

Radiation Chemistry in Solvent Extraction: FY2011 Research

Bruce Mincher
Stephen P. Mezyk
Leigh R. Martin

September 2011



The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

Radiation Chemistry in Solvent Extraction: FY2011 Research

**Bruce Mincher
Stephen R. Mezyk
Leigh R. Martin**

September 2011

**Idaho National Laboratory
Fuel Cycle Research & Development
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

**Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

ABSTRACT

This report summarizes work accomplished under the Fuel Cycle Research and Development (FCR&D) program in the area of radiation chemistry during FY 2011. The tasks assigned during FY 2011 included:

- Continue measurements free radical reaction kinetics in the organic phase.
- Continue development of an alpha-radiolysis program and compare alpha and gamma radiolysis for CMPO
- Initiate an effort to understand dose rate effects in radiation chemistry
- Continued work to characterize TALSPEAK radiation chemistry, including the examination of metal complexed ligand kinetics.

Progress made on each of these tasks is reported here. Briefly, the method developed to measure the kinetics of the reactions of the $\bullet\text{NO}_3$ radical with solvent extraction ligands in organic solution during FY10 was extended here to a number of compounds to better understand the differences between radical reactions in the organic versus aqueous phases. The alpha-radiolysis program in FY11 included irradiations of CMPO solutions with ^{244}Cm , ^{211}At and the He ion beam, for comparison to gamma irradiations, and a comparison of the gamma irradiation results for CMPO at three different gamma dose rates. Finally, recent results for TALSPEAK radiolysis are reported, summarizing the latest in an effort to understand how metal complexation to ligands affects their reaction kinetics with free radicals.

CONTENTS

| | |
|---|-----|
| ABSTRACT..... | iii |
| 1. INTRODUCTION..... | 1 |
| 2. RESULTS AND DISCUSSION..... | 1 |
| 2.1 Kinetics in the organic phase..... | 1 |
| 2.1.1 $\cdot\text{NO}_3$ radical kinetics in the organic phase..... | 1 |
| 2.2 Alpha radiolysis..... | 3 |
| 2.3 Dose rate effects..... | 4 |
| 2.4 Metal loaded ligand kinetics..... | 4 |
| 3. CONCLUSIONS AND FUTURE WORK..... | 8 |
| 4. INDICATORS OF PRODUCTIVITY..... | 9 |
| 5. LITERATURE CITED..... | 11 |

FIGURES

| | |
|---|---|
| Figure 1. pH dependence of DTPA speciation. Working TALSPEAK pH of ~ 3.6 shown as vertical line. Numbers correspond to individual DTPA species, with 1 being fully deprotonated and 6 being fully protonated..... | 5 |
| Figure 2. Arrhenius plots for temperature-dependent rate constants for $\cdot\text{OH}$ radical reaction with (a) DTPA Species 3, (b) DTPA Species 4, (c) DTPA Species 5, and (d) DTPA Species 6, with the species defined as shown in Figure 1..... | 6 |
| Figure 3. Absorbance measured for $(\text{SCN})_2^{\cdot-}$ at 475 nm for N_2O -saturated 52.1 μM KSCN with 100.4 μM DTPA buffered in the presence of 10 mM phosphate to 5.00 with 10.5 (blue top line), 20.6 (second green line), 30.3 (third red line) and 40.7 (bottom black line) μM Lu..... | 7 |
| Figure 4. Measured kinetics for $\cdot\text{OH}$ radical reaction with Lu-DTPA at pH 5.00. Data taken from peak values of transient absorbance kinetics of Figure 3. Solid line corresponds to fit of Equation (7), with $k_2 = (6.49 \pm 0.07) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | 8 |
| Figure 5. Summary of pH dependent Lu-DTPA and hydroxyl radical reaction rate constants, with TALSPEAK conditions indicated by (*) corresponding to a Lu-DTPA reactivity of $k_2 = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | 8 |

TABLES

| | |
|--|---|
| Table 1. Rate constants ($\text{M}^{-1} \text{ s}^{-1}$) for the reaction of $\cdot\text{NO}_3$ radical in organic and aqueous solution [2]..... | 2 |
|--|---|

Table 2. Rate constants ($M^{-1} s^{-1}$) for the reaction of $\cdot NO_3$ radical in organic and aqueous solution for additional compounds. 2

Table 3. Summary of Arrhenius parameters for $\cdot OH$ radical oxidation of different DTPA species. 2

SEPARATIONS AND WASTE FORMS/RADIATION CHEMISTRY PROGRAM

1. INTRODUCTION

During aqueous solvent extraction separations for fuel cycle applications both the aqueous and organic phases are irradiated with both high linear energy transfer (LET) alpha and low LET beta/gamma radiation. The deposition of this energy into the system results in adverse effects including degradation of ligands and loss of solvent extraction efficiency, production of radiolysis products that complex metals to decrease separation factors, and possible changes in physical characteristics of the solvent due to precipitates or polymers. For application in a nuclear solvent extraction process, components of the solvent formulation must have adequate radiolytic stability to ensure solvent recycle potential. The ligand decomposition yield should be sufficiently low, and the nature of the decomposition products sufficiently benign, that significant process efficiency is not lost with time and absorbed radiation dose. Therefore, a major effort in the separations campaign has been invested in understanding radiation chemistry in biphasic, acidic systems containing the ligands of most importance to the proposed future fuel cycle.

When a radiation event occurs in solution, direct interaction of the incident particle with a solution constituent will only happen in proportion to the abundance of that component. Therefore, the diluent is the most likely solution component to be affected. Diluent radiolysis produces ionic and radical species that diffuse through the solution to react with other diluent molecules, or the ligands designed to complex metal ions for separations. Radical reactions are especially important, and knowledge of the rate constants for these reactions, and their products, allows reaction mechanisms to be elucidated. Therefore, a successful radiation chemistry program will consist of a strong kinetics component, relying on pulse and steady state radiolysis, and a strong analytical chemistry component, relying on mass spectrometric, liquid chromatographic and other appropriate methods. These techniques have been employed in the work reported here.

In addition to the pulse and steady state radiolysis techniques, solvent extraction contacts are necessary to evaluate the changes in solvent extraction efficiency for irradiated solvents. All three techniques were used in FY11 to better understand the radiation chemistry of primarily the ligand octylphenyl-N,N-diisobutylcarbamoylmethyl phosphine oxide CMPO. This report also contains the latest data in regard to metal complexed DTPA radiolysis toward a better understanding of TALSPEAK chemistry.

2. RESULTS AND DISCUSSION

2.1 Kinetics in the organic phase

Conventional pulse radiolysis is conducted in the aqueous phase. However, in the irradiated solvent extraction system, an organic phase is in contact with the aqueous phase, and neutral radicals may also undergo reactions in that organic phase. Radicals such as $\cdot\text{OH}$ and $\cdot\text{NO}_3$ that are produced in the aqueous phase may diffuse across the phase boundary, or they may be produced *in-situ* from extracted acid and water. To model these reactions it is necessary to measure their kinetic constants in the organic phase.

2.1.1 $\cdot\text{NO}_3$ radical kinetics in the organic phase

Previously under this program techniques were developed for the generation and measurement of the $\cdot\text{NO}_3$ radical in the aqueous phase [1], and in the organic phase [2]. This was achieved using pulse-irradiated, N_2O -sparged, 6 M HNO_3 for aqueous applications and with 1.4 M tetrabutyl ammonium nitrate (TBANO₃) in *t*-butanol for organic applications. The absorbance maximum at 630 nm was used to measure the kinetic constants for the reaction of $\cdot\text{NO}_3$ radical with CMPO and DMDOHEMA in *t*-butanol

solution in FY10 [2]. The rate constant for the reaction of octanol in *t*-butanol solution was also determined at that time. These data are given in Table 1, along with the previously determined rate constants for these reactions in aqueous solution.

Table 1. Rate constants ($M^{-1} s^{-1}$) for the reaction of $\bullet NO_3$ radical in organic and aqueous solution [2].

| Analyte | <i>t</i> -BuOH | aqueous |
|----------|-------------------------------|-------------------------------|
| CMPO | $(9.33 \pm 0.59) \times 10^7$ | $(1.28 \pm 0.13) \times 10^8$ |
| DMDOHEMA | $(4.27 \pm 0.46) \times 10^8$ | $(2.22 \pm 0.10) \times 10^8$ |
| octanol | $(4.33 \pm 0.43) \times 10^8$ | 5.8×10^6 |

There is no obvious trend between solvents with the rate constant being lower in the organic phase for CMPO, and higher for DMDOHEMA and octanol. The rate constant for octanol is important since it represents the rate for $\bullet NO_3$ reaction with the diluents in the DMDOHEMA-based system. A fast rate of reaction with the diluent indicates that fewer radicals will be available to react with the ligand. For example, note that the rate constants for DMDOHEMA and octanol are nearly identical in the *t*-butanol solution. Since in the proposed solvent extraction process DMDOHEMA is used at a concentration of 0.65 M and octanol at 6.3 M, only approximately 10% of $\bullet NO_3$ radical yield in the organic phase would be available to react with the ligand under these conditions. This rate constant also explains why no $\bullet NO_3$ radical was detected in irradiated octanol solutions of TBANO₃, since the high concentration of octanol would quickly scavenge any produced radical [2].

Here (Table 2) we report new kinetic measurements in the organic phase for $\bullet NO_3$ radical reactions with additional compounds, and compare them to the aqueous phase.

Table 2. Rate constants ($M^{-1} s^{-1}$) for the reaction of $\bullet NO_3$ radical in organic and aqueous solution for additional compounds.

| Analyte | <i>t</i> -BuOH | aqueous |
|------------------|-------------------------------|-------------------------------|
| TBP | $(1.42 \pm 0.09) \times 10^7$ | $(4.3 \pm 0.7) \times 10^5$ |
| 1-butanol | $(1.74 \pm 0.44) \times 10^7$ | 1.9×10^6 |
| 1-propanol | $(1.03 \pm 0.21) \times 10^7$ | $(2.2 \pm 1.5) \times 10^5$ |
| <i>p</i> -xylene | $(7.40 \pm 1.15) \times 10^8$ | $(1.07 \pm 0.09) \times 10^9$ |
| anisole | $(7.12 \pm 0.93) \times 10^8$ | $(4.42 \pm 0.27) \times 10^9$ |
| toluene | $(9.03 \pm 1.07) \times 10^8$ | $(1.71 \pm 0.15) \times 10^9$ |

Two trends are noticeable in Table 2. First it can be seen that alcohols react with $\bullet NO_3$ radical at faster rates for longer carbon chain lengths, with the slowest rate being $\sim 1 \times 10^7 M^{-1} s^{-1}$ for propanol, and the fastest being $\sim 4 \times 10^8 M^{-1} s^{-1}$ for octanol. This suggests that the reaction is one of $\bullet H$ atom abstraction. In future experiments we will examine higher C-chain length alcohols, using alcohol addition to *t*-butanol solution. These results already allow us to predict that the reaction with the dodecane diluent used in solvent extraction to be fast. This dodecane rate constant will also be measured in continued work. Based upon the current results, diluents containing abundant $-CH_2-$ groups should scavenge $\bullet NO_3$ radical resulting in protection of the ligands, and these reactions will happen faster in the organic phase than in the aqueous phase. However, it should be kept in mind that nitrated alkanes, which will be produced by the scavenger reaction, have been implicated in solvent degradation for the PUREX process, as nitroalkanes are also metal complexing agents [3].

In the second trend noticeable in Table 2, compounds with phenyl rings react with $\cdot\text{NO}_3$ radical in organic solution more slowly than in aqueous solution. The reason for this change in rate constants for aromatic species is not understood at this time.

2.2 Alpha radiolysis

Most radiation chemistry studies have been performed using γ -sources for ease of contamination control and post-irradiation analytical chemistry. However, solvents used for the solvent extraction of metals from dissolved fuel will also be exposed to significant α -doses. It is therefore desirable to understand the effects of high LET radiation, and a α -radiolysis program was initiated in FY 2010 [2].

The linear energy transfer (LET) of the α particle is significantly greater than that of β or γ radiation. Massive, highly charged α -particles have short ranges and deposit 156 eV nm^{-1} for an energy of 5 MeV in water [4]. This energy deposition results in closely-spaced overlapping spurs, resulting in high localized concentrations of reactive species, many of which undergo recombination before they can diffuse into the bulk solution. The result is higher yields of molecular species and lower yields of radicals for α -radiation. Therefore, differences in the effects of irradiation between high and low LET sources might be expected.

Alpha-irradiation of samples is experimentally difficult. Isotopic irradiations such as with ^{244}Cm or ^{238}Pu result in α -emitter contaminated samples which can't be analyzed in most laboratories, even at DOE sites. Alternately, He ion beams may be used to avoid radiological contamination issues. However, the penetration depth of the He ion is small, resulting in the need to use very high dose rates with rapid stirring of irradiated samples to deliver a reasonable integrated dose to the samples. The dose rates used are very high by comparison to γ irradiations, which may introduce ambiguity in results. Therefore, during FY 11 we have investigated several methods to α -irradiate CMPO samples, for comparison to each other, and to γ -irradiated samples. The following α -irradiation techniques were used:

1. ^{244}Cm irradiations in a glovebox at INL
2. ^{211}At irradiations at Chalmers University, Göteborg, Sweden
3. He ion beam irradiations at NDRL, South Bend, IN
4. Reactor production of α -particles using B targets at UC Irvine

Post-irradiation samples were analyzed by HPLC and mass spec (TM-DESI-MS) to determine decomposition products and G -values (degradation yield) for the He ion beam-irradiated samples. Irradiations were performed for both CMPO in dodecane solution, and for CMPO in dodecane in contact with a nitric acid aqueous phase. The results of these irradiations were reported in detail [5] and only a summary is reported here.

In brief, it was found that the degradation yield of 0.1 M CMPO irradiated in dodecane (no aqueous phase) as determined by HPLC was the same for α (He ion beam) as for γ -irradiation, at $0.14 \mu\text{mol Gy}^{-1}$. This result was unexpected, since the higher LET α -radiation gives lower yields of reactive radical species than for γ -radiation. Despite the equivalent rate of decrease in CMPO concentration for the two radiation types, the products of irradiation as determined by mass spectrometry were different. For α -irradiation, a predominant reaction was the fission of the CMPO carbonyl-methylene bond to generate diisobutylformamide. In contrast, radiolysis by γ -irradiation favored cleavage of the CMPO methylene-phosphoryl bond, resulting in formation of octylphenylphosphinic acid. The acidic gamma product is generally believed to be responsible for the difficulties encountered in stripping irradiated CMPO solutions [6, 7, 8], and increases in both forward extraction and stripping distribution ratios were measured here for γ -irradiated samples. Unfortunately, solvent extraction experiments could not be run on He ion beam irradiated solutions due to the low volumes irradiated. However, the absence of acidic

products in He-irradiated solution suggests that less deleterious effects on solvent extraction performance would be found.

Samples of 0.1 M CMPO in dodecane were also irradiated in the presence of the nitric acid phase, using ^{244}Cm and ^{211}At isotopic irradiations, as well as with γ -rays. Lower G -values for the loss of CMPO were measured, at $0.04 \mu\text{mol Gy}^{-1}$ for γ -rays, and $0.034 \mu\text{mol Gy}^{-1}$ for ^{211}At . Thus, the radiolytic decomposition rate of CMPO in the presence of nitric acid is lower than for neat organic solution. Assuming that He ion beams and At- α particles are equivalent, this again suggests that α and γ irradiation G -values are similar.

For γ -samples, an increase in forward and stripping distribution ratios was still found, but the magnitude of the increases was lower when in the presence of the acid. The γ -irradiation in the presence of acid also favored fission of the N-carbamoyl bond, resulting in secondary amine products. These would not be expected to have deleterious effects on solvent extraction. It was not possible to measure the products of isotopically irradiated α -samples in the presence of acid, because no instruments at INL are available to perform analyses on α -contaminated samples. However, solvent extraction experiments showed that the forward extraction and stripping distribution ratios decreased rapidly for both ^{244}Cm and ^{211}At -irradiated samples. Continued investigation of the effects of α -irradiation is clearly warranted, especially for product identification. We are currently investigating the potential to perform analyses of α -contaminated samples at the University of Nevada, Las Vegas radiochemistry laboratories.

2.3 Dose rate effects

Recently, it was reported that the use of varying γ -dose-rates for the irradiation of 0.01 M 4-*t*-butyl-6,6'-bis(5,5,8,8,-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-bipyridine (MF2-BTBP) in cyclohexanone resulted in different effects on D_{Am} and D_{Eu} [9]. Although dose rate effects over the range encountered using isotopic irradiation would be unusual, it is important to identify if dose rate effects actually occur, because the dose rates to be encountered in the process are probably lower than most dose rates generated by γ -irradiators used under experimental conditions. To initiate these studies, the effect of dose rate on the radiolytic generation of nitrous acid was initially investigated [2]. It has been shown under previous work for this program that the radiolytic generation of HNO_2 in irradiated HNO_3 has consequences for both the nitration of ligands [10, 11] and metal oxidation states [12]. Thus, the magnitude of its yield is important. However, we reported that the HNO_2 yield was unchanged over the order-of-magnitude dose rate range available using the INL ^{60}Co irradiator [2].

During FY11 0.1 M CMPO dodecane solutions were irradiated at three different dose rates using three different ^{60}Co irradiators at NDRL. In each case, an identical G -value for the loss in CMPO concentration was measured. These results agree with expectations that dose rate effects would not exist over the range of dose rates encountered using isotope sources.

2.4 Metal Loaded Ligand Kinetics

The G -values for the radiolytic decomposition of metal-complexed crown ethers were previously reported to be higher than for crown ethers alone [13, 14]. Only Ershov et al. [15] have investigated the change in kinetics due to metal complexation, also using crown ethers. They found faster $\cdot\text{OH}$ radical rate constants and slower $\cdot\text{H}$ atom rate constants when 18-crown-6 was complexed with potassium. Therefore it was hypothesized here that the complexation of solvent extraction ligands by metals would alter their reaction rate constants with the important reactive species produced by radiolysis.

The ligand DTPA was chosen for the following experiments due to its water solubility, which allows for greater ease in rate constant determinations. The hydroxyl radical ($\cdot\text{OH}$) is the major oxidizing species produced in the radiolysis of water. Its reaction with complexing ligands such as DTPA (diethylenetriaminepentaacetic acid) could reduce the extraction efficiency of the minor actinides within

the TALSPEAK process. At the working pH of ~3.6, DTPA exists in several protonation states, as shown in Figure 1.

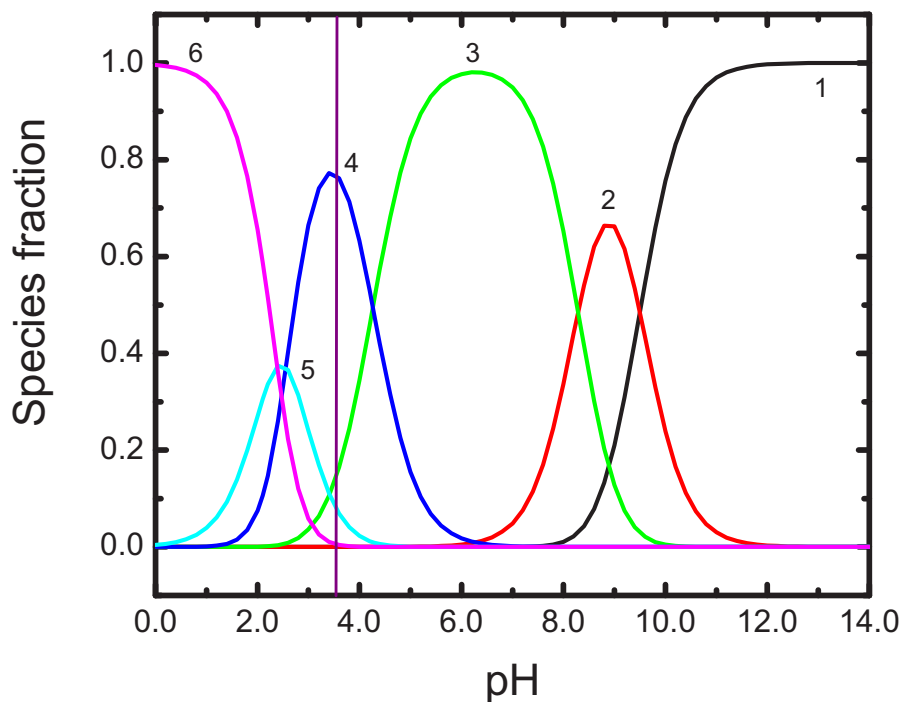


Figure 1. pH dependence of DTPA speciation. Working TALSPEAK pH of ~3.6 shown as vertical line. Numbers correspond to individual DTPA species, with 1 being fully deprotonated and 6 being fully protonated.

The reactivity of the hydroxyl radical with the different DTPA species was evaluated, over the pH range 1 – 6, and temperature range 5 – 40°C. These data are shown in Figure 2, with the corresponding Arrhenius parameters for these different species given in Table 3.

Table 3. Summary of Arrhenius parameters for $\cdot\text{OH}$ radical oxidation of different DTPA species.

| Species | $\ln(A)$ | $E_a / \text{kJ mol}^{-1}$ |
|---------|----------|----------------------------|
| 3 | 30.923 | 21.37 |
| 4 | 26.514 | 12.11 |
| 5 | 27.028 | 13.39 |
| 6 | 27.668 | 14.44 |

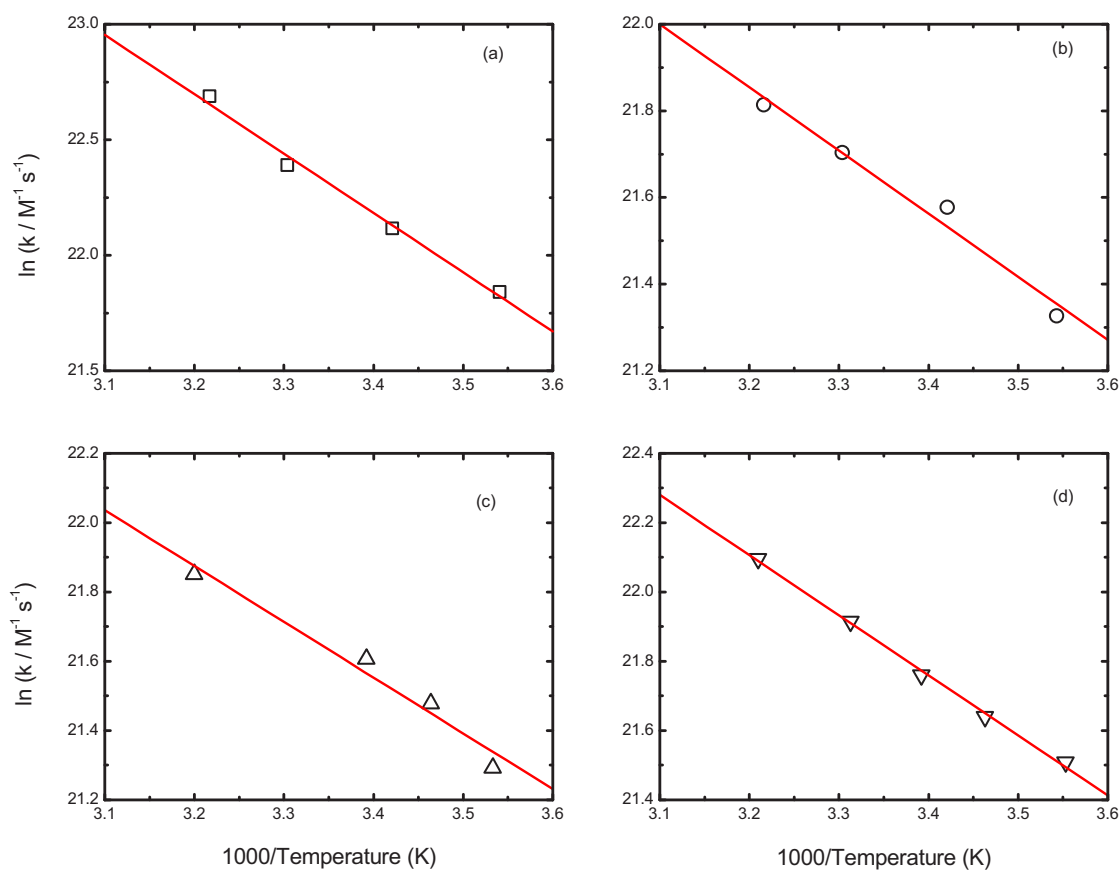


Figure 2. Arrhenius plots for temperature-dependent rate constants for $\cdot\text{OH}$ radical reaction with (a) DTPA Species 3, (b) DTPA Species 4, (c) DTPA Species 5, and (d) DTPA Species 6, with the species defined as shown in Figure 1.

These data allow the evaluation of $\cdot\text{OH}$ radical reactivity for lanthanide-complexed DTPA under TALSPEAK conditions. To date, we have obtained kinetic data for three lanthanides: Eu, Ce, and Lu. The europium analysis has been previously reported [2], while preliminary analyses for the Lu-DTPA complex data have been completed and are reported here.

The kinetic measurements were obtained using SCN⁻ competition kinetics, as no significant UV-visible absorption change upon direct irradiation of Lu/DTPA solutions was found. Typical solution conditions used N₂O-saturated water buffered (10 mM phosphate) to the desired pH containing 50.0 μM KSCN, 100.0 μM DTPA, and varying Lu concentrations over the range 10-50 μM . For this preliminary analysis, it was assumed that a 1:1 Lu:DTPA complex was formed under all conditions.

Hydroxyl radicals were generated from the decomposition of water by electron beam. Over the pH range investigated, DTPA species 1 and 2 may be discounted. Therefore, at room temperature (20.8°C) the $\cdot\text{OH}$ radical then react according to the competition shown in Equations 1-6, where k_2 is the rate constant for the reaction of the metal complexed species:



| | | |
|----------------|--|-----|
| •OH + Lu-DTPA | k_2 | (2) |
| •OH + DTPA-Sp3 | $k_3 = 4.28 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | (3) |
| •OH + DTPA-Sp4 | $k_4 = 2.31 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | (4) |
| •OH + DTPA-Sp5 | $k_5 = 1.51 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | (5) |
| •OH + DTPA-Sp6 | $k_6 = 1.79 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ | (6) |

Typical data for the measured transient absorbance of $(\text{SCN})_2^{\bullet-}$ observed at 475 nm is shown in Figure 3, for pH 5.0. This absorbance is seen to decrease with increasing amounts of Lu, indicating that more of the •OH radical is reacting with the metal complex through the reaction shown in Equation 2.

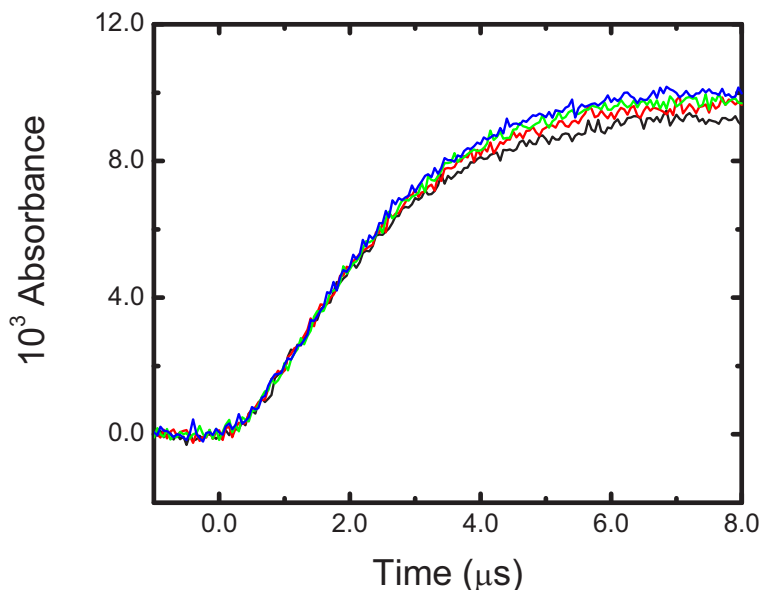


Figure 3. Absorbance measured for $(\text{SCN})_2^{\bullet-}$ at 475 nm for N_2O -saturated 52.1 μM KSCN with 100.4 μM DTPA buffered in the presence of 10 mM phosphate to 5.00 with 10.5 (blue top line), 20.6 (second green line), 30.3 (third red line) and 40.7 (bottom black line) μM Lu.

Using a standard competition kinetics analysis, an analytical equation for this chemistry can be derived:

$$\frac{1}{Y_{\text{SCN}^-}} = \frac{1}{Y_{\text{SCN}^-}^o} + \frac{1}{Y_{\text{SCN}^-}^o} * \frac{k_2 * [\text{Lu} - \text{DTPA}] + \sum k_i * f_i * [\text{DTPA} - i]}{k_1 * [\text{SCN}^-]} \quad (7)$$

where f_i corresponds to the fraction of free DTPA ligand at the measured pH, as determined from Figure 1, and $Y_{\text{SCN}^-}^o$ is the absorbance of this transient in the absence of any DTPA or Lu. Therefore, by plotting $1/Y_{\text{SCN}^-}$ against the [Lu] this equation can be fitted to derive k_2 . This is shown as the straight line in Figure 4. At this pH, a value of $k_2 = (6.49 \pm 0.07) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for this complex, which is faster than any of the individual DTPA species under these conditions. This is in agreement with results reported for Eu-DTPA [2].

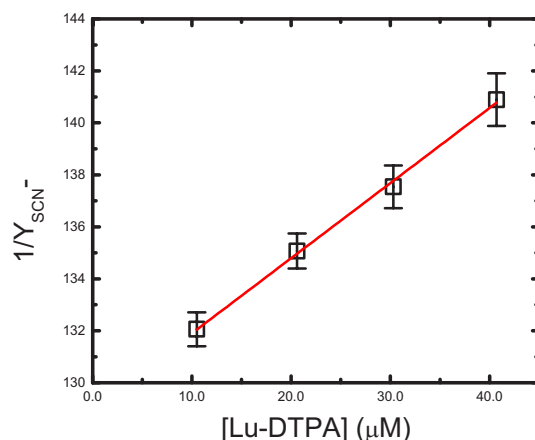


Figure 4. Measured kinetics for $\bullet\text{OH}$ radical reaction with Lu-DTPA at pH 5.00. Data taken from peak values of transient absorbance kinetics of Figure 3. Solid line corresponds to fit of Equation (7), with $k_2 = (6.49 \pm 0.07) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

These data were collected across the pH range 5.0 – 2.0, with this dependence shown in Figure 5. At more acidic pH the $\bullet\text{OH}$ radical reaction with the Lu-DTPA complex is slower. Based on this trend, under TALSPEAK pH conditions of 3.6, a value of $4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was determined.

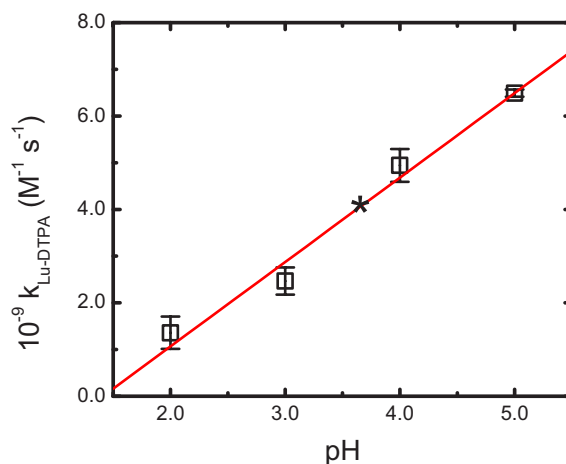


Figure 5. Summary of pH dependent Lu-DTPA and hydroxyl radical reaction rate constants, with TALSPEAK conditions indicated by (*) corresponding to a Lu-DTPA reactivity of $k_2 = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

It can be seen that the rate of reaction of the important oxidizing agent $\bullet\text{OH}$ radical with DTPA under TALSPEAK conditions is dependent on both pH and metal complexation. These analyses are currently being extended to the other measured lanthanide metals, as any attempt at modeling this complex system will require the rate constants for the light lanthanides.

3. CONCLUSIONS AND FUTURE WORK

The ability to measure rate constants for NO_3 reactions in the organic phase was an important accomplishment of the program for FY 2010. In FY11 this technique has allowed insights into the

radiation chemistry of the organic phase which have never been previously available. For example, organic rate constant comparisons with those in the aqueous phase $\cdot\text{NO}_3$ have revealed that this radical reacts by a different mechanism for aromatic versus saturated compounds. Continued work here will elucidate this mechanistic difference, and allow for the better prediction of conditions in the process.

Alpha radiolysis experiments using He-ion beams, ^{244}Cm and ^{211}At irradiation followed by HPLC, mass spec and solvent extraction analyses has begun to improve our understanding α -radiolysis, and has supported INL involvement in a recent NEUP grant issued to our collaborators. A major INL effort was to compare α and γ -radiolysis of CMPO. The results indicate that the rate of CMPO decomposition is similar for the two radiation types, and is decreased in the presence of the aqueous phase. Despite this consistency in the decomposition G -value for CMPO, the two types of radiation produce different radiolysis products and have different affects on solvent extraction performance. The publication of a report comparing α and γ -irradiation of CMPO was a successfully met Level 2 milestone for FY11 [5]. Continued irradiations and development of mass spec techniques will be performed to fully elucidate the mechanism of CMPO radiolysis; these techniques will have application to additional selected ligand investigations. Additionally, two systems have now been investigated for dose rate effects, with no differences identified in G -values over an order-of-magnitude change in γ -dose rates for loss in CMPO concentration or production of nitrous acid.

Initial attempts to measure the effects of metal complexation on the rate constant of the $\cdot\text{OH}$ radical with Lu-complexed DTPA have confirmed the hypothesis that metal complexation alters reaction rates with the reactive species produced by radiolysis. This indicates that precise modeling of the radiolytic decomposition of these ligands will require continued acquisition of kinetic constants under conditions relevant to the solvent extraction process. Work along these lines will continue during the next fiscal year.

In new work for FY12 we plan to initiate a study of the role of radical cation chemistry in irradiated solution. These cations are produced from solution components that are ionized during radiolytic production of electrons. They are a major radiolysis product for which the chemistry has not yet been investigated.

4. INDICATORS OF PRODUCTIVITY

The following peer-reviewed journal papers have been published since the inception of the INL FCR&D Radiation Chemistry program. Asterisked entries indicate invited contributions:

1. Mezyk, S.P.; Mincher, B.J., Radiolytic stability of nuclear reprocessing extraction ligands. Proceedings of the International Solvent Extraction Conference, ISEC 2011, Santiago, Chile, in press.
2. Swancutt, K.L.; Mezyk, S.P.; Tillotson, R.D.; Pailloux, S.; Chakravarty, M.; Paine, R.T.; Martin, L.R. 2011, Radiolytic degradation in lanthanide/actinide separation ligands- NOPOPO: Radical kinetics and efficiencies determinations. *Solvent Extr Ion Exch* **29**:637-654.
3. Swancutt, K.L.; Cullen, T.D.; Mezyk, S.P.; Elias, G.; Bauer, W.L.; Peterman, D.R.; Riddle, C.L.; Ball, R.D.; Mincher, B.J.; Muller, J.J. 2011. The radiation chemistry of the Cs-7SB modifier used in Cs and Sr solvent extraction. *Solvent Extr Ion Exch*. **29**:106-127.
4. Elias, G.; Mincher, B.J.; Mezyk, S.P.; Muller, J.; Martin, L.R. 2011. Toluene nitration in irradiated nitric acid and nitrite solutions. *Radiat. Phys. Chem.* **80**:554-560.
5. *Mincher, B.J.; Modolo, G.; Mezyk, S.P. 2010. The Effects of Radiation Chemistry on Solvent Extraction: 4. Separation of the minor actinides and considerations for radiation-resistant solvent systems. *Solvent Extr. Ion Exch.* **28**:415-436.

6. Elias, G.; Mincher, B.J.; Mezyk, S.P.; Cullen, T.; Martin, L.R. 2010. Anisole nitration during gamma-irradiation of aqueous nitrite and nitrate solutions. Free radical versus ionic mechanisms. *Environ. Chem.* **7**:183-187.
7. Mincher, B.J.; Cooper, W.J.; Mezyk, S.P.; Cole, S.K.; Fox, R.V.; Gardinali, P.R. 2010. Free radical chemistry of disinfection by-products. 3. Degradation mechanisms of chloronitromethane, dichloronitromethane and bromonitromethane. *J. Phys. Chem. A.* **114**:117-125.
8. *Mincher, B.J., Modolo, G., Mezyk, S.P. 2009. The Effects of Radiation Chemistry on Solvent Extraction: 3. A review of actinide and lanthanide extraction. *Solvent Extr. Ion Exch.* **27**:579-606.
9. Mincher, B.J., Elias, G., Martin, L.R., Mezyk, S.P. 2009. Radiation chemistry and the nuclear fuel cycle. *J. Radioanal. Nucl. Chem.* **282**:645-649.
10. Mincher, B.J.; Mezyk, S.P. 2009. Radiation chemical effects on radiochemistry: a review of examples important to nuclear power. *Radiochimica Acta* **97**:519-534.
11. *Mincher, B.J.; Modolo, G.; Mezyk, S.P. 2009. The Effects of Radiation Chemistry on Solvent Extraction: 2. A review of fission product extraction. *Solvent Extr. Ion Exch.* **27**:331-353.
12. Martin, L.R.; Mezyk, S.P.; Mincher, B.J. 2009. Determination of Arrhenius and thermodynamic parameters for the reaction of hydroxyl radical with lactic acid. *J. Phys. Chem. A.* **113**:141-145.
13. *Mincher, B.J.; Modolo, G.; Mezyk, S.P. 2009. The Effects of Radiation Chemistry on Solvent Extraction: 1. Conditions in Acidic Solution and a Review of TBP Radiolysis. *Solvent Extr. Ion Exch.* **27**:1-25.
14. Mincher, B.J.; Mezyk, S.P.; Martin, L.R. 2008. A pulse radiolysis investigation of the reactions of tributylphosphate with the radical products of aqueous nitric acid irradiation. *J. Phys. Chem.* **112**:6275-6280.
15. Cooper, W.J.; Mezyk, S.P.; Peller, J.; Cole, S.K.; Song, W.; Mincher, B.J.; Peake, B.M. 2008. Studies in radiation chemistry: Application to ozonation and other advanced oxidation technologies. *Ozone: Sci. and Eng.* **30**:58-64.
16. Mincher, B.J.; Herbst, R.S.; Tillotson, R.D.; Mezyk, S.P. 2007. γ -radiation effects on the performance of HCCD-PEG for Cs and Sr extraction. *Solvent Extr. Ion Exch.* **25**:747-755.
17. Mincher, B.J.; Mezyk, S.P.; Bauer, W.F.; Elias, G.; Riddle, C.L.; Peterman, D.R. 2007. FPX γ -radiolysis in the presence of nitric acid. *Solvent Extr. Ion Exch.* **25**:593-601.
18. Cole, S.K.; Cooper, W.J.; Fox, R.V.; Gardinali, P.R.; Mezyk, S.P.; Mincher, B.J.; O'Shea, K. 2007. Free radical chemistry of disinfection by-products. 2. Rate constants and degradation mechanisms of trichloronitromethane (Chloropicrin). *Environ. Sci. Technol.* **41**:863-869.

The following book chapters have been published since the inception of the INL FCR&D Radiation Chemistry program:

1. Mincher, B.J. *Degradation issues in aqueous reprocessing systems*, Ch. 104 in: Comprehensive Nuclear Materials, Allen, T., ed. Elsevier, *in press*.
2. Swancutt, K.L.; Mezyk, S.P.; Martin, L.R.; Paine, R.T. *Kinetics and Efficiencies of Radiolytic Degradation in Lanthanide/Actinide Separation Ligands – NOPOPO*. Ch. X in: Nuclear Energy and the Environment, ACS symposium series 1046, Wai, C. M. ; Mincher, B.J., Eds., 2010. pp. 232–242.
3. Mincher, B.J. *An overview of selected radiation chemical reactions affecting fuel cycle solvent extraction*. Ch 15 in: Nuclear Energy and the Environment, ACS symposium series 1046, Wai, C.M.; Mincher, B.J., Eds., 2010. pp. 181-192.
4. Mezyk, S.P.; Cullen, T.D.; Elias, G., Mincher, B.J. *Aqueous nitric acid radiation effects on solvent extraction process chemistry*. Ch. 16 in: Nuclear Energy and the Environment, ACS symposium

- series 1046, Wai, C.M.; Mincher, B.J., Eds., 2010. pp. 193-203.
5. Elias, G.; Mincher, B.J.; Mezyk, S.P.; Cullen, T.D.; Martin, L.R. *Nitration mechanisms of anisole during gamma irradiation of aqueous nitrite and nitrate solutions*. Ch. 17 in: Nuclear Energy and the Environment, ACS symposium series 1046, Wai, C.M.; Mincher, B.J., Eds., 2010. pp. 205-214.
 6. Martin, L.R.; Mincher, B.J.; Mezyk, S.P.; Elias, G.; Tillotson, R.D. *Effects of aqueous phase radiolysis on lactic acid under TALSPEAK conditions*. Ch. 20 in: Nuclear Energy and the Environment, ACS symposium series 1046, Wai, C.M.; Mincher, B.J., Eds., pp. 243-253.
 7. Takagi, J.; Mincher, B.J.; Yamaguchi, M.; Katsumura, Y. *Radiation chemistry in nuclear engineering*. Ch. 36 in: Charged Particle and Photon Interactions with Matter: Recent Advances, Applications, and Interfaces, Hatano, Y.; Katsumura, Y.; Mozumder, A., Eds. CRC Press, 2010

The following list of presentations is not all-inclusive, but rather is a special selection from among numerous invited talks:

1. Mincher, B.J.; Mezyk, S.P.; Elias, G.; Groenewold, G.S. *Radiation Chemistry Effects on Nuclear Solvent Extraction: Examples from CMPO radiolysis*. presented at the 14th International Congress on Radiation Research, Warsaw, Poland, 28 Aug-2 Sept, 2011.
2. Mincher, B.J.; Peterman, D.R.; Riddle, C.L.; Law, J.D.; Todd, T.A.; Mezyk, S.P. 2006. *Gamma Ray Radiolysis of the FPEX Solvent*, Actinide and Fission Product Partitioning & Transmutation Ninth Information Exchange Meeting, OECD Nuclear Energy Agency, Nimes, France.
3. Mincher, B.J.; *Radiation chemistry and the nuclear fuel cycle*, seminar presented at: Forschungszentrum Jülich, Germany, September 25, 2009.
4. Mincher, B.J.; *Radiation chemistry and the nuclear fuel cycle*, seminar presented at: ACSEPT, Actinide Separations and Partitioning Meeting, Bologna, Italy, September 21-23, 2009.
5. Mincher, B.J.; *Radiation chemistry and the nuclear fuel cycle*, presented at: Radiation Chemistry in the 21st Century; A Visionary Meeting, University of Notre Dame, Notre Dame, IN, USA, July 12-15, 2009.
6. Mincher, B.J.; *Radio-, and radiation chemistry at Idaho National Lab*, seminar presented at: the University of Tokyo, Tokyo, Japan, Nov. 23, 2008.
7. Mincher, B.J.; *The γ -radiolysis of ligands used in nuclear solvent extraction*, seminar presented at Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN, USA, 2007.
8. Mincher, B.J.; *The radiation chemistry of ligands used in fission product extraction*, seminar presented at University of Manchester, Manchester, UK, 2006.

5. LITERATURE CITED

1. Mincher, B.J.; Mezyk, S.P.; Martin, L.R. 2008, A pulse radiolysis investigation of the reactions of tributylphosphate with the radical products of aqueous nitric acid irradiation. *J. Phys. Chem.* 112:6275-6280.
2. Mincher, B.J.; Martin, L.R.; Mezyk, S.P. Radiation chemistry in solvent extraction: FY10 Research. INL Report FCR&D-SEPA-2010-0155.
3. Tahraoui, A.; Morris, J.H. 1995, Decomposition of solvent extraction media during nuclear reprocessing: literature review. *Sep. Sci. Technol.* 30: 2603-2630.
4. Pastina, B.; LaVerne, J.A. 1999, Hydrogen peroxide production in the radiolysis of water with heavy ions. *J. Phys. Chem. A* 103, 1592-1597.
5. Mincher, B.J.; Mezyk, S.P.; Groenewold, G.S.; Elias, G. A comparison of the alpha and gamma radiolysis of CMPO. INL Report FCR&D-SEPA-2011-000148.

6. Nash, K.L.; Rickert, P.G.; Horwitz, E.P. Degradation of TRUEX-dodecane process solvent. *Solvent Extr. Ion Exch.* 1989, **7**, 655–75.
7. Buchholz, B.A.; Nuñez, L.; Vandegrift, G.F. 1996, Effect of α -radiolysis on TRUEX-NPH Solvent. *Sep. Sci. Technol.* **31**: 2231-2243.
8. Chiarizia, R.; Horwitz, E.P. Hydrolytic and radiolytic degradation of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide and related compounds. *Solvent Extr. Ion Exch.* 1986, **4**, 677–723.
9. Fermvik, A.; Ekberg, C.; Englund, S.; Foreman, M.R.St.J.; Modolo, G.; Retegan, T.; Skarnemark, G. 2009, Influence of dose rate on the radiolytic stability of a BTBP solvent for actinide(III)/lanthanide(III) separation. *Radiochim. Acta* **97**:319-324.
10. Elias, G.; Mincher, B.J.; Mezyk, S.P.; Cullen, T.; Martin, L.R. 2010. Anisole nitration during gamma-irradiation of aqueous nitrite and nitrate solutions. Free radical versus ionic mechanisms. *Environ. Chem.* **7**:183-187.
11. Swancutt, K.L.; Cullen, T.D.; Mezyk, S.P.; Elias, G.; Bauer, W.L.; Peterman, D.R.; Riddle, C.L.; Ball, R.D.; Mincher, B.J.; Muller, J.J. 2011. The radiation chemistry of the Cs-7SB modifier used in Cs and Sr solvent extraction. *Solvent Extr Ion Exch.* **29**:106-127.
12. Mincher, B.J.; *Radiation chemistry and the nuclear fuel cycle*, seminar presented at: ACSEPT, Actinide Separations and Partitioning Meeting, Bologna, Italy, September 21-23, 2009.
13. Grigor'ev, E.I.; Mikhalitsyna, O.V.; Nesterov, S.V.; Trakhtenberg, L.I. 1994. Radiation stability of 15-crown-5 complexes with alkaline earth metal chlorides. *Mendeleev Commun.* **4**:66–67.
14. Grigor'ev, E.I.; Mikhalitsyna, O.V.; Nesterov, S.V.; Trakhtenberg, L.I. 1997. The effect of structure of crown ether complexes with alkaline-earth metal chlorides on their radiation resistance. *High Energy Chem.* **31**:16–19.
15. Ershov, B.G.; Seliverstov, A.F.; Sukhov, N.L.; Gordeev, A.V. 1987. Pulsed radiolysis of aqueous solutions of 18-Crown-6. *Khim. Vys. Energij* **21**: 119–122.