

***Radical Cations and Acid Protection during
Radiolysis***

Fuel Cycle Research & Development

***Prepared for
U.S. Department of Energy
Materials Recovery and Waste Form
Development Campaign
Bruce J. Mincher, Stephen P. Mezyk,
Christopher A. Zarzana
Idaho National Laboratory
9 Sept. 2016
FCRD-MRWFD-2016-00342***



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.

SUMMARY

Ligand molecules for used nuclear fuel separation schemes are exposed to high radiation fields and high concentrations of acid. Thus, an understanding of the complex interactions between extraction ligands, diluent, and acid is critical to understanding the performance of a separation process. The diglycolamides are ligands with important structural similarities to CMPO; however, previous work has shown that their radiolytic degradation has important mechanistic differences from CMPO. The DGAs do not enjoy radioprotection by HNO_3 and the kinetics of DGA radiolytic degradation are different. CMPO degrades with pseudo-zero-order kinetics in linear fashion with absorbed dose while the DGAs degrade in pseudo-first-order, exponential fashion. This suggests that the DGAs degrade by simple reaction with some product of direct diluent radiolysis, while CMPO degradation is probably multi-step, with a slow step that is not dependent on the CMPO concentration, and mitigated by HNO_3 . It is thus believed that radio-protection and the zero-order radiolytic degradation kinetics are related, and that these phenomena are a function of either the formation of strong acid complexes with CMPO and/or to the presence of the CMPO phenyl ring. Experiments to test both these hypotheses have been designed and partially conducted.

This report summarizes findings related to these phenomena for FY16, in satisfaction of milestone M3FT-16IN030104053. It also reports continued kinetic measurements for the reactions of the dodecane radical cation with solvent extraction ligands.

CONTENTS

SUMMARY	Error! Bookmark not defined.
CONTENTS.....	Error! Bookmark not defined.
FIGURES.....	v
ACRONYMS.....	Error! Bookmark not defined.
1. INTRODUCTION.....	1
2. EXPERIMENTAL	3
2.1 Mass Spectrometric Investigation of Ligand•HNO ₃ Complexes	3
2.2 Radical Cation Kinetics	3
2.3 Acid Extraction by Ligands	3
2.4 Steady-state Irradiations	3
2.5 Quantum Chemistry Calculations	4
3. RESULTS AND DISCUSSION.....	4
3.1 Radical Cation Measurements.....	4
3.2 Acid Complex Formation	5
3.3 Aromatic DGAs.....	7
4. CONCLUSIONS AND FUTURE WORK.....	7
5. REFERENCES	8

FIGURES

Figure 1. Correlation of calculated ionization potential difference between TODGA and various diluents for the proton transfer reaction , and the measured rate constant for the diluent radical cation reaction.....4

Figure 2. Positive ESI MS for the aqueous phase of a CMPO/dodecane solution that has been contacted with HNO₃, showing *m/z* 900 (red arrow), corresponding to [(CMPO)₂(HNO₃)Na]⁺...6

ACRONYMS

CMPO	octylphenyl(<i>N,N</i> -diisobutyl)-carbamoylmethylphosphine oxide
DGA	diglycolamide
DHDECMP	dihexyl(<i>N,N</i> -diethyl)-carbamoyl methyl phosphonate
ESI-MS	ElectroSpray Ionization Mass Spectrometry
EU	European Union
HEH[EHP]	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
HPLC	High Performance Liquid Chromatography
LEAF	Laser Electron Accelerator Facility
MeTODGA	methyltetraoctyldiglycolamide
SACSESS	SAfety of ACTinide SEparationS Systems
TODGA	tetraoctyldiglycolamide

RADICAL CATIONS AND ACID PROTECTION DURING RADIOLYSIS

1. INTRODUCTION

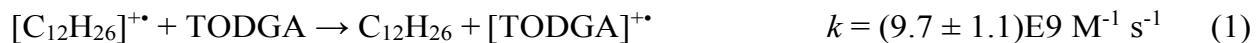
Ligand molecules for used nuclear fuel separation schemes are exposed to high radiation fields and high concentrations of acid. Thus, an understanding of the complex interactions between extraction ligands, diluent, and acid is critical to understanding the performance of a separation process. In general, acid and radiation are expected to degrade ligand molecules. However, steady state gamma-radiolysis experiments previously performed under this program showed that octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) was protected from radiolytic degradation in the presence of aqueous HNO₃. Measured $-G_{\text{CMPO}}$ decreased with increasing [HNO₃] in the aqueous phase, indicating that less CMPO molecules were destroyed as the concentration of HNO₃ increased. Neutral nitrate (from NaNO₃) did not provide this protection. This work also showed that at an aqueous phase [HNO₃] of 5 M, CMPO was practically stable in irradiated solution. [1] Table 1 shows $-G_{\text{CMPO}}$ for CMPO/dodecane samples irradiated in contact with a series of [HNO₃] and [NO₃⁻]. Although the diglycolamides are also amides with important structural similarities to CMPO, previous work here has also shown that they are not protected by HNO₃. [2,3,4]

Table 1. $-G_{\text{CMPO}}$ ($\mu\text{mol J}^{-1}$) for CMPO/dodecane samples irradiated over a series of [HNO₃] and [NO₃⁻]. HNO₃ data is from ref [1]. NO₃⁻ data are previously unpublished.

Concentration (M)	0.1	1.0	2.0	3.0	4.0	5.0
$-G_{\text{CMPO}}$ (HNO ₃)	0.18	-	0.11	0.07	0.05	0.01
$-G_{\text{CMPO}}$ (NO ₃ ⁻)	0.18	0.15	0.17	0.19	0.17	0.20

Another significant difference between CMPO and the DGAs is the disparate kinetics of radiolytic degradation. CMPO degrades with pseudo-zero-order kinetics, in linear fashion with absorbed dose, while the DGAs degrade in pseudo-first-order, exponential fashion. This suggests that the DGAs are degraded by reaction with some product of direct diluent radiolysis, while CMPO degradation is probably multi-step, with a slow step that is not dependent on the CMPO concentration.

Additional program work leading up to FY16 firmly established that the dodecane radical cation is produced in irradiated dodecane, and a method to measure the kinetics of its reactions was developed. [5, 6] With this method, it was shown that the dodecane radical cation undergoes reactions with both CMPO and TODGA with fast rate constants, shown assuming electron transfer, for TODGA in Eq. 1, and CMPO in Eq. 2:



If the resulting ligand radical cation then decays quickly to radiolysis products, [2] this would result in the measured pseudo-first-order kinetics observed for TODGA. Pre-equilibration of TODGA solutions with HNO₃ did not change the rate constant for this radical cation reaction, [6] implying no acid protection for TODGA, in agreement with steady state radiolysis findings. [2]

Since CMPO degradation is zero-order, either the CMPO radical cation is not actually produced as shown in Eq. 2, or its decay must be slow and rate limiting. An example of the first possibility is the hypothesis that a strong HNO₃ complex forms with CMPO to protect it from the electron transfer reaction. This would be consistent with the observed protection afforded by undissociated HNO₃, but not NO₃⁻ alone. If this complex reacts with the dodecane radical cation it could be decomposed to CMPO and a HNO₃ radical cation:



Thus, free CMPO would be regenerated by the dodecane radical cation reaction with the acid complex, both protecting CMPO from the degradation shown in Eq. 2, and potentially freeing its degradation from the pseudo-first-order kinetics suggested by Eq. 2. In this case some unidentified reaction would be responsible for the change in CMPO concentration with absorbed dose. Such an acid complex has been measured by mass spectrometry, and apparently it was strong enough that it did not decompose in the low acidity environment of an HPLC eluent. [7] However, pre-equilibration of CMPO solutions with HNO₃ did not change the rate of the radical cation reaction with CMPO (Eq. 2) [5], perhaps suggesting that the reaction rate with the CMPO•HNO₃ complex was equally fast.

A second hypothesis to explain zero-order kinetics for CMPO radiolytic degradation suggests that the aromatic ring stabilizes the CMPO radical cation produced in Eq. 2, and thus its decay is slow compared to the initial electron transfer reaction. This would then free the CMPO degradation rate from the initial CMPO concentration, resulting in the observed pseudo-zero-order kinetics. However, this proposed mechanism does not explain the acid protection of CMPO.

Based on this background, work in FY16 concentrated on attempts to characterize possible acid complexes of CMPO. Attempts to repeat the mass spectrometric verification of the CMPO•HNO₃ complex were made. Measurements of the back extraction of acidity from acid-loaded CMPO and TODGA solutions were also made. The rate constants for additional radical cation reactions were measured, as was steady state radiolysis experiments for aromatic DGA derivatives. The separate investigations into the kinetics of dodecane radical cation reactions and the nature of nitric acid radio-protection of CMPO have now converged into a single project since the two phenomena may be related. Many of the experiments reported here were made in collaboration with partners

at Forschungszentrum Jülich, Germany, as part of the DOE collaboration with the EU SACSESS program.

2. EXPERIMENTAL

2.1 Mass Spectrometric Investigation of Ligand•HNO₃ Complexes

A Bruker (Billerica, MA, USA) microTOFQ-II electrospray ionization quadrupole time-of-flight mass spectrometer was utilized in the ESI direct infusion mode. Samples were analyzed in the positive mode, with the capillary operated at a relative potential of 4.0kV. Other parameters were temperature 220°C; nebulizer gas and dry gas were both N₂; nebulizer pressure: 0.4 bar, dry gas flow: 4L/min; ESI flow rate: 3 μL/min. CMPO, and its analog dihexyl(*N,N*-diethyl)-carbamoyl methyl phosphonate (DHDECMP) were contacted with HNO₃ solutions, and the aqueous phases were analyzed. In addition to these acid-contacted solutions, water contacted solutions, and uncontacted solutions were also analyzed for comparison.

2.2 Radical Cation Kinetics

Picosecond electron pulse radiolysis/transient absorption experiments were performed at the Brookhaven LEAF facility. Samples of ligand in organic diluent were irradiated in 1.00 cm Suprasil semi-micro cuvettes. Methylene chloride was added as a scavenger to eliminate interference from solvated electron reactions. Time-resolved kinetics were obtained using an FND-100 silicon diode detector, digitized using a LeCroy WaveRunner 640Zi oscilloscope (8 bit, 4 GHz), providing 1-2 ns time resolution. Acid contacted measurements were performed on organic solutions after equal volumes of diluent/0.10-0.50 M CH₂Cl₂/ligand and acidic water were hand-shaken vigorously for 5 min followed by gravity phase separation for 10–20 min.

2.3 Acid Extraction by Ligands

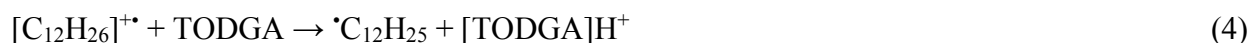
Dodecane solutions of 0.05 M CMPO or TODGA were contacted with (1.089 ± 0.001) M HNO₃ for 30 min, following which the post contact organic and aqueous phases were titrated with potassium hydrogen phthalate. The acid loaded organic phases were then stripped with two, 5 min water contacts, and the strip solution was also titrated.

2.4 Steady-state Irradiations

Irradiations were performed using a Nordion Gammacell 220, at a dose rate of 3.8 kGy h⁻¹. This dose rate was initially measured using standard Fricke procedures, and then subsequently corrected for ⁶⁰Co decay. The sample chamber temperature was approximately 30 °C. Samples of aromatic DGAs were irradiated across a series of absorbed doses, either as the 0.05 M DGA/dodecane phase only, or in contact with 0.01 M HNO₃, or 3 M HNO₃.

2.5 Quantum Chemistry Calculations

Electronic structure calculations using Gaussian 09 were performed by the Brookhaven collaborator to help elucidate the mechanism of the radical cation reaction with ligands. Molecular geometries and energies were determined with the B3LYP functional and 6-31g(d) basis set, using the Polarized Continuum Model for the solvent. Geometries were tested with frequency calculations to ensure that they had no negative frequencies, thus representing stable configurations at energy minima. From these the energies of electron transfer (TODGA oxidation, eq. 1) but also proton transfer (eq. 4) were determined:



3. RESULTS AND DISCUSSION

3.1 Radical Cation Measurements

In an attempt to better understand the reactions of the solvent radical cation, the kinetics of its reaction with TODGA were measured for a series of solvents over a range of calculated ionization potentials. These included 2,2',4,6,6'-pentamethylheptane (a branched dodecane), 1-dodecene, and cyclohexane, for comparison to the those measured for *n*-dodecane previously. It was postulated that the greater the difference between the ionization potentials of the diluent and the TODGA, the faster would be the electron transfer or proton transfer rate constant. According to calculations, both processes were energetically favorable. However, the correlation for electron transfer was weak ($r^2 = 0.57$). A better correlation ($r^2 = 0.997$) was found if the ionization potential for the proton transfer reaction was considered, for the saturated alkanes only. The 1-dodecene does not fit the curve, as shown in Fig. 1, implying additional mechanistic considerations for unsaturated radical cations.

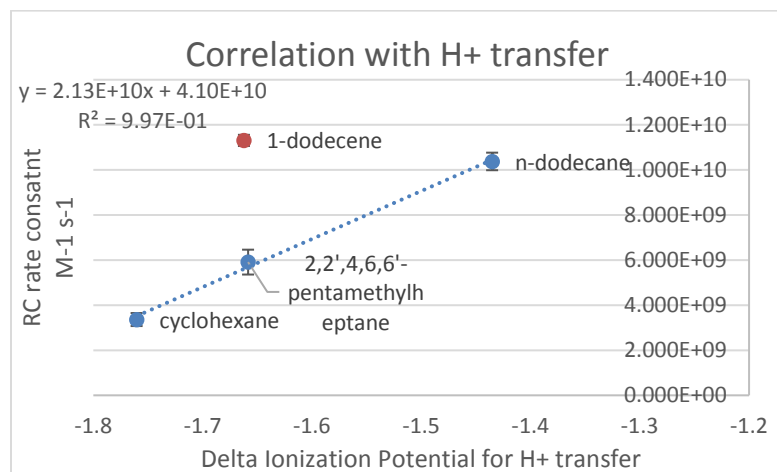


Figure 1. Correlation of calculated ionization potential difference between TODGA and various diluents for the proton transfer reaction, and the measured rate constant for the diluent radical cation reaction.

Radical cation kinetic measurements were also performed for octanol and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) in dodecane and these data are currently being analyzed.

3.2 Acid Complex Formation

Solutions of 0.05 M CMPO or 0.05 M TODGA were loaded by contacting them with 1 M HNO₃, and then titrated to measure the amount of acid that was extracted. These results are shown in Table 2. Volumes were kept consistent (2 mL always) so that the reported concentrations correspond to equivalents of acid present.

Table 2. Acid titration data (M) for acid loaded 0.05 M CMPO and TODGA solutions, and aqueous strips of the loaded organic solutions. All results are for triplicate titrations. The initial aqueous acid concentration was (1.089 ± 0.001) M.

	CMPO	TODGA
Post-contact aqueous [HNO ₃]	1.068 ± 0.000	1.083 ± 0.006
Post-contact organic [HNO ₃]	0.030 ± 0.001	0.008 ± 0.000
Change in aqueous [HNO ₃]	0.021	0.006
Strip of loaded organic [HNO ₃]	0.029 ± 0.000	0.007 ± 0.000

It can be seen that CMPO is indeed more basic than TODGA, extracting approximately three times as much acid. It was hypothesized that water stripping of loaded CMPO would not recover all the extracted acid due to formation of the postulated strong acid complex. A persistent complex was reported in ref [7], which remained intact in an HPLC eluent composed of 60 % phosphate buffer at pH 2.6/ 40 % 2-propanol containing 3.6 % octanol. Here; however, it can be seen that pure water quantitatively stripped the acid from both loaded ligands. While this result does not support the existence of the strong complex postulated in Eq. 3, it also does not eliminate that possibility. Such a complex may persist in more acidic solutions than neutral water.

In previous work, a nitric acid complex of CMPO was identified by mass spectrometry. [7] This species with *m/z* 900 was identified as an abundant ion in both phases of CMPO solutions when contacted with aqueous nitric acid, by direct infusion ESI-MS. This corresponds to a complex of the stoichiometry [(CMPO)₂(HNO₃)Na]⁺. This assignment was confirmed by collision induced dissociation, to produce an ion of *m/z* 837 which corresponds to loss of HNO₃.

This work was repeated in FY16 using electrospray ionization quadrupole time-of-flight mass spectrometry in the ESI direct infusion mode. A 1 mM CMPO/dodecane solution was contacted with the same volume of 15 mM HNO₃ for 90 seconds. The post-contact aqueous HNO₃ contained a significant ion at *m/z* 900. The ion at *m/z* = 900, is the [(CMPO)₂(HNO₃)Na]⁺ species that was previously seen. In addition, the [(CMPO)₂H]⁺ complex cation at *m/z* 815, the [(CMPO)₂Na]⁺ complex cation at *m/z* 837 and the [CMPO+H]⁺ ion at *m/z* 408 were detected.

The mass spectrum can be seen in Fig. 2. The presence of the m/z 900 ion suggests that CMPO can form stable complexes with oxoacids. This is consistent with the observation of significant acid in the organic phases of CMPO-dodecane / HNO_3 contacted experiments. A MS^2 spectrum of the $[(\text{CMPO})_2(\text{HNO}_3)\text{Na}]^+$ complex cation at m/z 900 generated the $[(\text{CMPO})_2\text{Na}]^+$ ion at m/z 837 by loss of 63 u ($-\text{HNO}_3$), and the $[\text{CMPO}(\text{HNO}_3)+\text{Na}]^+$ ion at m/z 493 by loss of 407 u ($-\text{CMPO}$); The latter ion evidently hydrates to the $[\text{CMPO}(\text{HNO}_3)(\text{H}_2\text{O})+\text{Na}]^+$ ion at m/z 511.

A similar analysis was performed for the non-aromatic dihexyl,*N,N*-diethyl)-carbamoyl methyl phosphonate (DHDECMP). In this work, the $(\text{DHDECMP})_2+\text{Na}]^+$ complex cation at m/z 749, the $[\text{DHDECMP}+\text{Na}]^+$ complex cation at m/z 386 and the $[\text{DHDECMP}+\text{H}]^+$ ion at m/z 364 were detected. In analogy with CMPO, an ion at m/z 812 for the $[(\text{DHDECMP})_2(\text{HNO}_3)+\text{Na}]^+$ ion was expected. Although this was present at very low intensity, the MS^2 results did not show a fragment ion that can be related back to the DHDECMP. If this acid complex also forms for DHDECMP, it is only at low yields. This supports the hypothesis that the aromatic ring on the CMPO molecule is involved in acid complexation.

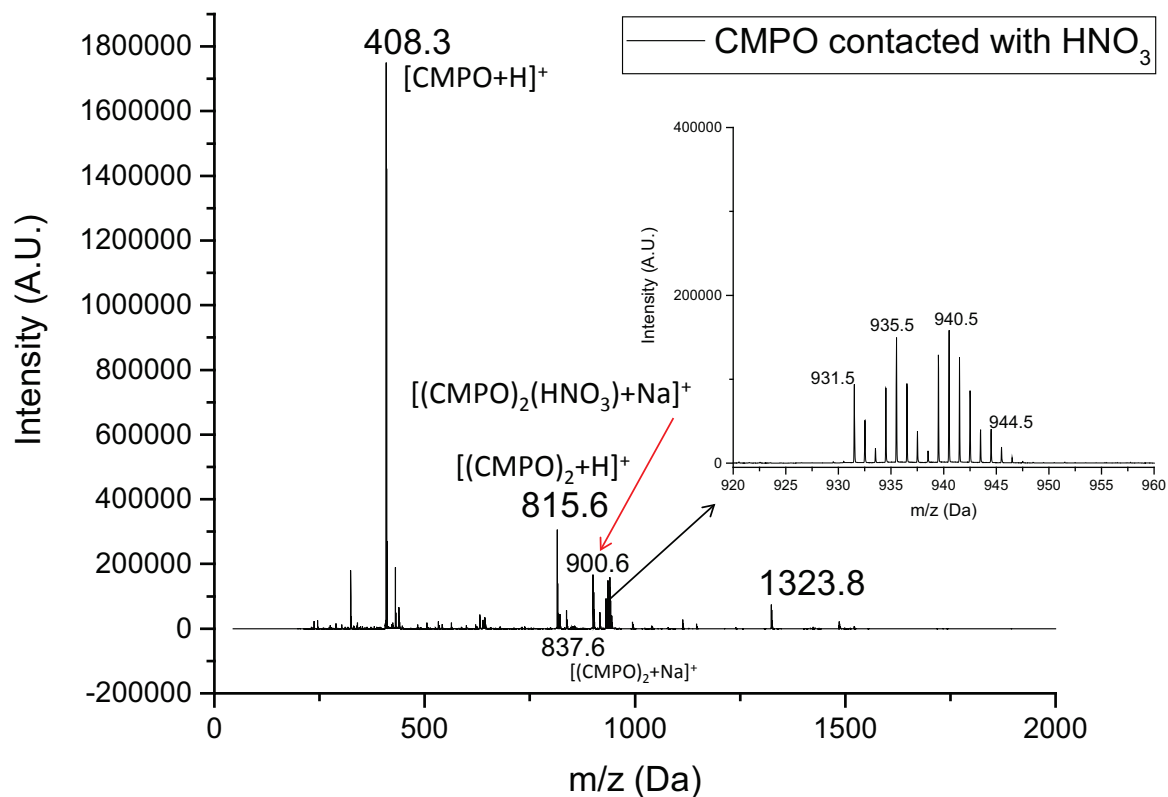


Figure 2. Positive ESI MS for the aqueous phase of a CMPO/dodecane solution that has been contacted with HNO_3 , showing m/z 900 (red arrow), corresponding to $[(\text{CMPO})_2(\text{HNO}_3)\text{Na}]^+$.

3.3 Aromatic DGAs

To investigate the postulated role of the phenyl ring in causing CMPO radiolysis to observe zero-order kinetics and/or nitric acid radio-protection, two aromatic DGAs were supplied by collaborators at Forschungszentrum Jülich. They are TODGA and MeTODGA derivatives that contain a phenyl ring on one methylene carbon (designated TWE-22 and TWE-15, respectively). These compounds were irradiated to a series of absorbed doses with 500 kGy maximum, as 0.05 M solutions in dodecane, 0.05 M in dodecane in contact with 0.1 M HNO₃, and 0.05 M in dodecane in contact with 3 M HNO₃. The irradiation campaign has been completed as of this writing, and the samples are currently being analyzed by mass spectrometry to determine $-G_{TWE}$ rates, and to obtain the reaction order of the degradation kinetics.

4. CONCLUSIONS AND FUTURE WORK

Although significant progress has been made in understanding the nature of nitric acid radio-protection of CMPO, the mechanism has not yet been fully elucidated. It is believed that radio-protection and the zero-order radiolytic degradation kinetics are related, and that these phenomena are a function of either the formation of strong acid complexes with CMPO and/or to the presence of the CMPO phenyl ring. Experiments to test both these hypotheses have been designed and partially conducted. Through titration of acid contacted organic solutions it was shown that CMPO extracts about 3 times as much acid as does TODGA, and that the complex $[CMPO(HNO_3)(H_2O)+Na]^+$ is detectable by mass spectrometry, while the non-aromatic (but also less basic) phosphonate DHDECMP does not form significant amounts of $[(DHDECMP)_2(HNO_3)+Na]^+$. An additional experiment investigating the radiolysis kinetics and radio-protection of DHDECMP is warranted. Aromatic DGAs have been irradiated in an alternate attempt to address the same question, and these samples are currently being analyzed.

Additional radical cation kinetics investigations have been conducted by pulse radiolysis, including the use of diluents in addition to dodecane. In preliminary work, a correlation was observed between the calculated ionization potentials for the proton transfer reactions to TODGA for these diluent radical cations and their rate constant for reaction with TODGA, perhaps suggesting that proton transfer, rather than electron transfer, is the mechanism by which ligand degradation is initiated.

5. REFERENCES

- 1 Mincher BJ, Mezyk SP, Elias G, Groenewold GS, Riddle CL, Olson LG. The radiation chemistry of CMPO: Part 1. Gamma radiolysis. *Solvent Extr Ion Exch* 2013; 31, 715-730.
- 2 Zarzana CA, Groenewold GS, Mincher BJ, Mezyk SP, Wilden A, Schmidt H, Modolo G, Wishart JF, Cook AR. A comparison of the γ -radiolysis of TODGA and T(EH)DGA using UHPLC-MS analysis. *Solvent Extr Ion Exch* 2015; 33, 431-447.
- 3 Galán H, Zarzana CA, Wilden A, Nuñez A, Schmidt H, Egberink RJM, Leoncini A, Cobos J, Verboom W, Modolo G, Groenewold G, Mincher BJ. Gamma-radiolytic stability of new methylated TODGA derivatives for minor actinide recycling. *Dalton Trans* 2015; 44, 18049-18056.
- 4 Roscioli-Johnson KM, Zarzana CA, Groenewold GS, Mincher BJ, Wilden A, Schmidt H, Modolo G. A study of the γ -radiolysis of di-dodecyl di-octyl diglycolamide using UHPLC-ESI-MS analysis. *Solvent Extr Ion Exch*, DOI 10.1080/07366299.2016.1212540
- 5 Mezyk SP, Horne GP, Mincher BJ, Zalupski PR, Cook AR, Wishart JF. The chemistry of separations ligand degradation by organic radical cations. *Procedia Chem*, accepted for publication.
- 6 Mezyk SP, Mincher BJ, Dhiman SB, Layne B, Wishart JF. The role of organic solvent radical cations in separations ligand degradation. *J Radioanal Nucl Chem* 2016; 307, 2445-2449.
- 7 Elias G, Groenewold GS, Mincher BJ, Mezyk SP. Determination of CMPO and identification of some radiolysis products using HPLC-UV and mass spectrometry. *J Chromatog A* 2012; 1243, 47-52.