

CONTINUOUS ELECTROPHORETIC SEPARATIONS OF  
RADIOACTIVE RARE EARTH MIXTURESI. SEPARATION OF  $^{144}\text{Ce}$ - $^{160}\text{Tb}$ - $^{170}\text{Tm}$  AND  $^{144}\text{Ce}$ - $^{152}\text{Eu}$ - $^{169}\text{Yb}$   
IN 0.05 M LACTIC ACID

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## INTRODUCTION

The continuous electrophoretic separations of mixtures of radioactive inorganic ions were first described by STRAIN *et al.*<sup>1-3</sup>. They successfully separated mixtures such as  $^{45}\text{Ca}$ - $^{32}\text{PO}_4^{3-}$  in 0.1 M lactic acid or 0.1 M acetic acid<sup>1</sup>, which served as basic electrolytes,  $^{90}\text{Sr}$ - $^{90}\text{Y}$  in 0.1 M lactic acid<sup>2</sup>,  $^{90}\text{Sr}$ - $^{90}\text{Y}$ - $^{32}\text{PO}_4^{3-}$ ,  $^{45}\text{Ca}$ - $^{90}\text{Y}$ - $^{32}\text{PO}_4^{3-}$ ,  $^{90}\text{Sr}$ - $^{90}\text{Y}$ - $^{144}\text{Ce}$ - $^{32}\text{PO}_4^{3-}$ ,  $^{137}\text{Cs}$ - $^{90}\text{Sr}$ - $^{90}\text{Y}$ - $^{60}\text{Co}$ - $^{32}\text{PO}_4^{3-}$ , and  $^{137}\text{Cs}$ - $^{90}\text{Sr}$ - $^{90}\text{Y}$ - $^{233}\text{U}$ - $^{95}\text{Zr}$ - $^{95}\text{Nb}$  also in 0.1 M lactic acid<sup>3</sup>. A continuous electrophoretic separation of radioactive Ac from inactive La has been published by LEDERER<sup>4</sup>.

In the present series, the continuous electrophoretic separations of radioactive rare earth mixtures on filter paper are described. Filter paper serves as a supporting and anticonvection medium, and at the same time shows the properties of an adsorptive capillary system. Considering the differences that exist between the continuous and discontinuous separation process occurring on an adsorptive supporting medium, which have been discussed in detail earlier<sup>5,6</sup>, the parallel treatment of the discontinuous or two-dimensional electrochromatographic separations will be considered in the present paper.

## EXPERIMENTAL

The apparatus used for continuous electrophoresis and for the discontinuous two-dimensional electrochromatography was described earlier<sup>5</sup>. The electrodes, consisting of Pt wires, are placed along the sides of a filter paper curtain, and are rinsed continuously with a solution of the basic electrolyte. The filter paper curtain is stretched freely between the two electrode channels in the wet chamber without cooling. Thus our apparatus represents a modification of GRASSMANN AND HANNIG'S apparatus<sup>7</sup>. The mixture to be separated is pumped continuously at a controlled rate by means of an electrically driven syringe\*.

\* Manufactured by Bender & Hobein, Munich, Germany.

The experimental conditions for the separations of the two rare earth mixtures, Ce-Tb-Tm and Ce-Eu-Yb, were the same, and so the results can be compared. The rare earths were first dissolved in nitric acid, evaporated to dryness, and then dissolved in 0.05 *M* lactic acid. The basic electrolyte was a 0.05 *M* solution of lactic acid. The filter paper used was Munktell No. 20/250. The distance between the electrode channels, *i.e.* the free width of the filter paper curtain was 300 mm, and the distance between the starting point and the lower edge of the paper, *i.e.* the free height of the curtain was 320 mm. The vertical speed of flow of the basic electrolyte, *i.e.* the time interval between the input and the outlet of the substance to be separated was 2  $\frac{3}{4}$  h.

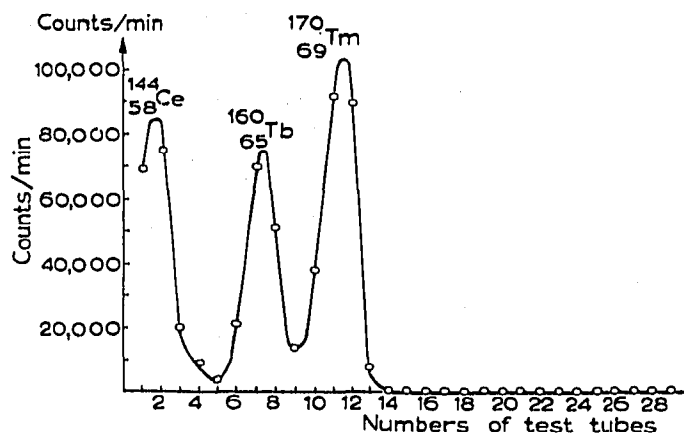
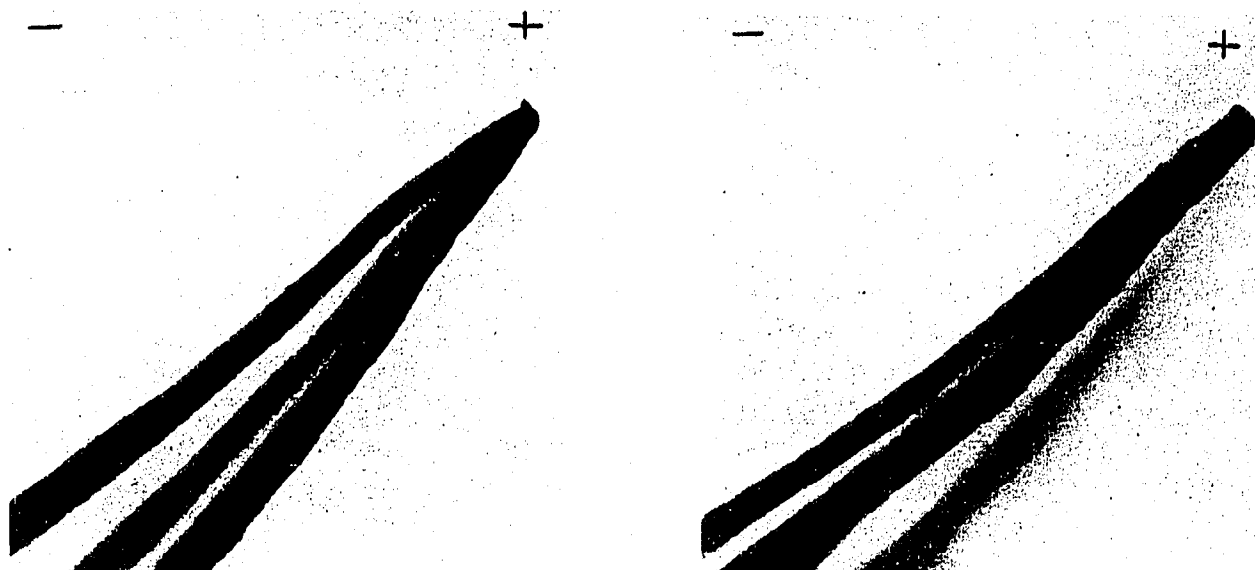


Fig. 1. Radioautograph of the continuous electrophoretic separation of  $^{144}\text{Ce}$ - $^{160}\text{Tb}$ - $^{170}\text{Tm}$ . The diagram below represents the activities of separated rare earths which were detected in the collecting glasses. Collecting time was 0.5 h. Electrolyte, 0.05 *N* lactic acid; paper, Munktell No. 20/250; voltage drop, 300 V; mean electrical field strength, 10 V/cm; current, 19 mA; pumping rate, 0.2 ml/h.

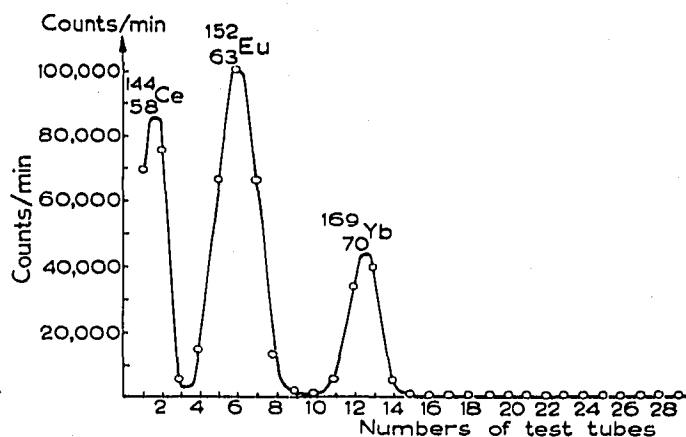


Fig. 2. Radioautograph of the continuous electrophoretic separation of  $^{144}\text{Ce}$ - $^{152}\text{Eu}$ - $^{169}\text{Yb}$ . The diagram below represents the activities of separated rare earths which were detected in the collecting glasses. Collecting time was 0.5 h. Electrolyte, 0.05 *N* lactic acid; paper, Munktell No. 20/250; voltage drop, 300 V; mean electrical field strength, 10 V/cm; current, 19 mA; pumping rate, 0.2 ml/h.

The electrode channels were sealed with a cellophane tape of  $\frac{3}{4}$  in. width, which acted as a membrane<sup>6</sup>. The voltage drop between the electrodes was 300 V, the mean electrical field strength being 10 V/cm, and the current 19 mA. The pumping rate of the rare earth solution was 0.2 ml/h.

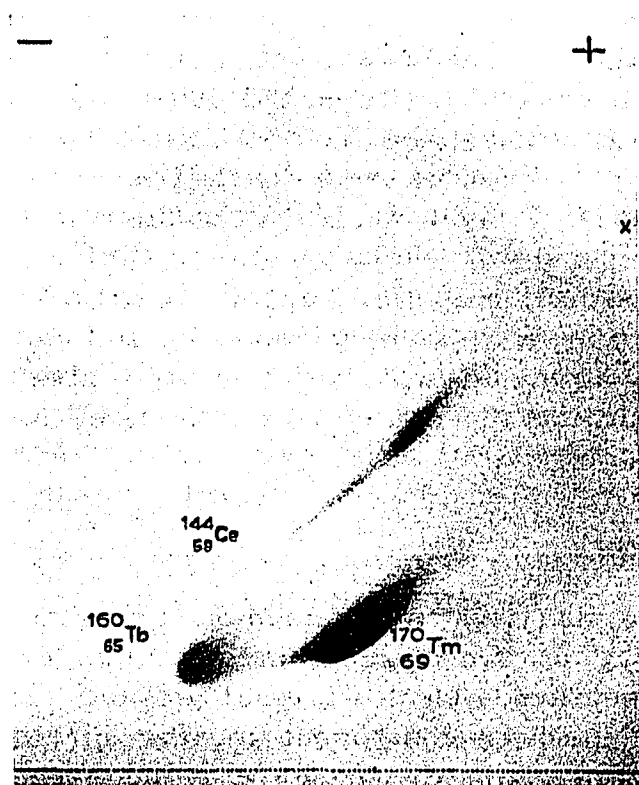


Fig. 3. Radioautograph of the two-dimensional electrochromatographic separation of  $^{144}\text{Ce}$ - $^{160}\text{Tb}$ - $^{170}\text{Tm}$ . Spots with no adsorption on the filter paper would reach the horizontal dotted line during the experiment.

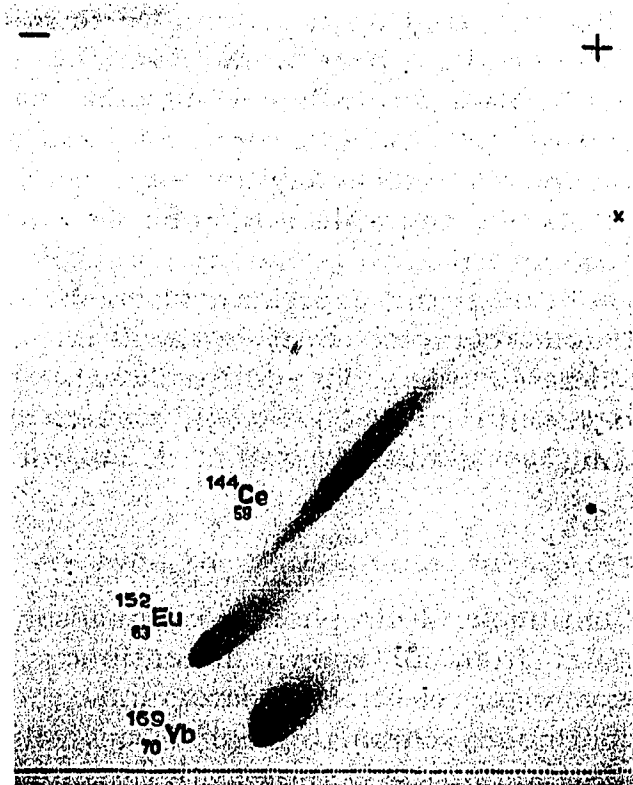


Fig. 4. Radioautograph of the two-dimensional electrochromatographic separation of  $^{144}\text{Ce}$ - $^{152}\text{Eu}$ - $^{169}\text{Yb}$ . Spots with no adsorption on the filter paper would reach the horizontal dotted line during the experiment.

The stationary state of the continuous separation process was reached after 5 h of operation, when all the components of the rare earth mixtures left the apparatus in a steady flow equal to the input pumping rate. A new set of collecting tubes was then introduced for a period of 30 min and the solutions evaporated on aluminium discs under an infrared lamp. The radioactivity of the aluminium discs was then measured by means of a Geiger-Müller counter with a mica window. To prepare the radioautographs, the filter paper curtain was dried in a stream of hot air, laid in a cellophane bag, and then exposed to a "Supervidox"\* X-ray film, 30 × 40 cm for about 16 h.

Figs. 1 and 2 represent radioautographs of the continuous separations of the mixtures  $^{144}\text{Ce}$ - $^{160}\text{Tb}$ - $^{170}\text{Tm}$  and  $^{144}\text{Ce}$ - $^{152}\text{Eu}$ - $^{169}\text{Yb}$  in 0.05 M lactic acid. Below each of the radioautographs there is a diagram showing the activities of the separated rare

\* Manufactured by VEB Fotochemische Werke, Berlin.

earths detected in the dried material from the collecting glasses. These activities correspond to a 0.5 h run, *i.e.* to 0.1 ml of the initial solution of the rare earths used.

The radioautographs of the discontinuous two-dimensional electrochromatographic separations of the two mixtures are represented in Figs. 3 and 4. All the experimental conditions were the same as for the continuous separations, except that only 0.02 ml of the rare earth solution was placed by means of a micropipette at the starting point in the form of a spot. This was done after a steady state of flow of the basic electrolyte and of the electric current had been reached. After a 2.5 h run the filter paper curtain was dried and radioautographed. The horizontal dotted line on the radioautographs represents the speed of flow of the basic electrolyte, *i.e.* all spots with no adsorption on the filter paper ( $R_F = 1$ ) would reach this line during the experiment.

Under the experimental conditions described, only Ce shows a considerable chromatographic effect on the filter paper, having a  $R_F$  factor about 0.60, and considerable tailing. Tb and Eu show a relatively strong adsorption (for Tb  $R_F$  is about 0.78 and for Eu about 0.79), whereas the adsorption of Tm and Yb is very faint (for Tm  $R_F$  is about 0.82 and for Yb about 0.95).

#### DISCUSSION

Continuous electrophoresis on an adsorptive capillary system differs in one important point from all known discontinuous one-way or two-way chromatographic, ion exchange, electrochromatographic, two-dimensional electrochromatographic, or continuous chromatographic separations: the slower component moving in the direction of the electric field, *i.e.* in the direction of the driving force, is in no way contaminated by the reversibly adsorbed fraction of the faster moving component during the continuous electrophoretic separation process. Particles or ions, which show different electrokinetic mobilities, follow separate tracks in the continuous electrophoretic process, and thus absolute separations can be achieved. This is of particular importance when an absolute separation of radioactive ions of high specific activities is desired. Moreover, by the continuous electrophoretic method, carrier-free preparations are possible even from a very dilute solution of a particular ionic species, and even though other ions may be present in considerable concentrations.

Although continuous electrophoresis is primarily considered to be a method for preparative separations, qualitative and quantitative analyses can in principle be readily carried out. This method can be used as an especially convenient analytical tool, in the case of the separation of radionuclides. When the stationary state of the continuous process is once reached, *i.e.* when all the radionuclides to be separated leave the apparatus in a steady flow, a new set of collecting glass tubes should be introduced for a known time. If the pumping rate of the continuously applied test solution is known, radiometric qualitative and quantitative analyses of the radionuclides from the collecting tubes can readily be performed in the usual manner.

A further advantage of continuous electrophoresis used for separating hazardous

radioactive materials lies in the fact that the process can be maintained fully automatically with relatively small expense.

According to the theory<sup>5</sup>, in the two-dimensional electrochromatographic technique the filter paper acts as an adsorptive capillary system. The two-dimensional discontinuous separation is a result of two simultaneous separations acting at right angles: the horizontal or electrochromatographic, and the vertical or chromatographic separation. The characteristics of the two-dimensional electrochromatographic separation process are the following: (1) particles travelling on the same track have identical electrophoretic mobilities; (2) particles travelling on different tracks have different electrophoretic mobilities; (3) particles moving in the vertical direction on the same horizontal front have the same chromatographic properties ( $R_F$ ).

In the discontinuous two-dimensional electrochromatographic process, only those components of a mixture that show identical electrophoretic, and at the same time, identical chromatographic properties are inseparable. In the continuous electrophoretic process, which may, or may not, be carried out in an adsorptive capillary system, all those components of a mixture that have identical electrophoretic mobilities are inseparable. In the continuous electrophoretic process chromatographic properties have no effect upon the separation.

The photographs reproduced in this article were from the photographic laboratory of the Institute Rudjer Bošković.

#### SUMMARY

Radioautographs of the continuous electrophoretic separations and of the two-dimensional electrochromatographic separations of two mixtures,  $^{144}\text{Ce}$ - $^{160}\text{Tb}$ - $^{170}\text{Tm}$  and  $^{144}\text{Ce}$ - $^{152}\text{Eu}$ - $^{169}\text{Yb}$ , in 0.05  $M$  lactic acid are given. Below each radioautograph of the continuous separation, the activities of the separated rare earths are presented in a diagram. These radioactivities detected in the collecting glasses correspond to a 0.5 hour run. From the diagrams of activities and from the radioautographs it is evident that the separation of both rare earth mixtures into components was complete.

The radioautographs of the discontinuous two-dimensional electrochromatographic separations show a relatively strong adsorption of Ce, Tb and Eu on the filter paper. These elements give spots with comet-like tailings.

The usefulness of the continuous electrophoretic separations of radionuclides for preparative carrier-free separations and radiometric qualitative and quantitative analyses is discussed.

#### REFERENCES

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