The Iodine Reaction of Rare Earth Elements. II.*
Colorimetric Determination of Acetate Ions by the Iodine Reaction of Rare Earth Elements

By Kenjiro KIMURA, Nagao IKEDA and Masayasu NOMURA

(Received June 28, 1952)

It has long been known that basic lanthanum acetate shows a blue color reacting with iodine(1). Krüger and Tschirch(2) applied this color reaction to the detection of acetate or lanthanum ions and reported its relatively high sensitivity. On the other hand, the application of this reaction to the quantitative analysis has long been the problem left to be solved. However, Hutchens and Kass(3) reported in their recent publication that successful results could be obtained on the microdetermination of acetate ions by this reaction.

The present authors(4) already noticed that similar color reactions occur when the basic acetate of praseodymium, neodymium or samarium reacts with iodine under the suitable conditions. In the present paper, they confirmed the method of Hutchens and Kass, then examined the possibility for the application of the corresponding reactions of praseodymium and neodymium to the same purpose.

Experimental

Materials.—The purity of the salts of lanthanum,(5) praseodymium(6) and neodymium(7) used was examined by the X-ray spectroscopic method. These salts are sufficiently pure for the practical use.

Use of Basic Lanthanum Acetate.

1. Development of the Color.—In a 5 ml. glass-stoppered test tube, put 1 ml. of standard solution of acetate ions(8), 1 ml. of lanthanum nitrate solution(9), 1 ml. of 0.1 N ammonia(10) and 1 ml. of 0.02 N iodine-potassium iodide solution. Heat the stoppered tube in boiling water for five minutes(11). By this procedure, the color of the

---

* Previous paper: Kimura and Ikeda, This Bulletin, **21**, 19 (1948).

(1) Damour, *Compt. rend.*, **43**, 976 (1856).

(2) Krüger und Tschirch, *Ber.*, **62**, 2776 (1929).

(3) Hutchens and Kass, *J. Biol. Chem.*, **177**, 571 (1949).

(4) Kimura and Ikeda, This Bulletin, **21**, 19 (1948). They also observed that basic propionate of lanthanum, praseodymium or neodymium also shows a blue color reacting with iodine.

(5) Lanthanum oxide, commercially supplied in Japan, was purified by the Prandtl's fractional precipitation method; cf. Prandtl und Losch, *Z. anorg. allgem. Chem.*, **127**, 209 (1923).

(6) Praseodymium oxide of the Auer-Gesellschaft was used.

(7) Neodymium oxide of the Auer-Gesellschaft was used.

(8) The standard solution was prepared as follows; dissolve 2.226 g. sodium acetate ($CH_3COONa \cdot 3H_2O$) in water and make the total volume 1 l. 1ml. of the solution corresponds to 1.00 mg. CH_3COOH.

(9) 1 ml. of the solution corresponds to 5.0 mg. of lanthanum.

(10) The *p*H value of mixture of 1 ml. of lanthanum nitrate solution and 1 ml. of 0.1 N ammonia is about 8.8. According to Hutchens and Kass, the *p*H value of this mixture must lie between 8.3 and 8.5.

(11) Heating time less than fifteen minutes does not affect the coloration.

solution becomes yellowish green to greenish blue according to the amounts of acetate ions present.

The absorption curve for the solution with color developed as above, measured by the Pulfrich photometer, is shown in Fig. 1. The absorption at 430 mμ(12) evidently results from the light absorption by excess iodine, and the absorption maximum at 610 mμ(13) is attributed to that by the iodine-basic lanthanum acetate compound. For the actual use, however, the authors selected the filter S66 because of its much lower absorption against excess iodine.

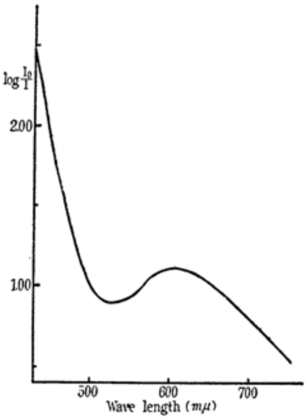

Fig. 1.—Absorption curve for the iodine-basic lanthanum acetate solution.
(0.5 mg. CH_3COOH/4 ml., Cell: 5 mm.)

The color thus obtained is very stable, and shows virtually no change even after 24 hours' standing.

2. Calibration Curve.—The solutions containing various amounts of acetate ions were treated in the way mentioned above, and the relation between the concentration of acetate ions and optical density was investigated. In Fig. 2 data obtained are presented graphically, showing the relation between optical density at 660 mμ and the amounts of acetate ions.

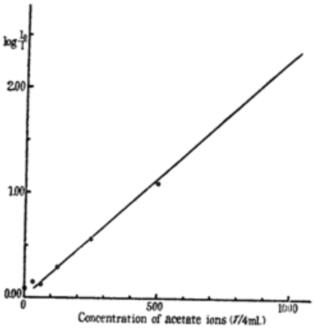

Fig. 2.—Calibration curve for basic lanthanum acetate.
(Filter: S66, Cell: 5 mm.)

As is evident from the figure, the Beer's law is adaptable in the concentration range of acetate ions between 60 γ and 500 γ (as CH_3COOH)(14) per 4 ml., i. e. the total volume of the colored solution. In this concentration range, the colored solution is clear, and the colorimetric determination of acetate ions by the Pulfrich photometer is possible.

When the concentration of acetate ions is smaller than 60 γ per 4 ml., the color caused by iodine reaction of basic lanthanum acetate is no longer observed and the resulting solution partly shows colloidal turbidity(15). The limit of identification for acetate ions by this method is 60 γ per 1 ml. of the original sample solution.

When the concentration is greater than 500 γ per 4 ml., deviations from the Beer's law occur.

3. Effect of Other Ions Present.—As for the effect of other ions present and the method for removing the interfering ions in this procedure, it was already studied in detail by Hutchens and Kass(16), and their methods seem to be valid.

In addition, citrate ions severely interfere with this color reaction.

Use of Basic Praseodymium Acetate.

It has been believed that the color reaction between iodine and basic acetates of rare earth elements is specific to lanthanum. However, Kimura and Ikeda(17) noticed that besides the basic acetate of lanthanum, those of praseodymium, neodymium and samarium take on an intense indigo color when properly treated with iodine. It allows the prediction that in such cases the colorimetric determination of acetate ions might be possible as in the case of lanthanum.

1. Development of the Color.—Although the acetate solution was treated under the same condition as in the case of lanthanum except the use of praseodymium nitrate instead of lanthanum nitrate, no transparent colored solution suitable for the quantitative analysis could be obtained.

Since it was already pointed out in the previous paper that the amount of ammonia used always plays an important role in the iodine reaction of rare earth elements, the authors tried the experiment with various concentrations of acetate ions and ammonia. The concentration of acetate ions should be high and that of ammonia should be low for the present purpose.

1 ml. of standard solution corresponding to 5 mg. acetate(14) was treated with 1 ml. of praseodymium nitrate solution(18), 1 ml. of ammonia of various concentrations and 1 ml. of 0.02 N

---

(12) It corresponds to the absorption of the filter S43.

(13) It corresponds to the absorption of the filter S61.

(14) The amount of acetate ions is represented as γ or mg. CH_3COOH in this paper.

(15) In the blank test, i. e. when no acetate ion is present, the resulting solution also shows colloidal turbidity to some extent.

(16) op. cit.

(17) op. cit.

(18) 1 ml. of the solution corresponds to 11.4 mg. of praseodymium.

iodine-potassium iodide solution in a 5 ml. glass-stoppered test tube. After 15 minutes'(19) heating in boiling water, the color of the resulting solution was observed. The results are listed in Table 1. It is revealed that the use of ammonia of 0.04—0.06 N gives a transparent colored solution suitable for the colorimetric determination. The pH values in this case are much smaller than those in the case of lanthanum.

Table 1

Concentrations of Ammonia (N)	Coloration and Precipitation	pH Values of the Mixed Solution of 1 ml. of Praseodymium Nitrate and 1 ml. of Ammonia
0.02	No coloration or precipitation	—
0.03		6.0
0.04	Transparent green solution	6.3
0.045		6.5
0.05		6.6
0.06		7.0
0.07	Blue precipitation	7.4
0.08		—

2. Calibration Curve.—The solutions containing various amounts of acetate ions were treated in the way mentioned above using 0.045 N ammonia, and the relation between the concentrations of acetate ions and optical density was checked by the Pulfrich photometer. The results are illustrated graphically in Fig. 3 showing optical density at 660 mμ versus the amount of acetate ions.

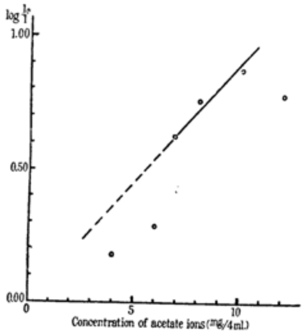

Fig. 3.—Calibration curve for basic praseodymium acetate.
(Filter: S66, Cell: 5mm.)

In the range of concentrations of 5—10 mg. acetate(14) per 4 ml., the transparent, yellowish green—bluish green solution was obtained. Beer's law is approximately adaptable in the range of 7—10 mg. per 4 ml., although the points on the graph are somewhat fluctuating. In smaller concentrations of acetate than 4 mg. per 4 ml., no coloration of the iodine reaction is observed. When it is larger than 10 mg. per 4 ml., blue precipitation occurs, and the colorimetric determination is no longer possible.

As is shown above, the sensitivity of this reaction in the case of praseodymium is much inferior to that in the case of lanthanum. Therefore, lanthanum nitrate should be used for the determination of acetate ions.

Use of Basic Neodymium Acetate.

The use of neodymium salt for the purpose of the determination of acetate ions was then investigated.

1. Development of the Color.—The mixture of 1 ml. of standard solution corresponding to 5 mg. acetate(14), 1 ml. of neodymium nitrate solution(20), 1 ml. of ammonia of various concentrations and 1 ml. of 0.02 N iodine-potassium iodide solution taken in a 5 ml. glass-stoppered test tube was heated in boiling water for ten minutes. Then, the color of the solution was observed. The results are shown in Table 2. The suitable range of concentrations of ammonia is 0.02—0.03 N, and the corresponding pH values are much smaller than those in the case of lanthanum and are almost similar to those in the case of praseodymium.

Table 2

Concentration of Ammonia (N)	Coloration and Precipitation	pH Values of the Mixed Solution of 1 ml. of Neodymium Nitrate and 1 ml. of Ammonia
0.01	No coloration or precipitation	5.7
0.02	Transparent green solution	6.0
0.03		6.4
0.04	Blue precipitation	6.8
0.05		—

2. Calibration Curve.—The solutions containing various amounts of acetate ions were treated in the way mentioned above using 0.02 N ammonia. The relation between the concentrations of

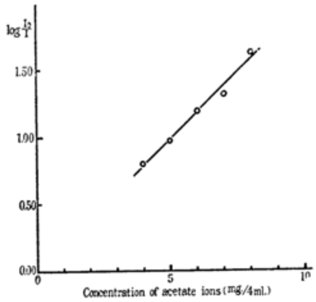

Fig. 4.—Calibration curve for basic neodymium acetate.
(Filter: S66, Cell: 5 mm.)

---

(19) In the case of praseodymium, fifteen minutes' heating is necessary to complete the color reaction, while five minutes' heating is sufficient in the case of lanthanum.

(20) 1 ml. of the solution corresponds to 7.0 mg. of neodymium.

Table 3

	Concentration of Ammonia used	pH Values of the Mixture of Nitrates and Ammonia	Concentration Range Available for the Colorimetric Determination	Limit of Identification
Lanthanum	0.1 N	8.8	60—500 γ/ml.*	60 γ/ml.*
Praseodymium	0.045 N	6.5	7—10 mg./ml.	4 mg./ml.
Neodymium	0.02 N	6.0	4— 8 mg./ml.	4 mg./ml.

* The volume is taken for the original sample solution.

acetate ions and optical density was checked by the Pulfrich photometer. Data are shown graphically in Fig. 4 representing optical density at 660 mμv ersus the amounts of acetate ions. In the concentration range of 4—8 mg.(14), Beer's law is adaptable. At smaller concentrations of acetate ions than 4 mg. per 4 ml., no coloration of the iodine reaction is observed. When it is larger than 8 mg. per 4 ml., blue precipitation occurs and the colorimetric determination is no longer possible.

The sensitivity of this reaction in the case of neodymium is much inferior to that in the case of lanthanum. It rather resembles to that in the case of preseodymium.

Conclusion

It is evident that the color reaction between iodine and the basic acetate of praseodymium or neodymium is applicable to the colorimetric determination of acetate ions as in the case of lanthanum. There are, however, partial differences between each case of them in the suitable concentration of ammonia and the sensitivity of the reaction. These are briefly tabulated in Table 3 for comparison.

The concentration of ammonia and the pH value suitable for quantitative analysis decrease in the order of lanthanum, praseodymium and neodymium, i. e., with the decrease of the basicity of the elements.

As for the sensitivity of the reaction for acetate ions, it is especially good in the case of lanthanum. In the case of praseodymium and neodymium, it resembles each other and are much inferior to that in the case of lanthanum.

Summary

The application of the color reaction between basic lanthanum acetate and iodine to the quantitative analysis has long been the problem left to be solved. Recently, hawever, Hutchens and Kass succeeded in application of this color reaction to the micro-determination of acetate ions with good results.

The present authors examined this method and confirmed that satisfactory results were obtained in its application. In addition, the authors found that the corresponding reactions for praseodymium and neodymium were applicable, too, to the same purpose, although in these cases the sensitivity was not so good as that in the case of lanthanum.

The authors wish to express their hearty thanks to Prof. Kin-ichiro Sakaguchi for his kind suggestions rendered during the course of this work.

Department of Chemistry, Faculty of Science,
Tokyo University and Department of
Agricultural Chemistry, Faculty of
Agriculture, Tokyo University