

Impact of radiolysis on morpholine-derived DAPhen ligands for the separation of americium(III) and europium(III)

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Materials

3-Nitrobenzotrifluoride (“F-3”) analytical grade was purchased from P&M Invest (Moscow) and was used as a solvent in the extraction experiments without further purification. Kerosene and nitric acid purchased from commercial sources and used without further purification.

1. Solvent Extraction

Extraction experiments were carried out in polypropylene Eppendorf tubes with a total volume of 1.5 mL. Equal volumes of the organic and aqueous phases (0.5 mL each) were used. Solutions of TOPO in kerosene or meta-nitrobenzotrifluoride (F-3) with a concentration of 0.25 mol/L were used as the organic phase for all extraction experiments. Phase contact was carried out for 10 minutes on a vortex shaker. The samples were then centrifuged (5 min, 12,000 rpm), and aliquots of 400 μ L from each phase were collected for analysis. The counting rates of aqueous and organic phases containing $^{241}\text{Am}^{\text{III}}$ and $^{152}\text{Eu}^{\text{III}}$ were determined using γ -spectrometer (ORTEC DSPec50 radiometric complex with a coaxial γ detector, Ametek). Measurements were performed on the γ -lines at 59.1 keV for $^{241}\text{Am}^{\text{III}}$ and 121.1 keV for $^{152}\text{Eu}^{\text{III}}$. The radionuclide contents in the initial aqueous phase were ~ 2500 and ~ 4000 Bq/mL for $^{241}\text{Am}^{\text{III}}$ and $^{152}\text{Eu}^{\text{III}}$, respectively. The distribution ratio (D) was calculated as the ratio of the counting rate in the organic phase to that in the aqueous phase. The separation factor $\text{SF}(M_1/M_2)$ was defined as the ratio of the distribution ratios of two different elements.

2. Irradiation of samples with ionizing radiation

Irradiation was carried out on the ILU-14 accelerator produced by the Budker Institute of Nuclear Physics of the Siberian Branch Russian Academy of Sciences in electronic mode. The ILU-14 facility generates a pulsed electron beam with an energy of 7.6 MeV. and the dose rate was 5 kGy/min. Dosimetric monitoring was carried out using films of a standard sample of absorbed dose photon and electron radiation doses (SSAD(Ph) 5/50; VNIIFTRI). Accordingly, the irradiation times required to achieve absorbed doses of 5, 10, 20, 50, and 100 kGy were 1, 2, 4, 10, and 20 minutes, respectively.

3. Identification of radiolysis products using HPLC–MS

The aliquots of organic phases contained ligands after radiolysis or ageing were diluted with acetonitrile (HPLC gradient grade, Sigma-Aldrich, USA) containing 1% formic acid (puriss. p.a., for HPLC, Fluka, Switzerland) until the final concentration of 10^{-5} mol/L. Experiments were carried out with Orbitrap Elite mass spectrometer (Thermo Fisher Scientific GmbH, Bremen, Germany) with electrospray ionization source. Samples were introduced into the ion source using a syringe pump at flow rate $3\mu\text{L min}^{-1}$. Mass spectra were acquired in a positive ionization mode. Sheath gas flow rates

were from 10 to 25 arbitrary units, auxiliary and sweep gas flow rate was set to zero, spray voltage 3.5 kV, capillary temperature 275 °C, S-Lens rf level 60%. Masses were analyzed in Orbitrap mass analyzer with 480 000 resolving power. Fragmentation was done by collision induced dissociation (CID) at normalized collision energy (NCE) 40. All spectra were registered continuously during 1 minute, then averaged. Results were processed using Thermo XCalibur 3.0 software.

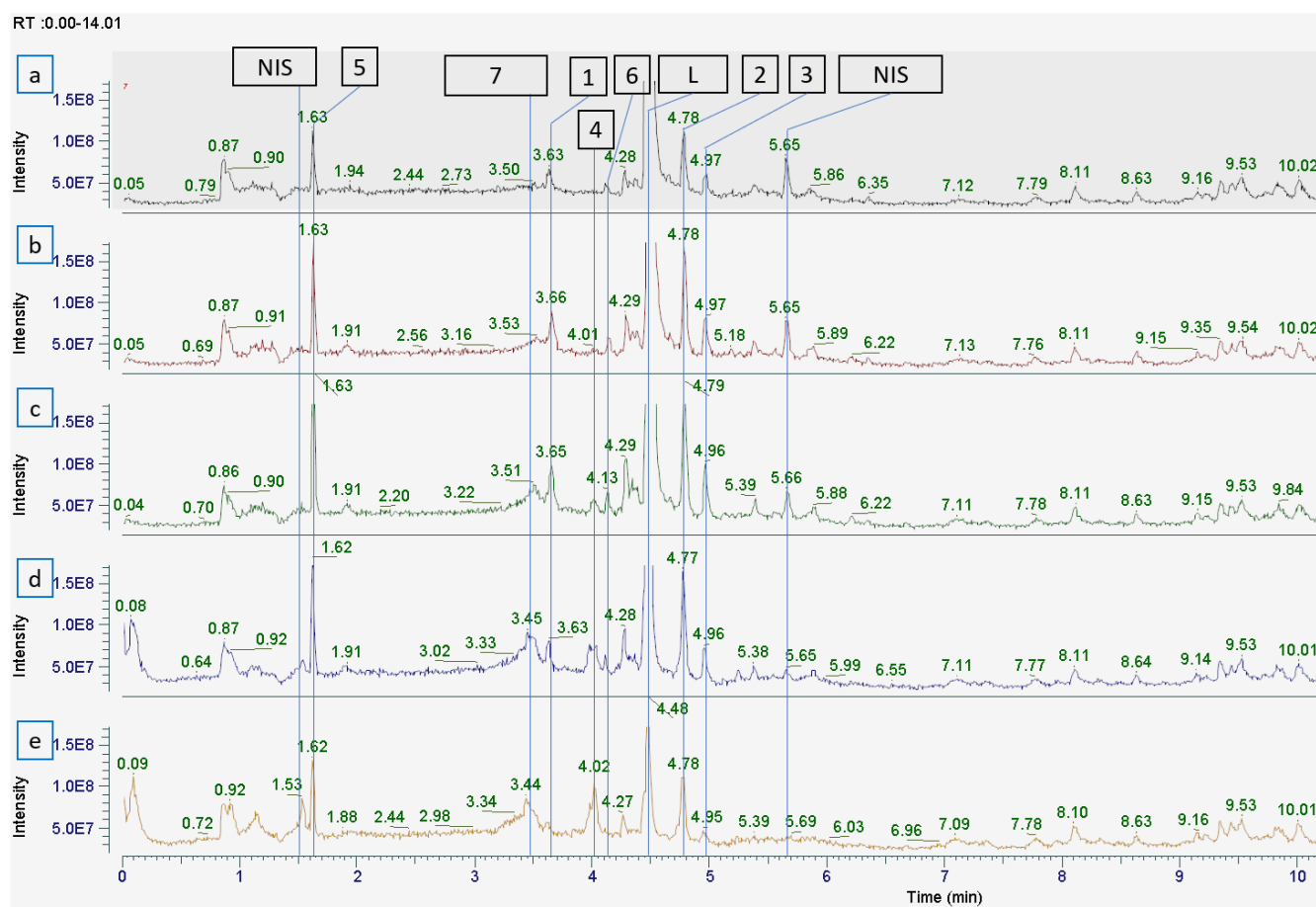


Figure S1 HPLC-MS chromatograms of radiolysis fragments of **L** (numbering as in the main article in **Scheme 1**, NIS is non-identified structure) after irradiation with doses of (a) 5 kGy, (b) 10 kGy, (c) 20 kGy, (d) 50 kGy, (e) 100 kGy