and reddish brown in dilute solutions. If all these recommended conditions are observed the personal factor, it is believed, will play a very small part toward obtaining reliable and satisfactory results.

Summary.

1. The application of palladious nitrate as an indicator for silver titrations has been tested and found to be satisfactory.
2. The sensitiveness of the indicator is little affected by dilution.
3. The stability of palladious iodide is greater than that of ferric sulfocyanate.
4. Excellent reproducibility and a satisfactory accuracy can easily be obtained for both tenth- and thousandth-normal concentrations of silver nitrate.
5. The use of gum arabic to avoid occlusion of silver nitrate and potassium iodide has given very good results and is to be recommended.
6. The application of palladious nitrate as an indicator apparently overcomes difficulties which arise with the Volhard method in the presence of mercury, palladium and other interfering metallic salts.
7. The errors of the method have been discussed.
8. Finally, the ease and rapidity with which the indicator and also the silver nitrate and potassium iodide solutions can be prepared are advantages.

ROCHESTER, N. Y.

OBSERVATIONS ON THE RARE EARTHS. V. HOLMIUM AND DYSPROSIUM.[1]

BY H. C. KREMERS AND C. W. BALKE.

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CONTENTS.—1. Introduction. 2. Frationation of the Bromates for the Concentration of Holmium and Dysprosium. 3. Fractionation of the Bromates for the Concentration of Holmium. 4. A Study of the Separation of Holmium from Yttrium. 5. Summary.

1. Introduction.

This investigation has had in mind a twofold purpose. The preliminary part of the work has had in view the development of better and more rapid methods of separation of the rare earth elements, since this is the most difficult portion of all rare earth work. Many of the rare earths have never been obtained in a pure state and it is, therefore, highly desirable to obtain methods of separation more nearly quantitative in nature. Accordingly, the yttrium group has been studied with attention directed toward a contentration of dysprosium and holmium and the separation of holmium from yttrium.

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[1] Part of a thesis submitted by H. C. Kremers to the graduate school of the University of Illinois as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

The second object in view in this investigation[1] was to obtain dysprosium material of a high state of purity having in mind a further study of its atomic weight. The dysprosium material used together with the material used in the study of the separation of holmium from yttrium was obtained from a previous investigation.[2] All of the material used was originally obtained from xenotime and gadolinite. These minerals were pulverized to pass a 100-mesh screen and decomposed with hydrochloric acid. The resulting rare earth chlorides were precipitated with oxalic acid and washed to remove the iron and beryllium in the case of the gadolinite. Another oxalate precipitation was usually resorted to remove all of the iron, silicia, etc. Since the most efficient preliminary separation of the yttrium group earths was found to be the bromates,[3] the earths were converted to the bromates as follows: The oxalates were moistened with concd. sulfuric acid and ignited to 400° in order to remove the excess of sulfuric acid. The anhydrous sulfates were then converted to the bromates by double decomposition with barium bromate. With the exception of the earths obtained from the gadolinite this preliminary fractionation had already been carried out before the present investigation was undertaken. The gadolinite material contained some 5 to 10% of cerium group earths.

2. Fractionation of the Bromates for the Concentration of Holmium and Dysprosium.

Some 12 kg. of rare earth oxalates obtained from part of 100 pounds of gadolinite were converted to the bromates as already described. These bromates were run through 50 recrystallizations in 3 parallel series. The 3 series showed a concentration of samarium, neodymium and praseodymium toward the insoluble end, dysprosium and holmium in the central portion and yttrium, erbium and thulium toward the soluble end.

At this point the dysprosium-holmium rich material was removed from each of the 3 parallel series and made into 3 new series which were labeled A, B, and C.

Series A was made up of the more soluble fractions of the material removed from the 3 parallel series, and contained dysprosium, holmium, yttrium and erbium. The concentration of erbium and yttrium was sought in this series.

Series B contained the fractions richest in dysprosium and holmium with small amounts of the less soluble neodymium and praseodymium bromates and the more soluble erbium and yttrium bromates. Dysprosium and holmium were concentrated in this series.

Series C was composed mainly of the less soluble bromates and contained, besides the bromates of dysprosium and holmium, terbium, neodymium

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[1] "Observations on the Rare Earths, VI," to be published later.

[2] Engle and Balke, THIS JOURNAL, **39**, 53 (1917).

[3] James, *Ibid.*, **30**, 979 (1908).

and praseodymium with traces of erbium and yttrium. Praseodymium and neodymium were concentrated in this series.

The 3 series were then fractionated in parallel. The concentration of the earths in the different series was observed and controlled mainly by the change in color although the solutions were frequently examined with the spectroscope. As the dysprosium and holmium bromates became more concentrated toward the less soluble end of series A, these fractions were removed from time to time and placed in series B, uniting them with the fractions which showed a similar color. From series C the more soluble dysprosium and holmium fractions were removed in the same way and added to the fractions in series B which most nearly matched them in color. In the same manner the yttrium and erbium which collected in the soluble end of series B were removed and placed in series A and the neodymium and praseodymium from the less soluble end of series B were added to series C. The 3 series were thus given some 30 recrystallizations which caused most of the dysprosium and holmium together with small amounts of the other earths present to collect in series B. This series was then recrystallized 60 times, several fractions being removed from both the soluble and insoluble ends. The fractions numbering 24 to 38 inclusive indicated the following colors and absorption lines:

Fraction No.	Color.	Absorption.	Earths present.
24	Pink	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
25–28	Flesh	Nd, Pr, Dy, Ho	Nd, Pr, Tb, Dy, Ho, Y
29–30	Yellowish pink	Nd, Pr, Dy, Ho	Nd, Pr, Tb, Dy, Ho, Y
31–32	Cream	Dy, Ho	Dy, Ho, Y
33	Cream	Dy (faint), Ho Er (faint)	Dy, Ho, Er, Y
34–38	Pale pink	Ho, Er	Ho, Er, Y

The equivalents of Fractions 31 and 33 were determined by the permanganate method of Gibbs[1] and gave the values 120.9 and 105.7, respectively. This indicated that Fraction 33 contained some 85% of yttrium. By a comparison of the absorption lines with a set of standard solutions the amounts of dysprosium and erbium in this fraction were estimated to be not more than 2 or 3%. This method was found to be fairly rapid for the concentration of dysprosium and even more satisfactory for holmium. The amount of dysprosium in this series was relatively small.

The sacrifice of material by this method was no greater or even less than in the other ordinary methods of fractionation. By the use of only one series, dysprosium and holmium would concentrate only very slowly, but by the above method the concentration of holmium and dysprosium was found to be more rapid. Considerable trouble was given by the cerium basis bromate[2] which continually separated out as a brown sludge. This

[1] *Am. Chem. J.*, 15, 546 (1893).

[2] James and Pratt, THIS JOURNAL, 33, 1326 (1911).

had to be filtered off from time to time and caused considerable delay in the fractionation. This experience shows that it is advisable to separate the cerium group earths completely from the yttrium group by the double sodium sulfate separation[1] before the bromate fractionation is begun.

3. Fractionation of the Bromates for the Concentration of Holmium.

In the previous investigations in this laboratory, some 12 fractions of holmium-rich material had been obtained from a large bromate series. This material was composed mainly of holmium and yttrium with small amounts of neodymium, praseodymium, terbium dysprosium and erbium. This series was recrystallized 65 times. Neodymium and praseodymium were frequently removed from the insoluble end and erbium and yttrium were removed at intervals from the more soluble end. Fractions 32 to 53 inclusive indicated the following colors and absorption lines:

Fraction No.	Color.	Absorption.	Earths present.
32-35	Yellow with purple tinge	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
36-38	Creamy yellow	Nd, Pr, Dy, Ho	Nd, Pr, Dy, Ho
39-49	Greenish yellow	Dy, Ho, Er	Dy, Ho, Er, Y
49-53	Pale pink	Ho, Er	Ho, Er, Y

This series contained holmium material with yttrium and traces of dysprosium and erbium.

4. A Study of the Separation of Holmium from Yttrium.

By fractionation of the bromates it was found that holmium and yttrium could be obtained free from the other earths. The bromate method was not found to be at all efficient for the separation of holmium from yttrium, and since considerable holmium-yttrium material was at hand it was decided to study methods for the separation of these two elements.

Fractional Precipitation with Lactic Acid.[2]—It was found that if the hydroxides of the rare earths were dissolved in lactic acid with a very small amount of nitric acid present and the resulting solution diluted and warmed on a steam bath for some hours, a very voluminous precipitate separated out, the composition of which was not determined. This behavior suggested a means for the possible separation of holmium from yttrium by fractional precipitation. Accordingly, 90 g. of moist hydroxide of the holmium-yttrium material having an equivalent of 97.5, were dissolved as described above and diluted to 3 liters. By warming this solution gently a portion of the rare earths was precipitated and filtered out. By repeating this process several times the material was split into seven fractions. Fractions 1 and 7 were analyzed and gave equivalents of 97.2 and 94, respectively. This method was accordingly abandoned, since no appreciable separation had taken place.

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[1] Engle and Balke, THIS JOURNAL, **39**, 53 (1917).

[2] Böhm, "Seltene Erden," p. 116.

Fractional Precipitation with Ammonium Carbonate.—This method was first tried by Dennis and Dales[1] on the yttrium group earths as originally obtained from the mineral sources. Some rapid separations were found to take place. These authors dissolved the earth hydroxides in a strong solution of ammonium carbonate and then partially neutralized the resulting solution with acetic acid until the point of precipitation was reached. A very dilute solution of acetic acid was then dropped in with constant stirring until part of the earths had precipitated. This fraction was then filtered off and the resulting solution again treated in a similar manner.

In the hope that this method would prove to be effective in the present problem 50 g. of moist hydroxides of yttrium-holmium material with an equivalent of 98.5 were accordingly dissolved in ammonium carbonate and fractionally precipitated by the above method. A spectroscopic examination of the fractions indicated no appreciable separation. Fraction 7 gave an equivalent of 101.5. It was evident that this method could thus not be successfully applied to the separation of holmium and yttrium.

Fusion of the Nitrates.—The separation of the earths by fusion of the nitrates depends upon the difference in their electropositive characters.[2] Twenty-five grams of the oxides of the holmium-yttrium material were dissolved in nitric acid and the solution evaporated to dryness. This was then fused until partial decomposition had taken place resulting in the formation of basic nitrates of the least electropositive portions of the mixture. After cooling, the fused mass was treated with water which dissolved the undecomposed nitrates but left the basic nitrates as an insoluble residue. The clear solution was then filtered off forming Fraction A. The basic salt, Fraction B, was again dissolved in nitric acid, evaporated to dryness and fused. Fraction A also was evaporated to dryness and fused. The insoluble portion of Fraction B formed Fraction C and the soluble portion of Fraction B was combined with the insoluble portion of Fraction A and the operation repeated.

After a series of 12 fusions the solutions of the different fractions indicated no appreciable separation by a spectroscopic examination.

According to the classification of the rare earths by Levy,[3] europium, gadolinium, samarium and terbium fall in between yttrium and holmium. Since very pure samarium[4] was at hand, it seemed possible that if this element were mixed with the holmium-yttrium material and the three earths fractionated by the nitrate fusion, the samarium would fall between the holmium and yttrium. The samarium could later be removed from the

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[1] This Journal, **24,** 425 (1902).

[2] Urbain, *Ann. chim.*, **19,** Sec. 7, 184 (1900).

[3] S. I. Levy, "The Rare Earths."

[4] Prepared by Mr. A. W. Owens.

holmium by means of the double sodium sulfate separation. Accordingly, 50 g. of samarium oxide were mixed with 25 g. of holmium-yttrium oxides and this mixture subjected to a series of 31 fusions. The original holmium-yttrium oxides had an equivalent of 98.6. The fractions gave the following absorptions and equivalents:

Fraction	*d*,	*e*.	*f*.	*g–j*.	*k*.	*l*,	*m*.	*n*.	*o*.
Absorption...........	Sa	Sa	SaHo	SaHo	SaHo	Ho	Ho	Ho	Ho
Atomic wt............	...	...	..	..	..	154.21	...	154.68	155.32

Most of the yttrium had concentrated toward the end showing the samarium lines. A very rapid concentration of holmium had taken place. This method was found to be the most efficient thus far tried. Work upon the separation of holmium from yttrium is being continued in this laboratory.

5. Summary.

1. The bromate method of fractionating the yttrium group earths for a more rapid concentration of dysprosium and holmium has been studied, and this method was found to be efficient for the concentration of holmium.

2. Some methods for the separation of holmium from yttrium were also studied. The fusion of the nitrates of a mixture of yttrium, holmium and samarium was found to give a very rapid concentration of holmium.

URBANA, ILLINOIS.

OBSERVATIONS ON THE RARE EARTHS. VI. THE PURIFICATION AND ATOMIC WEIGHT OF DYSPROSIUM.[1]

BY H. C. KREMERS, B. S. HOPKINS AND E. W. ENGLE.

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CONTENTS.—1. Introduction. 2. History of Dysprosium. 3. Fractionation of the Bromates for the Purification of Dysprosium. 4. Fractionation of the Ethyl Sulfates for the Purification of Dysprosium. 5. Preparation of Reagents Used in the Atomic-Weight Determinations. 6. Preparation of Dysprosium Oxide. 7. The Ratio of Dysprosium Sulfate to Dysprosium Oxide. 8. The Ratio of Dysprosium Oxide to Dysprosium Chloride. 9. The Ratio of Dysprosium Chloride to Silver. 10. Summary.

1. Introduction.

The object of the work described in this paper was to further purify dysprosium material already in a high state of purity. This purification was preliminary to a later object, namely, a further study of the atomic weight of dysprosium by the the use of the oxide-chloride ratio as used by Engle and Balke[2] and by a comparative study of this ratio with other ratios.

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[1] Part of a thesis submitted by H. C. Kremers to the Graduate School of the University of Illinois as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] THIS JOURNAL, 39, 53 (1917).