Electronic Supplementary Material (ESI) for Materials Advances.

Exploring How Exposure to Radiolysis and Harsh Chemical Reagents Impact Americium-241 Extraction Chromatography

SUPPORTING INFORMATION

Brian T. Arko,[1,2] David Dan,[1] Sara Adelman,[1,*] David B. Kimball,[1,*] Stosh A. Kozimor,[1,*] Marki M. Martinez,[1] Tara E. Mastren,[3] Daniel L. Huber,[1] Veronika Mocko,[1] Jung Rim,[1] Jenifer C. Shafer,[2,*] Benjamin W. Stein,[1] E. Miller Wylie II.[1]

[1]*Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)*

[2]*Department of Chemistry, Colorado School of Mines, Golden, CO 90401 (U.S.A.)*

[3]*Department of Nuclear Engineering, University of Utah, Salt Lake City, UT 84112 (U.S.A)*

**Corresponding author; sadelman@lanl.gov, dkimball@lanl.gov, stosh@lanl.gov, jshafer@mines.edu*

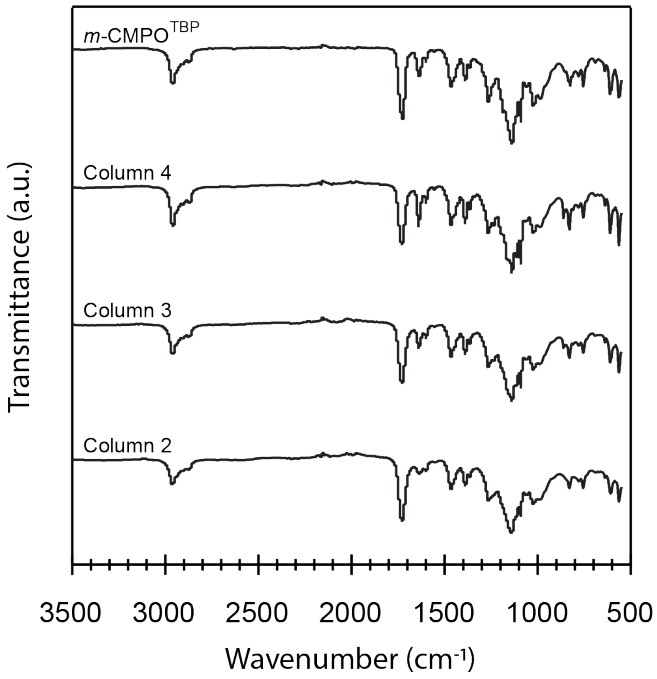

Figure S1. The IR spectra from '*pristine*' *m*-CMPO^{TBP} resin (*top*, no radiation nor acid exposure) and resin aliquots taken from active columns (2, 3, and 4) used in the CLEAR process ('*veteran*' resin samples that were exposed to acid and ^{241}Am). The ^{241}Am radiation dose received by the veteran resin decreased from Column #2 to Column #4.

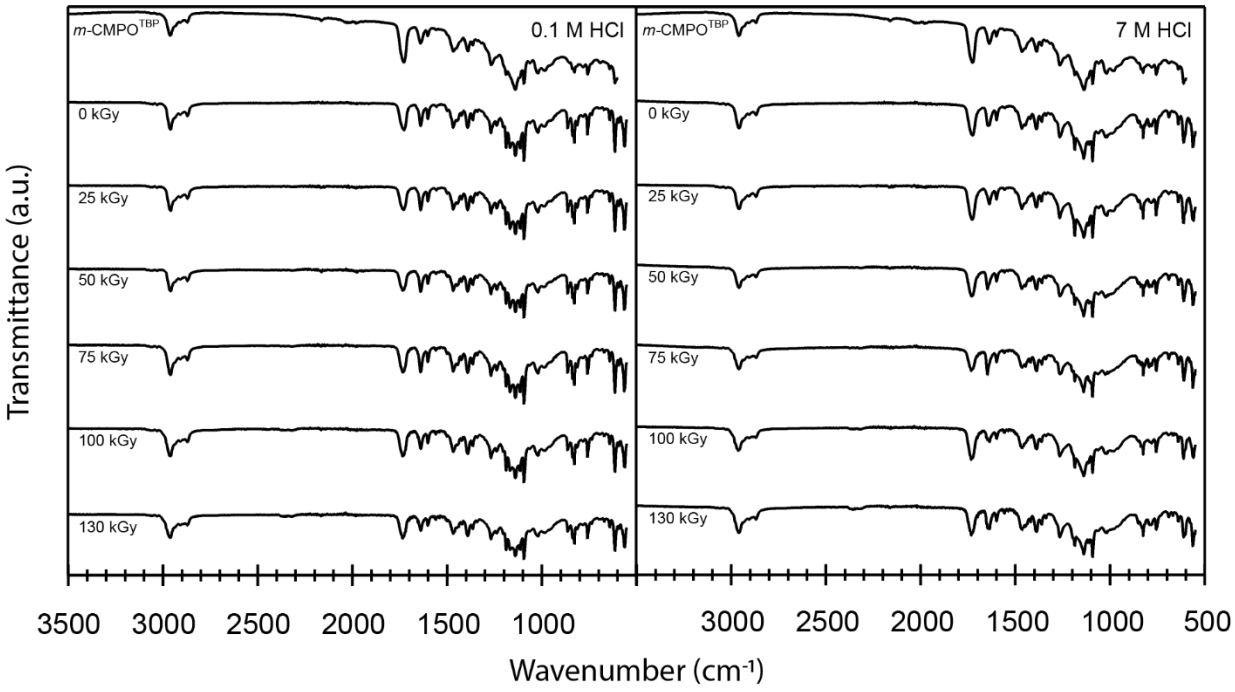

Figure S2*.* The IR spectra from '*pristine*' *m*-CMPO^{TBP} resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from *m*-CMPO^{TBP} resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose.

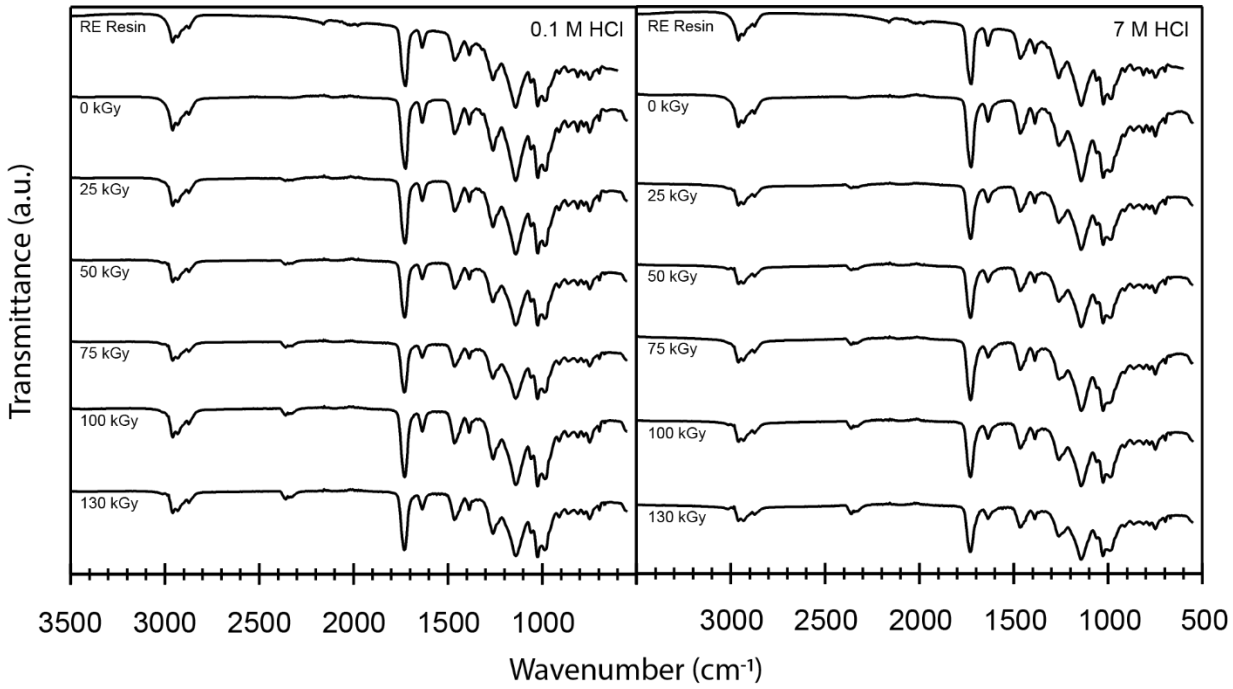

Figure S3. The IR spectra from '*pristine*' RE resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from RE resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose.

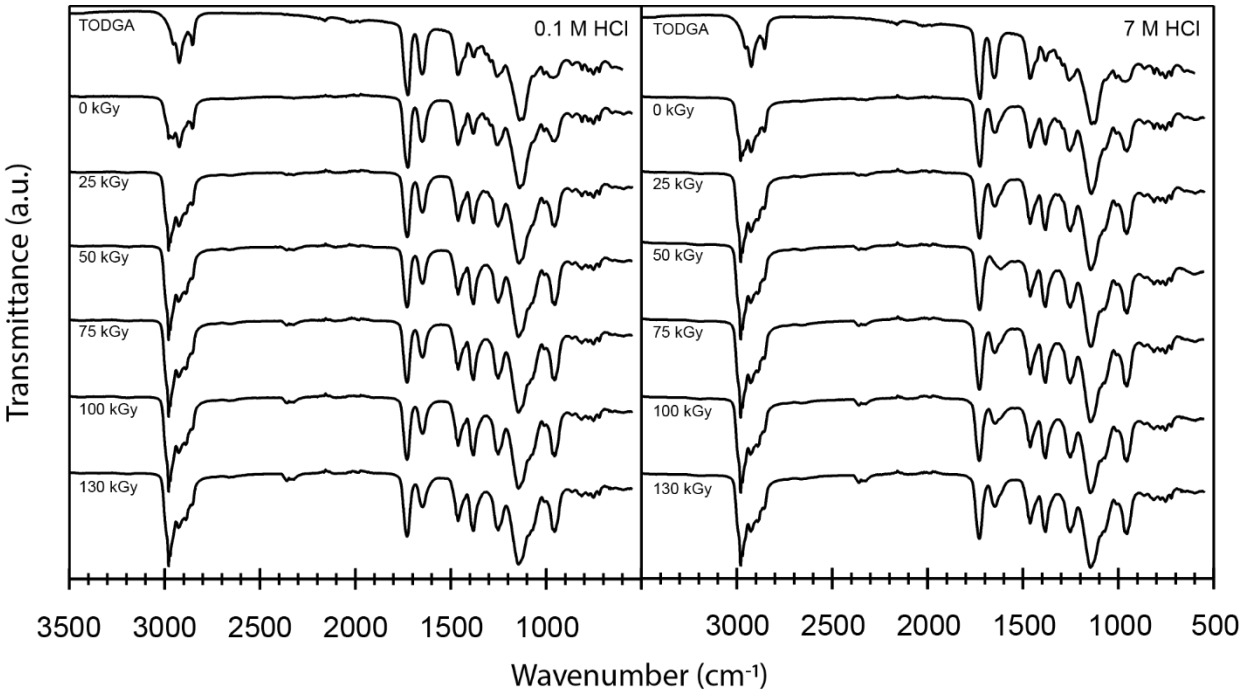

Figure S4*.* The IR spectra from '*pristine*' TODGA resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from TODGA resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose.

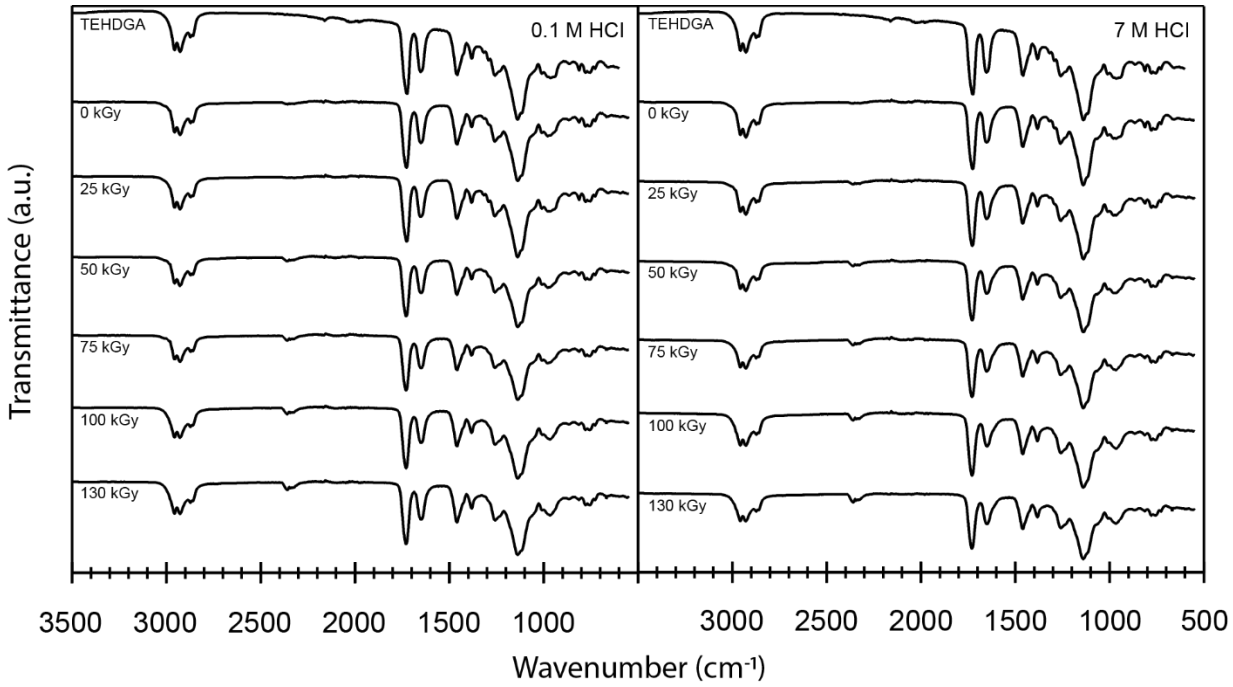

Figure S5*.* The IR spectra from '*pristine*' TEHDGA resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from TEHDGA resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose.

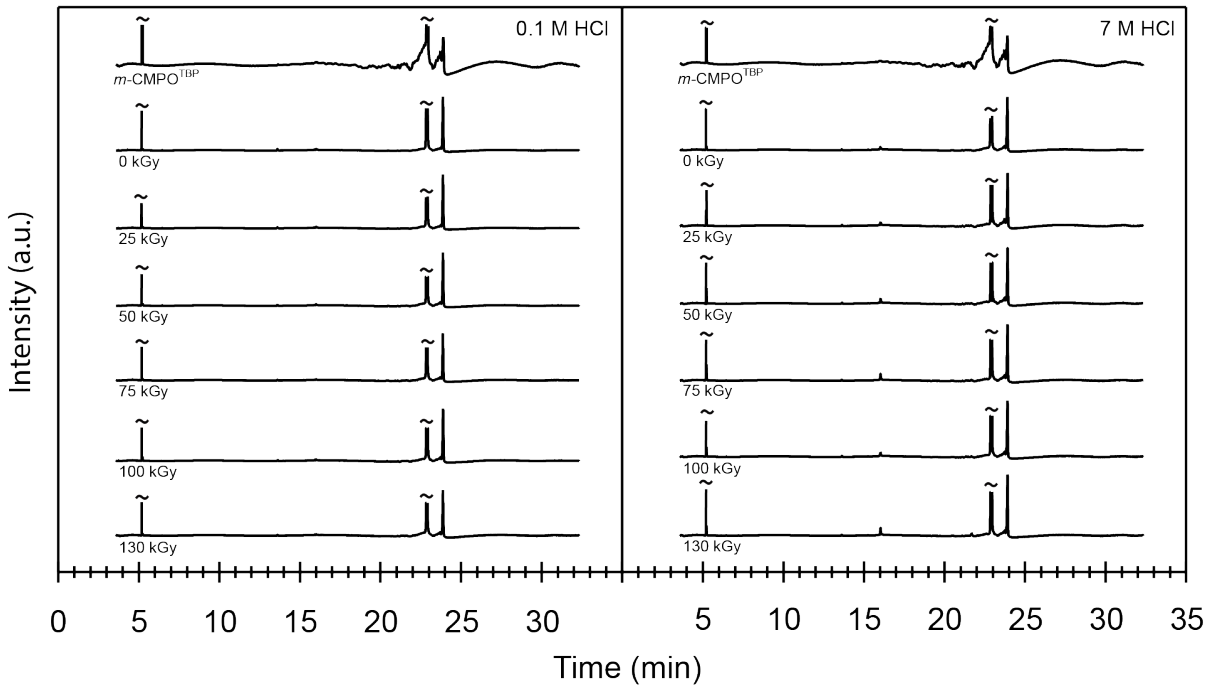

FIGURE S6. The GCMS chromatograms from '*pristine*' *m*-CMPO^{TBP} resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from *m*-CMPO^{TBP} resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All chromatograms are normalized to the *m*-CMPO intensity.

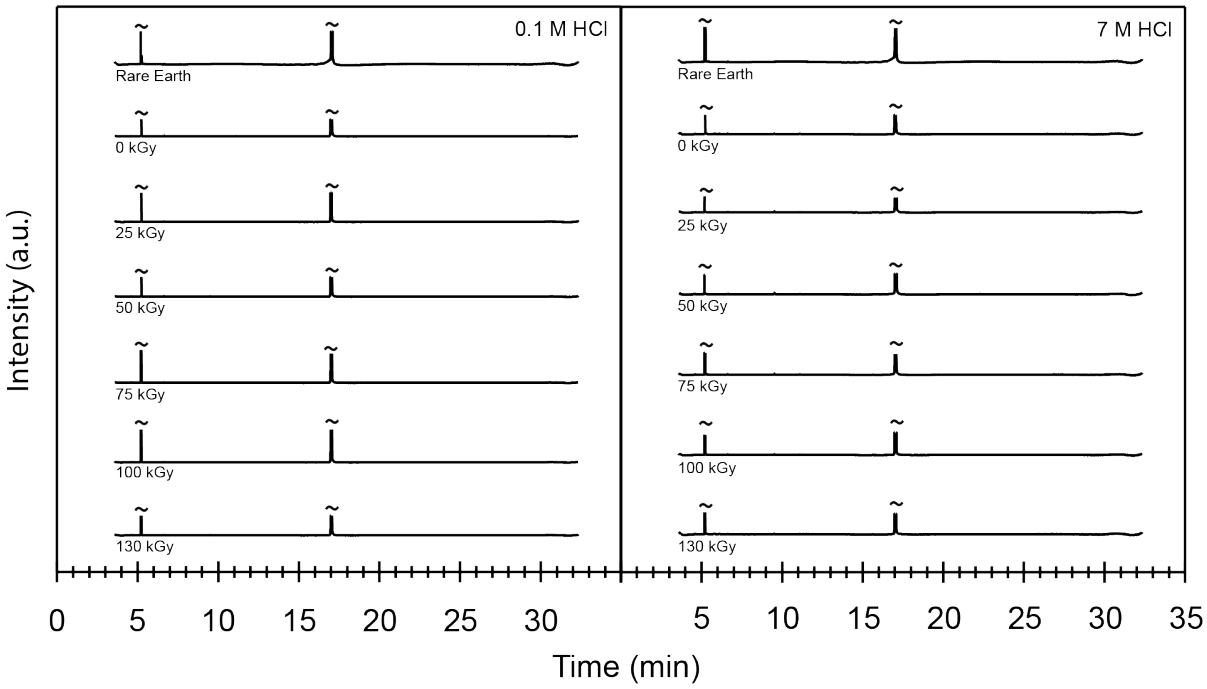

Figure S7*.* The GCMS chromatograms from '*pristine*' RE resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from RE resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All chromatograms are normalized to the RE intensity.

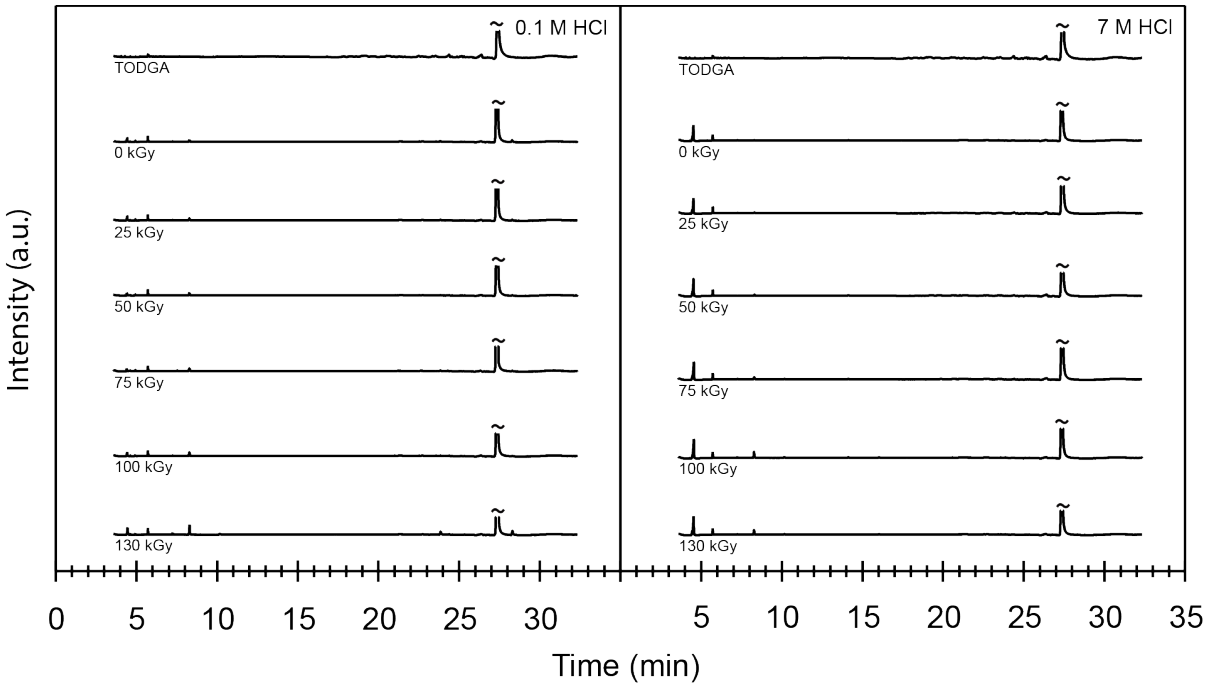

Figure S8. The GCMS chromatograms from '*pristine*' TODGA resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from TODGA resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All chromatograms are normalized to the TODGA intensity.

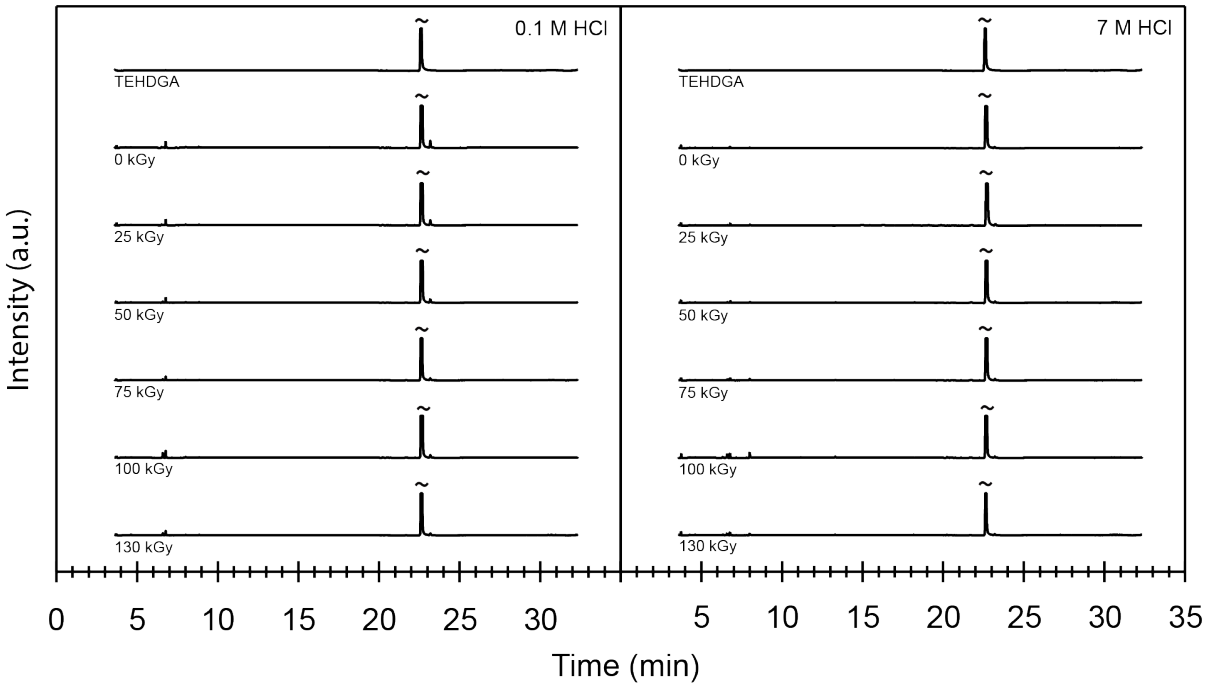

Figure S9*.* The GCMS chromatograms from '*pristine*' TEHDGA resin (*top*-no exposure to radiation or acid). The trace second from the top show spectra from TEHDGA resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All chromatograms are normalized to the TEHDGA intensity.

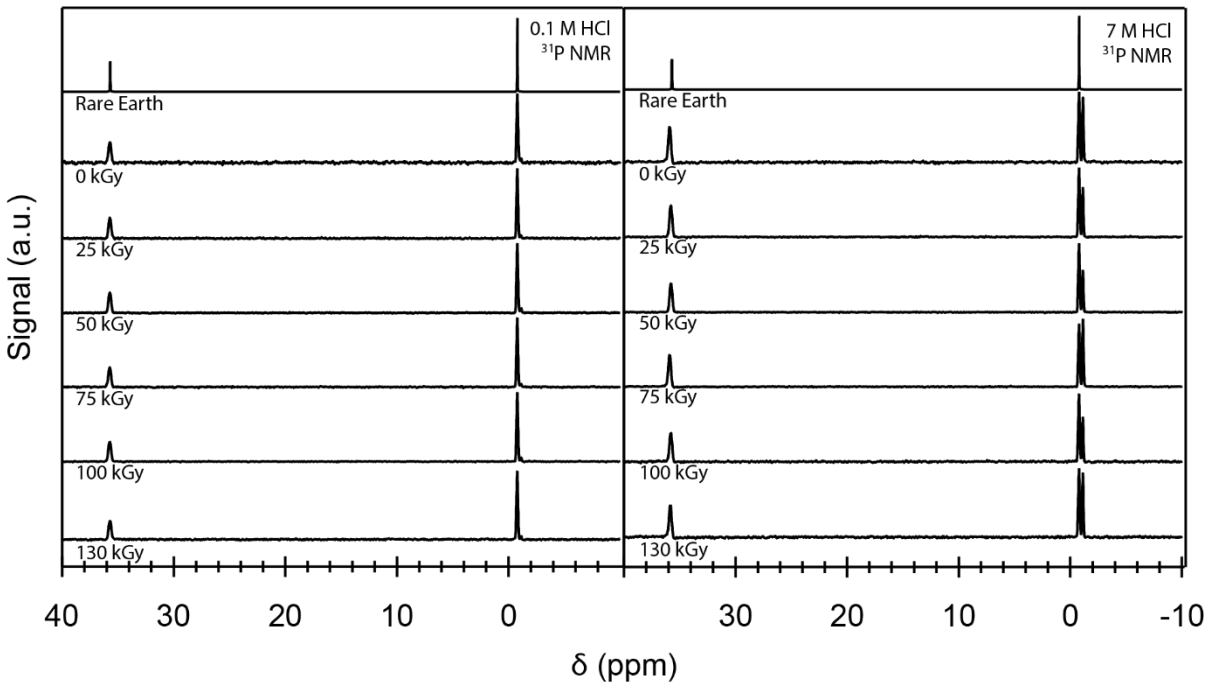

Figure S10. The ^{31}P NMR (^{1}H coupled) spectra from '*pristine*' RE resin (*top*-no exposure to radiation or acid). The trace second from the top shows spectra from RE resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All spectra were normalized to the TBP intensity.

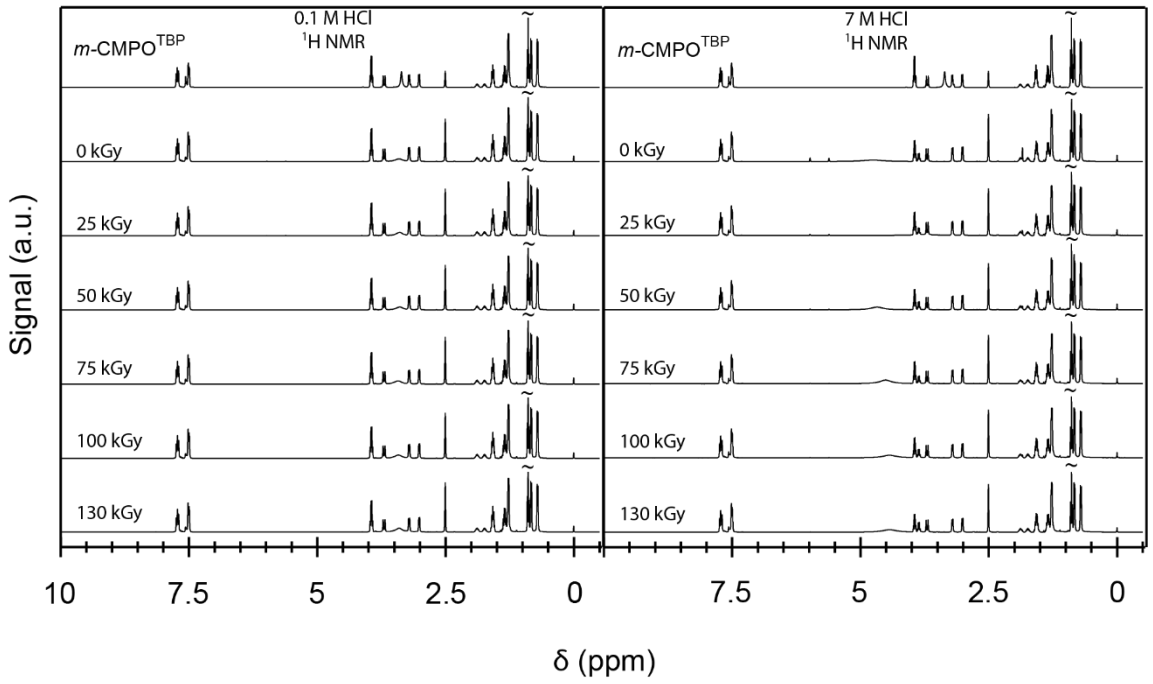

Figure S11. The ^{1}H NMR spectra from '*pristine*' *m*-CMPO^{TBP} resin (*top*-no exposure to radiation or acid). The trace second from the top shows spectra from *m*-CMPO^{TBP} resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All spectra were normalized to the δ 1 ppm intensity.

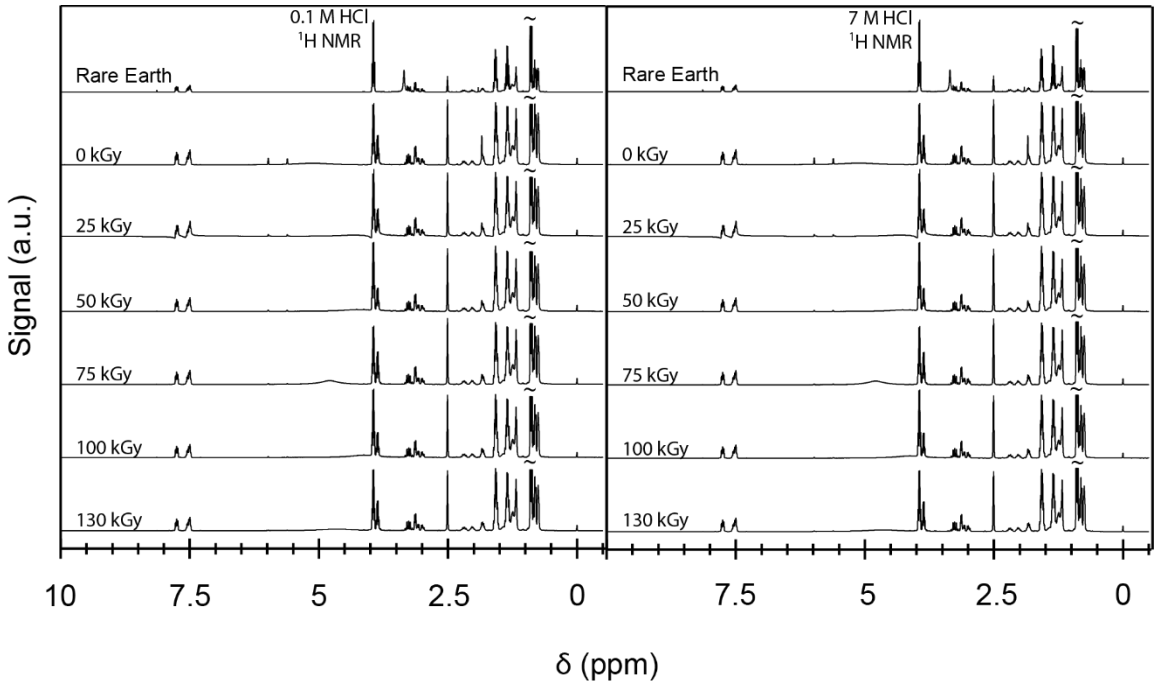

Figure S12. The ^{1}H NMR spectra from '*pristine*' RE resin (*top*-no exposure to radiation or acid). The trace second from the top shows spectra from RE resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All spectra were normalized to the δ 1 ppm intensity.

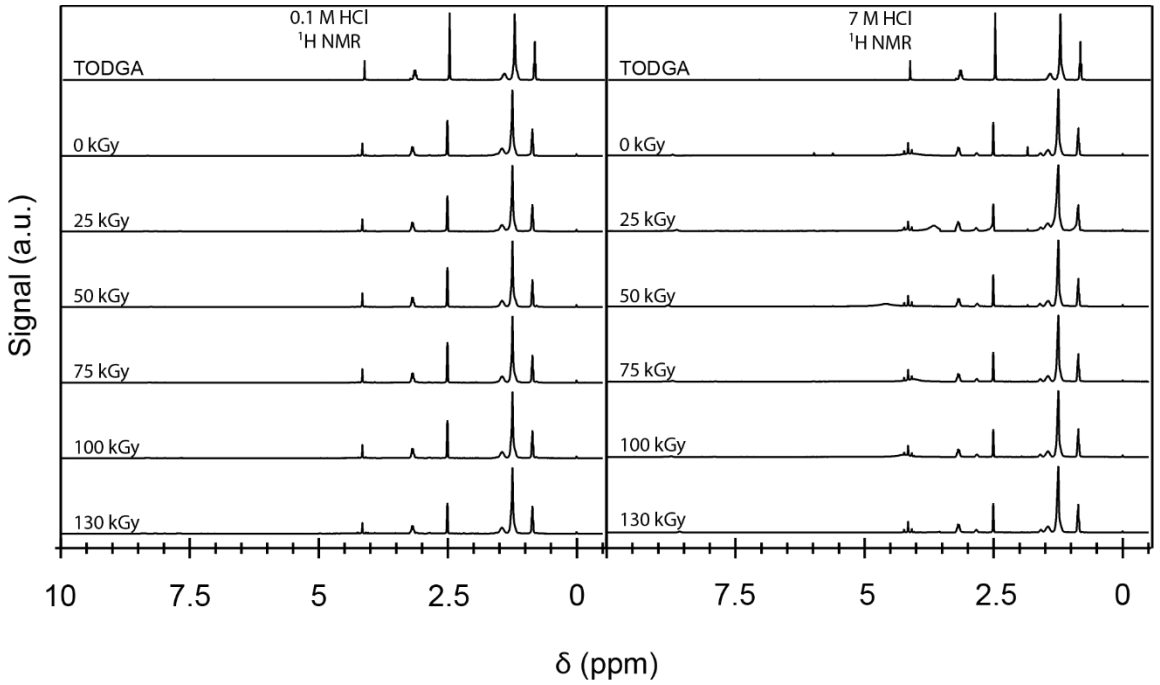

Figure S13. The ^{1}H NMR spectra from '*pristine*' TODGA resin (*top*-no exposure to radiation or acid). The trace second from the top shows spectra from TODGA resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All spectra were normalized to the δ 1 ppm intensity.

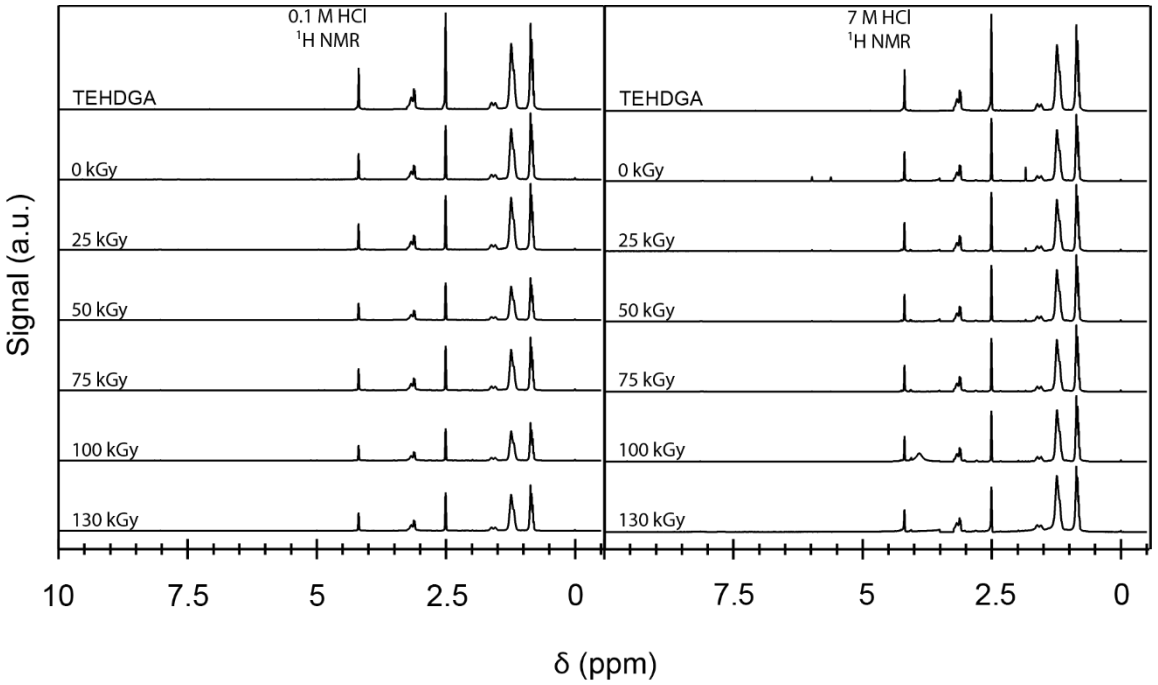

Figure S14*.* The ^{1}H NMR spectra from '*pristine*' TEHDGA resin (*top*-no exposure to radiation or acid). The trace second from the top shows spectra from TEHDGA resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All spectra were normalized to the δ 1 ppm intensity.

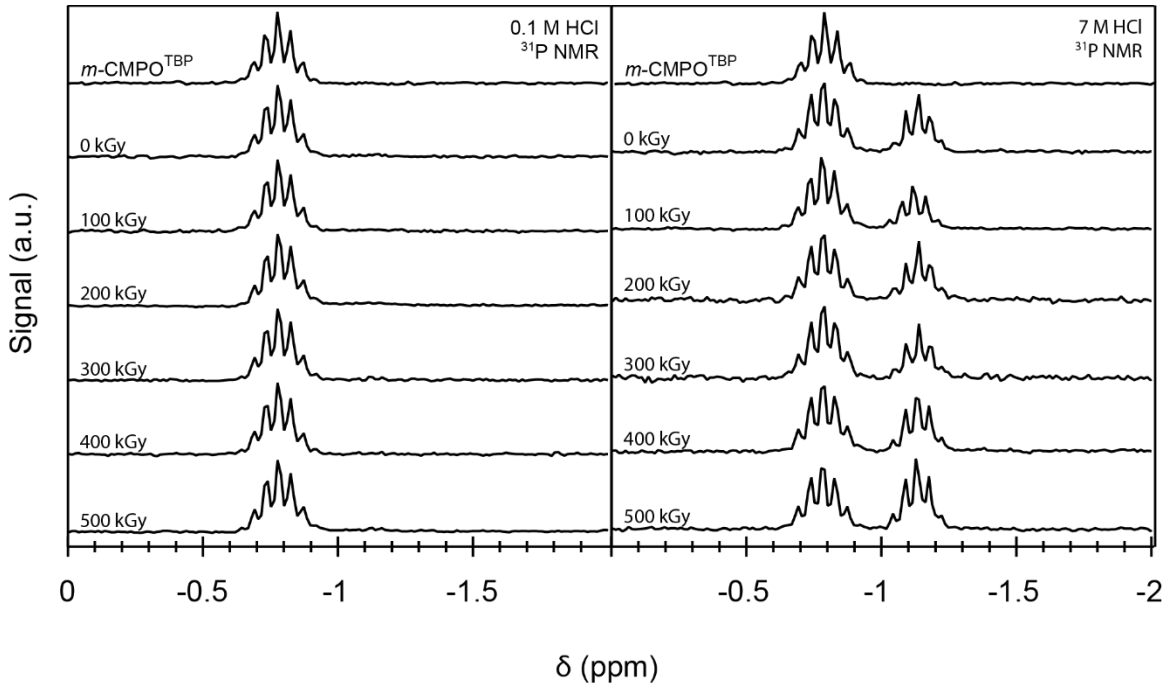

Figure S15. The zoomed in ^{31}P NMR (^{1}H coupled) spectra from '*pristine*' *m*-CMPO^{TBP} resin (*top*-no exposure to radiation or acid). The trace second from the top shows spectra from *m*-CMPO^{TBP} resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose.

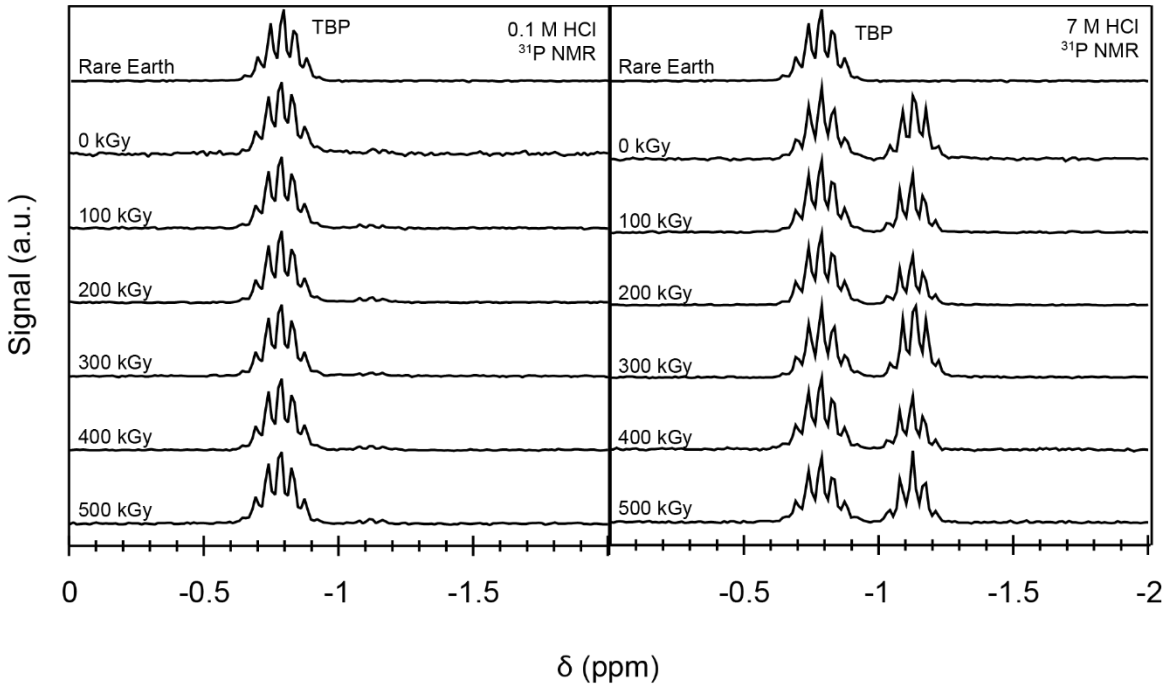

Figure S6*.* The zoomed in ^{31}P NMR (^{1}H coupled) spectra from '*pristine*' RE resin (*top*-no exposure to radiation or acid). The trace second from the top shows spectra from RE resin that was exposed to HCl (0.1 M *left*, 7 M *right*). Spectra from resins that were exposed to ^{137}Cs radiation are shown in the subsequent traces moving down the figure as a function of increasing dose. All spectra were normalized to the TBP intensity.

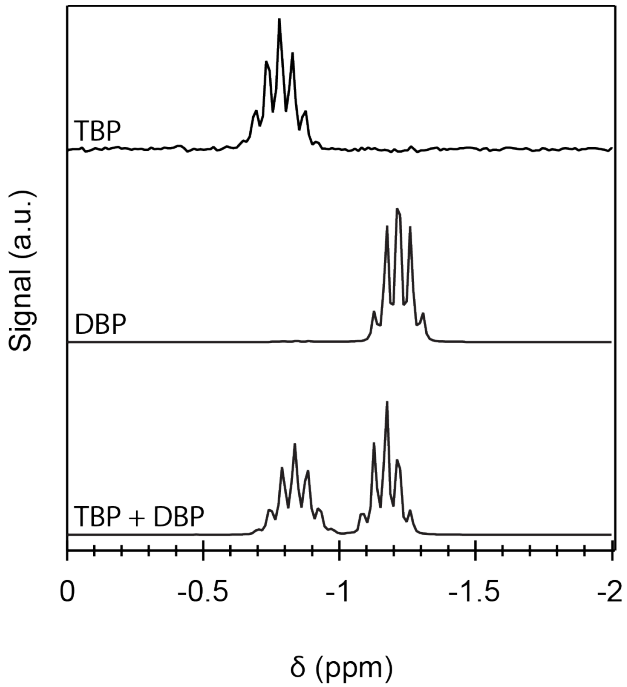

Figure S17. ^{31}P NMR spectra of DiButylPhosphate (DBP), TriButylPhosphate (TBP) and a mixture of pure TBP and pure DBP.

Table S1 Results verifying procedure with Nd/^{241}Am metal binding measurements using stable Eu traced with ^{155}Eu.

Resin	Metal Binding (mg M/g Resin)	
	^{155}Eu	**Eu ICP**
m-CMPO^{TBP}	16 ± 2	16 ± 1
Rare Earth	9 ± 2	10 ± 4
TODGA	38 ± 5	40 ± 9
TEHDGA	49 ± 9	53 ± 3