INL/EXT-16-38045

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Introduction

The extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) is a component used in both the Advanced TALSPEAK and ALSEP solvent extraction processes. The most likely compound formed via hydrolytic or radiolytic degradation of HEH[EHP] would be the phosphonic acid 2-ethylhexylphosphonic acid (H_2EHP) that is formed by cleavage of the P-O-R bond. Thus far, attempts to detect H_2EHP by gas chromatography or mass spectrometry have not been successful. The inability to detect this proposed degradation product in analytical samples is likely due to inadequate analysis techniques, lack of H_2EHP production, further decomposition of H_2EHP forming products not detectable by the employed analytical techniques, or a combination of all of the above scenarios.

In order to address this problem, commercially available alkylphosphonic acids were acquired and used as surrogates for H_2EHP in the gas chromatography and mass spectrometry analysis of samples. Once the ability to detect alkylphosphonic acid compounds was confirmed, these analytical techniques were used to confirm the production of H_2EHP in samples of HEH[EHP] exposed to nitric acid and nitric acid plus gamma radiation. This report provides a brief summary of results and serves as documentation of the completion the level four milestone M4FT-16IN030102025 “Investigate the hydrolytic and radiolytic degradation of HEH[EHP]”.

Experimental

All chemicals were reagent grade or higher (Sigma Aldrich) and used without further purification. Hexyl- and octyl-phosphonic acids were purchased (Strem) and used with further purification. Aqueous solutions were prepared using de-ionized water (MilliQ, 18 MΩ). All analyses are performed in triplicate unless otherwise noted.

The liquid cation exchanging extractant 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) was obtained from a commercial source (Yick-Vic Chemicals, China) and purified by a literature procedure. The final purity of the HEH[EHP] was greater than 98 % based on ^{31}P NMR analysis. NMR analyses utilized an Anasazi FT-90 MHz NMR spectrometer.

Due to the acidic functional group of the HEH[EHP] and the possibility of the generation of acidic degradation products, an aliquot of each solvent sample was diluted 100 fold with hexane and derivatized with 300 μL of an ~0.3 mol/L solution of diazomethane in hexane prior to analysis. This produced the methyl ester of the phosphoric or phosphonic acid functional groups in the target compounds. The samples were analyzed along with appropriate calibration and quality assurance samples for HEH[EHP] and degradation products.

For radiolysis experiments, samples (aqueous and organic) were held in septa-sealed scintillation vials and exposed to gamma irradiation using the GammaCell 220E irradiator which is equipped with a jig to hold the vials in fixed positions. The samples were sparged with air at a flow rate of 1 sccm using mass flow controllers (Sierra Instruments). The gamma dose rate delivered to each position on the irradiation jig was determined by standard Fricke dosimetry. The center-line gamma dose rate in the sample chamber is ~5.0 kGy/hr.

The gas chromatography analyses were performed on a Thermo Scientific Trace ULTRA gas chromatograph. The chromatograms were processed using Thermo Scientific Xcalibur software. The chromatographic separations were carried out utilizing a Thermo Scientific TG-35MS capillary column (30m x 0.32mm ID x 0.5µm film). Analytical conditions were set at 2.0 mL/min constant flow with helium as the carrier gas and an 80 mL/min split flow. Oven operating conditions started with a 2 min hold at 70°C, followed by a ramp at 20°C/min to 240°C then 40°C/min to 280°C, finished with an 8.25 min hold at 280°C. A Thermo AS3000 auto sampler was used for all injections, employing a 1 µL hot injection with the inlet set at 250 °C and 5 second pre-injection dwell time. The FID was held constant at 250°C. The fuel gas for the FID is a mixture of 350 mL/min air and 35 mL/min hydrogen with 30 mL/min nitrogen as a makeup gas.

Electrospray mass spectrometry analyses were performed using a Dionex (Sunnyvale, CA, USA) ultra-high performance liquid chromatograph (UHPLC) with an Ultimate 3000 RS pump, 3000 RS autosampler, 3000 RS column compartment, and a 3000 RS diode-array detector. Chromatographic separation was achieved using 1 µl injections on a Phenomenex (Torrance, CA, USA) Kinetex 1.7 µm EVO C18 50mm ×2.1 mm column maintained at 50 °C. The mobile phase was an isocratic mix of 50% Optima LC-MS water with 0.1% formic acid (Fisher) and 50% Optima LC-MS isopropyl alcohol (Fisher) with 3% 1-octanol (Signa-Aldrich) with a flow rate of 200 µL/min. The analytes were detected using a Bruker (Billerica, MS, USA) micrOTOFQ-II electrospray ionization quadrupole time-of-flight mass spectrometer, operating in negative ionization mode.

Results and Discussion

A nominally 1 M HEH[EHP] in dodecane solution was prepared for these experiments. One volume of this solution was contacted with 4 M HNO_3 for 30 days (HEH[EHP] Hydrolysis, Table 1). Another volume was irradiated in contact with 4 M HNO_3 to an absorbed dose of 890 kGy (HEH[EHP] Radiolysis, Table 1) using a GammaCell 200E ^{60}Co irradiator located at the Idaho National Laboratory (INL). A third volume (HEH[EHP] Neat, Table 1) was used as a control.

Table 1: HEH[EHP] sample descriptions

Sample	Description
HEH[EHP] Neat	1 M HEH[EHP] in dodecane
HEH[EHP] Hydrolysis	HEHEHP Neat sample contacted with 4M HNO_3 for 30 days.
HEH[EHP] Radiolysis	HEHEHP Neat sample contacted with 4M HNO_3 and irradiated to 890 kGy.

^{31}P NMR Spectroscopy Analysis. The production of H_2EHP via hydrolytic or radiolytic degradation of HEH[EHP] was initially monitored using ^{31}P NMR spectroscopy. Figure 1 shows the ^{31}P NMR spectrum of a 1 M HEH[EHP] solution (HEH[EHP] Neat) dissolved in n-dodecane. The peak at 32.3 ppm corresponds to HEH[EHP]. The peak at δ = 141 ppm corresponds to trimethylphosphite ($P(OCH_3)_3$) dissolved in deuterated chloroform. The $P(OCH_3)_3$ solution is held in a co-axial NMR tube insert and serves as a peak shift standard for all experiments. In addition to HEH[EHP], Figure 1 also shows a very minor resonance at approximately δ = -0.3 ppm that is attributed to bis-(2-ethylhexyl)phosphoric acid (HDEHP). The HDEHP is an impurity that is not entirely removed during the purification of the "as-received" HEH[EHP].

Figure 2 shows the ^{31}P NMR spectrum of a sample of H_2EHP dissolved in n-dodecane, with the phosphorous resonance of H_2EHP at δ = 37.3 ppm. The ^{31}P NMR spectra of HEH[EHP] (δ = 32.3 ppm) and H_2EHP (δ = 37.3 ppm) are easily resolved. However, based upon the sensitivity of the NMR technique, the detection of trace amounts of hydrolytic or radiolytic degradation products of HEH[EHP] is expected to be challenging. The ^{31}P NMR spectrum of the HEH[EHP] Hydrolysis sample is presented

in Figure 3. No peaks corresponding to H_2EHP are noted, which indicates that no significant hydrolytic degradation of HEH[EHP] has occurred.

The ^{31}P NMR spectrum of the irradiated HEH[EHP] sample (HEH[EHP] Radiolysis) is presented in Figure 4. This NMR spectrum indicates that significant radiolytic degradation (~10-15% based upon peak integration) of the HEH[EHP] in solution has occurred. However, no peak corresponding to the production of H_2EHP was detected. It should be noted that the broadening of the HEH[EHP] phosphorous resonance observed in the irradiated solution makes the detection of a low concentrations of H_2EHP difficult.

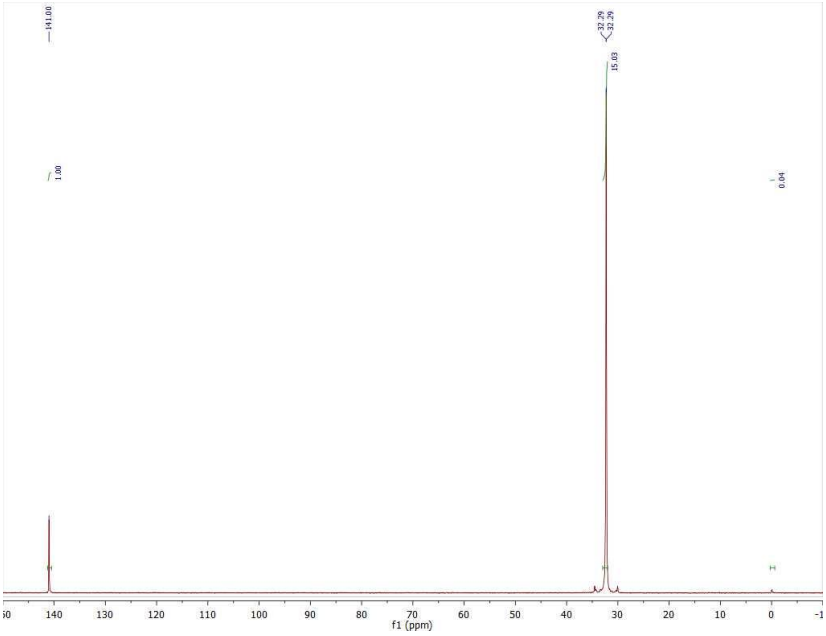

Figure 1. ^{31}P NMR spectrum of a 1 M HEH[EHP] solution in n-dodecane. The phosphorous resonance of HEH[EHP] occurs at 32.3 ppm. The resonance at 141 ppm is due to the trimethylphosphite internal peak shift standard which is held in a co-axial insert.

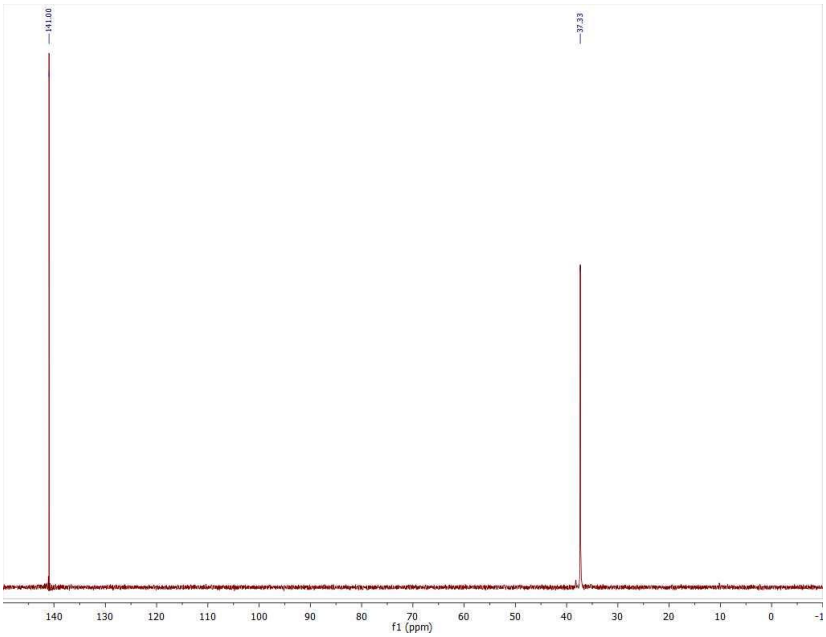

Figure 2. ^{31}P NMR spectrum of a ~1 M H_2EHP solution in n-dodecane. The phosphorous resonance of H_2EHP] occurs at 37.3 ppm. The resonance at 141 ppm is due to the trimethylphosphite internal peak shift standard which is held in a co-axial insert.

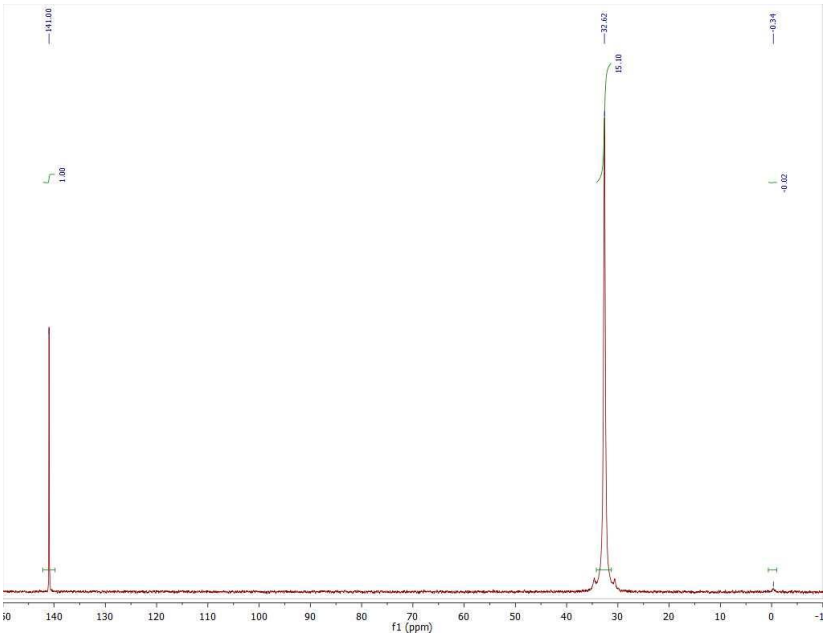

Figure 3. ^{31}P NMR spectrum of a hydrolyzed 1 M HEH[EHP] solution in n-dodecane following approximately thirty days contact with 4 M HNO_3. The phosphorous resonance of HEH[EHP] occurs at 32.3 ppm. The resonance at 141 ppm is due to the trimethylphosphite internal peak shift standard which is held in a co-axial insert.

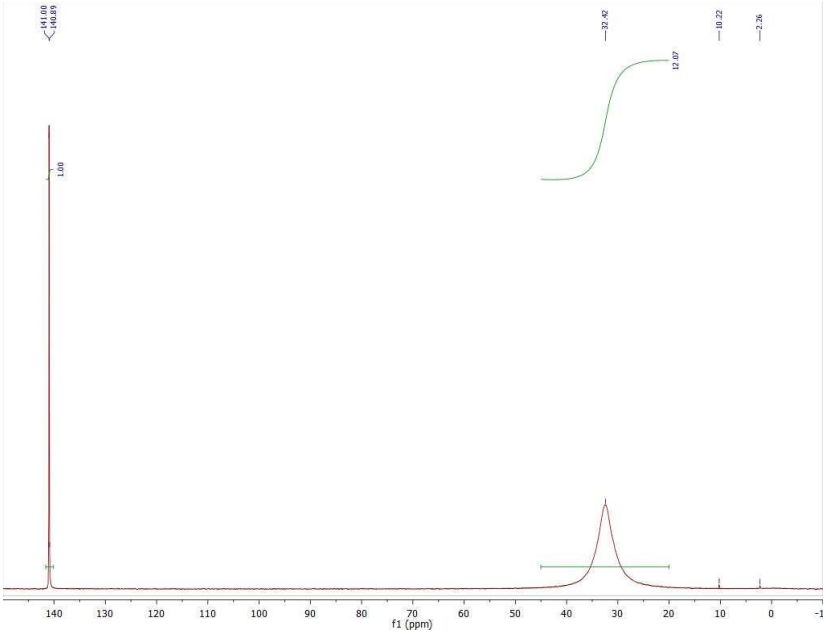

Figure 4. ^{31}P NMR spectrum of a 1 M HEH[EHP] solution n-dodecane following exposure 890 kGy absorbed gamma dose. The phosphorous resonance of HEH[EHP] occurs at 32.3 ppm. The resonance at 141 ppm is due to the trimethylphosphite internal peak shift standard which is held in a co-axial insert.

Gas Chromatography Analysis. Samples of neat, hydrolyzed, and irradiated samples of 1 M HEH[EHP] in dodecane were derivatized using diazomethane for gas chromatography analysis. Commercially available alklyphosphonic acids were also derivatized. A calibration curve generated for the gas chromatography-flame ionization detection (GC-FID) analysis of the dimethyl ester of octyl-phosphonic acid (chosen as a surrogate for H_2EHP) is shown in Figure 5. This calibration curve suggests that detection of H_2EHP is possible by gas chromatography. Based on the proposed degradation species being a branched ethylhexyl phosphonic acid as opposed to the straight chain octyl or hexyl phosphonic acids in this study, it is likely that the retention time on the degradation species would be slightly different from the straight chain analogs. With this in mind, the hydrolyzed and radiolyzed spectral data have been searched for eluted peaks exhibiting a similar fragmentation pattern.

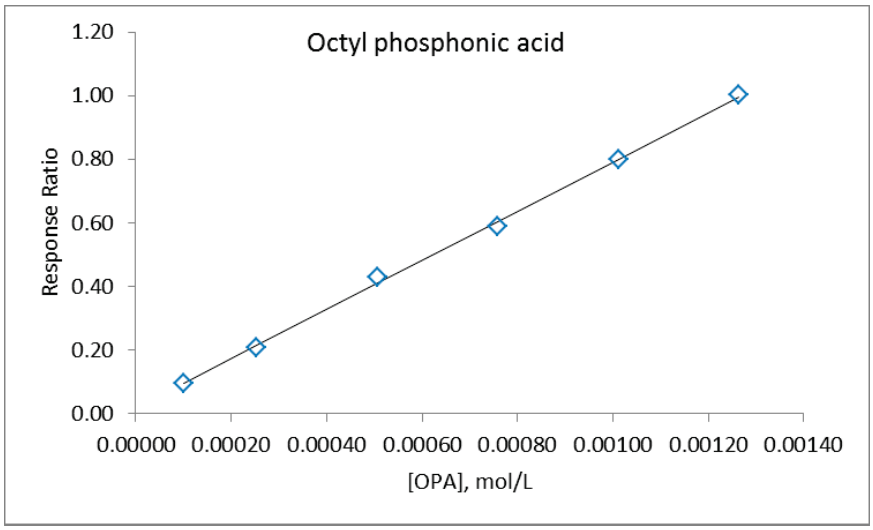

Figure 5. Calibration curve for the GC-FID detection of the dimethyl ester of octyl-phosphonic acid.

In the current study, the octyl-phosphonic acid dimethyl ester has retention times of GC-FID: 9.81 min and GC-MS: 8.92 min. In the hydrolysis sample there is a peak at GC-FID: 9.06 min and GC-MS: 8.23 min. The mass spectral data exhibits a similar fragmentation pattern between each of these peaks with a 124 m/z base peak, and share (with some abundance shifts) 79 m/z, 94 m/z, 110 m/z, 165 m/z, plus others. These facts together offer reasonable data to support that this is likely the proposed degradation product of 2-ethylhexyl phosphonic acid.

There is a corresponding peak in the irradiated sample as well; unfortunately it appears as a shoulder to another peak in the mass spectral data, and as a single peak in the FID chromatography. The mass spectrum does exhibit the same characteristics as found in the hydrolyzed samples. The concentration of HEH[EHP] and H_2EHP determined in the analyzed samples are shown in Figures 6 and 7, respectively. The dimethyl ester of H_2EHP was quantitated using the calibration curve generated using the octyl-phosphonic acid dimethyl ester (see Figure 5).

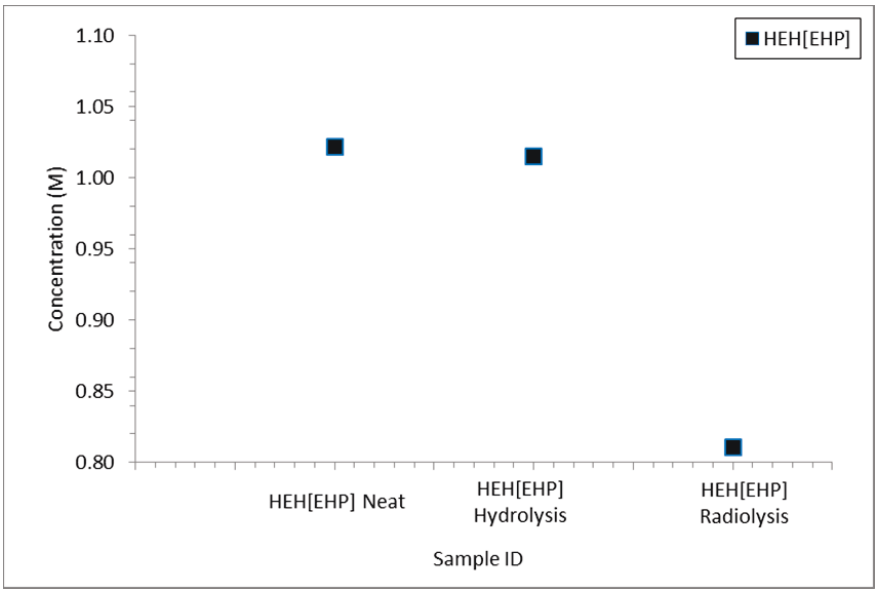

Figure 6. Concentration of the dimethyl ester of HEH[EHP] in neat, hydrolyzed, and irradiated samples of HEH[EHP] determined by GC-FID.

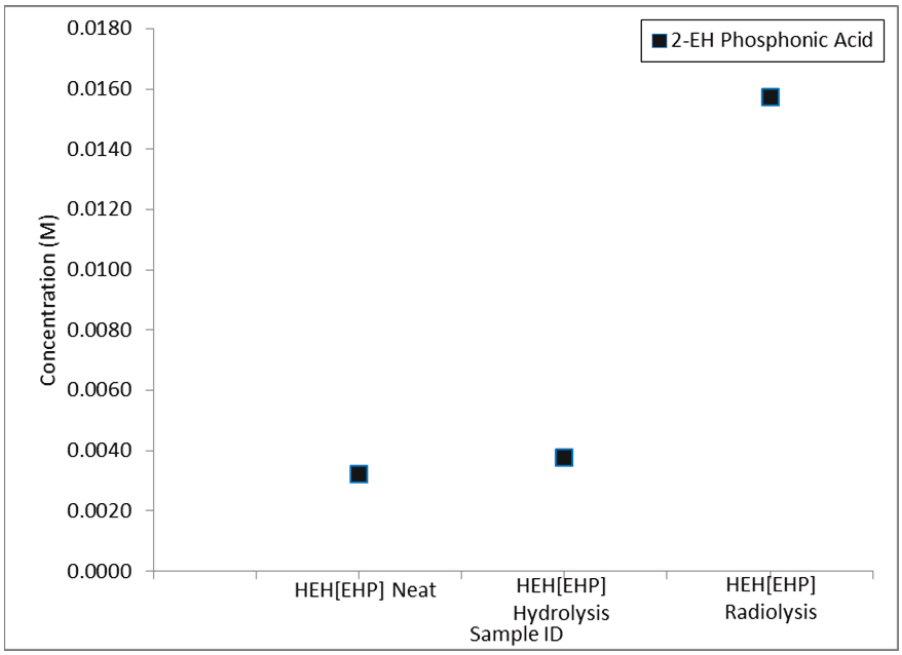

Figure 7. Concentration of the dimethyl ester of H_2EHP in neat, hydrolyzed, and irradiated samples of HEH[EHP] determined by GC-FID.

Electrospray mass spectrometry analysis. HEH[EHP] concentration was measured in all three samples (Figure), and showed a decrease in the samples from the HEH[EHP] Hydrolysis and HEH[EHP] Radiolysis experiments, compared to the HEH[EHP] Neat sample, similar to what was observed in the GC-FID analysis. This result indicates that, as expected, HEH[EHP] is degraded by both hydrolysis and radiolysis. The extent of degradation is higher in the HEH[EHP] Radiolysis sample than in the HEH[EHP] Hydrolysis sample, but we do not have measured rates of hydrolysis, so we cannot directly compare the influence of hydrolysis and radiolysis on the degradation of HEH[EHP].

H_2EHP was detected using UHPLC-ESI-MS (ion $m/z = 193.3$) in all three samples. More H_2EHP was detected in the HEH[EHP] Hydrolysis and HEH[EHP] Radiolysis samples than in the HEH[EHP] Neat sample. Significantly, there was more H_2EHP detected in the radiolyzed sample than in the hydrolyzed sample, mirroring the trend in HEH[EHP] degradation, indicating that although H_2EHP is present as a contaminant in HEH[EHP] it is also formed by hydrolysis and radiolysis of HEH[EHP] (Figure).

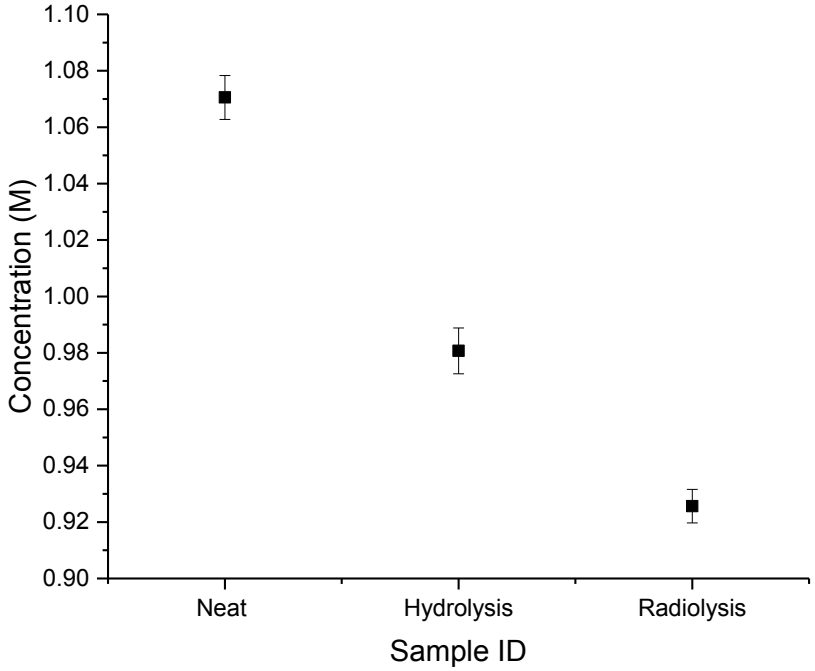

Figure 8. Measured concentration of HEH[EHP]. HEH[EHP] Neat corresponded to a nominal concentration of 1 M HEH[EHP] in dodecane, which was actually 1.07 M when measured using the UHPLC/ESI-MS. HEH[EHP] Hydrolysis is the HEH[EHP] Neat sample exposed to nitric acid, and HEH[EHP] Radiolysis is the HEH[EHP] Neat sample exposed to a γ radiation field. HEH[EHP] is degraded by acid contact and radiation exposure.

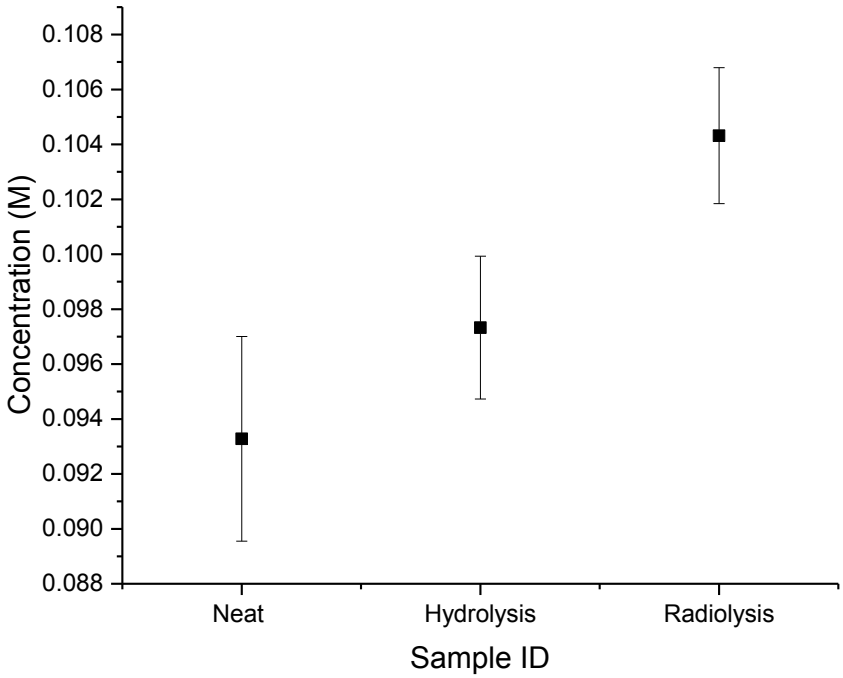

Figure 9. Measured concentration of 2-ethylhexyl phosphonic acid (H_2EHP) in the three samples. H_2EHP is present in the HEH[EHP] sample, and increases due to hydrolysis and radiolysis. H_2EHP was quantified using a calibration generated with octyl-phosphonic acid (H_2OP), which functioned as a surrogate for H_2EHP.

Octyl-phosphonic acid (H_2OP) was selected as a surrogate for (H_2EHP), since H_2OP is available commercially, and there should be very little difference in ionization efficiency and degradation chemistry from substituting an octyl group for the ethyl-hexyl. A set of calibration curves (Figure 10) were constructed for HEH[EHP] and H_2OP to evaluate the sensitivity of the UHPLC-ESI-MS analytical method towards H_2EHP. These measurements show that the method is approximately 2.3 times more sensitive to HEH[EHP] as it is to H_2OP, and thus H_2EHP.

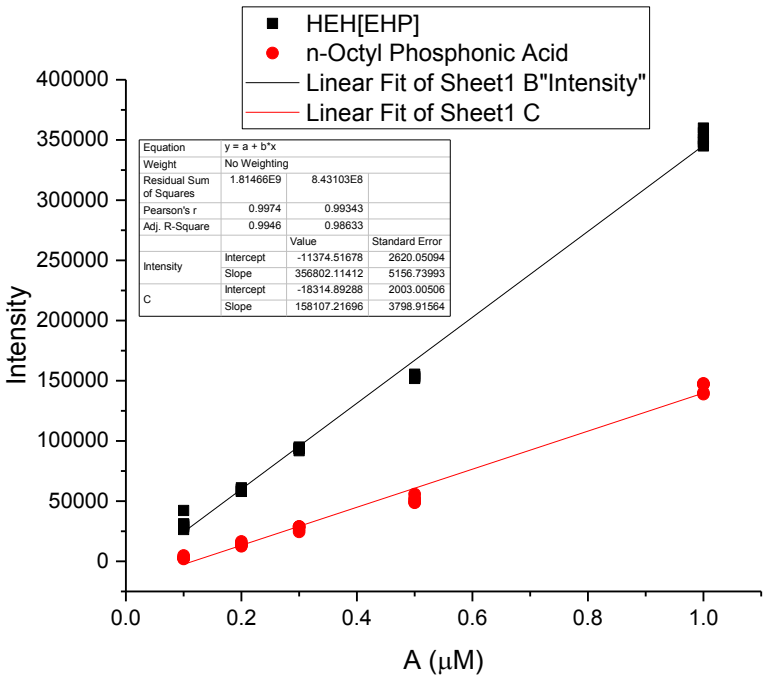

Figure 10. Calibration curves for HEH[EHP] and H_2OP. The instrument sensitivity to HEH[EHP] is 2.3 times that of H_2OP. It is expected that H_2EHP and H_2OP respond about the same.

Conclusions

H_2EHP is formed from the hydrolysis and radiolysis of HEH[EHP]. However, detection of H_2EHP in degraded HEH[EHP] samples is challenging due to three factors. Under the conditions used, which are similar to previous experiments, there is very little degradation of HEH[EHP] which results in the limited production of the H_2EHP degradation compound. Additionally, the amount of H_2EHP detected is significantly less than the amount of HEH[EHP] lost; coupled with the already low amount of HEH[EHP] lost, this means there is very little H_2EHP present in the samples. Finally, the analytical methods employed are more sensitive to HEH[EHP] relative to H_2EHP. Samples must be diluted to prevent saturation of the instrumentation, but because there is substantially more HEH[EHP] than H_2EHP in the samples and the method is more sensitive to HEH[EHP] than H_2EHP, the level of sample dilution required to measure HEH[EHP] can reduce the amount of H_2EHP to below the method detection limit. Therefore, an additional method should be developed to measure H_2EHP in the presence of large amounts of HEH[EHP].