

## **Effect of gamma-radiolysis on the synergistic extraction behaviour of diamides of dipicolinic acid and chlorinated cobalt dicarbollide**

**Joseph Lapka, Emily Wade, Alena Paulenova**

Oregon State University  
Corvallis, OR, United States

### **Abstract**

*The effects of gamma radiolysis on the synergistic extraction behaviour of chlorinated cobalt dicarbollide (CCD) and three diamidic derivatives of dipicolinic acid were investigated. In all extraction mixtures the combination of CCD and the ortho isomer of N,N'-diethyl-N,N'-ditoyl-dipicolinamide proved to be the most resilient to radiation changes in both non-saturated and nitric acid saturated solutions with distribution ratios of both increasing in either case for americium, while a noticeable decrease in extraction was observed for europium with an acid saturated solution. In mass spectroscopy studies the meta and para isomers show significant degradation in their spectra relative to the ortho isomer, which is reflected in their extractions of americium and europium.*

## Introduction

The study of the effects of radiation damage is of great importance in the nuclear waste management industry. Several widely used extractants such as TBP are known to have degradation products that are undesired and add hindrance to separation processes [1]. As a result, the radiolytic stability of any material to be subjected to the conditions created by such an industry requires significant investigation before any large scale usage can be carried out.

The first extraction process based on the use of extremely stable anions of dicarbollylcobaltate for separation of caesium and strontium directly from PUREX raffinate was invented by Czechoslovakian researchers [2,3]. Further, in co-operation with Russian scientists of Khlopin Radium Institute [4], the technological process based on the acidic form of chlorinated cobalt dicarbollide (CCD), was developed. The latest development of this process arises from the collaborative efforts between the Khlopin Radium Institute and Idaho National Laboratory and has been dubbed UNEX [5]. The process requires a higher polar organic solvent for the dissolution of CCD. Originally the process utilised nitrobenzene, though it has now been replaced trifluoromethylphenyl sulfone ( $\text{CF}_3\text{C}_6\text{H}_5\text{SO}_2$ , FS-13) which has been to exhibit excellent chemical and radiolytical stability [6].

The current version of the UNEX process utilises an extractant consisting of 0.08 M HCCD, 0.007-0.02 M PEG-400 and 0.02 M diphenyl-N,N-di-n-butyl-carbamoylmethylphosphine oxide (CMPO in FS-1) and provides simultaneous extraction of Cs, Sr, An and Ln from aqueous  $\text{HNO}_3$  solutions. However, due to limited solubility of CMPO and its metal complexes in the organic phase, the CMPO-based UNEX extractant is of a limited utility for processing acidic solutions containing higher quantities of actinides and lanthanides [8]. Therefore, alternative extractants for Ln and An are under development and to be tested on their synergistic effect in extraction mixture with HCCD with the aim to optimise as the UNEX process to each specific HLW source under study, including the specific stripping protocols.

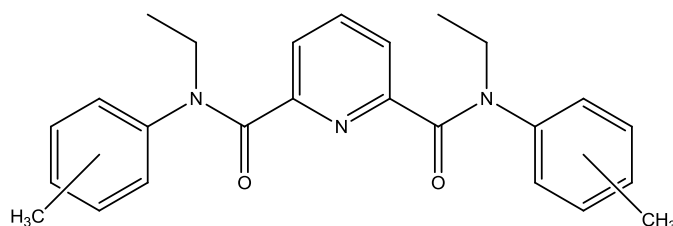
Present research has led to the development of new N-containing reagents and methods with significant potential for accomplishing separation of trivalent metals from wastes such as substituted malonic diamides (DIAMEX) [7] and tetra-alkyl-diglycolamides (TODGA) [8,9]. Substituted diamides of dipicolinic acid are of interest due to their pyridine nitrogen in proximity to the carbonyl allowing it to possibly participate in co-ordination. Previously it was reported that among other dipicolinamides, N,N'-diethyl-N,N'-ditolyl-dipicolinamide (EtTDPA) shows the best extractability toward americium with a slight extraction preference over europium [10]. A significant synergistic effect was observed in the extraction of trivalent metals by different dipicolinamides (DPA) in the presence of CCD [11], leading to some diamides of dipicolinic acid being proposed instead of CMPO as components of a modified UNEX solvent with the ultimate goal of increasing the separation of the trivalent actinides and lanthanides [12].

Recently, results on the investigation of extraction of Am and lanthanides (Ln) with different dipicolinamides as a function of their structure and nitric acid concentration [13] and their synergistic effect with chlorinated cobalt dicarbollide (CCD) on extraction of Am and Ln with diamides [14] were reported. The aim of the present work was to investigate the effect of radiolysis on the extraction performance of mixtures isomers of the diethyl-ditolyl-diamides of dipicolinic acid and CCD to indentify the effect of varying the methyl group position on the exterior aromatic rings on stability, extractability, synergism and selectivity towards the separation of Am from lanthanides.

## Experimental

### *Synthesis of organic ligands*

N,N'-diethyl-N,N'-ditolyl-dipicolinamides (EtTDPA, Figure 1) were synthesised by the reaction of thionyl chloride with 2,6-pyridinedicarboxylic acid (dipicolinic acid). The acyl chloride was then reacted with the desired isomer of N-ethyltoluidine to produce the desired EtTDPA molecule [15].

**Figure 1: Structure of EtTDPA**

Chemicals used in the synthesis of EtTDPA were purchased from TCI Co. LTD and of analytical grade used without further purification. The purities of the synthesised ligands were checked by elemental analysis.

### **Radiolysis**

Isomers of EtTDPA were dissolved in a trifluoromethylphenyl sulfone (FS-13, Marshallton Research Laboratories) solution containing the protonated chlorinated cobalt dicarbollide ion (HCCD, Katchem) in concentrations of 0.01 M and 0.02 M EtTDPA and CCD respectively. Half of the sample solutions were saturated with 3 M HNO<sub>3</sub> prior to radiolysis. The organic phases were then placed in sealed 7 mL quartz vials for irradiation. Samples were irradiated in the Oregon State University cobalt-60 irradiator (Gammacell) with a centreline dose of 0.45 kGy/hr. Individual vials were removed when the desired dose was achieved and placed into refrigeration to limit possible hydrolysis effects until all samples could be analysed.

### **Extraction procedure**

Organic phases of each desired dose rate were pre-equilibrated with an aqueous phase of 3 M nitric acid, which was identical to that used during extractions minus the metal of interest. After being contacted with nitric acid both phases were mixed for 4 minutes followed by centrifugation to separate phases. The organic phase was then contacted with a fresh portion of nitric acid and spiked with radiotracer levels of <sup>152/154</sup>Eu or <sup>241</sup>Am and again shaken for 4 minutes. The aqueous:organic volume ratios for the phases were 1 to 1 in each extraction experiment. Portions of the aqueous and organic layers were then taken and placed into vials for counting. The count rates of both metals were measured using a Cobra NaI 3 × 3" well gamma-ray spectrometer. Distribution ratios and separation factors of studied metals were determined as the ratio of the gamma ray counts in the organic and aqueous phases:

$$D = \frac{A_{\text{org}}}{A_{\text{Aq}}}; SF = \frac{D_{\text{Am}}}{D_{\text{Eu}}} \quad (1)$$

### **Mass spectroscopy**

Aliquots of irradiated solutions were diluted with acetonitrile to micromolar concentrations and placed in 1 mL autosampler vials. Analyses were performed on a Waters LC/MS electrospray spectrometer equipped with a reverse phase <sup>18</sup>C separation column. Scans were taken in positive ion mode with a range of 100-1 000 mass to charge units.

## **Results and discussion**

### **Extraction behaviour**

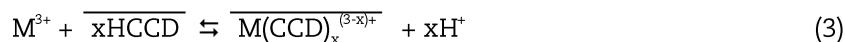
The synergistic extraction of trivalent cations from acidic solutions by mixtures of CCD and dipicolinamides takes place by a combination of two different mechanisms. Diamides such as EtTDPA are neutral ligand extractants which require a balance of charge to the extracted metal

cation. In the case of nitric acid the counter charge is provided by the nitrate ion, giving the mechanism of extraction:

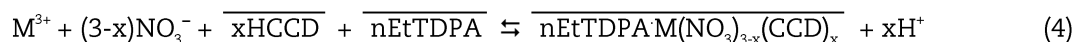


where overbars indicate species contained in the organic phase.

CCD exists in the organic phase of polar diluents as the acidic HCCD form. The extraction of cations is indirectly provided by CCD, acting as a charge balancer in the organic phase during a liquid-liquid cationic exchange mechanism [16]:



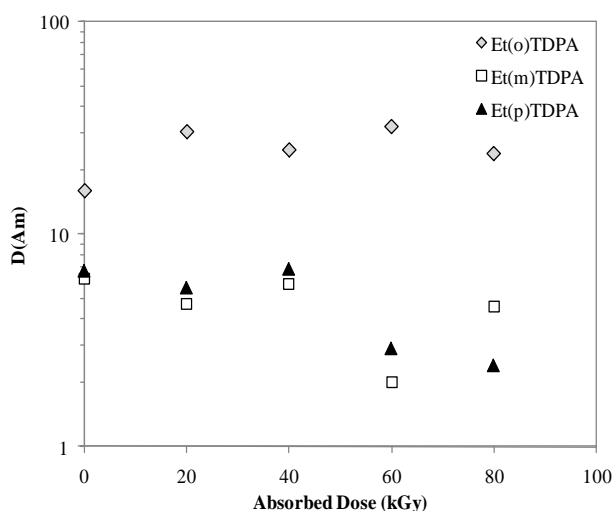
The overall sum of these two equations can then be written as:

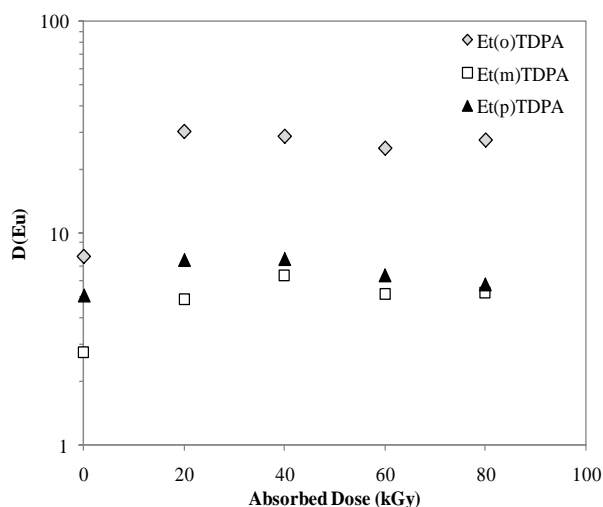


As seen in Eq. (4), at lower acid concentrations, extraction by the ionic CCD mechanism dominates, forming the complex  $[M \cdot nEtTDPA](CCD)_3$ . At higher acidities the increase in the nitrate ion concentration drives the neutral extraction mechanism with CCD anions being replaced by nitrate groups. Depending on the acidity, the possible complexes present in solution are  $[M \cdot nEtTDPA](CCD)_3$ ,  $[M(NO_3) \cdot nEtTDPA](CCD)_2$ ,  $[M(NO_3)_2 \cdot nEtTDPA](CCD)$  and  $[M(NO_3)_3 \cdot nEtTDPA]$  [17].

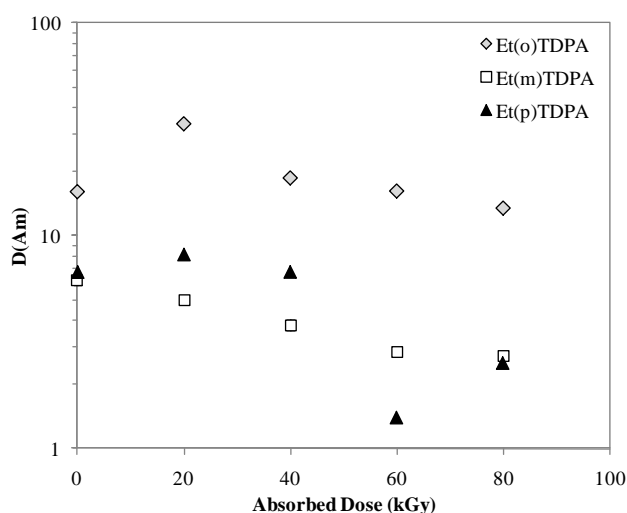
Previous experiments have shown that the americium and europium extraction capabilities of isomers of EtTDPA from 3 M nitric acid were not greatly affected with absorbed doses of up to 125 kGy [18], and in fact remain relatively constant at each dose though no attempts at stripping were made. However, the concentrations of the ligands were 20 times higher than in the current work. The extractions of americium and europium from 3 M nitric acid with irradiated non-acid saturated solutions are shown in Figures 2 and 3. In both cases the ortho isomer of EtTDPA retains a strong extraction capability for both metals, with the distribution of europium increasing to similar levels to that of americium at 20 kGy, and retaining that level as was seen with americium. This causes a dramatic decrease in the separation factor between americium and europium, with almost no preference for either metal. Though there is a slight increase in Eu extraction for both Et(m)TDPA and Et(p)TDPA up to 40 kGy, the effect is significantly less that observed for Et(o)TDPA. As with Et(o)TDPA a significant decrease in separation factor occurs for both Et(m)TDPA and Et(p)TDPA.

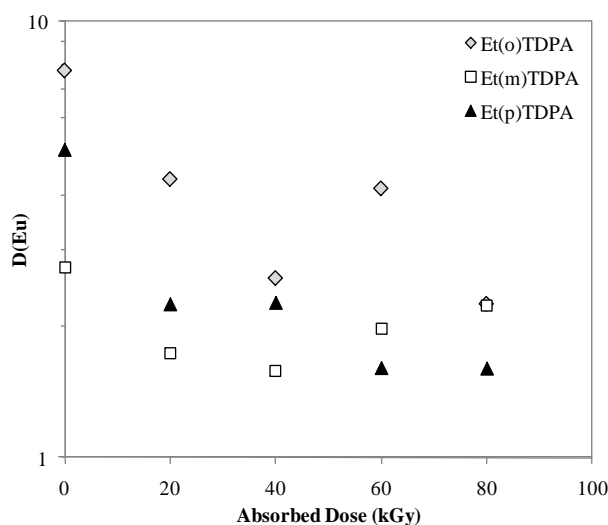
**Figure 2: Distribution of Am from 3 M HNO<sub>3</sub> with non-acid saturated irradiated EtTDPA + CCD**



**Figure 3: Distribution of Eu from 3 M HNO<sub>3</sub> with non-acid saturated irradiated EtTDPA + CCD**

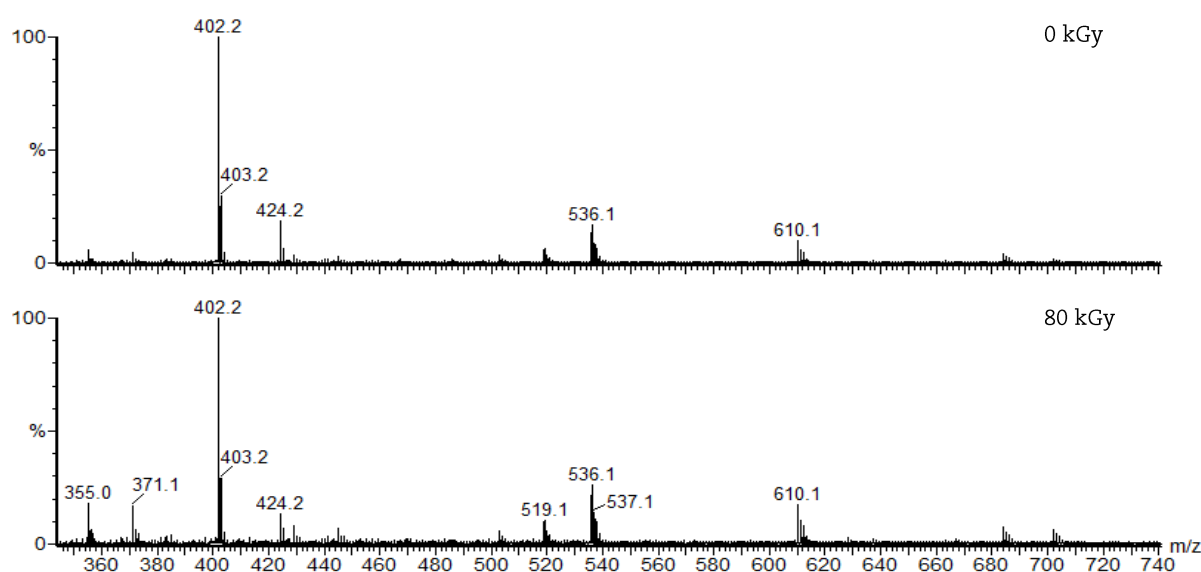
Solutions saturated with nitric acid prior to irradiation show somewhat similar americium extraction behaviour than that seen with non-saturated solutions (Figure 4). At lower doses there is a slight increase in extraction seen particularly with Et(o)TDPA, while all isomers decrease in distribution ratio at doses. The overall behaviour in europium extractions (Figure 5) is an exponential decrease in distribution ratio with increasing dose though it is somewhat erratic. The irregular behaviour seen throughout these extractions would be suspect, however it was previously also seen by a different researcher performing similar experiments within our research group [19]. Unlike in the non-acid saturated case the separation factors actually increase due to the significant decrease in europium particularly for Et(o)TDPA increasing to value of over 7 compared to 2 at 0 kGy. These results show that while the radiation products of EtTDPA do not cause significant changes in extraction capability [18], the products do interfere with the synergistic behaviour of EtTDPA and CCD.

**Figure 4: Distribution of Am from 3 M HNO<sub>3</sub> with acid saturated irradiated EtTDPA + CCD**

**Figure 5: Distribution of Eu from 3 M HNO<sub>3</sub> with acid saturated irradiated EtTDPa + CCD**

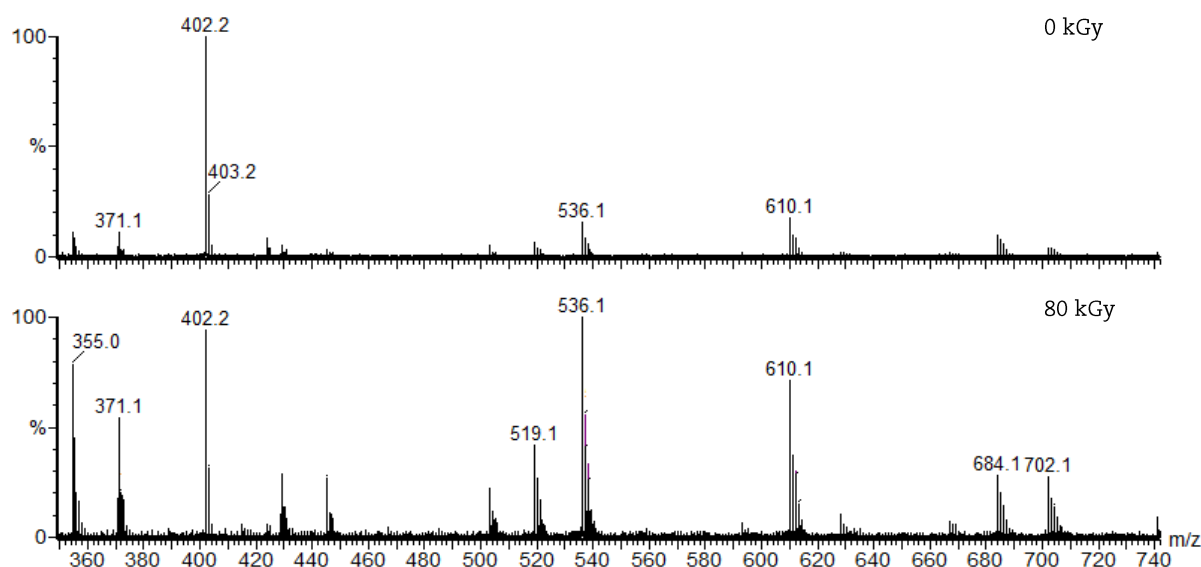
### Mass spectroscopy

In order to better understand the extraction behaviour, electrospray ionisation mass-spectroscopy was performed on nitric acid saturated solutions of EtTDPa isomers. The molecular mass of EtTDPa is approximately 401 daltons, thus it should be expected that the main peak will be the adduct of EtTDPa and a proton  $[\text{EtTDPa}][\text{H}^+]$  at 402 m/z. This peak is indeed observed and it is the largest peak for all isomers at 0 kGy as seen in the top of Figure 6. Also observed is the  $[\text{EtTDPa}][\text{Na}^+]$  adduct at 424.2 m/z. The most interesting peaks in the spectra are those at 355.0, 371.1, 536.1 and 610.1 m/z. These peaks were not found in mass spectroscopy experiments done in non-acid saturated solutions, and are found in the spectrums of every isomer regardless of irradiation time. However, ortho is unique in that the relative intensities of these ions actually decrease at lower doses (up to 45 kGy). At higher doses such as 85 kGy they have greater abundance than what was seen at 0 kGy.

**Figure 6: Averaged ion current mass spectrum of irradiated Et(o)TDPa at 0 and 80 kGy**

Both Et(m)TDPA and Et(p)TDPA behave similar to each other yet significantly different from Et(o)TDPA. At 0 kGy the peak intensities of 536.1 and 610.1 are slightly higher than with Et(o)TDPA, and since these peaks were only seen with saturated with nitric acid it is consistent with the fact that both the meta and para isomers extract nitric acid better than the ortho. Also unlike Et(o)TDPA, doses of radiation cause significant changes in the mass spectra with increasing intensities of the minor peaks rather than lowering as was seen for Et(o)TDPA at 45 kGy. In fact at 80 kGy the  $[\text{EtTDPA}][\text{H}^+]$  adduct is no longer the dominant peak in the spectrum but rather the 536.1 as seen in Figure 7. Although these peaks have yet to be identified their broad isotope pattern indicates that they contain a significant number of carbons and are probably higher charge species of a compound greater than the 1 000 m/z range used in this experiment.

**Figure 7: Averaged ion current mass spectrum of irradiated Et(p)TDPA at 0 and 80 kGy**



## Conclusion

The three isomers of EtTDPA in mixtures with CCD were found to exhibit significantly different behaviour under varying radiolysis conditions. In all cases the ortho isomer of EtTDPA shows significantly higher metal extraction than seen with the meta and para isomers. Non-acid saturated solutions saw a significant decrease in separation factor between americium and europium with Et(o)TDPA, while acid saturated solutions saw more than a three-fold increase with the same ligand. Mass spectroscopy revealed that only minor changes occurred to the composition of Et(o)TDPA solutions, while Et(m)TDPA and Et(p)TDPA saw a significant decrease in the ratio of unaffected ligand, ultimately interfering with the synergistic behaviour of EtTDPA and CCD.

## References

- [1] Sugo, Y., Y. Sasaki, S. Tachimori, "Studies on Hydrolysis and Radiolysis of N,N,N',N'-Tetraoctyl-3-oxapentane-1,5-diamide", *Radiochim. Acta.*, 90 (3), 161 (2002).
- [2] Rais, J., P. Selucky, M. Kyrs, *Journal of Inorganic Nuclear Chemistry*, 38, 1376 (1976).
- [3] Rais, J., et al., *Journal of Inorganic Nuclear Chemistry*, 38, 1742 (1976).
- [4] Galkin, B.Y., et al., *Proceedings of ISEC-88*, Vol. 4, Moscow, Nauka, 215-219 (1988).
- [5] Romanovskiy, V.N., et al., "The Universal Solvent Extraction (UNEX) Process. I. Development of the UNEX Process Solvent for the Separation of Cesium, Strontium, and the Actinoids from Acidic Radioactive Waste", *Solv. Extr. Ion Exch.*, 19 (1), 1 (2001).
- [6] Todd, T.A., et al., "Development and Characterization of a Universal Solvent Mixture for the Separation of Cesium, Strontium, Actinides and Rare Earth Elements from Acidic Radioactive Waste", *Proceedings of the International Solvent Extraction Conference (ISEC 2002)*, Cape Town, South Africa, March (2002), pp. 1216-1221.
- [7] Serrano-Purroy, D., et al., "First Demonstration of a Centrifugal Solvent Extraction Process for Minor Actinides from a Concentrated Spent Fuel Solution", *Sep. Purif. Technol.*, 45 (3) 157-162 (2005).
- [8] Zhu, Z.X. et al., "Cumulative Study on Solvent Extraction of Elements by N,N,N',N'-Tetraoctyl-3-oxapentanediamide (TODGA) from Nitric Acid into n-dodecane", *Anal. Chim. Acta.*, 527 (2), 163-168 (2004).
- [9] Modolo, G. et al., "Development of a TODGA-based Process for Partitioning of Actinides from a PUREX Raffinate, Part I: Batch Extraction Optimization Studies and Stability Tests", *Solv. Extr. Ion Exch.*, 25 (6), 703-721 (2007).
- [10] Babain, V.A., et al., "Extraction of Am and Eu with N,N'-substituted Pyridine-2,6-Dicarboxamides in Fluorinated Diluents", *Radiochemistry*, 48, (4), 369-373 (2006).
- [11] Alyapyshev, M.Yu., V.A. Babain, I.V. Smirnov, "Extractive Properties of Synergistic Mixtures of Dipicolinic Acid Diamides and Chlorinated Cobalt Dicarbolide", *Radiochemistry*, 46 (3), 270-271 (2004).
- [12] Romanovskiy, V.N., V.A. Babain, M.Yu. Alyapyshev, "Radionuclide Extraction by 2,6-pyridinedicarboxylamide Derivatives and Chlorinated Cobalt Dicarbolide", *Sep. Sci. Technol.*, 41 (10), 2111-2127 (2006).
- [13] Paulenova, A., et al., "Extraction of Lanthanides with Diamides of Dipicolinic Acid from Nitric Acid Solutions", *I. Sep. Sci. Technol.*, 43 (9) 2606-2618 (2008).
- [14] Paulenova, A., et al., "Extraction of Lanthanoids with Diamides of Dipicolinic Acid from Nitric Acid Solutions. II. Synergistic Effect of Ethyl-tolyl Derivates and Dicarbolide Cobalt", *Solv. Extr. Ion Exch.*, forthcoming (2009).
- [15] Nikitskaya, E.S., V.S. Usovskaya, M.V. Rubtsov, "Tertiary Amines of some Heterocycles as Possible Hypotensive Substances", *Russian J. General Chem.*, 28, 161-166 (1958).



- [16] Dozol, J.F., M. Dozol, R.M. Macias, "Extraction of Strontium and Cesium by Dicarbollides, Crown Ethers and Functionalized Calixarenes", *J. Inclus. Phen. Macrocyclic Chemistry*, 38, 1-22 (2000).
- [17] Rais, J., et al., "Feasibility Studies on  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$  and  $^{152,154}\text{Eu}$  Extractions with Boron Compounds", *Proceedings of the 2<sup>nd</sup> NUCEF Int. Symposium; NUCEF'98 Safety Research and Development of Base Technology on Nuclear Fuel Cycle*, Volume 99-004, Issue 1, 215-240, November (1998).
- [18] Lapka, J.L., A. Paulenova, "The Radiolytic and Thermal Stability of Diamides of Dipicolinic Acid", *Separation Science and Technology*, 45, 1706-1710 (2010).
- [19] Paulenova, A., et al., *NRC7 – 7<sup>th</sup> International Conference on Nuclear and Radiochemistry, Budapest, Hungary, 24-29 August (2008).*