

RAPID SEPARATION OF INDIVIDUAL RARE-EARTH ELEMENTS FROM FISSION PRODUCTS*

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Abstract

A microprocessor-controlled radiochemical separation system has been developed to rapidly separate rare-earth elements from gross fission products. The system is composed of two high performance liquid chromatography columns coupled in series by a stream-splitting injection valve. The first column separates the rare-earth group by extraction chromatography using dihexyldiethylcarbonylmethylenephosphonate (DHDECMP) adsorbed on Vydac C₈ resin. The second column isolates the individual rare-earth elements by cation exchange using Aminex A-9 resin with α -hydroxyisobutyric acid (α -HIBA) as the eluent. With this system, fission-product rare-earth isotopes with half-lives as short as three minutes have been studied.

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1. Introduction

Until recently the chemical similarity of rare-earth elements has made the study of rare-earth radionuclides with short half-lives difficult. Historically, rare-earth separations were performed using conventional ion-exchange resins or extraction-chromatography columns. Both had only moderate efficiency and required long (several hours) separation times. In order to decrease the separation time, pressurized reservoirs were used to increase the solvent flow rate. However, with conventional resins, which have slow kinetics, as the flow rate increases the column efficiency decreases.

Recent developments in high performance resins along with pumps and valves capable of operating at high pressure (70 - 800 atm) have allowed the rapid separation (<30 min) of individual rare-earth elements.^(1,2) When the rare-earth isotopes are produced by fission, the separation time is lengthened significantly because a rare-earth group separation is usually required before the individual elements can be purified.

In this paper we describe an automated radiochemical separation system having the capability of rapidly (within 10 min) isolating individual rare-earth elements from fission products.

2. Experimental

In this study, fission product radionuclides were obtained from the spontaneous fission of ^{252}Cf ; using two 100 μg electrodeposited ^{252}Cf

sources⁽³⁾ which are located in a specially designed hot cell.⁽⁴⁾

The ²⁵²Cf sources are mounted in a pressurized (~2 atm) cylindrical chamber (8.25 cm inside diameter X 7.6 cm long) which is coupled by a He-jet transport system⁽⁵⁾ to a collection chamber with a 25 m teflon capillary tube (inside diameter ~0.8 mm). The sample chamber is continuously fed by a He-gas stream containing NaCl aerosols. Recoil fission fragments from the ²⁵²Cf are thermalized in the chamber, attach themselves to the NaCl aerosols and are swept through the capillary into the sample chamber which is continuously evacuated by a mechanical vacuum pump with a capacity of 76 L/s. The aerosols, some with the fission fragments attached, exit the capillary at sonic velocity and impinge on a magnetic tape which can be moved under microprocessor control. This tape exits the vacuum chamber through an interlock device to a wash chamber where the fission products are dissolved.

2.1 Rare-earth separation

A schematic diagram of the separation system is shown in Fig. 1.

The rare-earth group is separated with an extraction chromatography column. The individual rare-earth elements are then separated with a cation exchange column. All stages of the separation chemistry are under the control of a microprocessor.

The fission products, dissolved in ~1 mL of warm 3.0 M HNO₃, are placed onto an extraction chromatography column using an injection valve. The extraction chromatography column consists of 20 μM Vydac C₈^a resin

^aPurchased from Separations Group, Hesperia, Calif.

which is saturated with dihexyldiethylcarbonylmethylenephosphonate⁽⁶⁾ (DHDECMP). This column, which is slurry packed,⁽⁷⁾ is 5.0 cm long and 3.2 mm inside diameter. A pump capable of operating up to 300 atm delivers DHDECMP-saturated 3.0 M HNO₃^b at a flow rate of 5.0 mL/min to the precolumn. Experiments have shown that the rare-earth elements from La through Dy are adsorbed on the DHDECMP column while most (~97%) other fission products were washed through within ~1 min under the above conditions. The rare-earth fraction was then eluted by injecting ~2 ml of H₂O onto the column using the sample-injecting valve. The yield through this separation step is ~25% with ~3% contamination from other fission products (Tc, Ru, I).

By minimizing the volume and acidity of the separated rare-earth sample, optimized resolution of the individual rare-earth elements can be achieved in the final separation step. The output from the DHDECMP column passes through a pneumatically operated stream-splitting/sample-injection valve which is connected to a cation exchange column. The rare-earth fraction from the DHDECMP precolumn is captured in a sample loop in the injection valve and is sequentially injected onto the cation exchange column where the individual rare-earth elements are separated. The cation exchange column is a 25 cm long X 3.2 mm inside diameter stainless steel tube which is slurry packed⁽⁷⁾ with 11.5 µm Aminex A-9^c cation exchange resin.

^bSolubility is ≤0.5 g/L.

^cPurchased from Bio Rad Laboratories, Richmond, Calif.

By elevating the temperature of the Aminex A-9 column from 17°C (ambient) to 90°C we increased the resolution between individual rare-earth elements by ~50%. We have therefore operated the cation exchange column at 90°C using water jacketed columns heated with a thermostatically controlled water bath.

Two high-pressure pumps, capable of operating to 800 atm, were used under microprocessor control to deliver α -hydroxyisobutyric acid (α -HIBA) of varying concentration and pH to the cation exchange column. The flow rate to this column is 1.2 mL/min. The α -HIBA gradient starts at pH-3.2, 0.7M α -HIBA, which allows the rare-earth elements to adhere to the column, and smoothly increases to pH-5.0, 1.0 M α -HIBA in seven minutes eluting the rare-earth elements in inverse order of atomic number (Z). The yield through this column is estimated to be >90%. Thus the yield through the entire system is >22%.

The individual radioactive rare-earth elements are monitored with a shielded NaI(Tl) detector which is positioned at the outlet of the cation exchange column. The detecting system is a 1-1/2" X 1-1/2" NaI(Tl) crystal having a 3/16" hole drilled diametrically through it which is coupled to a log-rate meter and a strip chart recorder. The eluant from the cation exchange column passes through the hole in the detector providing a near 4π counting geometry.

Figure 2 is a chromatogram of a rare-earth separation obtained from the NaI(Tl) spectrometer. The start time corresponds to the end of

a 5.0 min fission product collection period. It should be noted that the first element, Gd, is eluted at 5.5 min and the group is completely separated within 10 min.

To illustrate the speed and purity of a typical rare-earth radioelement separation from fission-products the gamma-ray spectrum, obtained with a 107 cm³ open-end coaxial Ge(Li) spectrometer, of the Pm fraction is shown in Fig. 3. In this spectrum gamma-rays in the decay of ¹⁵²Pm, ¹⁵³Pm and ¹⁵⁴Pm, with half-lives ranging from ~3 to ~15 min are observed. This spectrum was acquired 9 min after the end of the fission-product collection and was counted for 4 min. Even though the two elements Sm and Nd are adjacent to Pm in the elution sequence only the 104- and 197-keV gamma-ray peaks can be identified as being emitted in the decay of ¹⁵⁵Sm and ¹⁵⁷Sm, respectively, and only the 276-keV gamma-ray can be attributed to the decay of ¹⁵²Nd. From the intensities of these contaminant peaks, the radiochemical purity of the Pm fraction is estimated to be ~99% with ~1% contamination resulting from the Sm and Nd activities.

3. Discussion

In summary, a rapid fission-product rare-earth separation system has been developed which is based on two liquid chromatography columns coupled in series and operated under microprocessor control. The ²⁵²Cf spontaneous fission isotope was used as the source of fission products in these experiments. A He gas-jet transport arrangement was used to rapidly transfer the fission products from the shielded ²⁵²Cf hot-cell to the chemistry laboratory. To date, experiments with this

system have identified individual rare-earth fission products with half-lives as short as ~ 3 min. We are presently working to further decrease the separation time sufficiently so that rare-earth activities with 1 min half-lives can be studied.

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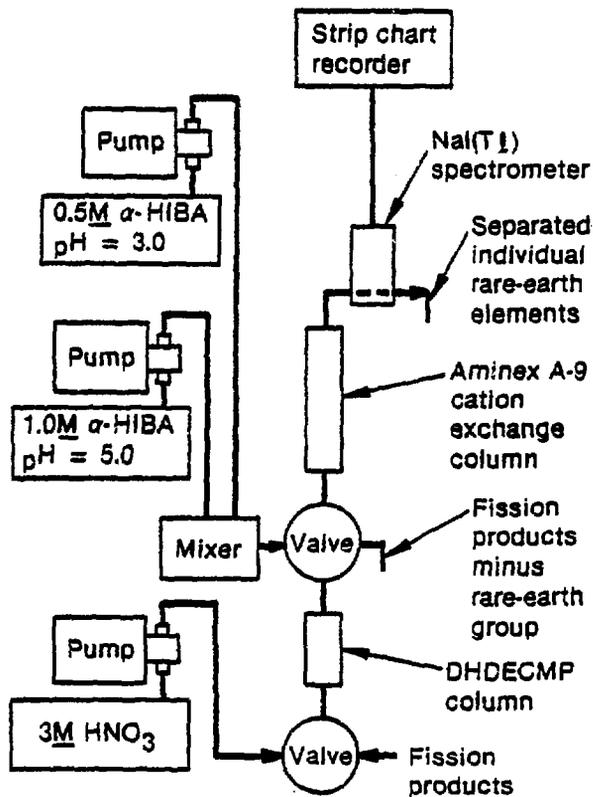
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Figure Captions

Fig. 1 Schematic diagram of high pressure liquid chromatography system.

Fig. 2 Chromatogram of a separation of individual fission-product rare-earth elements produced by the fission of ^{252}Cf .

Fig. 3 A Ge(Li) gamma-ray spectrum of the Pm fraction of the rare-earth elements separated from fission-products produced by the fission of ^{252}Cf . The gamma-ray peaks are identified by the following key: (a) 4.1 min ^{152}Pm ; (b) 7.5 min ^{152}Pm ; (c) 15 min ^{153}Pm ; (d) 5.4 min ^{153}Pm and (e) 2.7 min ^{154}Pm .



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