

Electrophoretic separation of some actinide and lanthanide elements*

Up to now, the data on the electrophoretic separation of lanthanide elements is rather scarce^{1,2}. Therefore we have studied the potentialities of this method for separation between actinide and lanthanide elements. The study of the actinide elements was restricted to americium and curium, since, of the transplutonium elements, these two are the most difficult to separate by ion exchange techniques.

Experimental

The electrophoresis apparatus was obtained from the Locarte company³. In this apparatus, 2 cm wide strips of Whatman 3 MM paper are sandwiched between two polished aluminium plates, 78 cm long. To provide electrical insulation, polythene sheets are placed between the paper strips and the metal plates. The metal plates are pressed together with a pressure of 6 p.s.i. and are cooled by the circulation of water through the plates. In our set-up the circulating water is cooled by a separate refrigerator. The ends of the paper strips are tapered to form wicks and dip in the electrode cells. A voltage, up to a maximum of 10,000 V, can be applied over the paper strips.

In our experiments, all the elements studied were radioactive and were used in tracer concentration. They were americium-241, curium-244, cerium-144, europium-152 + 154, gadolinium-153, terbium-160 and thulium-170. The β - and γ -emitting lanthanides were measured with a Geiger-Müller tube or with a NaI(Tl)-crystal. The α - and γ -emitting actinides were counted with a proportional counter or a scintillation counter. In many cases a 400-channel γ -ray spectrometer was used to check the separation.

After completion of the electrophoresis, the paper strips were cut into sections of 0.5 cm, which were counted for relative activities with the appropriate counter. Reproducibility of the measurements was quite satisfactory.

Various complexing agents in different concentrations were used in the experiments. In addition the solutions usually contained a buffer substance for stabilizing the acidity of the solution.

Results

α -Hydroxyisobutyric acid as a complexing agent. As this acid has often been used as a complexing agent in the separation of the lanthanides or the transplutonium elements on cation-exchange columns⁴, it was also used in our first electrophoresis experiments. For these experiments we chose americium and europium, since these two elements occupy corresponding places in the actinide and lanthanide series, respectively.

The best separation was obtained at pH = 3.2 using a concentration of 0.05 M of the complexing agent (0.046 M of the acid and 0.004 M of its ammonium salt; no other buffer was added to the solution). The voltage over the paper strip was 9 kV, current 6 mA, and was applied for 1, 2, 3 and 4 h, respectively.

The results are given in Table I, which lists the relative concentrations of the radioactive tracers in each section of paper in counts per minute. Both elements move

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TABLE I

MIGRATION DISTANCES OF AMERICIUM AND EUROPIUM IN 0.046 *M* α -HYDROXYISOBUTYRIC ACID AND 0.004 *M* OF ITS AMMONIUM SALT (pH = 3.2) AT 1, 2, 3 AND 4 HOURS, RESPECTIVELY

Voltage 9 kV; current 6 mA. The concentrations are given in counts/min of the radioactive tracers.

Migration distance $\times 0.5$ cm	1 h		2 h		3 h		4 h	
	Am	Eu	Am	Eu	Am	Eu	Am	Eu
1	—	—	—	—	—	—	—	—
2	30	—	—	—	—	—	—	—
3	82	—	—	—	—	—	—	—
4	349	78	—	—	—	—	—	—
5	649	92	59	—	—	—	—	—
6	72	257	113	—	—	—	—	—
7	—	356	116	—	—	—	—	—
8	—	1121	275	—	—	—	—	—
9	—	2096	477	47	—	—	—	—
10	—	188	126	73	150	—	—	—
11	—	—	—	208	181	—	—	—
12	—	—	—	667	372	—	—	—
13	—	—	—	1164	644	—	—	—
14	—	—	—	422	616	—	30	—
15	—	—	—	—	493	—	124	—
16	—	—	—	—	63	—	190	—
17	—	—	—	—	—	—	233	—
18	—	—	—	—	—	—	269	—
19	—	—	—	—	—	—	59	—
20	—	—	—	—	—	126	—	—
21	—	—	—	—	—	82	—	51
22	—	—	—	—	—	111	—	92
23	—	—	—	—	—	169	—	131
24	—	—	—	—	—	340	—	200
25	—	—	—	—	—	572	—	265
26	—	—	—	—	—	695	—	590
27	—	—	—	—	—	948	—	652
28	—	—	—	—	—	1058	—	336
29	—	—	—	—	—	804	—	53

to the cathode, europium somewhat faster than americium, with the result that a complete separation between these two elements is possible.

Experiments were carried out on a mixture of americium and curium and the same complexing agent. No pH value was found, however, where a separation was obtained. But, under the same experimental conditions as those described above, a complete separation between americium or curium and the lanthanides studied was obtained. Fig. 1 shows the results of a 3 h electrophoresis, the applied voltage again being 9 kV, the current amounting to 6–8 mA. The lanthanides move to the cathode faster than americium and curium.

EDTA as a complexing agent. Since no separation between americium and curium could be obtained with α -hydroxyisobutyric acid, we decided to look into the possibilities offered by EDTA (ethylenediaminetetraacetic acid), which was found by FUGER^{5,6} to give, in ion exchange experiments, separations superior to those so far obtained with α -hydroxyisobutyric acid or other organic hydroxy acids.

It did not appear to be possible to perform the separation with EDTA, without adding a buffer to the solution. The reason for this is, that during electrophoresis a

change in the acidity of the solution in the electrode cells occurs which causes an acidity-gradient over the paper strip and, as was found in the experiments to be described here, the behaviour of both americium and curium changes from cationic to anionic in a very small pH range. Therefore the acidity of the solution has to be fixed

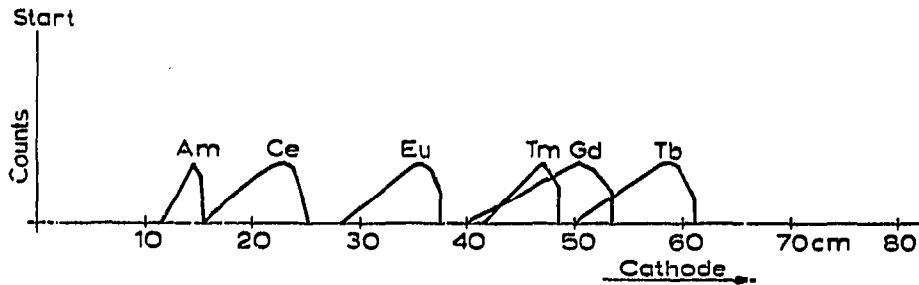


Fig. 1. Electrophoresis of americium and different lanthanides in a 0.05 *M* α -hydroxyisobutyric acid solution, pH 3.2.

very accurately. FUGER, in his ion exchange experiments, found that glycine stabilizes the acidity very well. It has not yet been possible to fix the pH so accurately that either americium or curium is at its iso-electric point and therefore does not migrate in the electrical field.

An 0.001 *M* solution of EDTA was prepared, containing 0.1 *M* glycine. The pH was adjusted to 1.6 by the addition of perchloric acid. A potential of 3000 V was applied over the paper strip (approximately 38 V/cm) for 4 h, causing a current through the paper of 30 mA. Both americium and curium move to the cathode, americium somewhat faster than curium (see Fig. 2). A separation of the peaks of

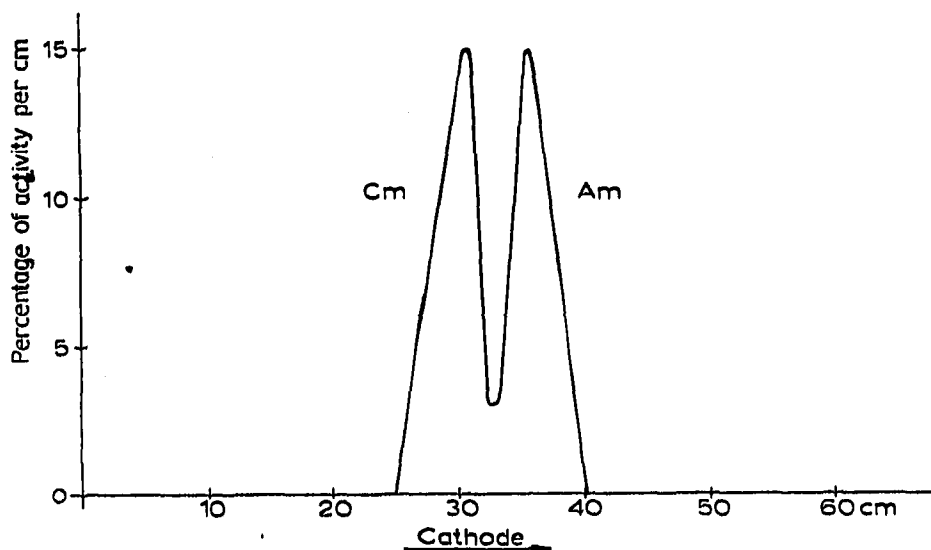


Fig. 2. Electrophoretic separation between americium and curium in a solution containing 0.001 *M* EDTA as complexing agent and 0.1 *M* glycine as buffer. Voltage 3 kV; current 30 mA; duration 4 h, pH = 1.6 obtained by the addition of perchloric acid.

americium and curium is obtained. At higher pH values both americium and curium move to the anode and no separation between the elements is obtained. This begins to occur at pH 1.7.

At pH 1.6 not only is a separation between americium and curium obtained, but also between these elements and the lanthanides studied, as is shown in Fig. 3 (the curium peak is not plotted in this figure, but would be to the left of the americium peak as in Fig. 2). The duration of the electrophoresis was 2.5 h and in this case an

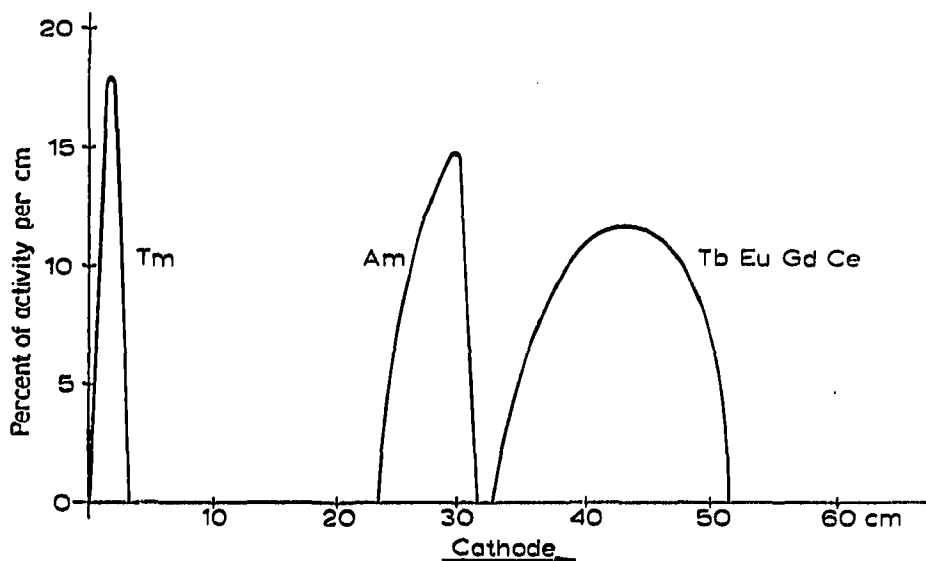


Fig. 3. Electrophoretic separation between americium and different lanthanides. Duration 2.5 h; other conditions as in Fig. 2.

americium fraction was obtained, completely separated from the lanthanides. The same result was also obtained at higher pH values. As an example, Fig. 4 gives the result obtained at pH 9 (after the addition of sodium hydroxide to the solution), where all metal ions present move to the anode. In this last case, the potential applied over the paper was also 3000 V, giving a current through the strip of 4 mA. The duration

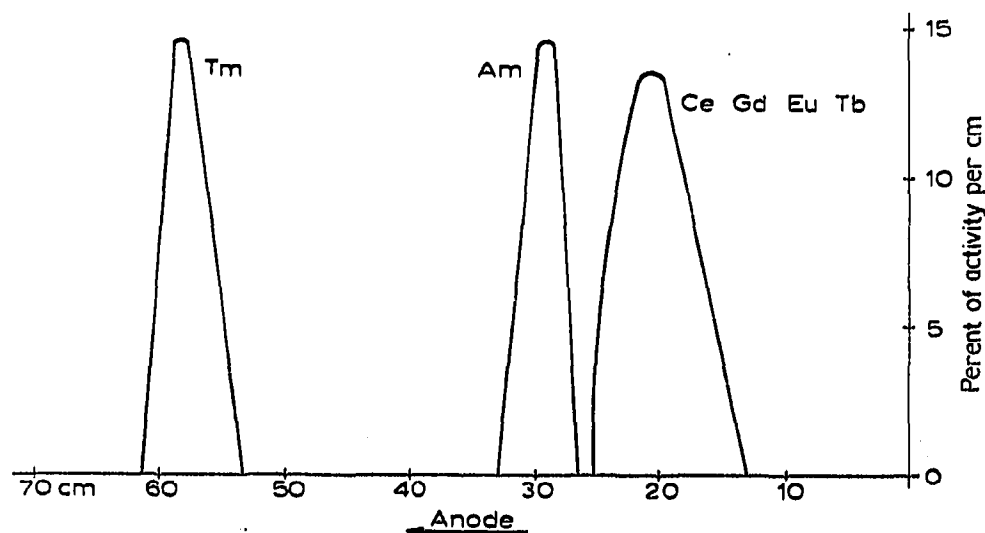


Fig. 4. Electrophoretic separation between americium and different lanthanides. The solution contained 0.001 M EDTA as complexing agent and 0.1 M glycine as buffer. Voltage 3 kV; current 4 mA; duration 2.5 h. pH = 9 obtained by the addition of sodium hydroxide to the solution.

of electrophoresis was 2.5 h. Here, as in the acid solution, americium could be separated from the lanthanides present, the difference being that now the elements move to the anode.

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Reactor Centrum Nederland, Petten (The Netherlands)

W. KRAAK*
G. D. WALS

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* Present address: Institut for Atomenergi, Kjeller, Norway.

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Quantitative analysis of lithium, potassium and caesium chlorides by paper chromatography and flame spectrophotometry

Paper chromatography of alkali metal ions has been the subject of much research involving work on inorganic¹⁻²⁶ as well as organic salts^{7,12,27-32}. We do not, however, consider that a sufficiently simple method, giving separation of the cations in reasonable quantities (*ca.* 6 mg) for their individual determination, has so far been reported in the literature. We have therefore here examined the paper chromatography of lithium, potassium and caesium chlorides, in order to determine the most suitable experimental conditions for quantitative evaluation of the results. This was attained by using two different eluants and applying first the descending method and then the ascending method on the same chromatogram. The first eluant, consisting of butyl alcohol (I), has the advantage of separating lithium alone, while the second eluant, consisting of a mixture of hydrochloric acid, methanol and butanol (II), permits the separation of caesium from potassium. Lithium must be removed first from the chromatogram, as this cation eluted with (II) would contaminate both Cs⁺ and K⁺.

After separation, the cations extracted from the strip are individually determined quantitatively by means of flame spectrophotometry.

In order also to obtain data on the behaviour of sodium and rubidium chlorides, the possibility of separating these two cations by the eluants (I) and (II) was examined. It was observed, however, that Na⁺ in the amounts considered here (10-15 mg) shows

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