NOTES

The Separation of Lanthanons by Paper Precipitation Chromatography with 8-Quinolinol. II. The Separation and Detection of Lanthanum, Cerium, Praseodymium and Uranium

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It was shown in the preceding paper[1] that the use of an aqueous *n*-butyric acid solution saturated with isobutanol (as a developer) made it possible to obtain rare earth ions on oxine-impregnated filter paper in the form of separated circular bands of precipitates.

In the present study, a modified developer composed of a *n*-butyric acid solution and a water-miscible organic solvent has been applied to the separation of ions from mixtures containing lanthanum, cerium(III), praseodymium and uranyl ions. It has been found that the separation is much improved by the use of the new developer when a small amount of uranyl ions is added to the sample solution.

Experimental

The apparatus, the method of development and the preparation of the sample were essentially the same as have been reported previously,[1] but some changes were made:

1) The distance between the liquid surface of the developer and the oxine-impregnated filter paper was 3.5~4.0 mm. when a container 6 cm. in diameter was used. The width of the strip at the center of the filter paper disk was 3.5~4.0 mm., larger than that of the strip used in the previous study.[1]

2) Oxine (1.000±0.003 g.) in 80 ml. of ethanol was used to impregnate 100 sheets of filter paper (Toyo Filter Paper No. 5B, 9 cm. in diameter). In order to obtain reproducible results, it is essential to keep the oxine content in the filter paper disk as constant as possible.

3) A *n*-butyric acid solution (1~3%) could be used as the developer when a small quantity of uranyl nitrate (ca. 1 mg./ml. as uranium) was added to the sample solution, although the results were not satisfactory because of the low dissolution. *n*-Butyric acid solutions containing various organic solvents were examined and found to be much more useful for the separation of ions.

4) A 2.5% solution of *n*-butyric acid was used as one of the components of the developer. This concentration of the acid is higher than that used in the previous study.[1]

5) After development, the chromatograms were exposed ammonia vapor in order to insure the precipitation of the oxinates. The color of the cerium band thereupon changed from yellow to violet, but most of the cerium which had been coprecipitated together with the other rare earth elements (contaminants of the other rare earth bands) remained unchanged. The distribution of cerium was determined in detail by spraying about a 3 N aqueous solution of potassium chromate.

Development.—Table I shows the results obtained with mixtures in water of organic solvents and 2.5% *n*-butyric acid in various proportions (20±1°C).

There is almost no change in the chromatogram when only a small quantity of the organic solvent (shown by ±) is added. Then the development is gradually improved as the quantity of organic

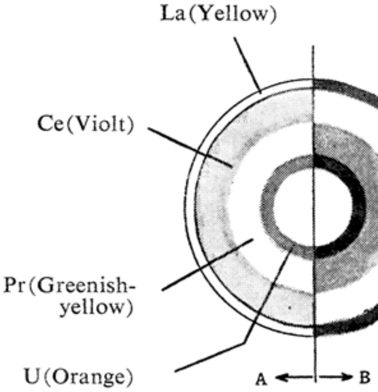

Fig. 1. Chromatogram and its radioautogram.
A. Chromatogram of uranyl and three rare earth element ions.
B. Radioautogram: chromatogram was irradiated with thermal neutrons (ca. 1×10^{11} n/cm^2/sec., 5 hr.) and attached to the photographic plate from 90 till 170 hr. after irradiation.

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[1] H. Nagai, This Bulletin, 33, 715 (1960).

TABLE I.* RESULTS OF DEVELOPMENT WITH VARIOUS SOLVENTS

Volume ratio of the 2.5% *n*-butyric acid solution	300	200	100	60	30	10	5	2	1	1	1
Volume ratio of the organic solvent	1	1	1	1	1	1	1	1	1	2	3
Dioxane				±	+	⧺	⧺	M	S		
n-Propanol		±	+	+	⧺	⧺	M	M	S		
Isopropanol		±	+	⧺	⧻	⧺	M	M	S		
Ethanol	±	+	⧺	+	+	+	+	+	M	M	S
Methanol			±	+	+	⧺	⧺	+	M	S	

* This table is explained below.

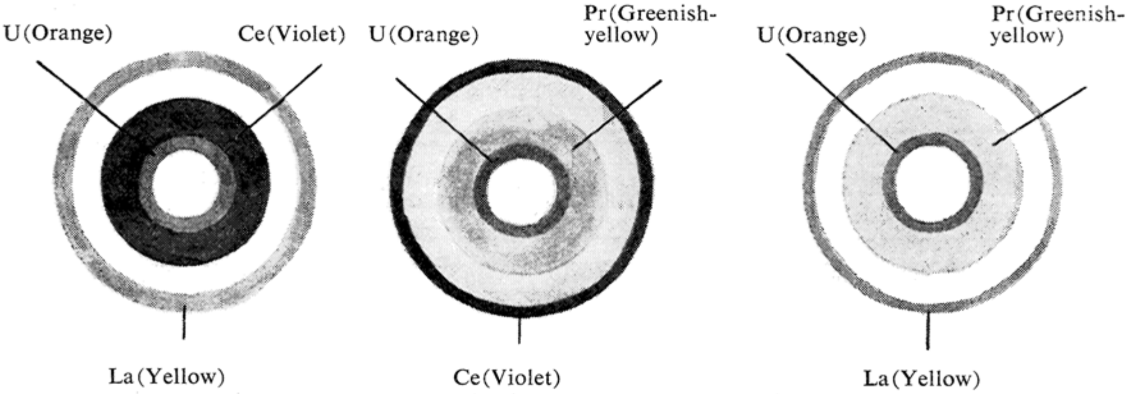

Fig. 2. Chromatograms of ternary mixtures.

solvent is increased (the degree of improvement is indicated by +, ⧺, and ⧻). When the mixing ratio of organic solvent is increased beyond this region, some of the bands begin to dissolve before the completion of the development; the chromatogram obtained is an intermediate one between the precipitation- and soluble-type chromatograms. This region is indicated as M. When the mixing ratio of the organic solvent is increased further, the chromatogram finally comes to be a true soluble type (indicated as S). In the present study, the author does not deal with these regions, M and S.

When a sample solution containing uranyl, praseodymium, cerium and lanthanum ions was developed in precipitation chromatography with a suitable developer, the bands of the components were formed in the order described above counting from the center to the periphery (Fig. 1). Table I shows that a 30 : 1 mixture of 2.5% *n*-butyric acid and isopropanol is the best developer. In this case, however, a considerable amount of the lanthanum ions was retained in the praseodymium and cerium bands. This defect was reduced by adding dioxane to the developer. The best result, in this experiment, was obtained with a developer composed of 2.5% butyric acid, isopropanol and dioxane in a volume ratio of 50 : 4 : 1. It is important to stop the development immediately after the formation of the bands of all the components; thus, in order to obtain satisfactory results, the development is stopped when the uranyl band formed begins to dissolve slightly. The results of the development were as follows.

When all of the four cations were present, the only band which could be obtained in an almost pure state was the uranyl band (the innermost). The lanthanum band (the outermost) was slightly contaminated by cerium. The praseodymium and the cerium bands, between the two bands mentioned above, however, almost entirely overlapped one another, and a considerable quantity of lanthanum was contained in these bands, although the characteristic color of each band could still be observed (praseodymium, a greenish yellow, and cerium, violet).

Better results were obtained with samples containing three kinds of ions, two kinds of rare earth ions and the uranyl ion. The uranyl ion was separated in an almost pure state in all cases, and the separation of praseodymium and cerium, which had been almost impossible before, was possible, though the separation was not satisfactory. Concerning the separation of lanthanum and cerium the lanthanum band was found to be almost pure; the cerium band, however, was contaminated by a considerable quantity of lanthanum. The separation of lanthanum and praseodymium was most satisfactory in these experiments; the amount of lanthanum in the other band was much less than that in the case of the separation of cerium and lanthanum. Figure 2 shows these chromatograms.

Discussion

Optimum Mixing Ratio. — When chromatograms were obtained with a series of organic solvents, with various mixing ratios the area of a band was the largest at the optimum mixing ratio. It might be that the rate of precipitation was the slowest in this solution, as in the case of the other precipitation reactions.

The Estimation of the Separation of Ions.— In order to estimate the degree of the separations, the following methods were employed; observation under day- and ultraviolet-light, a radioautogram, and spraying with a potassium chromate solution. A radioautogram is a very convenient way to find out the distribution of the components (Fig. 1), but several months are necessary to determine the distribution of cerium. The potassium chromate spray can, however, give almost the same results as the long exposure-radioautography does.

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