Separation of Lanthanons by Paper Precipitation Chromatography with 8-Quinolinol. I. Separation and Detection of Lanthanum, Cerium and Praseodymium (Part 1)

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(Received September 30, 1959)

The separation of lanthanons by paper chromatography and its analogous column method was studied by Lederer[1-4] and Pollard et al.[5,6], and the separation was effective to some extent. However, the separation of adjacent elements was very difficult, although a few elements have been separated. The difficulties were principally caused by considerable tailing and the close R_f values of the elements. On the other hand, precipitation chromatography with 8-quinolinol (oxine), which the author has studied[7-12], involved fundamentalf actors to reduce these difficulties. The procedure of precipitation chromatography is as follows. One drop of the test solution is applied at the center of a circular filter paper, previously impregnated with oxine, and developed with an adequate developing solvent. As the developing solvent penetrates into the filter paper, the oxine contained in the filter paper dissolves and reacts with the cations in the test solutions; the phenomenon can be compared with the dropwise addition of the precipitating agent to the test solution in the precipitation titration. Accordingly, from the analogous deduction of the precipitation titration, the cation which forms the most stable metal complex with oxine precipitates at the central part of the filter paper. By the precipitation the reaction product is removed from the reaction system. Therefore the reaction proceeds in such a way as to cause the predominant precipitation of the same kind of complex salt to continue, until the greater part of this cation was consumed. Then the deposition of the next stable complex salt in the test solution follows. Such a course of precipitation prevents the overlapping of the bands corresponding to each cation in the test solution.

In addition to the advantage described above, this chromatographic procedure scarcely ever causes any tailing. This phenomenon is probably due to the following reason: when the test solution is applied on the filter paper, nuclei of the precipitate of the cations are formed and grow smoothly during the entire development. On the other hand, the difficulties caused by the coprecipitation are encountered in this procedure, especially, when the lanthanons are treated. Accordingly, an improved procedure was devised so as to utilize the advantages of precipitation chromatography and to avoid as much as possible the coprecipitation of the elements.

Experimental

Apparatus.—The apparatus used for developing the chromatogram is illustrated in Fig. 1.

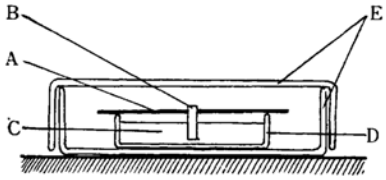

Fig. 1

A is a sheet of filter paper impregnated with oxine, which was prepared as follows. One hundred sheets of circular filter paper 9 cm. in diameter (Toyo filter paper No. 5B) were dipped in an ethanolic solution of oxine containing ca. lg. oxine in 80 ml. of ethanol (95%). After about 10 min. the paper was taken out, and dried in the open air. When the paper was almost dry, it was placed in an electric drier and completely dried. After storage for a few days in a closed vessel, the paper was used for the experiment. B is a narrow strip of untreated filter paper, 1~1.5 mm. in width, inserted in a slit cut at the center of the oxine-treated filter paper where one drop of the test solution, saturated with isobutanol, had been spotted. C is the developing solvent. D is a small Petri dish (the container for the developing solvent). E is a large Petri dish (12~13 cm. in diameter).

Preparation of Test Solutions.—The available

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6) F. H. Pollard, J. F. W. McOmie and H. M. Stevens, ibid., **1954**, 3435.
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8) H. Nagai, ibid., **77**, 1267 (1956).
9) H. Nagai, ibid., **77**, 1794 (1956).
10) H. Nagai, ibid., **78**, 285 (1957).
11) H. Nagai, ibid., **78**, 840 (1957).
12) H. Nagai, ibid., **78**, 1334 (1957).

lanthanon material consisted of lanthanum oxide, praseodymium oxide, and cerous nitrate. Aqueous nitrate solutions were prepared by evaporating to dryness ca. 10 mg. of the required oxide or nitrate with a few drops of 2 N nitric acid, and dissolving the residue in water to produce the test solution containing ca. 10 mg. cation in 1 ml. solution. The following binary mixtures were prepared similarly: La-Ce, La-Pr and Ce-Pr.

Development. — Acetic acid-butanol system has been successfully used in a number of cases as the developing solvent for precipitation chromatography in the separation of many metallic cations, but it seemed to show insufficient separability in the case of lanthanons, though identification of each element in binary systems was possible with some difficulty. The lanthanum-cerium system developed with 0.5% acetic acid (by volume) saturated with isobutanol, and the cerium-praseodymium system developed with ca. 0.01% acetic acid and isobutanol (saturation) gave bare identification of the cations. In the separation of lanthanum and praseodymium, 0.01% acetic acid (saturated with isobutanol) was the most suitable solvent for the identification of praseodymium, while ca. 0.5% acetic acid (saturated with isobutanol) was the most suitable for the identification of lanthanum. The use of a solution more concentrated than 2% acetic acid (saturated with isobutanol) as the developing solvent caused irregular deformation of the chromatogram early in the development and then the bands of the chromatogram completely dissolved; thus the identification of the components of the test solution was scarcely ever possible.

Solution of *n*-butyric acid saturated with isobutanol showed far better results in the separation of lanthanons. Solutions of 0.005, 0.01, 0.05, 0.1, 0.5, 1, 2, 3, 5 and 10% *n*-butyric acid (by volume) saturated with isobutanol were used as developing solvent. The results were as follows. When the test solution was developed with 0.005 or 0.01% solution the innermost band was formed without leaving any blank space at the center of the chromatogram, and the bands showed practically no migration during the development. By the use of the solutions of 0.05 and 0.1% *n*-butyric acid, a blank area appeared at the central portion of the chromatogram, and, although the bands migrated a little on development, the results resembled the foregoing two cases. In the development with more than 1% *n*-butyric acid, the appearance of the bands resembled rather the chromatograms of the perfectly dissolved type than the precipitation chromatogram. When solutions of 1, 2 and 3% were used, the patterns of the chromatograms resembled one another, and the most desirable results were obtained generally in these cases (Fig. 2).

When 5% *n*-butyric acid (saturated with isobutanol) was used, the bands mixed together appreciably. And when 10% *n*-butyric acid (saturated with isobutanol) was used, the confusion of the bands became more marked, but the deformation of the chromatogram, which was observed at a higher concentration of acetic acid, was not observed in the *n*-butyric acid system.

Fig. 2.

The temperature of the developing solvents was 20±1°C. After the development was finished, the chromatogram was subjected to reaction with ammonia vapor so as to stabilize the metal oxinates, and investigated under both visible and ultraviolet light.

Discussion

When the acetic acid system (saturated with isobutanol) was used as the developing solvent, cerium and praseodymium were identified most readily by the use of 0.01% acid. Since the R_f values of cerium and praseodymium hitherto reported have been the same, this can be regarded as an improvement, though their complete separation has met with little success. On the other hand, lanthanum-praseodymium and lanthanum-cerium whose R_f values were reported to be somewhat different from each other (but the real separation was very difficult owing to their considerable tailing), showed rather better separation at a higher concentration of acetic acid (ca. 0.5% acetic acid).

When the *n*-butyric acid system (saturated with isobutanol) was used as the developing solvent, the separation of cations was achieved at a higher concentration than in the case of the acetic acid system. Accordingly, the chromatogram appeared to be somewhat soluble rather than of complete precipitation but a distinct difference was observed from the perfectly dissolved chromatogram. It was far superior to that of the acetic acid system described above.

These phenomena might be explained as follows. Precipitation chromatography inherently possesses the characteristic of exaggerating the separation factor among the cations, but the coprecipitation is apt to compensate for the advantage of the precipitation chromatography, as the author pointed out at the beginning of this paper. One way to minimize the influence of coprecipitation was to increase the acidity of the developing solvent. When the acidity reached a concentration adequate to prevent coprecipitation and to maintain the ability to form complex salts, the best separability could be expected. Even if the complex salts thus formed do not precipitate completely, their diffusion (migration) velocities in the filter paper decrease so markedly by complex formation that they can not migrate together with the developing front where the reaction between the complexing agent and the cation is predominantly taking place. Accordingly, it would be reasonable to say that the reaction product (the complex salt formed) was taken out of the reaction system as in the case of precipitation. Thus, the advantages of precipitation chromatography are still retained while its minor disadvantage, coprecipitation, is avoided.

The author wishes to thank Professor T. Sasaki, Tokyo Metropolitan University, Professor N. Saito, the University of Tokyo, Professor J. Yoshimura, Kyushu University, Professor R. Matuura, Kyushu University, Professor K. Ochiai, Kumamoto University, and Assistant Professor H. Kimizuka, Fukuoka Gakugei University, for their encouragement and numerous suggestions throughout the investigation. Also the author expresses hearty thanks to Professor S. Misumi for the gift of lanthanons. The cost of this research was defrayed from the Scientific Research Fund of the Ministry of Education.

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