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Use of solid extraction chromatography for determination of uranium in sea water and brine

S.P. Prabhu[a,*], T.L. Prasad[b], D.D. Rao[a]

[a]*Radiation Safety Systems Division, Bhabha Atomic Research Centre, Mumbai 400085, India, Tel. +91 22 25592138; email: spprabhu@barc.gov.in (S.P. Prabhu)*
[b]*Desalination Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

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ABSTRACT

Bench scale field trials were initiated for the development of effective technology for recovery of uranium from sea water using acrylonitrile absorbents synthesized by radiation grafting. One of the important needs is to ensure quality assurance for the accurate measurement of heavy metal ion concentrations from lean solutions such as sea water and brine. Efforts have been made at Bioassay Laboratory of Radiation Safety Systems Division in India to improve the radiochemical separation and detection techniques for rapid, sensitive and accurate estimation of uranium in sea water samples. The earlier method using ion exchange had disadvantages of being lengthy and required use of sulphuric acid. Hence, a method was developed for estimation of uranium concentration in natural sea water and brine (desalination plant effluents) samples by solid extraction chromatography (SEC) using UTEVA resin (Uranium and TEtraValents Actinides). This resin consists of dipentyl pentylphosphonate sorbed onto an inert polymeric support. Using SEC technique, the complete analysis results are available within a day and as the resin is very specific for uranium extraction from the samples, it is easier to eliminate interfering transition ions like vanadium and iron from the samples. This paper reports the standardization of radiochemical procedure for uranium from sea water and brine samples and its determination by alpha spectrometry.

Keywords: Sea water; Brine; Uranium; Solid extraction chromatography; Alpha spectrometry

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1. Introduction

Uranium is a ubiquitous, primordial radionuclide and its concentration in the environment strongly depends on the geological matrix (varies between 0.1 and 500 ppm) [1]. Researchers are taking renewed interest on the recovery of uranium from sea water and other alternative resources [1,2] to complement the uranium locally deposited as terrestrial ore. With its lean but clean resource, ocean can serve as a potential source for uranium and other valuable heavy metals for a long run. The uranium content of oceans is of the order 4.5×10^9 tonnes [2]. Sea water is an electrolyte with pH of 8–8.5 and uranium predominantly

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*Corresponding author.

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exists as uranyl tricarbonate complex. Scientists in the USA, Japan, Korea and India are exploring the use of uranium found in sea water as a potential secondary source for future energy demands [3]. Polymer matrices have been synthesized by Post Irradiation Grafting (PIG) of acrylonitrile and converting it suitable for uptake of uranium from sea water [4–6]. These polymeric adsorbents, however, extract some of the transition elements like vanadium from sea water. The uranyl solutions extracted from sea water are stored in the glass lined Mild Steel (MS) storage vessels with MS lids. The storage in these vessels leads to leaching out of iron into the solution. Thus, in addition to estimating uranium concentration, it was necessary to eliminate the interference by these ions in the samples. The ion exchange using sulphuric acid had disadvantages of being too lengthy and required the use of sulphuric acid [7]. Therefore, in present study, SEC technique is used for neat separation of uranium from the lean solution. The technique employs the use of UTEVA resin consisting of dipentyl pentylphosphonate sorbed onto an inert polymeric support made of porous silica or an organic polymer. This paper reports the procedure standardized and estimation of uranium concentrations in the sea water, brine and product elute samples received from Recovery of Uranium from Sea Water pilot program (RUSWapp) facility. The paper also highlights the advantages of solid extraction chromatography over ion-exchange technique.

2. Materials and methods

2.1. Reagents

In all experiments, analytical grade reagents and deionized water were used. The following reagents were used: nitric acid (concentrated and 3 M), hydrochloric acid (9, 5 and 1 M), ammonia solution (25%), sulphuric acid (0.5 M) and ammonium sulphate (3.5 M), 5 mg/ml iron carrier solution (iron nitrate in 1 M nitric acid). The extraction resin used was 1 g of UTEVA resin (Eichrom Technologies) of 100–150 μm particle size (Fig. 1). The radioactive tracer solution used was ^{232}U procured from NPL (Reference: E08020077). Working standard of 21.6 mBq/ml was prepared by diluting this NPL standard with 3 M HNO_3.

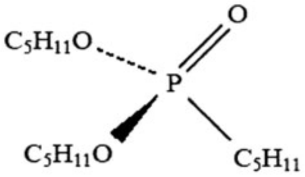

Fig. 1. Dipentyl pentylphosphonate (DP[PP])).

2.2. Standardization

For the purpose of standardization, 0.3 mL of ^{232}U standard was added to each of the 10 samples of 100-mL sea water in Borosil glass beakers along with varying amounts of iron(III) carrier solution (5–25 mg) and evaporated to dryness. After complete evaporation, 5 mL of conc. HNO_3 was added and again evaporated to dryness. For sample preparation, the residue formed after evaporation was dissolved in 5 mL of 3 M HNO_3 + 1 M $Al(NO_3)_3$ and loaded onto UTEVA column preconditioned with 3 M HNO_3 at a flow rate of ~1 drop/s. The UTEVA column was sequentially washed with 3 M HNO_3, 9 M HCl and 5 M HCl. The

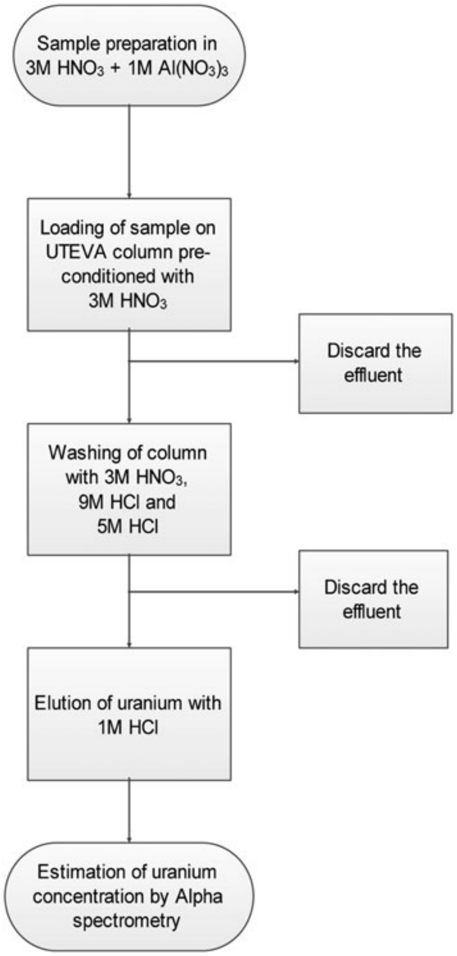

Fig. 2. Flowchart of procedure standardized using UTEVA resin.

Table 1
The effect of the presence of iron(III) on ^{232}U recoveries

Amount Fe (mg)	^{232}U recovery (%) Set-I	^{232}U recovery (%) Set-II
5	98.1	95.5
10	93.5	94.9
15	83.3	92.3
20	97.2	87.4
25	81.7	89.5

Table 2
Uranium concentration observed in sea water and brine samples of different locations

Sample ID	Volume taken for analysis per set (mL)	Set-I Uranium concentration (ppb)	Set-II Uranium concentration (ppb)	Average uranium concentration (ppb)	Remarks
DD/A&N/SW1	100	3.0 ± 0.5	3.2 ± 0.5	3.1 ± 0.7	Sea water
DD/A&N/SW2	50	4.7 ± 0.9	5.7 ± 1.1	5.2 ± 1.4	Do
DD/SL/SW1	100	3.3 ± 0.6	3.7 ± 0.5	3.5 ± 0.8	Do
DD/MLD/SW1	180	3.2 ± 0.4	3.4 ± 0.6	3.3 ± 0.7	Do
DD/BLR/SW1[a]	50	0.24 ± 0.06	0.31 ± 0.06	0.3 ± 0.08	Process water
DD/CJ/SW1	150	1.9 ± 0.3	2.3 ± 0.4	2.1 ± 0.5	Sea water
DD/LTE/BR1	200	6.4 ± 0.6	5.3 ± 0.6	5.8 ± 0.8	Brine

[a] Sample counted for 4 d in alpha spectrometer (MDA = 6 ppb).

adsorbed uranium was finally eluted using 1 M HCl, electroplated and estimated by alpha spectrometry. Flow chart for the procedure standardized is given in Fig. 2. The sea water and brine samples used are from natural sea water from different locations, as reported in our earlier paper [8]. The TDS (Total Dissolved Solids) varies from 20,000 to 50,000 ppm with pH of around 8.5.

2.3. Alpha spectrometry technique

Estimation of uranium was done using alpha spectrometry as given below. The sources were prepared by electrodepositing uranium on to a 2.5-cm dia stainless steel planchette in ammonium sulphate–sulphuric acid medium at pH 2.2, for 2–3 h. A constant voltage of 6 V was applied and the current flowing through the circuit was 300 mA. At the end of electrodeposition, before switching off the current, few drops of ammonia were added to the plating solution, to neutralize the H^+ ions formed. The source planchette was washed with alcohol and heated directly on the flame till it is red hot. The sample source is measured using a Passivated Ion Implanted Planar Silicon (PIPS) detector. The active surface area of the detector is ~450 mm^2, depletion thickness 100 μm, efficiency of the system ~15% and resolution 40 keV at 5.15 MeV $^{239+240}$Pu alpha energy. The detector is coupled to a 4 K multi-channel pulse height analyzer. The distance between the stainless steel planchette and the detector surface was kept 10 mm. These samples were counted for 16–96 h.

2.4. Extraction of uranium from sea water and brine by polymeric grafted adsorbents

Grafting of the adsorbents was carried out using a PIG technique i.e. sheets were irradiated prior to immersing them in grafting solution. Irradiation of substrate sheets was carried out with electron beam energies of 1.25 and 2 MeV, using departmentally available as well as private Electron Beam Centres accelerators. The electron beam irradiated substrate sheets were immersed in solution mixture of acrylonitrile and

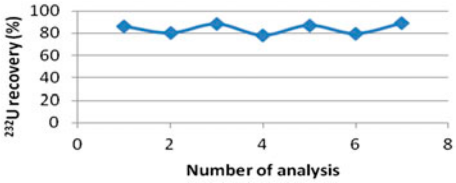

Fig. 3. ^{232}U recovery in sea water and brine samples using UTEVA technique.

Table 3
Comparison of analytical steps and time required for ion-exchange and UTEVA technique

Ion-exchange technique	Time required	UTEVA technique	Time required
Evaporation and acid digestion of sample	5-10 min	Evaporation and acid digestion of sample	5–10 min
Evaporation after addition of 0.2 N H_2SO_4 to the above residue	5–10 min		
Residue dissolved in 0.2 N H_2SO_4 (2 mL) + 0.6 N $(NH_4)_2SO_4$ (2 mL)	30 min	Residue dissolved in 5 mL of 3 M HNO_3 + 1 M $Al(NO_3)_3$	30 min
Preparation of ion-exchange column	5–10 min	Preparation of UTEVA column	5–10 min
Washing of ion-exchange column with 8 M HCl	15 min		
Column separation for uranium using ion-exchange technique	360–420 min	Column separation for uranium using UTEVA technique	100–140 min
Total time required for sample preparation and uranium separation	420–495 min (7–8 h)		140–190 min (2–3 h)

dimethyl formamide in 70:30 ratios at 55–60˚C for 3–4 h. Subsequently, the cross-linked cyano groups were substituted with amidoxime groups [6].

Uranium concentration in sea water, brine and product elute samples received from RUSWapp facility [8] was estimated using the solid extraction chromatography method standardized in the present study.

3. Results

Table 1 shows uranium recoveries when varying amount of iron (III) was added in duplicates using UTEVA technique. The results show that the chemical recovery of uranium was unaffected by the presence of iron between 5 and 25 mg. The average radiochemical recovery obtained using the SEC technique in the presence of iron was 91.3 ± 5.7%.

The technique standardized was applied for estimation of uranium in seven sea water/brine samples RUSWapp facility. The uranium concentration observed in these samples ranged from 0.3 to 5.8 ppb (Table 2) with average recovery of 84% and range of 78–89% (Fig. 3). Table 3 shows the time required for separation of uranium from sample using ion-exchange as well as UTEVA technique.

The UTEVA technique standardized was also applied to 15 product elute samples. These samples of 1–25 ml of aliquots were taken in duplicates (depending upon the concentration of uranium expected in these samples) and analysed using SEC technique and estimated by alpha spectrometry. Results of the product elute samples obtained using ion-exchange technique and UTEVA technique are given in Tables 4a and 4b. *t*-Test for paired data was conducted using

Table 4a
Uranium concentration for laboratory scale elution

Sample no.	pH	Location of submergence/source	Code	Uranium concentrations by alpha spectrometry (ppb) Ion-exchange technique	UTEVA technique
1	7.80	Brine from MED; 2 MeV	DD/MED/TK28/BR1	8.6 ± 3.4	8.2 ± 3.5
2	7.64	Do	DD/MED/TK20/BR1	11.9 ± 4.8	10.6 ± 4.4
3	7.64	Do	DD/MED/TK7/BR1	17.4 ± 4.5	18.8 ± 5.0
4	7.82	Do	DD/MED/TK14/BR1	40.0 ± 14.0	41.1 ± 2.6
5	1.47	Cirus jetty; 1.25 MeV	LE/CJ/0.05/RC1/3	11.6 ± 5.7	7.6 ± 1.5
6	0.00	Do	LE/CJ/5/RC1/3	15.4 ± 4.2	16.1 ± 2.8
7	0.29	Do	LE/CJ/0.5/RC1/3	22.4 ± 13.6	22.8 ± 5.2
8	6.84	Filtrate after precipitation	LS/PPT2/50/A2/FL1	36.8 ± 15.6	32.3 ± 3.8
9	7.01	Do	LS/PPT1/RT/A1/FL1	58.4 ± ± 19.2	50.5 ± 7.7

Table 4b
Uranium concentration for pilot scale elution done using contactor assemblies (1 m × 1 m × 1 m)

				Uranium concentrations by alpha spectrometry (ppb)	
Sample no.	pH	Location of submergence/source	Code	Ion-exchange technique	UTEVA technique
1	0.21	Cirus jetty; 2 MeV	DD/RLE8/C1A1/F5	455.8 ± 59.51	532.8 ± 51.7
2	0.00	Do	ER/C1A1/F4	491.2 ± 71.8	500.9 ± 82.8
3	0.19	Do	ER/C1/F1	591.2 ± 71.9	570 ± 60.1
4	0.21	Do	DD/RLE1/C1A1/F5	591.8 ± 69.2	630.3 ± 73.7
5	0.00	Do	DD/LEV44	3,280.0 ± 423.2	2,988 ± 486.5
6	0.00	Do	DD/LS/RLEVP1	23,667.1 ± 1,048.3	23,904 ± 1,547

Origin Pro 6.1 to compare the results obtained using ion-exchange & SEC technique. The *t*-test analysis showed that results obtained by SEC and ion-exchange technique are not significantly different at 95% confidence level.

4. Conclusion

The proposed SEC method, which uses UTEVA resin to separate uranium, has been applied to sea water and brine samples as well as the product elute samples received from RUSWapp facility. It was observed that UTEVA technique would not only rapidly separate uranium from the sea water, brine and product elute samples but also eliminate the interfering ions like iron present in these samples. The separation technique standardized is simple, rapid and has good sensitivity and reproducibility. The results of the measurements were comparable with those obtained using ion-exchange technique. Estimation of the separated uranium by alpha spectrometry was also simple, with a Minimum Detection Activity (MDA) of 20 ng for a counting time of 24 h and sample volume of 1 mL.

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References

[1] M. Konstantinou, I. Pashalidis, Speciation and spectrophotometric determination of uranium in seawater, Mediterr. Mar. Sci. 5 (2004) 55–60.

[2] K. Jungseung, T. Costas, T.M. Richard, O. Yatsandra, S. Tomonori, J.J. Christopher, D. Sheng, S. Erich, Recovery of uranium from seawater: A review of current status and future research needs, Sep. Sci. Technol. 48 (2013) 367–387.

[3] Generation IV Roadmap cross-cutting fuels and Materials R&D Scope report, Nuclear Energy Research Advisory Committee and Generation IV International Forum (2002).

[4] Y.K. Bharadwaj, K. Virendra, K.S.S. Sarma, S.A. Khader, S. Sabharwal, Development of electron beam grafted co-polymer membranes for recovery of uranium from seawater: Process parameter standardization, BARC/2006/E/004, Bhabha Atomic Research Centre, Trombay, Mumbai – 400 085, 2006, pp. 29.

[5] T.L. Prasad, P.K. Tewari, S. Sathiyamoorthy, Recovery of uranium from reject streams of desalination plants, Presented at 18th annual conference of Indian Nuclear Society, November 21–24, 2007, Nuclear Fuel Complex, Hyderabad.

[6] T.L. Prasad, N.K. Prasad, P.K. Tewari, D. Sathiyamoorthy, 2012, Technology to harvest uranium from Sea—Development of radiation grafting reactor systems, Founder's day Special Issue of BARC news letter, October 2012, pp. 172–177.

[7] A. Suja, P.D. Sawant, S.M. Wankhede, D.D. Rao, T.L. Prasad, Technology to harvest uranium from seawater and its estimation by laser fluorimetry, Indian Chem. Eng. 56 (2014) 87–96.

[8] T.L. Prasad, A.K. Saxena, P.K. Tewari, D. Sathiyamoorthy, An engineering scale study on radiation grafting of polymeric adsorbents for recovery of heavy metal ions from seawater, Nuclear Eng. Technol. 41(8) (2009) 1101–1108.