Separation of Am^{III} from Eu^{III} Using an Improved System of Flow-counterbalanced Capillary Electrophoresis

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Separation of $^{241}Am^{III}$ from $^{152,154}Eu^{III}$ was carried out using an improved system of flow-counterbalanced capillary electrophoresis in a thiocyanate medium. In this system, Eu^{III} was electrophoresed in the opposite direction to Am^{III} due to a combination of (1) the difference in the moving velocities of Eu^{III} and Am^{III}, and (2) a constant flow in the capillary caused by a difference in the water levels of the inlet and outlet of the sample solution.

The separation of minor actinides (MA) from lanthanides (Ln) is very important in the reprocessing portion of the nuclear energy cycle. However, the chemical behavior of Ln^{III} is very similar to that of MA^{III}, which includes species such as ^{241}Am, ^{243}Am, and ^{244}Cm.

Arisaka et al. showed that the distribution behavior of Cm^{III} on an anion-exchange resin was very different from that of Eu^{III}.[1] The disparity between the sorption behavior of Eu^{III} and Cm^{III} was explained on the basis of their inner-sphere hydration numbers and the coordination extent of chloride ions around Eu^{III} and Cm^{III} in both the solution and the resin phases. Ikeda et al. showed that separation of MA^{III} (Am^{III} and Cm^{III}) from Ln^{III} (Ce^{III}, Nd^{III}, Tm^{III} and Yb^{III}) could be accomplished using a tertiary pyridine resin in hydrochloric acid–alcohol mixed solvent solutions.[2,3] These results show that solvents with low activity around MA^{III} and Ln^{III}, such as a mixed solvent (alcohol/H_2O), as well as high ion strength solutions, are favorable for effective separation of MA^{III} from Ln^{III}. Khopkar and Mathur determined the formation constants (β_1 and β_2) for thiocyanate complexes of La^{III}, Eu^{III}, Tb^{III}, Pu^{III}, Am^{III}, and Cm^{III} in an ammonium ion medium.[4] From their results, it was shown that the β_2 values of MA^{III} are higher than those of Ln^{III}. In order to distinguish the chemical behavior of Ln^{III} and MA^{III}, the interactions of Eu^{III} and Am^{III} with thiocyanate ions were investigated in mixed solutions (CH_3OH/H_2O) by Mori et al.[5] Furthermore, the moving velocities of the two species, Eu^{III} and Am^{III}, were investigated by paper electrophoresis in the same mixed solvent system.[5] It was revealed that the velocity of Eu^{III} in the region $[SCN^-] = 0.20$–0.60 M for X_{MeOH} (mole fraction of methanol in the mixed solvent) $= 0.23$ was considerably greater than that of Am^{III}.

The difference in the electrophoresis velocities of Eu^{III} and Am^{III} may be favorable for separation of Am^{III} from Eu^{III} using capillary electrophoresis (CE). CE has been widely used for simultaneous high-resolution separation of ionic substances with similar chemical properties, such as rare earth elements.[6–9] However, this technique has thus far proved unfavorable for treatment of larger sample amounts. Chankvetadze et al. devised an ingenious technique, flow-counterbalanced capillary electrophoresis (FCCE),[10] for carrying out separation of ionic analogous materials. The technique takes advantage of counter flow provided by the pressure difference between both ends of the capillary and makes possible continuous separation.[11,12]

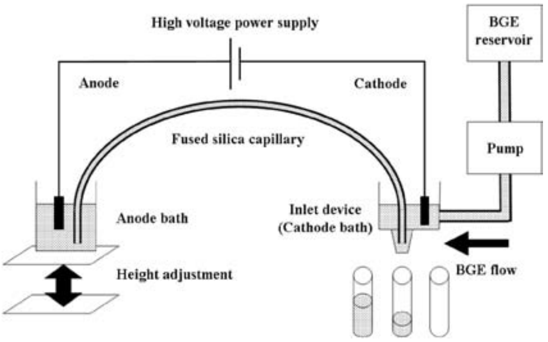

Figure 1. An improved system of FCCE with height adjustment.

In this study, an improved system of FCCE was used to separate Am^{III} from Eu^{III}. This system is not due to pressure difference but due to height difference between liquid levels of cathode and anode baths. So, it is a simpler device than the reported device.[11,12] The system consists of a power supply, a fused silica capillary, an inlet (cathode bath) and an outlet (anode bath) for the solution, a height adjustment device, and a peristaltic transfer pump for the background solution, as shown in Figure 1. The size of the fused silica capillary was 80.5 cm × 75 µm (i.d.). The capillary was first washed with 0.10 M HCl and water and then filled with a background electrolyte aqueous solution (BGE, 0.10 M $HClO_4$ + 1.00 M NaSCN) because the mixed solvent of methanol/H_2O was not suitable in long time capillary electrophoresis; then, a sample solution of 0.10 M $HClO_4$ (20–25 nL) containing $^{152,154}Eu^{III}$ and $^{241}Am^{III}$ was injected at the cathode side of the capillary using a hydrodynamic technique (the difference between the water levels of inlet and outlet, ΔH, was 10 cm, and the injection time, Δt, was 15 s). The BGE was also injected at the cathode side of the capillary using the same technique ($\Delta H = 10$ cm, $\Delta t = 180$ s); thus, the sample solution was located at 5.4 cm from the cathode side of the capillary. Using the height adjustment facility, the cathode side of the capillary was set at 0.0–5.0 cm higher than the anode side. The CE was operated at room temperature (298 ± 1 K) by application of +3.0 kV. Owing to the concentration of electrolytes and the pH of the BGE, the electroosmotic flow (μ_{EOF}) was very small.[13] The migrating sample solution was collected in tubes through the inlet device from the cathode side at regular intervals, and the radioactivity of the samples was measured using a NaI(Tl) scintillation counter or a high-pure Ge detector.

Figure 2 shows an electropherogram of Eu^{III} and Am^{III} in the FCCE system with various height differences between the

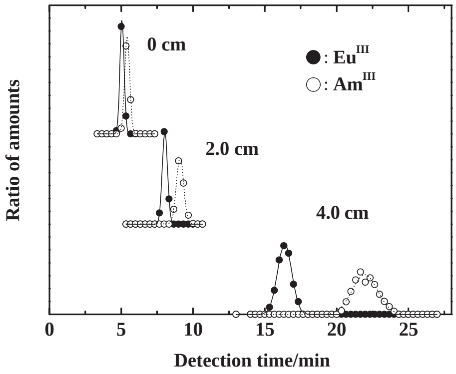

Figure 2. Electropherogram of FCCE (with height differences of 0, 2.0, and 4.0 cm) of Eu^{III} and Am^{III} in an aqueous solution of 0.10 M $HClO_4$ + 1.00 M NaSCN.

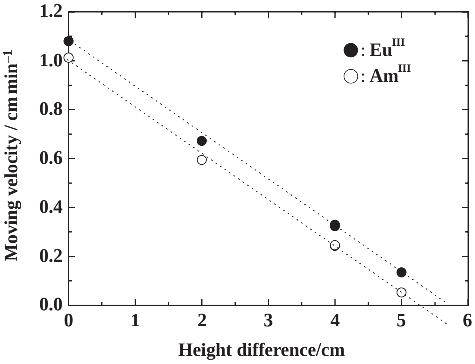

Figure 3. Moving velocity of Eu^{III} and Am^{III} in FCCE in an aqueous solution of 0.10 M $HClO_4$ + 1.00 M NaSCN.

cathode and anode sides of the capillary. The moving velocities of Eu^{III} and Am^{III} were calculated from the detection peak, as shown in Figure 3. It should be noted that the moving velocity of Eu^{III} was greater than that of Am^{III}, and the difference between the moving velocities of Eu^{III} and Am^{III} was constant at any height difference. Hydrodynamic flow from the cathode to the anode in the capillary occurs when the cathode side of the capillary is higher than the anode side. Thus, the moving velocities of Eu^{III} and Am^{III} which are electrophoresed from anode to cathode decrease as the height difference increases; this is shown in eqs 1 and 2:

$$v_{\mathrm{Eu}} = v_{\mathrm{eff,Eu}} - v_{\mathrm{h}} \tag{1}$$

$$v_{\mathrm{Am}} = v_{\mathrm{eff,Am}} - v_{\mathrm{h}} \tag{2}$$

where v_{Eu} and v_{Am} are the moving velocities of Eu^{III} and Am^{III} in the FCCE system with height difference, $v_{\mathrm{eff,Eu}}$ and $v_{\mathrm{eff,Am}}$ are the moving velocities without height difference, and v_{h} is the moving velocity of the hydrodynamic flow. When $v_{\mathrm{eff,Eu}} > v_{\mathrm{h}} > v_{\mathrm{eff,Am}}$, Eu^{III} should move from the anode to the cathode while Am^{III} moves from the cathode to the anode.

On the basis of these considerations, the following experiment was carried out in order to achieve complete separation of Am^{III} from Eu^{III}. Sample solutions of equal volumes of the BGE containing $^{152,154}Eu^{III}$ and $^{241}Am^{III}$ were injected at the cathode side and the anode side of the capillary using the hydrodynamic method. The height was adjusted so that the cathode side of the capillary was set 5.5 cm higher than the anode side. After operation of the FCCE system by application of +3.0 kV for 60 min, the radioactivities of the solution in the anode bath and the solution from the inlet device (cathode bath) were measured.

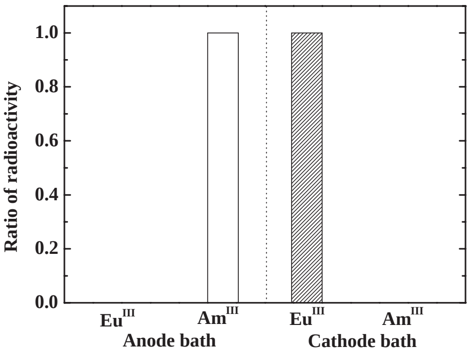

Figure 4. Complete separation of Am^{III} from Eu^{III} using FCCE in an aqueous solution of 0.10 M $HClO_4$ + 1.00 M NaSCN.

Figure 4 shows the ratio of radioactivity attributable to $^{152,154}Eu^{III}$ and $^{241}Am^{III}$ in the solutions collected from the anode and cathode baths. Only Am^{III} was detected in the anode bath, while only Eu^{III} was detected in the cathode bath. This result demonstrates that Am^{III} moved in the opposite direction from Eu^{III} during FCCE and that Am^{III} was completely separated from Eu^{III}.

The FCCE separation technique for Am^{III} and Eu^{III} provides high separability while creating little radioactive waste. Furthermore, by utilizing the FCCE technique with hydrodynamic flow, continuous separation of different radionuclides with different CE moving velocities is possible.

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