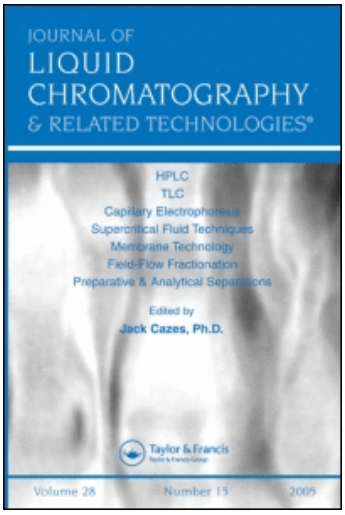

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Determination of Radiolysis Products in Zirconium Salt of Di-(2-Ethylhexyl) Phosphoric Acid by High Performance Liquid Chromatography/Mass Spectrometry

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ABSTRACT

A liquid chromatography with an electrospray ionization-mass spectrometry (LC-ESI-MS) method is described for the quantitative measurement of di-(2-ethylhexyl) phosphoric acid (D2EHPA), mono-(2-ethylhexyl) phosphoric acid (M2EHPA) in zirconium salt of di-(2-ethylhexyl) phosphoric acid (Zr-D2EHPA). During the solvent extraction process of radioactive waste, the Zr-D2EHPA extractant may be degraded to D2EHPA, M2EHPA, and PO_4^{-3} etc. Amounts of D2EHPA and M2EHPA in Zr-D2EHPA must be monitored because the production of

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these compounds means degradation, which leads to a decrease in the extraction yield. Retention behavior for D2EHPA and M2EHPA is studied with a Phenomenex LUNA-C_{18} (4.6 mm × 25 cm) analytical column and methanol/H_2O (50 mmol CH_3COONH_4) by LC. Optimum conditions of eluent for the determination of D2EHPA and M2EHPA irradiated with ^{60}Co γ-rays of Zr-D2EHPA are methanol : H_2O (50 mmol CH_3COONH_4) = 80 : 20 ratio in the SCAN mode of the MS for D2EHPA and Methanol : H_2O (50 mmol CH_3COONH_4) = 75 : 25 ratio in the SIM mode of the MS for M2EHPA. Di-(2-ethylhexyl) phosphoric acid and M2EHPA compounds are well separated within 10 min. Dynamic ranges are 10–100 $\mu g\,mL^{-1}$ for D2EHPA and 10–200 $\mu g\,mL^{-1}$ for M2EHPA, respectively. The detection limits are 1 $\mu g\,mL^{-1}$ in the SCAN mode of the MS for D2EHPA and 1 $\mu g\,mL^{-1}$ in the SIM mode of the MS for M2EHPA in this system with a 20 μL sample loop.

Key Words: Radiolysis products; γ-Irradiation; Zirconium salt; HPLC/MS.

INTRODUCTION

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is a useful extractant for the treatment of high-level liquid waste. The improvement of the extraction of some metals by D2EHPA in the presence of zirconium (Zr).[1] Weaver detected an increase in the extracting power of organophosphorus acids towards various elements when the organic phase contained Zr.[2] Zirconium salt of di-(2-ethylhexyl) phosphoric acid (Zr-D2EHPA) shows more powerful extraction properties for the lanthanides than those of the original D2EHPA in 1 M HNO_3 solutions.[3] Zirconium salt of di-(2-ethylhexyl) phosphoric acid is the new type of effective extractants for the extraction of alkaline earth, rear earth, and transplutonium elements from the nitric acid solution. Zirconium increases the capacity of D2EHPA at extraction of some elements, especially Am and Cm. Zirconium salt of di-(2-ethylhexyl) phosphoric acid is used in the solvent extraction process for radioactive waste.[4] One of the significant problems associated with solvent extraction of highly radioactive materials is the radiation damage to the organic solvent. Radiolysis property analysis of extractants used in radioactive waste treatment is necessary to get the data for the estimation of design life in a high-level radioactive atmosphere. This compound may be degraded to D2EHPA, mono-(2-ethylhexyl) phosphoric acid (M2EHPA) and PO_4^{-3} by radioactive materials. Amounts of D2EHPA and M2EHPA in Zr-D2EHPA must be monitored because the production of these compounds means degradation, which leads to a decrease in the extraction yield. In the present study, Zr-1 M D2EHPA/dodecane was exposed to gamma rays from

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a ^{60}Co source (95,000 Ci) and the yields of the degradation products were determined by the liquid chromatography/mass spectrometry (LC/MS) method.

The purpose of this investigation is to optimize the method for the determination of D2EHPA and M2EHPA using high performance LC/MS.

EXPERIMENTAL

Chemicals and Reagents

Di-(2-ethylhexyl) phosphoric acid (>95%), *n*-dodecane and H_2SO_4 (Merck), phosphoric acid 2-ethylhexyl ester (mono- and di-ester mixture) (TCI), $Zr(SO_4)_2 \cdot H_2O$, 99.99% (Aldrich) were used without further purification. All other reagents were of reagent grade. Double distilled water was used throughout. Di-(2-ethylhexyl) phosphoric acid stock solution was prepared by dissolving 1100 mg of D2EHPA in 10 mL acetone and the calibration standard solutions were prepared by diluting the stock solution in acetone. HPLC grade methanol and H_2O (50 mmol CH_3COONH_4) were used for the preparation of eluents. The two mobile phases prepared as eluents were: (A) methanol : H_2O (80 : 20, v/v) and (B) methanol : H_2O (75 : 25, v/v).

Purification of Mono-(2-Ethylhexyl) Phosphoric Acid

Mono-(2-ethylhexyl) phosphoric acid was purified by the following Acharya's method.[4] Di-(2-ethylhexyl) phosphoric acid and M2EHPA mixtures (D2EHPA content: 60%, M2EHPA content: 40%) (10 mL) were treated with 60 mL of 1 M NaOH and stirred vigorously so as to obtain a single phase. Then 10 mL of acetone was added to obtain a homogeneous solution. The pH of the solution was adjusted to between 7.5 and 10.5 by adding a few drops of 1 M NaOH or 1 M HCl. To it, 30 mL of 1 M $BaCl_2$ was added very slowly with vigorous shaking. A white precipitate of barium mono-(2-ethylhexyl) phosphate (BaM2EHPA) immediately separated out and was filtered off. The BaM2EHP precipitate was washed thoroughly with water and ethanol to completely remove NaD2EHPA and $Ba(D2EHPA)_2$. The BaM2EHPA precipitate was equilibrated with 50 mL of 1 M HCl in a separating funnel to regenerate M2EHPA and $BaCl_2$. The organic layer containing M2EHPA was diluted with diethyl ether and washed several times with water, followed by evaporation of the diethyl ether to leave behind pure M2EHPA. This three-stage separation gave M2EHPA of 99% purity. The purity of M2EHPA was checked by LC and was analyzed as 99%.

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Preparation of Zirconium-1 M Di-(2-Ethylhexyl) Phosphoric Acid

The complete bonding of 1 M D2EHPA/dodecane in the form of Zr-1 M D2EHPA/dodecane was reached through the one fold mixing of 1 M D2EHPA/dodecane solution with 1 M H_2SO_4, containing 15 g L^{-1} of Zr in the form of $Zr(SO_4)_2$, corresponding to the mole ratio of 1/6 of 1 M D2EHPA/dodecane, shaken for 4 hours. The received extractants were rinsed in 0.5 M HNO_3 and they were filtered with Whatman ISP filter paper to remove residual aqueous droplets. The concentration of zirconium in the organic phase was calculated from the difference between zirconium concentration in the aqueous phase before and after extraction. Zirconium concentration was analyzed by ICP (Jobin-yvon model JY 38 plus).

Irradiation of Zirconium Salt Di-(2-Ethylhexyl) Phosphoric Acid with ^{60}Co γ-Rays

Zirconium-1 M D2EHPA/dodecane were irradiated with ^{60}Co γ-rays source (95,000 Ci) in a gamma irradiation facility at Korea Atomic Energy Research Institute (KAERI). The samples of 20 mL of Zr-1 M D2EHPA/dodecane were taken in a scintillation vial and exposed to radiation from a ^{60}Co source (95,000 Ci). Irradiation was carried out in an atmosphere of air at an ambient temperature. The samples were irradiated to an absorbed dose of 1×10^5, 1×10^6, 1×10^7, and 1×10^8 rad. The liquid products were determined by LC/MS.

Sample and Standard Preparation

A series of diluted standards were made of D2EHPA and M2EHPA with concentrations of 15, 55, 85, and 110 μg mL^{-1} in acetone. Di-(2-ethylhexyl) phosphoric acid (>95%) and M2EHPA (>99%) standards (110 μg mL^{-1}) were made by dilution in acetone. Samples were prepared by dilution with acetone giving around 70 μg mL^{-1} and these were used for LC–MS analyses.

Apparatus and Chromatographic Conditions

Chromatography was performed using a Hewlett-Packard 1100 series system (Hewlett-Packard, USA): a Model HP G1313A autosampler, a HP G1311A quaternary pump, a HP G1316A column thermostat set at 30°C, and a HP G1315A diode array UV/VIS detector (254 nm) coupled in series with

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the HP G1946A mass selective detector (MSD), equipped with a HP G1948A electrospray-interface were used. The analytical column was a LUNA-C_{18} (4.6 mm × 25 cm) (Phenomenex, USA). The data was analyzed using the HP G1033A data handling system (Hewlett-Packard, USA). The mobile phases were methanol : H_2O (50 mmol CH_3COONH_4) = 80 : 20 for analysis of D2EHPA and methanol : H_2O (50 mmol CH_3COONH_4) = 75 : 25 for analysis of M2EHPA.

The flow-rate was 0.7 mL min^{-1} and the injection volume was 20 μL. Ionization mode was electrospray ionization (ESI) positive, fragmentor voltage was 100 V, drying gas flow was 10 L min^{-1}, drying gas temperature was 350°C, and drying gas pressure was 40 psi. The MS used was a HP G1946A (Hewlett-Packard, USA). The scan range was 50–800 amu. A scan time of 0.9 s and an interscan time of 0.1 s was used. The source and transfer line temperature was 100°C. The data was processed using personal computer-based HP G1033A software. Table 1 shows the LC/MS analytical conditions for the determination of D2EHPA in γ-irradiated Zr-1 M D2EHPA/dodecane solvent.

RESULTS

Determination of Synthetic Solution of Di-(2-Ethylhexyl) Phosphoric Acid and Mono-(2-Ethylhexyl) Phosphoric Acid

Chromatography was performed on a C_{18} column using a methanol : H_2O contained 50 mmol CH_3COONH_4 gradient and satisfactory retention and resolution is achieved for D2EHPA and M2EHPA. A total ion chromatogram of the synthetic solution of D2EHPA and M2EHPA are shown in Fig. 1.

Table 1. Liquid chromatography/MS conditions for the determination of D2EHPA in γ-irradiated Zr-1 M D2EHPA/dodecane solvent.

System	Hewlett-Packard 1100 series
Analytical column	Phenomenex LUNA-C18 (4.6 mm × 25 cm)
Eluent (for D2EHPA)	MeOH : H_2O (50 mmol CH_3COONH_4) = 80 : 20
Eluent (for M2EHPA)	MeOH : H_2O (50 mmol CH_3COONH_4) = 75 : 25
Flow rate	0.7 mL min^{-1}
Ionization mode	ESI positive
Fragmentor voltage	100 V
Drying gas flow rate	10 L min^{-1}
Drying gas temperature	350°C
Drying gas pressure	40 psi

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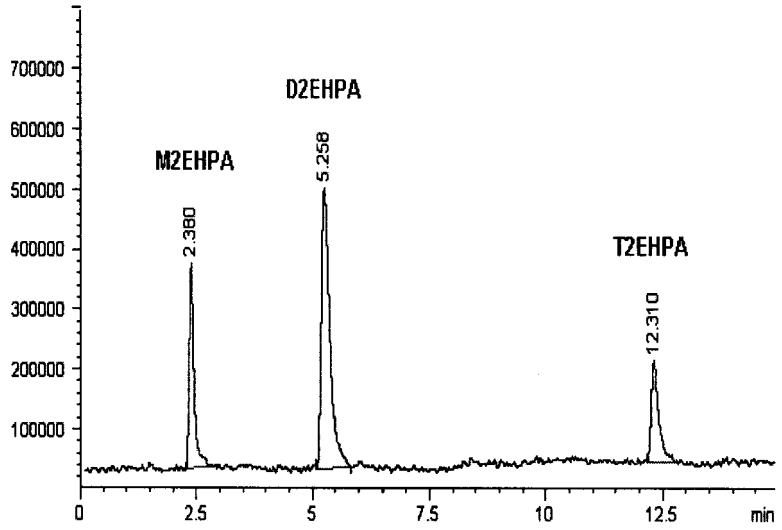

Figure 1. Total ion chromatogram for D2EHPA and M2EHPA in synthetic solution.

Mono-(2-ethylhexyl) phosphoric acid peak was at 2.3 min, D2EHPA peak was at 5.2 min, and tri-(2-ethylhexyl) phosphoric acid (T2EHPA) peak was also shown at 12.3 min. Tri-(2-ethylhexyl) phosphoric acid was also shown in the synthetic solution of D2EHPA and M2EHPA. HPLC grade methanol and H_2O (50 mmol CH_3COONH_4) were used for the preparation of eluents. The mobile phase prepared as an eluent was methanol : H_2O (80 : 20, v/v). The optimum condition for these compounds is methanol : H_2O (50 mmol CH_3COONH_4) = 80 : 20 ratio. To confirm the reproducibility of D2EHPA and M2EHPA, the synthetic solution of 34.8 $\mu g\,mL^{-1}$ of D2EHPA and 60 $\mu g\,mL^{-1}$ of M2EHPA were analyzed five times, respectively, and the results are shown in Table 2. The retention time of D2EHPA and M2EHPA peaks and the reproducibility peak area of D2EHPA and M2EHPA were 0.34–1.11% and it shows favorable results. The detection limit is 1 $\mu g\,mL^{-1}$ (in SCAN mode) for D2EHPA and 1 $\mu g\,mL^{-1}$ (in SIM mode) for M2EHPA in this system with a 20 μL sample loop. The calibration data of D2EHPA and M2EHPA give straight lines as in Fig. 2.

Determination of Radiolysis Products of Zirconium-1 M Di-(2-Ethylhexyl) Phosphoric Acid/Dodecane

Chromatography was performed on a C_{18} column using a MeOH/H_2O (50 mmol CH_3COONH_4) gradient and satisfactory retention and resolution is

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Table 2. Precision for the determination of D2EHPA and M2EHPA in LC.

	D2EHPA (34.8 μg mL^{-1})		M2EHPA (60 μg mL^{-1})	
	Retention time (min)	Area	Retention time (min)	Area
1	5.25	3,279,040	2.38	404,571
2	5.23	3,360,580	2.32	407,597
3	5.26	3,357,520	2.35	407,330
4	5.20	3,357,280	2.40	405,295
5	5.24	3,308,230	2.35	407,243
Average	5.24	3,332,530	2.36	406,407
SD	0.023	36,998.43	0.031	1,376.08
RSD (%)	0.44	1.11	1.31	0.34

achieved for D2EHPA and M2EHPA in a gamma irradiated solution of Zr-D2EHPA. A total ion chromatogram of D2EHPA and M2EHPA in a γ-rays irradiated solution of Zr-D2EHPA is shown in Fig. 3.

Di-(2-ethylhexyl) phosphoric acid peak (in Scan mode) was at 5.3 min. HPLC grade methanol and H_2O (50 mmol CH_3COONH_4) were used for the preparation of eluents. The mobile phases prepared as eluents was methanol : H_2O (80 : 20, v/v). Mono-(2-ethylhexyl) phosphoric acid peak was at 3.1 min (in SIM mode). HPLC grade methanol and H_2O (50 mmol CH_3COONH_4) were used for the preparation of eluents. The mobile phases prepared as eluents was methanol : H_2O (75 : 25, v/v) for the complete separation of the D2EHPA peak and the M2EHPA peak. We used larger samples for the analysis of M2EHPA, because the M2EHPA concentration is much smaller than the D2EHPA concentration.

We confirmed the mass spectrum of M2EHPA obtained in optimum conditions, and the strongest ion peak was analyzed quantitatively in the SIM mode (characteristic ion = 233.1 m/z). A LC of Zr-1 M D2EHPA/dodecane exposed to gamma rays up to an absorbed dose of 1×10^8 rad shows D2EHPA and M2EHPA (Fig. 3). The liquid products observed in the radiolysis of Zr-1 M D2EHPA were D2EHPA and M2EHPA. Twenty milliliter of Zr-1 M D2EHPA/dodecane was taken in a scintillation vial and exposed to radiation from a ^{60}Co source (95,000 Ci). Irradiation was carried out in an atmosphere of air at an ambient temperature. The samples were irradiated to an absorbed dose of 1×10^5, 1×10^6, 1×10^7, and 1×10^8 rad. The assignment of M2EHPA and D2EHPA in the ESI-PI mass spectra of total ion chromatogram of Zr-1 M D2EHPA/dodecane, exposed to gamma rays to an absorbed dose of 1×10^8 rad,

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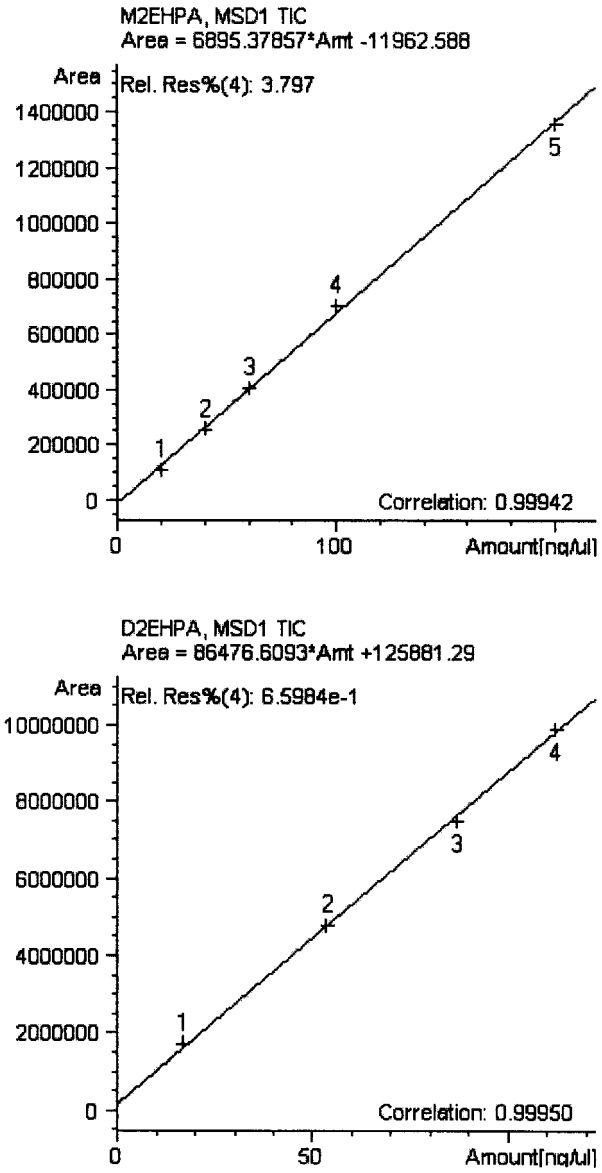

Figure 2. Calibration curves of M2EHPA (upper) and D2EHPA (lower).

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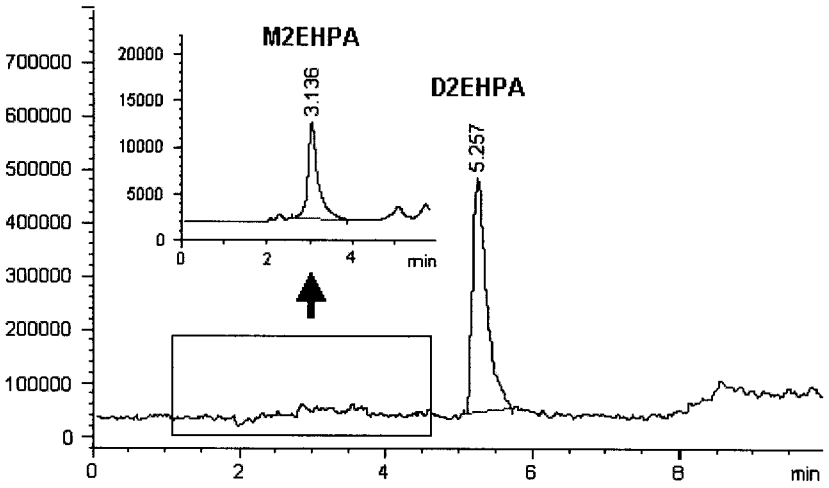

Figure 3. Total ion chromatogram for D2EHPA (in SCAN mode) and M2EHPA (in SIM mode) in γ-irradiated Zr-1 M D2EHPA ($Zr = 15\,g\,L^{-1}$) sample solution. sample: 1×10^8 rad.

is shown in Table 3 and Fig. 4. Since we may assume the sequential radiolysis of D2EHPA proceeds to yield orthophosphoric acid via M2EHPA, like that of the radiolysis of D2EHPA, D2EHPA $\rightarrow$ M2EHPA $\rightarrow$ H_3PO_4. The yields of M2EHPA products determined by total ion chromatography are shown in Fig. 3, as a function of absorbed dose.

The radiation yields of Zr-1 M D2EHPA/dodecane revealed similar patterns to those of D2EHPA decomposed radiolytically by a stepwise splitting

Table 3. Assignment of detected M2EHPA and D2EHPA in the ESI-PI mass spectra.

Analyte	Retention time (min)	Ion cluster (m/z)	Assignment
M2EHPA	3.1	211	$M^+ + H$
		233	$M^+ + Na$
		255	$M^+ + 2Na$
		256	$2M^+ + H$
D2EHPA	5.3	323	$M^+ + H$
		345	$M^+ + Na$
		645	$2M^+ + H$

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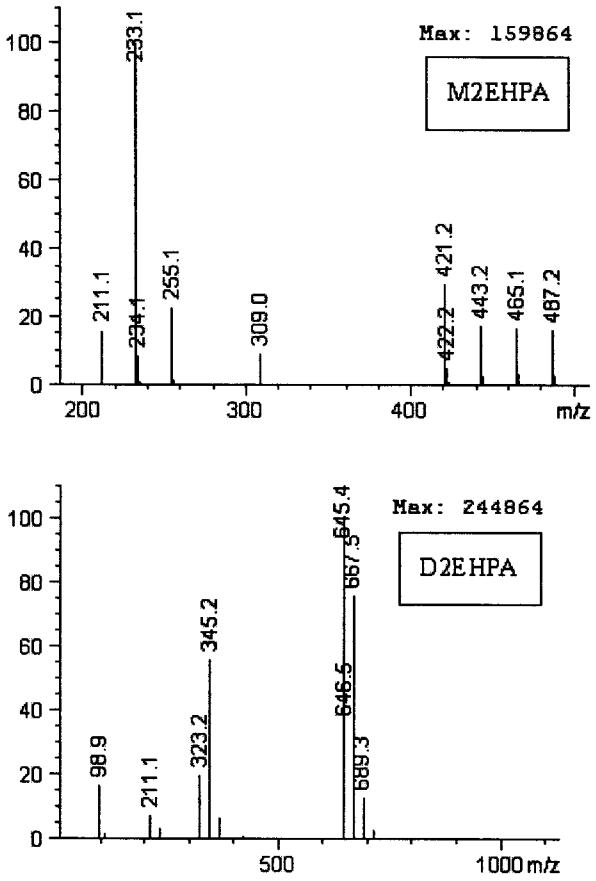

Figure 4. APCI-PI mass spectra of M2EHPA (upper) in a 80 : 20, Methanol : H_2O (50 mmol CH_3COONH_4) and D2EHPA (lower) in a 75 : 25, Methanol : H_2O (50 mmol CH_3COONH_4).

of two ester bonds to orthophosphoric acid. M2EHPA yields were increased as the absorbed dose Zr-1 M D2EHPA/dodecane increased. HPLC grade methanol and H_2O (50 mmol CH_3COONH_4) were used for the preparation of eluents. The mobile phases prepared as eluent was methanol : H_2O (75 : 25, v/v). In the present work, interest was centered on the liquid products of the radiolysis, especially D2EHPA and M2EHPA. The yields of D2EHPA and M2EHPA are listed in Table 4. The analysis of M2EHPA is difficult in this mixture. A comparison with synthetic D2EHPA–M2EHPA mixture was

Table 4. Determination of D2EHPA and M2EHPA in γ-irradiated Zr-1 M D2EHPA/*n*-dodecane/1 M HNO_3.

	Radian			
Compound (%)	1×10^5	1×10^6	1×10^7	1×10^8
D2EHPA	31.64	31.01	29.71	24.53
M2EHPA	0.35	0.34	0.33	0.39

Note: Irradiation source: ^{60}Co, absorbed dose unit: rad; Zr-1 M D2EHPA/dodecane (Zr = 15 g L^{-1}).

carried out. The D2EHPA and M2EHPA yields are based on the energy absorbed by the Zr-1 M D2EHPA from the gamma rays. An increase in exposure is generally accompanied by a decrease in yield.

This analysis technique is simple and more effective than other analysis methods for the determination of radiolysis products of Zr-1 M D2EHPA/dodecane.

CONCLUSION

A LC/MS for quantifying degradation products in Zr-D2EHPA solutions were analyzed. Degradation phenomena of Zr-D2EHPA caused by radiolysis are remarkable above 3.6×10^5 rad. The optimum instrument conditions for analyzing D2EHPA in Zr-1 M D2EHPA/dodecane are as follows: Flow rate is 0.7 mL min^{-1}, Eluent is MeOH : H_2O (50 mmol CH_3COONH_4) = 80 : 20 for D2EHPA and MeOH : H_2O (50 mmol CH_3COONH_4) = 75 : 25 for M2EHPA. Although these conditions produce the most usable analysis in this LC/MS system, they may vary somewhat in other systems. Phenomenex LUNA-C18 (4.6 mm × 25 cm) analytical column and Methanol/H_2O (50 mmol CH_3COONH_4) eluent by LC. Optimum conditions of eluent for the determination of D2EHPA and M2EHPA in irradiated with ^{60}Co-rays of Zr-D2EHPA are methanol : H_2O (50 mmol CH_3COONH_4) = 80 : 20 ratio in the SCAN mode of the MS for D2EHPA and methanol : H_2O (50 mmol CH_3COONH_4) = 75 : 25 ratio in the SIM mode of the MS for M2EHPA. Di-(2-ethylhexyl) phosphoric acid and M2EHPA compounds are well separated within 10 min. Dynamic ranges are 10–100 μg mL^{-1} for D2EHPA and 10–200 μg mL^{-1} for M2EHPA, respectively. The detection limits are 1 μg mL^{-1} in the SCAN mode for D2EHPA and 1 μg mL^{-1} in the SIM mode for M2EHPA in this system with 20 μL sample loop.

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