Journal of Chromatography A, 1499 (2017) 1–20

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review article

# A review on solid phase extraction of actinides and lanthanides with amide based extractants

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ARTICLE INFO

*Article history:*
Received 10 November 2016
Received in revised form 14 March 2017
Accepted 17 March 2017
Available online 19 March 2017

*Keywords:*
Solid phase extraction
Amides
Separation
Actinides
Radioactive wastes

ABSTRACT

Solid phase extraction is gaining attention from separation scientists due to its high chromatographic utility. Though both grafted and impregnated forms of solid phase extraction resins are popular, the later is easy to make by impregnating a given organic extractant on to an inert solid support. Solid phase extraction on an impregnated support, also known as extraction chromatography, combines the advantages of liquid-liquid extraction and the ion exchange chromatography methods. On the flip side, the impregnated extraction chromatographic resins are less stable against leaching out of the organic extractant from the pores of the support material. Grafted resins, on the other hand, have a higher stability, which allows their prolong use. The goal of this article is a brief literature review on reported actinide and lanthanide separation methods based on solid phase extractants of both the types, i.e., (i) ligand impregnation on the solid support or (ii) ligand functionalized polymers (chemically bonded resins). Though the literature survey reveals an enormous volume of studies on the extraction chromatographic separation of actinides and lanthanides using several extractants, the focus of the present article is limited to the work carried out with amide based ligands, viz. monoamides, diamides and diglycolamides. The emphasis will be on reported applied experimental results rather than on data pertaining fundamental metal complexation.



**Contents**



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http://dx.doi.org/10.1016/j.chroma.2017.03.035
0021-9673/

**Nomenclatures**

| | |
|---|---|
| ADHA | P-amino-*N,N*-dihexyl acetamide |
| α-HIBA | Alpha hydroxyl isobutyric acid |
| An | Actinide |
| C4DGA | Diglycolamide-functionalized calix[4]arene |
| CMPO | Octyl-(phenyl)-*N,N*-diisobutyl carbamoyl methyl phosphine oxide |
| DB2EHM | Di-bis-(2-ethylhexyl)malonamide |
| DEHAA | Di-2-ethyhexyl acetylamide |
| DEHBA | Di-2-ethylhexyl butyramide |
| DEHiBA | Di-2-ethyhexyl isobutryamide |
| DGA | Diglycolamide |
| DIAMEX | Diamide extraction |
| DIDPA | Di-isodecylphosphoric acid |
| DMDBTDMA | *N,N*'-dimethyl-*N,N*'-dibutyl tetradecyl malonamide |
| DMDOHEMA | *N,N*'-dimethyl-*N,N*'-dioctyl-2-(2-hexyloxy-ethyl)-malonamide |
| $D_w$ | Weight distribution coefficient |
| EC | Extraction chromatography |
| EDHBA | 4-Ethoxy-*N,N*-dihexyl-butanamide |
| EDTA | Ethylenediamine tetraacetic acid |
| ERIX Process | Electrolytic reduction and ion exchange process |
| HAN | Hydroxylamine nitrate |
| HDEHP | Bis-2-ethylhexyl phosphoric acid |
| HEDTA | *N*-(2-Hydroxyethyl)-ethylenediamine triacetic acid |
| HLW | High level waste |
| HN | Hydrazine |
| $K_d$ | Distribution coefficient |
| Ln | Lanthanide |
| MCF | Mesostructured cellular foams |
| MAREC | Minor actinide recovery by extraction chromatography |
| PUREX | Plutonium uranium reduction extraction |
| RTIL | Room temperature ionic liquid |
| SHLW | Simulated high level waste |
| TBP | Tri-*n*-butyl phosphate |
| T2EHDGA | *N,N,N*',*N*'-tetra-2-ethylhexyl diglycolamide |
| T-DGA | Tripodal diglycolamide |
| THOREX | Thorium extraction |
| TODGA | *N,N,N*',*N*'-tetraoctyl diglycolamide |
| TRPO | Trialkyl phosphate oxide |

## 1. Introduction

In view of the fast dwindling natural resources of fossil fuels, nuclear energy is slowly emerging as one of the major alternative energy resources [1]. However, due to the limited availability of the naturally occurring fissile material ($^{235}$U), the future of the nuclear energy program largely depends upon the availability of the man-made fissile materials such as $^{239}$Pu and $^{233}$U. To sustain the nuclear power programme beyond the availability of the naturally occurring $^{235}$U, it is imperative, therefore, to follow the closed nuclear fuel cycle option [1–3]. The closed nuclear fuel cycle emphasizes on the reprocessing of the spent nuclear fuel using a suitable methodology. During reprocessing of the spent fuel, valuable activation products such as $^{239}$Pu (formed in uranium based fuel) and $^{233}$U (formed in thorium based fuel) are recovered in the well-known hydrometallurgical processes, PUREX (Plutonium Uranium Reduction EXtraction) and THOREX (THORium EXtraction), respectively [4]. Though the TBP (tri-*n*-butyl phosphate) based PUREX process has been the workhorse of the nuclear fuel reprocessing industry for the past several decades, continued R&D efforts have identified a few drawbacks associated with the use of TBP which have raised concerns [5–10]. The main problems of TBP are (i) its vulnerability to high radiation field and deleterious nature of its degradation products affecting the product recovery, (ii) its solubility towards aqueous phase, and (iii) non-incinerable nature of the spent solvent, thus, yielding large volumes of secondary wastes. To overcome these draw-backs, amide based extractants have been studied for possible application in the nuclear reprocessing since the work of Siddall [11,12]. These extractants offer several advantages over TBP, especially with respect to the (i) innocuous nature of their degradation products, viz. carboxylic acids/amines, and (ii) the possibility to incinerate the used solvent leading to reduced volume of secondary wastes [11–15]. Additionally, the physico-chemical properties of this class of ligands can be tuned by the judicious choice of alkyl groups. Systematic studies have been undertaken to investigate (i) linear *N,N*-dialkyl amides as alternatives to TBP in the PUREX process [16–18], and (ii) branched chain *N,N*-dialkylamides as alternatives to TBP in the THOREX process [18–22].

Though the reprocessing of spent nuclear fuel gives fissile nuclear materials such as $^{239}$Pu, it also leads to the generation of large volumes of highly radioactive liquid waste, known as High Level Waste (HLW) which contains >95% of the total radioactivity of all radioactive wastes. The HLW generated during the reprocessing of the spent nuclear fuel contains the un-extracted U, Pu (from the PUREX losses), bulk of the minor actinides (Am, Np, Cm), a host of fission product elements like lanthanides (Lns), Tc, Pd, Zr, I, Cs, Sr and activation products such as Ni, Sb, Zr [23–27]. Fission products are highly radioactive (beta/gamma emitters) and pose serious threat to the human life as well as to the ecology. The challenge for the final disposal of HLW is largely due to the radiotoxicity associated with the minor actinides (Ans), which are alpha emitters and have half-lives in the range of few hundreds to millions of years. At present, the most accepted strategy for the management of HLW is to vitrify the waste oxides in borosilicate glass matrices followed by disposal in deep geological repositories [28–30]. Due to the long half-lives of the minor Ans, the surveillance of HLW containing vitrified blocks for such a long period is a daunting task. An alternative/complimentary concept is the **P&T** (**P**artitioning and **T**ransmutation), which is being explored by several countries worldwide for the safe disposal of HLW. The **P&T** process envisages the complete removal of minor Ans from HLW and their subsequent burning in high flux reactors/accelerators in suitable chemical forms [31–36]. After removing the minor Ans along with the long-lived fission products, the residual waste can be vitrified and buried in sub-surface repositories at a much reduced risk and cost. The successful application of this approach is expected to reduce the stringent requirements for geological repository capacity substantially.

## 2. Novel extractants for actinide separations

Separation scientists have been engaged in the development of new extractants for actinide partitioning from HLW for the past few decades [37–39]. In this context, several organophosphorus as well as amide based extractants have been developed and evaluated systematically (Fig. 1). Amongst the organophosphorus compounds, octyl-(phenyl)–*N,N*-diisobutyl carbamoyl methyl phosphine oxide (CMPO) has been investigated extensively [38–43]. The bifunctional nature of CMPO facilitates the extraction of trivalent Ans (Am and Cm) at a moderate acidity of 3–4 M $HNO_3$. However, the stripping of the extracted An ions from the loaded