

# CONTINUOUS ELECTROPHORETIC SEPARATIONS OF RADIOACTIVE RARE EARTH MIXTURES

## III. SURVEY OF EXPERIMENTS IN 0.05 *M* LACTIC ACID

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### INTRODUCTION

In our previous reports<sup>1,2</sup> some continuous electrophoretic separations of three-component and five-component rare earth mixtures in 0.05 *M* lactic acid were described. These results gave us some indications that in the series of the rare earths there might be a relationship between the cathodic mobilities of the rare earths and their atomic numbers, or their ionic radii respectively. The experiments reported here confirm this presumption and at the same time give complete information about the separability in 0.05 *M* lactic acid of mixtures of rare earths with atomic numbers from 57 to 71.

### EXPERIMENTAL AND RESULTS

The experiments here described were carried out in successive runs without changing the filter paper curtain, and without switching off the electric current. The first solution, containing a particular rare earth, was pumped onto the starting point of the curtain during 10 min. Electrophoresis was then continued for a period of 2 h without applying the rare earth solution to the curtain. At the end of this period a set of collecting glasses was inserted, and the next rare earth solution was pumped onto the starting point of the curtain for 10 min. Then during a period of 2 h the first rare earth applied was collected and its distribution in the collecting glasses was estimated by an appropriate method. Afterwards the solution of the third rare earth was applied to the curtain during 10 min, and at the same time the previously applied rare earth was collected during 2 h in a new set of glasses, and so on.

In this way all the rare earths were applied to the curtain in successive runs at intervals of 2 h, each particular rare earth solution being pumped separately onto the starting point of the curtain during a period of 10 min, and the distribution of each of the rare earths was estimated in the corresponding set of collecting glasses. The apparatus<sup>3,5</sup> and general experimental conditions<sup>1</sup> have been described previously.

The diagram shown in Fig. 1 represents the distribution curves of the rare earths at the outlet of the filter paper curtain as estimated by G.M. counting of the effluent in the collecting glasses. In accordance with the experimental procedure, the activities correspond to a 10 min continuous run. Because of the short half lives of Pr, Sm, Dy and Ho, these rare earths were not applied in a radioactive form, and so only

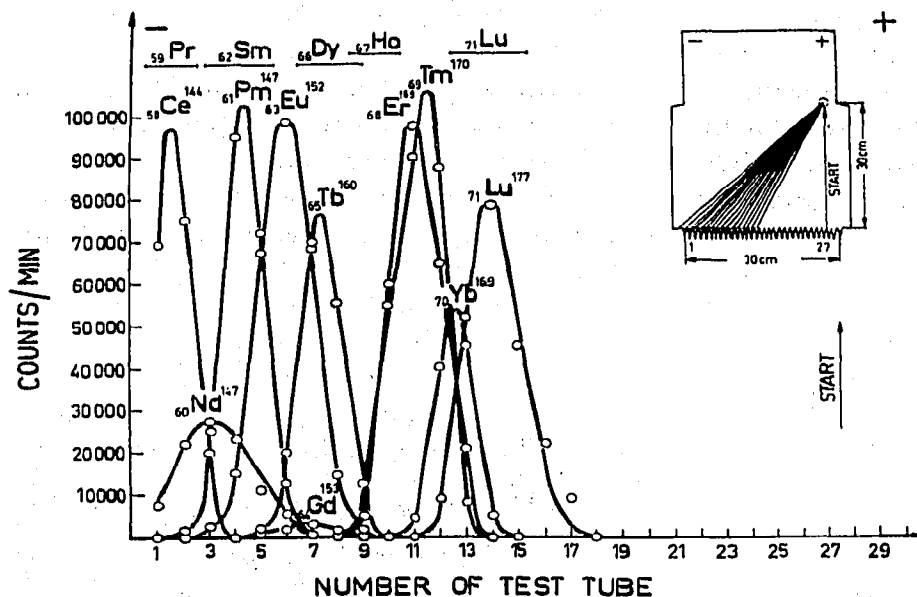


Fig. 1. Distribution curves of the rare earths at the outlet of the filter paper curtain as estimated by G.M. counting of the contents of the collecting glasses. For inactive rare earths only the width of the bands is indicated in the diagram. The activities correspond to a continuous run of 10 min. The dimensions of the filter paper curtain and the position of the starting point is sketched. Electrolyte, 0.05 *M* lactic acid; paper, Munktell No. 20/250; voltage drop, 300 V; mean electric field strength, 10 V/cm; electric current, 20 mA; pumping rate, 0.2 ml/h; time in which each sample is pumped on the curtain, 10 min.

the width of their bands in the collecting glasses could be estimated. In this case it was supposed that the peaks of their distribution curves were in the middle of the respective bands.

Fig. 2 represents a diagram in which the atomic numbers of the rare earths are plotted *vs.* the appearance of the peaks of the distribution curves of the rare earths

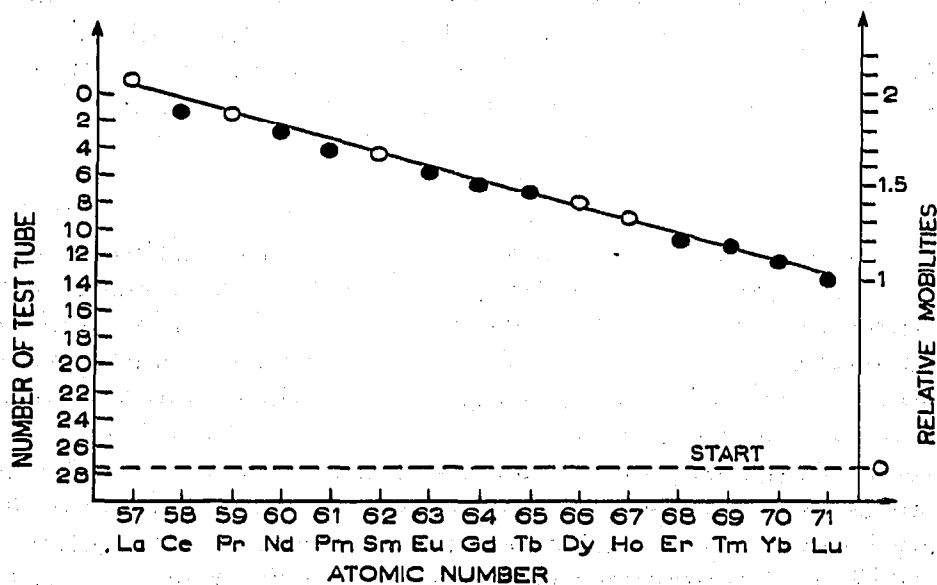


Fig. 2. Plot of atomic numbers of rare earths *vs.* their relative electrophoretic mobilities in 0.05 *M* lactic acid. ● = radioactive rare earths; ○ = inactive rare earths. The positions of the peaks of the distribution curves at the outlet of the apparatus were taken from Fig. 1.

at the outlet of the apparatus. The position of the peaks was estimated from the experimental data given in Fig. 1. At the same time the atomic numbers of the rare earths were plotted against the cathodic electrophoretic mobilities relative to that of lutetium. These relationships give a straight line in the diagram.

Using the data for the ionic radii of the rare earths reported by SEABORG<sup>6</sup>, which give an approximately linear relationship between the atomic numbers of these elements and their ionic radii, the diagram in Fig. 3 was constructed. Like the

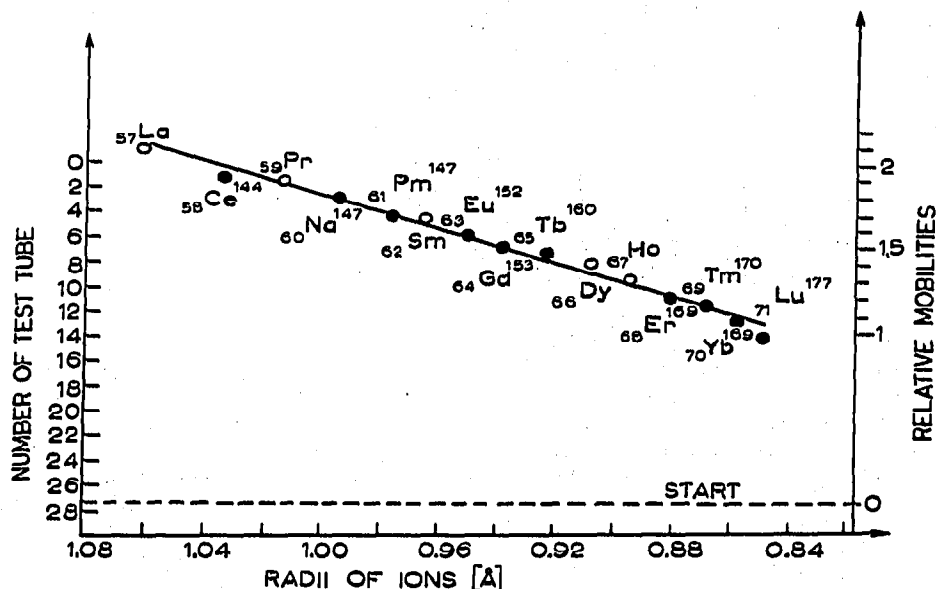


Fig. 3. Plot of ionic radii of rare earths *vs.* their relative electrophoretic mobilities in 0.05 *M* lactic acid. The values of the ionic radii were taken from SEABORG<sup>6</sup>. ● = radioactive rare earths; ○ = inactive rare earths.

previous diagram, this figure shows that a straight line relationship exists between the radii of ions of rare earths and their cathodic electrophoretic mobilities. From the experimental results presented here, it is obvious that the cathodic electrophoretic mobilities of the rare earths in 0.05 *M* lactic acid are directly proportional to their ionic radii, respectively indirectly proportional to their atomic numbers.

#### DISCUSSION

In 0.05 *M* lactic acid it was not possible to separate rare earth mixtures containing more than five components, even with an apparatus that was considerably enlarged in the horizontal direction<sup>2</sup>. Nevertheless, in order to obtain relative mobilities by the continuous electrophoretic method for as many as 15 rare earths in successive experiments, it was necessary to maintain the experimental conditions as constant as possible from experiment to experiment.

With a given voltage drop at the electrodes it is essential that the electric current remain constant from experiment to experiment, because this seems to be the most convenient indication of the constancy of the temperature in the filter paper curtain and of evaporation and consequently of the constancy of the vertical speed of the background electrolyte, provided the filter paper curtain is not changed during the whole set of experiments. The variation of the vertical speed of flow of the back-

ground electrolyte from sheet to sheet of filter paper, even if these were of the same quality and of the same batch, appeared in our experiments to be too considerable to give comparable results in successive experiments.

We tried to ascertain relative electrophoretic mobilities of rare earths using continuous electrophoresis in a moist chamber with a membrane blocking the continuously rinsed vertical electrodes, despite the fact that the paths travelled by the substances in this technique show smaller or greater curvatures in the sense of an apparent acceleration depending on experimental conditions<sup>4,5</sup>. Because of the relatively great electrophoretic mobilities of the rare earths in 0.05 *M* lactic acid, the small conductivity of the background electrolyte, the relatively small electric field strength used, and a relatively great vertical speed of flow of the background electrolyte, the paths travelled were very close to straight lines<sup>1,2</sup>. In this particular case the relative distances travelled in the horizontal direction are directly proportional to the relative electrophoretic mobilities.

In our experiments the use of radioactive rare earths proved very useful because it enabled us to work with very dilute solutions, which give minimum distortion of the electric field strength in the area of the travelling spot and allowed relatively accurate estimations of the peaks of the distribution curves determined in the collecting glasses. In a few cases, where radioactive rare earths were unsuitable because of their short half lives, the width of the bands in the collecting glasses could only be estimated; in these cases it was assumed that the peaks of the distribution curves were in the middle of the respective bands.

Although the experiments described here were actually carried out discontinuously in successive runs in intervals of 2 h, every rare earth solution being pumped separately onto the starting point of the curtain during 10 min, the results correspond to continuous runs. The angles of inclination of the paths travelled are, according to the theory<sup>3,5</sup>, only a function of the mobilities, if the electric field strength and the vertical speed of the background electrolyte are constant. The quantity of the material which drips out of the apparatus corresponds in this particular case to only a 10 min continuous run, but the time between input and output of the substance depends on the vertical speed of the background electrolyte and on the sorbability of the curtain for the particular substance under given experimental conditions.

Our results show that in the direction of increasing atomic number, or decreasing ionic radius respectively, the cathodic mobility decreases linearly. This decrease of the cathodic mobility indicates that the capacity of the rare earths to form complexes with lactic acid increases.

This result seems to be in accordance with various reports in the literature concerning other complexes and different techniques.

LEDERER<sup>7</sup> reported on one-dimensional electrochromatographic experiments with all the rare earths using 1% citric acid as electrolyte. He obtained the same sequence of rare earths but no linearity. SHVEDOV AND STEPANOV described some continuous electrophoretic separations of mixtures of some rare earths that appear among fission products. From their results it is obvious that the sequences, so far reported, both in citric acid<sup>8</sup> and in trilon B<sup>9,10</sup> are in accordance with our results. The same refers to ion exchange using as eluent lactic acid or lactates<sup>11-14</sup>, citrate<sup>11</sup> or EDTA<sup>11</sup> solutions, and to extraction of nitrates with tributyl phosphate<sup>15</sup>, or extraction of acetylacetonates with acetylacetone<sup>16</sup>.

## SUMMARY

Using continuous electrophoresis the relative mobilities of rare earths in 0.05 *M* lactic acid were estimated. Within the series of rare earths with atomic numbers ranging from 57 to 71 a relationship was found between the cathodic mobilities of these rare earths and their atomic numbers, or their ionic radii respectively. This relationship is presented in diagrams which give straight lines. In the direction of increasing atomic number, or decreasing ionic radius respectively, the cathodic mobility decreases, indicating that the capacity of these rare earths to form complexes with lactic acid increases. At the same time information about the continuous electrophoretic separability of rare earth mixtures in 0.05 *M* lactic acid for preparative purposes is given. Various problems concerning the determination of relative mobilities using the continuous electrophoretic method are discussed in detail.

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