# THE PAPER ELECTROPHORETIC SEPARATION OF RARE EARTHS USING 1% CITRIC ACID AS ELECTROLYTE

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In a preliminary note[1] we have described the separation of several mixtures of rare earths using 1% citric acid as electrolyte. The study of all the rare earths was not possible at that time because of two technical difficulties: the technique employed (DURRUM technique with paper strips holding one sample only) did not permit the measurement of comparative mobilities, which is important when two ions do not separate, and we did not dispose of a complete collection of rare earth elements.

In spite of these limitations we employed paper electrophoresis to separate the mixture Nd–Pm–Sm[2] and to prepare Ac free from La by a continuous method[3].

Recently we have obtained an apparatus which allows the comparison of the movement of several spots run side by side thus permitting the examination of rare earths which do not move with very different speeds. Also we have been able to obtain a complete collection of rare earth oxides from Johnson, Matthey & Co. (London) varying in purity from 95% to 99%.

This paper is thus a continuation of the studies previously described[1–3]. Relatively few separations of yttrium earths were found possible under the conditions employed.

## TECHNIQUE

The large model paper electrophoresis apparatus of Jouan (Paris) was used holding a paper sheet 25 cm long and 28 cm wide in a horizontal moist chamber. The paper used was No. 302 d'Arches. Sheets of the required dimensions for the apparatus were dipped into 1% citric acid solution, blotted between filter papers and clamped into the apparatus which contained 400 ml of 1% citric acid in each electrode chamber.

300 volt were applied for 3½ hours with a current of initially 6 ma which rose usually to 10–11 ma.

The rare earth oxides were dissolved in 1*N* $HNO_3$ and precipitated with 1*N* $NH_4OH$. The hydroxides were filtered off, washed twice with distilled water and transferred back to the original beaker and dissolved in sufficient 1% citirc acid to produce a clear solution (with warming on the water bath). Under these conditions all rare earths except Ce give colourless solutions. Ce produces a yellow solution.

5 microlitres of the rare earth solution are then placed on the paper which had been mounted in the electrophoresis apparatus beforehand. The spots were placed about 3 cm from the anode end.

After electrophoresis the paper is blotted to remove excess liquid and dipped

*References p. 89.*

into an alcoholic ammoniacal hydroxyquinoline solution. The paper is then viewed both in daylight and ultraviolet light.

To test the uniformity of the migration of spots placed next to each other on the paper, a mixture of La and Y was prepared and five spots placed next to each other allowing 8 cm on each side and 3 cm between the spots. The movement of La after 2 ½ hours with 300 volt was 110, 110, 107, 106 and 105 mm (average 107.6) and that of Y 96, 97, 96, 95, 95 (average 95.8 mm); in both cases the variation being about 2 %–3 % of the total distance.

## RESULTS

To minimise differences due to variations from one sheet to another as many rare earths as possible were placed on the same sheet in mixtures of two or three per spot. On the first sheet used to compare all lanthanum earths the following solutions were run side by side: Pr alone; Eu and Ce; Sm, Nd and La, two spots of each solution being placed on the paper. The distances moved in mm were:

| | |
|---|---|
| La | 137, 138 |
| Ce | 120, 122 |
| Pr | 115, 117 |
| Nd | 112, 113 |
| Sm | 100, 101 |
| Eu | 96, 97 |

The distances measured were those of the centres of the spots; the two values being the distances of duplicate analyses on the same sheet. Fig. 1 shows the size of spots and degree of separation obtained.

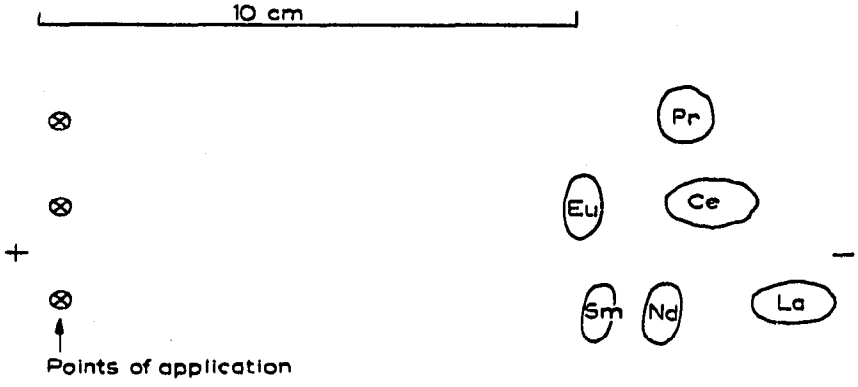


Fig. 1. Movement of lanthanum earths in 1 % citric acid with 300 volts for 3 ½ hours. The following solutions were electrophorised (top to bottom): Pr, Eu–Ce, Sm–Nd–La.

Three spots of the mixture Sm–Nd–La were also run side by side on another sheet and moved as follows:

| | |
|---|---|
| La | 133, 136, 135 |
| Nd | 109, 109, 111 |
| Sm | 100, 99, 101 |

*References p. 89.*

Eu, Gd and Tb were compared on one sheet and moved

| | |
|---|---|
| Eu | 106, 106 mm |
| Gd | 104, 103 |
| Tb | 103 |

For establishing the sequence of the yttrium earths three sheets were run holding mixtures of lower and higher atomic weight earths as well as La as reference. The distances moved varied somewhat from one sheet to another and are given below.

| | | | | | |
|---|---|---|---|---|---|
| (1) La | 161, 162 mm | (2) La | 155, 158 mm | (3) La | 161, 156, 161, 156 mm |
| Gd | 117, 117 | Gd | 118, 120 | Ce | 140, 141 |
| Dy | 114, 113 | Tb | 115, 115 | Y | 122, 125 |
| Ho | 111, 113 | Dy | 117, 116, 113 | | |
| Tm | 106, 105 | Yb | 104, 105 | Er | 110, 112, 109 |
| Lu | 102, 102 | Lu | 106, 105, 102 | Yb | 99, 101 |

Fig. 2 shows the separations obtained on sheet 3.

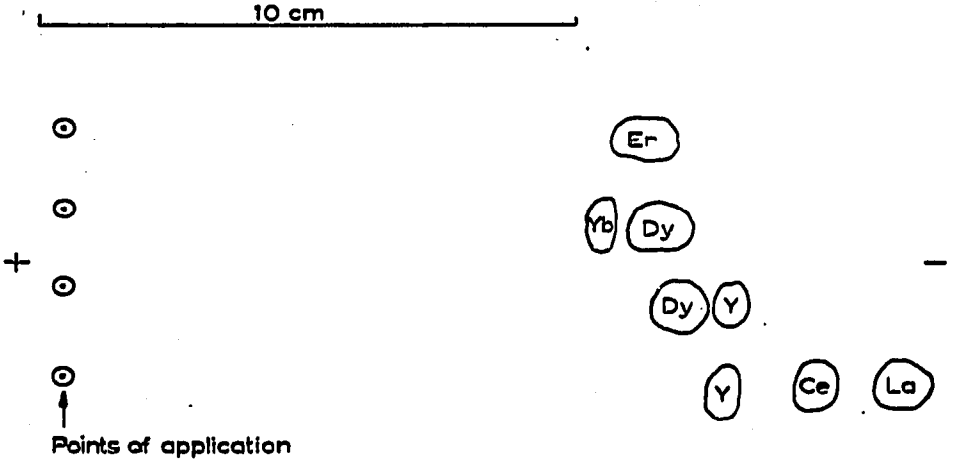


Fig. 2. The movement of some rare earths mixtures in 1 % citric acid with 300 volts for 3½ hours. The following solutions were electrophorised (top to bottom): Er, Dy–Yb, Y–Dy, La–Ce–Y.

La being the fastest moving element shows the greatest variation of mobility from sheet to sheet as, under the conditions used, it moves into a zone in which liquid flow is greater than in the centre region of the electropherogram. In order to

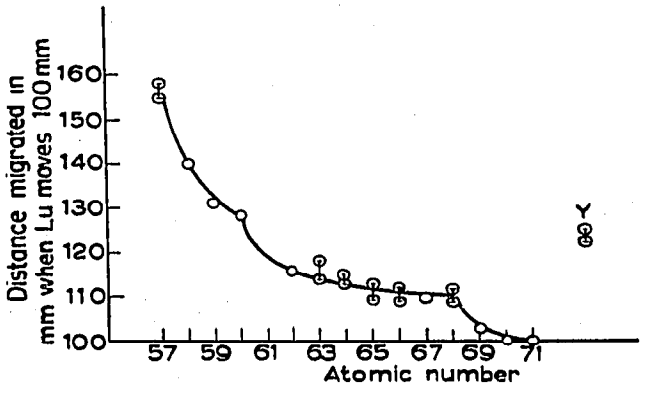


Fig. 3. Relative electrophoretic mobilities plotted against atomic numbers.

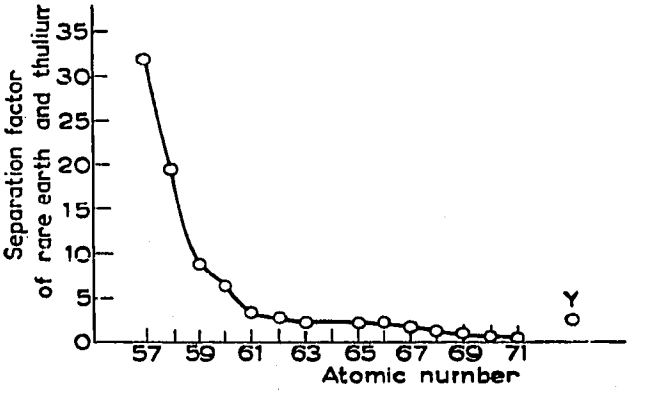


Fig. 4. Ion exchange separation factors (compared with Tm) of a glycolic acid elution. (From STEWART[4].)

*References p. 89.*

compare mobilities from one sheet to another we referred always to the slowest moving rare earth. Lu and Yb move with practically the same speeds and all mobilities were recalculated to a movement of 100 mm for Lu and Yb.

Fig. 3 shows the mobilities plotted against the atomic numbers of the rare earths. Similar relative data exist for ion exchange sequences with glycolic acid elution (STEWART[4]). These are shown in Fig. 4. The agreement between the two seems to be rather good, except for the position of Y which moves much faster than in the ion exchange sequence.

## SUMMARY

All rare earths have been electrophorised in 1% citric acid on paper with 300 volt for 3½ hours. The sequence is similar to that on ion exchange columns. Few separations of yttrium earths were recorded.

## REFERENCES

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[2] H. LANGEVIN-JOLIOT AND M. LEDERER, *J. Phys. Radium*, 17 (1956) 497.
[3] M. LEDERER, *Anal. Chim. Acta*, 11 (1954) 145.
[4] D. C. STEWART, *Peaceful Uses of Atomic Energy Conference (Geneva 1955)*, Vol. VII, p. 373.

Received March 30th, 1957