



## Assessment of monoamide extractants and solid supports as new extraction chromatographic materials



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### ABSTRACT

The potential of monoamide-based extraction chromatographic materials for actinide recovery was assessed by monitoring uranium partitioning into six different materials. These materials were comprised of two solid supports (Amberlite XAD 4 and XAD 7) coated with one of three extractants: di-2-ethylhexyl butyramide (DEHBA), di-2-ethylhexyl isobutyramide (DEHiBA), or di-2-ethylhexyl acetylamine (DEHAA). This report considers differences in uranium partitioning depending on the solid support, extractant, aqueous phase conditions and amount of extractant coating on a given support. Studies indicate the acetyl amide extractant coated onto XAD 7 is a top candidate for further investigation. This is an interesting finding as the acetyl amide is not generally considered a particularly useful extractant for solvent extraction separations due to its tendency to form a third phase. This information contrasts the general paradigm that a given extractant can be equally useful for extraction chromatographic or solvent extraction separations and indicates that the development of future classes of extraction chromatographic materials should carefully consider the role of alkyl groups in their optimization. Additionally, the efficacy of the developed monoamide materials are compared with more classically utilized organophosphorous materials to consider opportunities for advancement in *f*-element separations.

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### 1. Introduction

Some of the most popular classes of extraction chromatographic materials for *f*-element separations are supplied by Eichrom® and use carbamoyl phosphine oxide (TRU resin), di-amyl-amyl phosphonate (UTEVA resin), bis-2-ethylhexyl phosphoric acid (HDEHP), or diglycolimides (DGA) supported on an Amberlite GC-371 polyacrylic backing [1]. These materials have shown selectivity, versatility and currently represent gold standard materials for *f*-element separations via extraction chromatography [2]. Many of the extractants used by Eichrom® are organophosphorous and several of them have been considered aggressively for separations of used nuclear fuel on a solvent extraction platform. However, organophosphorous reagents have their own pitfalls in a solvent extraction system. The radiolytic and hydrolytic degradation products have a tendency to limit material recyclability and third phase formation places an apparent ceiling on processing limits and increases potential criticality hazards [3]. The management of organophosphorous materials in fuel reprocessing requires the addition of several wash steps to remove degradation products and their deleterious effects from the separations process [4]. This

has encouraged consideration of monoamides as an attractive alternative to organophosphorous based materials in solvent extraction applications because of their apparently benign degradation products and simplified synthetic routes [5–9]. Their comparatively simple synthesis encourages consideration of a multiplicity of monoamides with different alkyl side chains.

A recent review from our research group has captured many relevant aspects of monoamides as potentially useful extractants for solvent extraction separations [10]. Siddall pioneered the study on monoamide extractants as potential candidates for replacing TBP in the early 1960s [11]. Recognizing their potential as hexavalent/tetravalent actinide extractants, Siddall reported the extraction efficiency of altering the R and R' groups on the monoamides. When comparing the extraction of Np(IV), UO<sub>2</sub>(VI), or Pu(IV) by various monoamides, he noted that the extraction of a hexavalent or tetravalent cation could be tuned by altering the alkyl groups on the monoamide. Another important conclusion from this work was the demonstration of monoamide synthesis as both straight forward and inexpensive.

Studies in France and India have compared monoamides of differing alkyl compositions (straight chained versus branched) [3,12,13]. It was observed that straight chained extractants selectively extracted hexavalent cations over tetravalent while the opposite was seen for extractants with branched chains [12]. The

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impact on solubility and third phase formation was studied by altering the  $\beta$ -carbon side chains. The conclusion from these studies is the bis-2-ethylhexyl side chain favors both solubility and, generally, displays a resistance to third phase formation [14]. The degradation products of the more promising extractants have also been studied. To date, the degradation products reported are only simple carboxylic acids and amines [9]. Their only adverse side effect is the reduction of the concentration of extractant, but even that is minimal.

Solvent extraction has been the primary technology used in nuclear fuel reprocessing. However, column chromatography has been shown to be an effective technology for separations work as well [15–17]. Proven to be a useful extraction method and one that could generate less secondary waste, column chromatography is a viable option as a complementary extraction technique to solvent extraction. This requires the study of not only the appropriate monoamide extractants, but choosing a compatible support system.

This manuscript reports the impact of varying the alpha-C chain of the monoamide and the concentration of acid on the extraction of U. To understand the impact the solid support has on extraction and to optimize uranium extraction under various conditions, the following parameters were studied: different resin materials, the amount of extractant loaded on each resin, and the amount of resin in the system.

## 2. Experimental

### 2.1. Materials

Solutions of nitric acid were prepared from high purity, ACS reagent grade, concentrated nitric acid provided by Fisher Scientific. Dilutions were prepared using 18 M $\Omega$  de-ionized nanopure water. The  $^{233}\text{UO}_2(\text{NO}_3)_2$  was available from stocks at the Colorado School of Mines. The activity of the uranium stock solution was verified by liquid scintillation counting to be  $8.5 \times 10^3$  Bq/mL. Tracer experiments were completed using 5  $\mu\text{L}$  of the uranium mother solution.

Extractants studied were di-2-ethylhexyl butyramide (DEHBA), di-2-ethylhexyl isobutyramide (DEHiBA), and di-2-ethylhexyl acetamide (DEHAA). Each extractant was synthesized in house following a procedure published by Thiollet and Musikas [18]. Purity was qualitatively determined via  $^1\text{H}$  NMR and FTIR.

Resin materials, XAD 7 and XAD 4, were provided by Rohm & Hess. The resin material was washed before coating with the extractant. The washing procedure included rinsing the resin with 18 M $\Omega$  de-ionized nanopure water until the rinse was neutral as indicated by pH paper. The resin was then dried in an oven overnight at 80  $^\circ\text{C}$  to remove residual water. Coating was assessed as weight percent of extractant contributing to the total weight of the coated resin. The resin material was weighed and submerged in methanol to prevent site saturation upon contact with the extractant solution. The extractant was weighed prior to dissolution in methanol and was then contacted with the methanol wetted resin. The mixture was placed in an oven overnight at 55  $^\circ\text{C}$  to encourage solvent evaporation. After drying, the sample was weighed to assess the total percent coated. Successful extractant coating was verified by FTIR analysis of the non-coated and coated resins. In the analysis, the addition of the 1645  $\text{cm}^{-1}$  peak, representing the monoamide C=O stretch, indicated the presence of the monoamide material on the resin.

### 2.2. Batch experiments

For batch experiments, the resin was weighed into an Eppendorf microcentrifuge tube and contacted with an acid solution of

appropriate concentration and volume. The resin was allowed to equilibrate with the acidic aqueous phase for ten minutes prior to addition of the uranium spike. The samples were vortex mixed for 60 min and centrifuged for 5 min. A 100  $\mu\text{L}$  aliquot was then removed from each sample and placed into 3 mL Ecoscint LSC cocktail for measurement using a Packard 2500 Liquid Scintillation counter. Each sample was measured in triplicate and standard deviations presented in the figures are one sigma of the standard deviation on the triplicate measurement. The conditions studied included varying the acid concentration (2–6 M  $\text{HNO}_3$ ); varying the weight percent of extractant coated on the resin (40–70% weight percent); and comparing the total amount of resin in the system between 50 mg and 100 mg resin while maintaining 1 mL total volume. The total uranium extracted was assessed as a  $K_d$  as well as percent extracted. The  $K_d$  was calculated using Eq. (1) while percent extracted was calculated by measuring the difference between the activity in the solution before and after extraction.

$$K_d = \left( \frac{[\text{U}]_i - [\text{U}]_f}{[\text{U}]_f} \right) \left( \frac{\text{Vol}_{\text{aq}} (\text{mL})}{\text{mass}_{\text{resin}} (\text{g})} \right) \quad (1)$$

## 3. Results/discussion

The three extractants, Fig. 1, studied provide the opportunity to examine the impact of the alkyl substituent on uranium uptake. All three extractants have the same side chains, 2-ethylhexyl; DEHBA and DEHiBA both have a 4-carbon chain on the alpha-amide carbon. The branching of the DEHiBA side chain is an interesting comparison with DEHBA which has a straight chain off the alpha carbon. DEHAA also has a straight chain off the alpha carbon, however, it is only a 2-carbon chain. Studying the three extractants in parallel allows a direct comparison to be made between branching off the alpha-carbon and a straight chain off the alpha-carbon as well as chain length off the alpha-carbon.

In addition to studying different extractants, two types of resin were examined as well. Fig. 1 shows the backbone of each resin. The XAD 4 resin has a styrene divinylbenzene backbone with an average pore size of 100  $\text{\AA}$  and a surface area of 750  $\text{m}^2/\text{g}$ . The XAD 7 resin has a polyacrylic ester backbone with an average pore size of 300–400  $\text{\AA}$  and a surface area of 380  $\text{m}^2/\text{g}$ . Examining both resins under similar conditions will provide insight into how the pore size, surface area, and the solid support–extractant interface impacts uranium uptake.

### 3.1. Nitric acid uptake

Partitioning of a positively charged metal ion to a lipophilic solid phase using a solvating extractant requires the presence of an anionic counter ion. For this study, nitrate was chosen as the counter ion. Nitrate aqueous media are also common for used nuclear fuel separation since nitrate easily dehydrates and forms weak complexes with uranium in the aqueous phase. The properties make it a nearly ideal supporting anion for uranium recovery using solvating extractants from molar nitrate concentrations. Furthermore, in current reprocessing systems, nitric acid is used to dissolve uranium oxide fuel post irradiation. In this study, the impact of nitric acid concentration on the uptake of uranium was monitored for the 40 weight percent resin material. Data relevant to this investigation are presented in Fig. 2.

Both the XAD 7 and XAD 4 resins generally showed an increase in uranium uptake with increasing nitric acid concentration. The only ligand that did not follow this trend was the acetyl amide. In this case, the maximum  $K_d$  was observed at an acid concentration of 3 M for the XAD 7 resin material and, like with the other

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