Paper electrophoresis of oxine–metal complexes

MICHL[1] has shown that pyridine–acetic acid buffers not only have the advantage that they are volatile and that the increase in pH is constant, but also that separations of Cu^{++} and Cd^{++} are possible if this buffer is used; this is no doubt due to the formation of pyridine complexes of one or both of the metals.

POLLARD *et al.*[2] have used oxine in butanol–acetic acid mixtures for the paper chromatography of cations, notably of rare earths. However, no reference was found as to the possibilities of oxine–acetic acid buffers in the separation of inorganic cations by paper electrophoresis.

As with pyridine–acetic acid mixtures, the pH values increase linearly with the amount of acetic acid added to 1% oxine as shown in Table I.

TABLE I

pH VALUES OF MIXTURES OF OXINE AND ACETIC ACID

pH value	*% Acetic acid*	*% Oxine*
3.1	10	1
3.48	5	1
3.62	3	1
3.8	1	1

No interesting separations of transition elements such as Fe, Cu and Cd could be obtained as these ions precipitate in acetic acid–oxine while, when the pH is decreased by addition of HCl to about 2, they move as non-complexed cations.

The migration of the rare earths was found to be similar to that recorded in 1% citric acid[3]. La moves fastest, followed by the other rare earths approximately in the order of their atomic numbers. However, round spots without comets could only be obtained in the mixture 10% acetic acid–1% oxine. As in citric acid, there are fairly large differences between the mobilities of Nd and Sm, also between the mobilities of gadolinium earths and yttrium earths. In a moist-chamber apparatus (constructed by Jouan, Paris) with a paper length of 23 cm, separations of the following mixtures could be obtained: La–Y–Sc; La–Ce and Nd–Sm (see Fig. 1). The spots are readily revealed by drying the paper and then exposing it to an atmosphere of NH_3 which then yields fluorescent spots as described by POLLARD *et al.*[2]. However, the mixture acetic acid–oxine does not yield migration differences which are better than citric acid[3]; in the case of La–Ce–Pr the separation is even worse.

The variables of one of the successful separations, namely Nd–Sm, were studied in detail with a moist-chamber apparatus, 70 cm in length, using Whatman No. 31 extra thick paper. With 1000 V applied to the electrode vessels the paper burns through. With 750 V evaporation is excessive and the amount of liquid flow from the

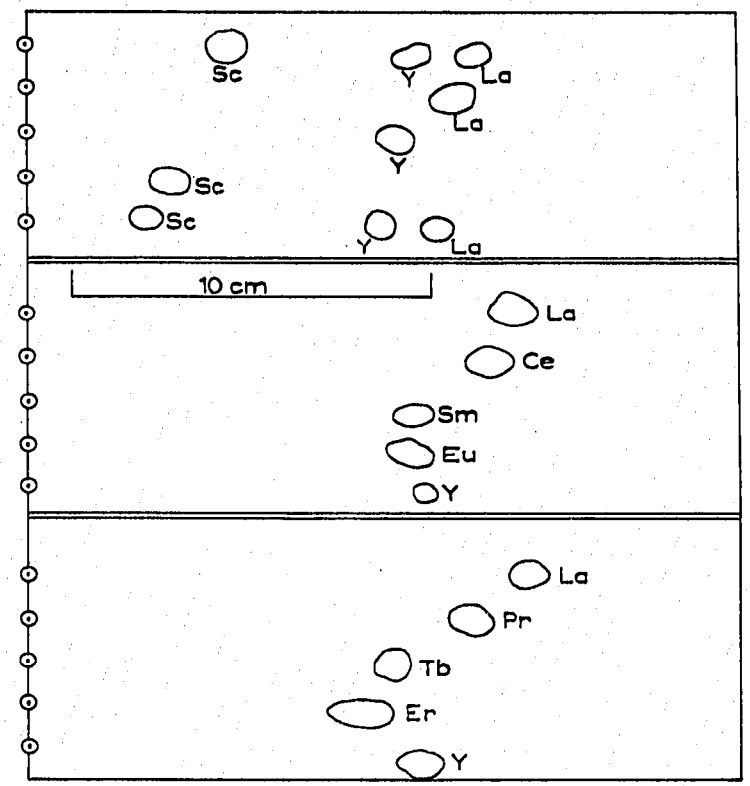

Fig. 1. The paper electropherograms with different pure rare earths and rare earth mixtures are run in the Jouan moist-chamber apparatus with 300 V for 4 ½ h with 10% acetic acid–1% oxine. Points of application are on the left. The movement is cationic. Paper: Arches 304. Three electropherograms, each with five spots are shown.

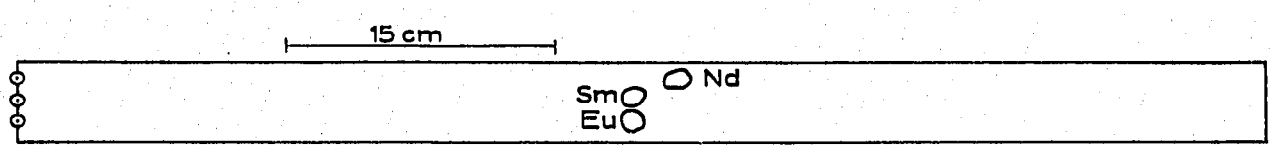

Fig. 2. Migration of spots of Nd, Sm and Eu placed side by side on Whatman No. 31 extra thick paper 70 cm long, and run with 300 V for 25 h.

electrode vessels is so large as to diminish the migration differences. The best separations are obtained with low voltages, 150–450 V and adequate times. Fig. 2 shows the migration of Nd, Sm and Eu with 300 V for 25 hours.

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Received February 25th, 1959