



Supercritical fluid extraction of uranium and thorium employing dialkyl amides



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ABSTRACT

N,N-dialkyl aliphatic amides with varying alkyl groups viz. N,N-dibutyl-2-ethyl hexanamide (DBEHA), N,N-dibutyl-3,3-dimethyl butanamide (DBDMBA), N,N-dihexyl octanamide (DHOA), N,N-di-sec-butyl pentanamide (DBPA), N,N-dibutyl octanamide (DBOA), have been evaluated for supercritical fluid extraction (SFE) of uranium and thorium from nitric acid medium as well as from tissue paper matrix. The trend in extraction efficiency could be correlated to the structure of the amides and the amide complex of uranium/thorium. Straight chain amide DBOA was found suitable for SFE of both uranium and thorium. Under optimised conditions (200 atm. pressure, 323 K temperature, 30 min static time followed by 30 min dynamic time, 0.5 M amide in methanol), (94 ± 3)% uranium and (85 ± 4)% thorium could be extracted from 4 M nitric acid medium. For tissue paper matrix, under optimised conditions (200 atm pressure, 323 K temperature, 45 min static time followed by 30 min dynamic time, 0.2 M amide in methanol) (87 ± 7)% uranium and (88 ± 7)% thorium were extractable. For the amide having branching at C_α, DBEHA, extraction efficiency of thorium was as low as 7% for 2 M HNO₃ medium while extraction efficiency of uranium was still 95%. For tissue paper matrix, extraction efficiency for uranium with 0.2 M DBEHA (in methanol) was 86% while only 11% thorium was extractable under same conditions. This fact could be exploited for separation of thorium and uranium.

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1. Introduction

Extraction and purification of actinides from various matrices is of utmost importance to the nuclear industry. Owing to the importance of uranium as nuclear fuel material, it is of interest to study the extraction behaviour of uranium in terms of separation, pre-concentration and purification during various stages of nuclear fuel cycle. As India possesses vast reserves of thorium (360,000 tonnes) in contrast to modest quantity of uranium (60,000 tonnes) [1], there is a need to develop capabilities on all aspects of thorium fuel cycle, i.e. mining, fuel fabrication, reprocessing and waste management. In this context development of processes for separation and purification of thorium from various matrices, liquid as well as solid, is of utmost importance. Conventionally employed processes like solvent extraction and ion exchange result in the generation of large amount of secondary liquid volume. In recent decades, supercritical fluid extraction (SFE) has emerged as a promising alternative to solvent extraction owing to its inherent potential of

minimisation of liquid waste generation and simplification of the extraction process. The supercritical fluids (SCF) possess hybrid properties of liquids as well as of gases [2]. Liquid like solvating characteristics enable extraction while gas like characteristics such as diffusivity, viscosity and surface tension facilitate rapid mass transfer, faster completion and deep penetration inside solid matrix. Also, SFE offers other attractive features such as favourable modification of solvent properties like density and viscosity by tuning the pressure/temperature conditions of the system. Carbon dioxide is widely employed as supercritical fluid owing to its moderate and easily attainable critical constants (critical pressure = 72.9 atm, critical temperature = 304.3 K) and other attractive properties, such as, non-toxicity, chemical and radio-chemical stability, environment friendliness, being easily recyclable and less expensive. Organic compounds are readily soluble in supercritical carbon dioxide (SC CO₂), whereas metal ions have poor solubility due to charge neutralization requirement and weak solute-solvent interactions. SFE of metal ion could be performed by complexation with suitable organic reagents to form non-polar compounds which are readily soluble in SC CO₂. The first results on SFE of metal ion (copper) were reported by Laintz et al. [3] in 1992. SFE of actinides was reported employing various organophosphorus

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reagents and β -diketones [4–6]. We have also investigated SFE of actinides (uranium, thorium) from acidic solutions [7] as well as from tissue paper matrix employing various organophosphorus reagents [8,9] and β -diketones [10]. Direct dissolution and SFE of uranium from various solid uranium oxides [11] was also investigated by us. Systematic study of the SFE of uranium employing crown ethers and calixarenes has been reported by us [12,13].

In the early 1960s, Siddal proposed N,N-dialkyl aliphatic amides to be an alternative to TBP in the reprocessing of spent nuclear fuel [14–16]. In spite of wide scale application of TBP for spent fuel reprocessing, it suffers from several disadvantages like deleterious nature of degradation products, its non-incinerability leading to large amount of secondary waste volume, high aqueous solubility and third phase formation probability. Dialkyl amides, on the other hand, offer several advantageous features like innocuous nature of degradation products (mainly carboxylic acids/amines), possibility of complete incineration of the used extractant leading to reduction in volume of secondary waste. Also, physico-chemical properties of this class of extractants can be tuned by the judicious choice of alkyl groups.

Detailed solvent extraction studies investigating the applicability of dialkyl amides for reprocessing applications have been reviewed [17]. However, only limited studies on SFE of uranium/thorium from solids viz. oxide/nitrate employing amides exist in literature [18–20] where a single amide (either DHOA or D2EHIBA) was compared with other organophosphorus reagents, diketones etc. This prompted us to carry out the present study on SFE of uranium and thorium employing set of amides, with different structural features. Attempt has been made to rationalise the extraction efficiency trend with structure of uranium and thorium complex. SFE of uranium/thorium employing amides has been carried out from nitric acid medium and effect of molarity of nitric acid on the extraction maxima has been studied. As a representative of assorted solid matrix, tissue paper loaded with uranium/thorium nitrate was also taken for the study. Systematic study of effect of various parameters on uranium/thorium extraction efficiency has been carried out.

2. Materials and methods

2.1. Materials

CO₂ gas employed for preparing supercritical fluid was of 99.9% purity. High purity U₃O₈ and ThO₂ (both having purity \geq 99.9%) were used for preparation of standard solution. Arsenazo III (Merck, Germany) was used in the spectrophotometric determination of uranium/thorium. Sulphamic acid (Merck, Germany) was of 99% purity. A.R. grade nitric acid, chloroform, methanol and hexane

were used. Amides (listed in Table 1) were obtained from Department of Chemistry, Delhi University, whose purity was confirmed by IR spectra and were used as such.

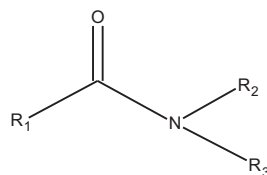
2.2. SFE set-up and procedure

Uranium standard solution was prepared by dissolving U₃O₈ powder in 4 M nitric acid. For preparation of thorium standard solution, accurately weighed ThO₂ powder was taken in a platinum crucible. ThO₂ powder was dissolved by adding 2 mL concentrated nitric acid and 0.5 mL of 0.2 M HF and heating under IR-lamp. The clear solution thus obtained was evaporated to near dryness. 3 mL of 4.0 M nitric acid was added and again evaporated to near dryness. The evaporation process was repeated twice to ensure complete removal of HF. The final solution was made up with 4 M nitric acid. Accurately weighed amount of the uranium/thorium nitrate solution, containing \sim 1 mg uranium/thorium, was sprinkled on a tissue paper kept in a petridish and air dried for 45 min. The details of the SFE set-up have been described elsewhere [9]. SFE was carried out in the in-situ mode of complexation where the uranium/thorium solution (1 mL, in nitric acid)/tissue paper containing known amount of uranium/thorium along with amide solution (1 mL, of required molarity, in methanol) were taken in the extraction vessel. The extraction vessel was loaded in the SFE set-up and after achieving the desired temperature in thermostat; CO₂ from delivery pump was flown until desired pressure was attained. The extraction vessel was maintained at desired pressure and temperature conditions for certain time, without performing collection of extract (static time). Subsequently, extraction was performed by flowing SC CO₂ for certain time (dynamic time) and collecting the extract in collection tube containing chloroform. After extraction, system was depressurized to atmospheric pressure and the extraction vessel was unloaded. The uranium/thorium amount left unextracted was determined spectrophotometrically (Section 2.4).

2.3. Solvent extraction study

For solvent extraction, 1 mL of uranium/thorium solution (1 mg, in 4 M HNO₃), amide solution (1 mL, in methanol) and 2 mL of hexane were taken in a beaker and magnetically stirred for 1 h. The solution was transferred to separating funnel and allowed to settle for 30 min. Subsequently, the aqueous phase was separated and uranium/thorium were determined by the procedure as described in Section 2.4. The distribution ratio (D) is the ratio of concentration of uranium/thorium in the organic phase to the concentration of uranium/thorium in the aqueous phase after solvent extraction. Uranium/thorium concentration in the organic phase was, in turn

Table 1
Amides used in the study



Amide	R ₁	R ₂ , R ₃
N,N-dibutyl-2-ethylhexanamide, DBEHA	CH ₃ (CH ₂) ₃ (C ₂ H ₅)CH	C ₄ H ₉
N,N-dibutyl-3,3-dimethylbutanamide, DBDMBA	(CH ₃) ₃ CCH ₂	C ₄ H ₉
N,N-dihexyloctanamide, DHOA	CH ₃ (CH ₂) ₆	C ₆ H ₁₃
N,N-di-sec.butylpentanamide, DBPA	CH ₃ (CH ₂) ₃	CH(CH ₃)(C ₂ H ₅)
N,N-dibutyloctanamide, DBOA	CH ₃ (CH ₂) ₆	C ₄ H ₉

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