consumption of reagent, flexibility and safety with respect to hazardous samples.

A number of solid phase extractants (SPE) like chelating resin, cellulose, silica gel, metal hydroxides, activated carbon, *etc.* have been investigated for the separation and preconcentration of inorganic metal ions. Appropriate organic ligands can be chemically or physically supported on various substrates, thus providing complexing or chelating sorbents for the separation and preconcentration of metal ions.¹³ Naphthalene is known as an excellent extractant at high temperatures but cannot be applied to thermally unstable complexes. Several workers have used solid phase extraction based on adsorption of metal chelates on microcrystalline naphthalene, which is more rapid and convenient and has been applied to many types of metal complexes. Sanjay Kumar *et al.*¹⁴ used solid phase extractant (a homogeneous mixture of TOPO and naphthalene) for separation of uranium in geological samples and achieved determination by laser induced fluorimetry method. Naveen Kumar *et al.*¹⁵ used oxine supported on microcrystalline naphthalene for preconcentration of uranium and other metal ions and achieved determination by ICP-OES. Several other works¹⁶⁻²¹ have also used chelating agent supported on microcrystalline naphthalene for the separation of uranium from different matrices.

The reagent 2,3-dihydroxynaphthalene (2,3-H₂ND) is a well-known O-O' type bi-dentate ligand. It has been used as an extractant in liquid-liquid solvent extraction for several elements like uranium,²² thorium,²³ rare earth elements,²⁴ molybdenum,²⁵ manganese,²⁶ and iron, *etc.* Tarafder *et al.*²² used this reagent for liquid-liquid solvent extraction of uranium in silicate rock samples. However, an extant literature survey shows that no such report is available for solid phase extraction of uranium on microcrystalline naphthalene with this cited reagent. This prompted the authors to undertake a detailed study to establish a method to separate and preconcentrate uranium in water samples by solid phase extraction using the extractant, 2,3-dihydroxynaphthalene (2,3-H₂ND) in the presence of a counter cation such as cetyltrimethylammonium bromide (CTAB) on microcrystalline naphthalene. Based upon this separation and preconcentration technique, a highly effective and alternative method for the LED fluorimetric determination of ultra-trace

level (sub-ppb) uranium in water samples has been developed.

In the present paper, details of a systematic study have been encompassed on the development of a solid phase extractive LED fluorimetric method for the determination of uranium in water samples.

Experimental

Apparatus

One pulsed LED (light emitting diode) fluorimeter (Model: UA-2, make: Quantalase India Pvt. Ltd., Indore, India) was used for fluorescence measurement of uranium in aqueous medium at the $\lambda_{\text{excitation}}$ and $\lambda_{\text{emission}}$ of 405 and 516 nm, respectively. Similarly, one pellet fluorimeter (Model: FL 6224A, make: Electronics Corporation of India Ltd., Hyderabad, India) was used for fluorescence measurement of uranium in solid (pellet) medium at the $\lambda_{\text{excitation}}$ and $\lambda_{\text{emission}}$ of 365 and 565 nm, respectively. One pH meter (Model: LI-120, make: ELICO, Hyderabad, India) was used for pH measurement. A muffle furnace was used for the fusion of the flux at 850°C.

Standards and reagents

U₃O₈ standard (1 mg mL⁻¹): Weighed 0.25 g U₃O₈ (dried at 105°C) in 250 mL volumetric flask, dissolved in 7.5 mL conc. HNO₃, diluted with water and made up to the mark with distilled water to obtain 1 mg mL⁻¹ U₃O₈ solution. Then the 1 µg mL⁻¹ U₃O₈ solution was prepared by diluting the stock solution. This was further diluted to prepared ppb level U₃O₈ working standard solution.

Preparation of 2,3-dihydroxynaphthalene 1% (w/v) was done by dissolving 1 g in 100 mL ethyl acetate. Sodium acetate 10% (w/v), potassium hydroxide 5% (w/v), cetyltrimethylammonium bromide (CTAB) 1% (w/v) and Na₂EDTA 10% (w/v) were prepared in aqueous solutions separately. Naphthalene (scintillation grade) solid, tetra sodium pyrophosphate buffer 5% (w/v) solution (adjusted pH ~7 using a few drops of 1:1 *ortho*-phosphoric acid) was used for fluorescence enhancing reagent for uranium. Unless otherwise stated, all reagents and chemicals used were of AR/GR grade of standard make.

General Procedure

Pretreatment of samples

Water (ground water) samples were collected from different field areas of eastern India in pre-washed polyethylene bottles. All the water samples were filtered through a 0.45-µm pore size membrane filter to remove suspended particulate matter and acidified with 1% nitric acid.

Solid phase extraction and determination of uranium

To a 250-mL water sample taken in a 500-mL beaker containing up to 10 µg uranium was added with 5 mL of 1% 2,3-dihydroxynaphthalene (2,3-H₂ND) in ethyl acetate. This was stirred well with a magnetic stirrer. Then, 5 mL of 1% cetyltrimethylammonium bromide (CTAB) was added followed by the addition of 2.0 g naphthalene, which was melted at 80–90°C and stirred continuously for about 10 min in the heated condition. To this was then added with 10 mL of 10% CH₃COONa, 3 mL of 10% Na₂EDTA solution and 5 mL of 5% KOH, and the pH was adjusted in the range of 10–12 and stirred continuously for another 20 min in the heated condition (at molten naphthalene temperature, ~80°C). After cooling, the solid mass containing the uranium ion associated complex

Fig. 1 Plot of % recovery of 10 µg uranium vs. pH of the solution at the time of solid phase extraction (amount of 2,3-H₂ND/ 0.31×10^{-3} mol, amount of CTAB/ 0.14×10^{-3} mol, amount of naphthalene/ 15.6×10^{-3} mol, stirring time: 30 min).

adsorbed on microcrystalline naphthalene was filtered through Whatman filter paper 41. The filter paper containing a solid mass in a platinum crucible was charred in a muffle furnace at 700°C for about 1 h in order to destroy the organic matter completely; otherwise the organic matter quenches the uranium fluorescence in aqueous solution. The solid mass was treated with a few ml of diluted HNO₃ and dried. This was digested with 2 mL pyrophosphate buffer (5%), which was also used as a fluorescence enhancing reagent and taken in a 10-mL volumetric flask and made up to the volume with distilled water. The fluorescence intensity was then measured in an LED based fluorimeter. The process blank was also run in a similar way. A wide calibration curve (not shown here) comprising fluorescent counts against known concentrations of standards up to 1000 ppb was prepared and calculated the concentration of uranium for an unknown sample solution from the calibration curve.

Results and Discussion

During the last few decades, separation and preconcentration based on solid-liquid extraction with microcrystalline naphthalene modified with different chelates has received great attraction. As has already been discussed in the prelude of the paper, several workers have used solid phase extraction of uranium on microcrystalline naphthalene modified with different chelates.¹⁴⁻²¹ However, solid phase extraction of uranium on microcrystalline naphthalene with the bi-dentate chelate 2,3-dihydroxynaphthalene in the presence of cetyltrimethylammonium bromide has not so far been reported in the existing chemical literature. This prompted authors to explore the present study for separation and preconcentration of uranium in water samples followed by its LED fluorimetric determination.

In what follows are given details of studies on the variables affecting the solid-liquid extraction of uranium from a sample solution.

Effect of pH on the extraction of uranium

In order to show the effect of pH on the extraction of uranium as uranium-2,3-dihydroxynaphthalene (2,3 H₂ND) complex on microcrystalline naphthalene, a set of solutions containing 10 µg uranium each was studied over a pH range of 1 to 12. Under optimized conditions, it was found that the extraction of uranium was observed from pH 5 to 12, but the maximum

Fig. 2 Plot of % recovery of 10 µg uranium vs. amount of 2,3-H₂ND/ 10^{-3} mol (amount of CTAB/ 0.14×10^{-3} mol, amount of naphthalene/ 15.6×10^{-3} mol, pH: 10 – 12, stirring time: 30 min).

efficiency and reproducibility of the extraction was achieved in the range of pH 10 – 12, which is shown in Fig. 1. This indicates that the uranium-2,3-dihydroxynaphthalene (2,3-H₂ND) complex was adsorbed on microcrystalline naphthalene quantitatively and the recovery of uranium was more than 95%.

Effect of concentration of 2,3-dihydroxynaphthalene (2,3-H₂ND)

In order to investigate the effect of the amount of 2,3-H₂ND on the quantitative extraction of uranium, the extraction studies were conducted by varying the amounts of 2,3-H₂ND from 0.1 to 10 mL of 1% (w/v) 2,3-H₂ND) for 10 µg uranium, keeping the other parameters constant. The results showed that the percentage recovery of uranium in terms of fluorescence intensity increases gradually with the increasing concentration of chelates. At the reagent concentration of 0.125×10^{-3} mol, the uranium-2,3-H₂ND complexes were adsorbed on microcrystalline naphthalene quantitatively. However, in order to allow for reagent impurity and the scope for the complexation of higher amounts of uranium, a concentration of 0.31×10^{-3} mol (5 mL of 1% 2,3-H₂ND) is recommended. This is illustrates in Fig. 2. Uranium forms its anionic complex with 2,3-dihydroxynaphthalene at the alkaline pH.²²

Effect of cetyltrimethylammonium bromide (CTAB)

The effect of CTAB on the complexation of uranium with 2,3-H₂ND and its subsequent solid phase extraction on microcrystalline naphthalene was studied by varying its concentration from dilute to concentrate solution. It was found that 10 mL of 0.01 M (0.1×10^{-3} mol) solution was required for the complete extraction of 10 µg uranium. However, in the presence of higher amounts of uranium and for reagent impurities, 5 mL of 1% CTAB (0.14×10^{-3} mol) is recommended. It was observed that a 100% retention of the uranyl-2,3-H₂ND complex took place only in the presence of CTAB. In the absence of CTAB, only ~60% retention of the uranyl-2,3-H₂ND complex took place on microcrystalline naphthalene. This indicates that a part of the uranyl complex with 2,3-H₂ND is negatively charged and in the presence of positively charged CTA⁺, neutral ion-associated complex is formed. Earlier, Tarafder *et al.*²² reported that 3 moles of 2,3-H₂ND and 2 moles of CTAB took part in the formation of an uranyl ion associated complex. In the case of 2,3-H₂ND, 2 moles are present within the co-ordination sphere and 1 mol is present as an adductant. The tentative composition of the ion-associated complex is formulated as (CTA)₂[UO₂(ND)₂].H₂ND. The stoichiometry

Fig. 3 Plot of % recovery of 10 µg uranium vs. amount of naphthalene/10⁻³ mol (amount of 2,3-H₂ND/0.31 × 10⁻³ mol, amount of CTAB/0.14 × 10⁻³ mol, pH: 10 – 12, stirring time: 30 min).

between UO₂²⁺, 2,3-H₂ND and CTAB is 1:3:2.

It is pertinent to mention here that the extracted species (CTA)₂[UO₂(ND)₂]-H₂ND on microcrystalline naphthalene is destroyed by ignition or perchloric acid treatment in order to remove the organic matter, which otherwise quenches uranium fluorescence. The fluorescence of free uranyl ions are enhanced by the addition of fluorescence enhancing reagent (FER). The excitation and emission spectra of uranyl ions in phosphate medium had already been reported in earlier literature.²⁷⁻²⁹

Effect of the amounts of naphthalene

In order to adsorb uranyl-2,3-dihydroxynaphthalene complexes quantitatively, the amount of naphthalene was also chosen carefully. In order to investigate the effect of the amount of naphthalene on the quantitative recovery of 10 µg uranium, the recovery studies were conducted by varying the amounts of naphthalene from 0.5 to 5 g (3.9 – 39 × 10⁻³ mol). It was found that uranium could be recovered quantitatively (95%) with 1 g naphthalene. However, in order to allow for reagent impurity and the scope for the adsorption of higher amounts of uranium, 2 g (15.6 × 10⁻³ mol) naphthalene is recommended. This is shown in Fig. 3.

Effect of stirring time

In order to investigate the effect of stirring time on the extraction efficiency, the experiments were carried out from 5 to 60 min. A total of 30 min stirring time was sufficient for the quantitative extraction of 10 µg uranium. Hence, a 30-min stirring time is recommended. Figure 4 illustrates this.

Effect on the sequence of the addition of reagents

It is important to mention here that the anionic complex of uranium with 2,3-H₂ND is kinetically so stable that once formed at lower pH, *i.e.*, slightly acidic to neutral condition, it is not broken even in alkaline condition. Hence, it is always recommended that the reagent 2,3-H₂ND is first added to the uranium solution and then the pH of the medium is raised to 10 – 12, where the solid phase extraction of uranium is carried out quantitatively.

Effect of electrolytes

The role of sodium acetate has no effect on quantitative extraction of uranium on microcrystalline naphthalene except its buffering capacity at the pH of 4 – 6. As has already been mentioned in the previous paragraph that uranium forms a kinetically stable anionic complex with 2,3-H₂ND in slightly

Fig. 4 Plot of % recovery of 10 µg uranium vs. stirring time/min (amount of 2,3-H₂ND/0.31 × 10⁻³ mol, amount of CTAB/0.14 × 10⁻³ mol, amount of naphthalene/15.6 × 10⁻³ mol, pH: 10 – 12).

acidic to neutral medium *i.e.*, in the pH range 4 – 6. Na₂EDTA is used to mask the quenchers, like Ca, Fe, Mn, Cu, Co, Cr, Ni, *etc.* Similarly, the role of KOH is to increase the pH of the solution to 10 – 12, where to maximize the extraction efficiency.

Effect of diverse ions

In order to investigate the effects of common co-existing ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe³⁺, Al³⁺, Ti⁴⁺, Mn²⁺, Cu²⁺, Co²⁺, Ni²⁺, Pb²⁺, Cr³⁺, *etc.*) in water samples on the recovery of uranium, a set of natural water samples were taken for the determination of uranium by the proposed method. Tables 1A and 1B shows the typical composition of natural water samples analyzed in this laboratory by different classical and instrumental techniques. The possibility cannot be ruled out that the adsorption of other co-existing ions present in water samples on microcrystalline naphthalene may interfere in the determination of uranium by LED/laser fluorimetry. Direct determination of uranium by laser/LED fluorimetry method in phosphate medium is not possible because of several quenching elements, like Ca, Fe, Mn, Cu, Co, Cr, Ni, *etc.* if present above the tolerance level. Detailed studies on this quenching behavior of these elements have already been carried out in several works.^{27,28} The transition group elements generally present in a water sample at trace (ppb) levels (as shown in Table 1B), which are masked by Na₂EDTA, do not interfere in the determination of uranium by the proposed method because the tolerance levels of most of the quenching elements are at the ppm level. After preconcentration of the water sample by the proposed method, if Ca, Al, Fe, *etc.* are present above the tolerance level (Ca and Al forms white precipitate in the presence of phosphate buffer, Fe quenches uranium fluorescence above the ratio of Fe to U:100), then uranium can be extracted by conventional liquid-liquid solvent extraction using aluminum nitrate as a salting out agent prior to LED fluorimetry determination.¹¹ The tolerance limits of the common co-existing species in water samples by the proposed method are shown in Table 2.

Validation and application of the method

In order to validate the method developed and in order to attest the efficacy of the extractive system, the proposed method was thoroughly applied to a set of water samples. The proposed method has been applied for the determination of uranium in water samples containing varied matrix *i.e.*, low TDS to high TDS collected from different field areas of eastern India for uranium exploration work. The results are shown in Table 3. In the direct determination of uranium in water samples, if present at sub ppb levels, the instrument (LED fluorimetry) yields

Table 1A Concentration ($\mu\text{g mL}^{-1}$) of major species in natural water samples (N.D. = Not detected)

Sample No.	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	TDS	pH
1	13	<1	10	<10	N.D.	80	10	<10	80	7.3
2	30	2	42	25	N.D.	166	82	30	400	7.3
3	45	1	56	15	N.D.	139	110	40	370	7.0
4	21	<1	12	<10	N.D.	97	14	<10	100	7.2
5	15	<1	14	<10	N.D.	80	14	<10	95	7.2
6	54	2	10	35	N.D.	123	131	30	390	7.1
7	35	1	28	<10	N.D.	209	17	<10	200	7.5
8	15	1	24	<10	N.D.	118	23	<10	130	7.0
9	38	1	54	42	N.D.	139	173	30	460	7.0
10	13	<1	16	<10	N.D.	80	16	<10	100	7.5

Table 1B Concentration (ng mL^{-1}) of trace elements in natural water samples

Sample No.	Fe	Al	Cu	Zn	Pb	Co	Bi	Cr	Ni	B	Mo	V	As	Se	U
1	500	10	<5	236	5	<5	<5	<5	<5	<5	5	10	<5	7	<1
2	300	14	<5	17	14	<5	<5	<5	<5	<5	<5	59	22	6	<1
3	470	17	<5	30	12	<5	<5	<5	<5	<5	6	40	11	14	<1
4	590	10	<5	21	9	<5	<5	<5	<5	<5	13	10	20	10	<1
5	410	18	<5	14	13	<5	<5	<5	<5	<5	5	12	18	<5	<1
6	110	30	<5	65	16	<5	8	<5	<5	<5	<5	37	29	<5	<1
7	150	19	<5	39	14	<5	9	<5	<5	<5	5	19	11	9	<1
8	140	26	<5	23	13	<5	5	<5	<5	<5	5	15	15	10	1
9	1050	30	<5	20	16	<5	7	<5	<5	<5	7	41	20	21	5
10	1320	23	<5	52	14	<5	14	<5	<5	<5	8	15	14	14	10

Table 2 Effect of diverse ions on the determination of 1 ppm uranium by the proposed method

Sl. No.	Elements/species	Tolerance limit, ppm
1	Na, K, Ca, Mg, Rb, Sr, Ba, Cu, V, Mo, Zn, Pb, Al, HCO ₃ ⁻ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	1000
2	Fe, Mn, Cr, Co, Ni	100

imprecise results *i.e.*, with low precision (the fluorescence signal is marginally above that of process blank). However, when preconcentrated by solid phase extraction with microcrystalline naphthalene, uranium can be comfortably determined *i.e.*, fluorescence signal much above that of process blank and yields high precision, which are shown in Table 3. Therefore, preconcentration improves the precision and reliability of results.

In the absence of certified reference material for water samples, standard addition method has been applied to validate the percentage recovery values of this method, taking into consideration ground water samples that contain uranium below the determination limit of the method. The results are also shown in Tables 3 and 4. The result indicates that the recoveries were reasonable for trace uranium analysis in the range 95 – 100% with precision 1 – 12% RSD. The above standard addition method has been applied in order to nullify the matrix effect as well as the loss of analyte during several steps involved in the recommended procedure for recovery studies, which is defined as the addition of a known amount of analyte to a sample and then determining what percent of the amount added is detected. Similarly, the reliability of the results was also compared by analyzing the same water samples by pellet fluorimetry involving standard separation technique like co-precipitation using aluminum phosphate as a carrier.³⁰ The results of the study are also shown in Table 4. The results in

Tables 3 and 4 indicate that the method developed is quite effective in the solid phase separation and preconcentration of uranium for their accurate determination by LED fluorimetry method.

Conclusions

The proposed solid phase extraction of uranium with microcrystalline naphthalene combined with LED fluorimetry determination is an effective alternative method for separation and preconcentration of trace and ultra-trace level uranium determination in water samples. At the alkaline pH of 10 – 12, uranium is separated and preconcentrated from sample solutions by means of its complex formation with 2,3-dihydroxynaphthalene in the presence of CTAB, which adsorbed on microcrystalline naphthalene quantitatively. The method is highly effective for the determination of uranium in those water samples where uranium is present below the determination limit of the instrument. The higher preconcentration factor (100 fold) can also be achieved by concentrating a 1-L water sample into a 10-mL volume by the proposed method. The detection limit and determination limit of the proposed method are 0.025 and 0.1 ppb respectively in aqueous solution based on 3σ and 10σ of ten replicate measurements of blank sample, where σ denotes standard deviation of the measurements. The developed method provides freedom from hazardous large amounts of the salting out agents like aluminum nitrate used in liquid-liquid solvent extraction of uranium in the conventional pellet fluorimetry method. The proposed method is simple, rapid and eco-friendly and can be applied to a variety of water samples, including seawater and effluents on a routine basis.

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Table 3 Results of uranium in water samples collected from the eastern part of India

Sample No.	U determined by present method ^a		U added/ ng mL ⁻¹	U found/ ng mL ⁻¹	U recovery, %	U determined by direct method ^a	
	U/ng mL ⁻¹	RSD, %				U/ng mL ⁻¹	RSD, %
1	0.08	10	10	10.0	99	<1	25
2	0.1	8	10	10.1	100	<1	17
3	0.4	4	10	10.3	99	<1	20
4	0.2	5	10	10.2	100	<1	20
5	0.8	5	10	10.6	98	<1	30
6	0.8	6	10	10.5	97	<1	25
7	0.5	10	10	10.5	100	<1	32
8	1.1	5	10	11	99	1	12
9	5.0	7	10	15.2	101	5	8
10	10.2	6	10	20.0	99	10	5

a. No. of three replicate determinations ($n = 3$).

Table 4 Results of traces of uranium in different water samples

Sample No.	U found by proposed method ^b /ng mL ⁻¹	RSD, %	U found by standard addition method ^b /ng mL ⁻¹	RSD, %	U found by pellet fluorimetry method ^{ab} /ng mL ⁻¹	RSD, %
1	1.8	6	1.9	8	1.9	10
2	0.5	10	0.6	12	0.5	14
3	1.2	5	1.0	10	1.2	8
4	5.3	7	5.1	8	5.2	10
5	10.2	6	9.9	8	10.5	8

a. Separation and preconcentration of uranium by co-precipitation using aluminum phosphate as a carrier. b. No. of three replicate determinations ($n = 3$).

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