## Summary.

1. Only one yttrium sodium sulfate exists at 25°.

2. There is a great tendency for the solution to remain in a metastable condition for many months.

3. The efficacy of sodium sulfate for the separation of the cerium and yttrium earths depends upon the concentration. If the solution be too concentrated the yttrium earths will be precipitated to a very great extent.

DURHAM, N. H., February 8, 1913.

---

# SOME QUANTITATIVE SEPARATIONS OF NEODYMIUM.

BY T. O. SMITH AND C. JAMES.

Received March 7, 1913.

During the separation of the crude rare earths as oxalates from acid solutions of minerals, it has been observed that varying amounts of other elements, such as titanium, uranium, etc., accompany the precipitate. It, therefore, seemed advisable to study this matter from the quantitative standpoint. Neodymium was chosen, because it so happened that plenty of pure material was at hand; and also, because of its position in the series, it would seem to give results that would be in accord with the other members of the group.

A standard neodymium chloride solution was prepared from the pure oxalate in the following manner: The oxalate was ignited to the oxide, $Nd_2O_3$, in a weighed platinum dish and the exact weight of the oxide found. It was then carefully dissolved in a slight excess of hydrochloric acid and the excess of the latter removed by gentle evaporation to dryness. The salt so obtained was dissolved in water, diluted to a known volume and the strength of the solution calculated.

This standard solution was then further checked by measuring out 50 cc., diluting, heating to boiling, and precipitating with oxalic acid. The precipitated oxalate was allowed to stand an hour, washed with cold water, dried and ignited to the oxide. This showed that the solution contained 0.002876 gram $Nd_2O_3$ per cc. It was found to check perfectly with the calculated result. A standard neodymium chloride solution might therefore be prepared by simply dissolving a known weight of the oxide in the required amount of hydrochloric acid and diluting to the desired volume.

## Separation of Titanium.

To prepare a standard titanium solution, dry titanium dioxide was treated with hot sulfuric acid, forming basic titanium sulfate, $(TiO)SO_4$. Any considerable excess of acid was evaporated off. The granular white mass of basic sulfate was put into solution by repeated decantations with dilute sulfuric acid. The final solution contained about 4 cc. of concentrated sulfuric acid per liter. This amount of acid, however, was not sufficient to hold the titanium in solution for a very great length of time. The solution was standardized by precipitating with ammonia and weighing as titanium dioxide. It was found to contain 0.003174 gram $TiO_2$ per cc.

To effect the separation, the standard solutions of neodymium chloride and basic titanium sulfate were poured with stirring into a boiling oxalic acid solution. At first a voluminous precipitate was formed which soon became granular upon digesting at about 100° with occasional stirring. The granular precipitate filtered well and was thoroughly washed with a cold, 5% oxalic acid solution and finally with water.

The data follow:

| No. of sample. | Gram $TiO_2$ taken. | Gram $Nd_2O_3$ taken. | Gram $Nd_2O_3$ found. |
|---|---|---|---|
| 1 | 0.1587 | 0.1438 | 0.1437 |
| 2 | 0.1587 | 0.1438 | 0.1437 |
| 3 | 0.07935 | 0.1438 | 0.1432 |
| 4 | 0.1587 | 0.1438 | 0.1416 |
| 5 | 0.23805 | 0.1438 | 0.1437 |
| 6 | 0.1587 | 0.1438 | 0.1438 |
| 7 | 0.1587 | 0.1438 | 0.1438 |
| 8 | 0.07935 | 0.1438 | 0.1439 |
| 9 | 0.1587 | 0.1438 | 0.1437 |
| 10 | 0.23805 | 0.1438 | 0.1407 |

An attempt was made to separate titanium from neodymium by the following procedure: The mixed solutions were precipitated by ammonia and the hydroxides carefully washed with hot water. They were then treated with dilute nitric acid. The solution was evaporated to dryness on the water bath and the free acid driven off in the air bath at 105°. The neodymium was then taken up with hot water while the titanium was left behind. In view of the results obtained, as well as the amount of time and work involved, this method is not to be recommended.

## Separation of Glucinum.

A glucinum nitrate solution was standardized by precipitating the hydroxide with ammonia and igniting to the oxide. It was found to contain 0.003824 gram GlO per cc. The glucinum and neodymium salts were mixed in dilute solution, heated to boiling and the neodymium precipitated by the addition of a slight excess of oxalic acid. The oxalate was washed with cold water and weighed as the oxide.

The data follow:

| No. of sample. | Gram GlO taken. | Gram $Nd_2O_3$ taken. | Gram $Nd_2O_3$ found. |
|---|---|---|---|
| 1 | 0.0956 | 0.1438 | 0.1438 |
| 2 | 0.1912 | 0.1438 | 0.1436 |
| 3 | 0.2868 | 0.1438 | 0.1438 |

## Separation of Uranium.

A standard uranium solution was prepared by the method of precipitating hydrated ammonium uranate from a uranyl solution and igniting to uranoso-uranic oxide. The salt used was uranyl nitrate, $UO_2(NO_3)_2$, and the solution prepared contained 0.001208 gram $U_3O_8$ per cc.

Varying amounts of this solution together with the standard neodymium solution were diluted to 250 cc. and heated to boiling. The neodymium was precipitated by the addition of a slight excess of oxalic acid. The solution was kept hot for about fifteen minutes to allow the voluminous precipitate to become granular. It was then set aside for a half hour, or longer, after which it was filtered, ignited and weighed.

The data follow:

| No. of sample. | Gram $U_3O_8$ taken. | Gram $Nd_2O_3$ taken. | Gram $Nd_2O_3$ found. |
|---|---|---|---|
| 1 | 0.0604 | 0.1438 | 0.1440 |
| 2 | 0.1208 | 0.1438 | 0.1439 |
| 3 | 0.1812 | 0.1438 | 0.1440 |

## Separation of Barium.

A standard barium chloride solution was prepared by the usual method of precipitating and weighing the sulfate. The neodymium was separated as the oxalate as in previous cases and the barium in the filtrate also estimated.

The data follow:

| No. of sample. | Gram $BaSO_4$ taken. | Gram $Nd_2O_3$ taken. | Gram $BaSO_4$ found. | Gram $Nd_2O_3$ found. |
|---|---|---|---|---|
| 1 | 0.0900 | 0.1438 | 0.0900 | 0.1432 |
| 2 | 0.1800 | 0.1438 | 0.1799 | 0.1430 |
| 3 | 0.2700 | 0.1438 | 0.2697 | 0.1433 |

## Separation of Zirconium.

Zirconium oxychloride was dissolved in water to which had been added a few drops of hydrochloric acid to keep it in solution. By precipitating the hydroxide with ammonia and igniting to the oxide this solution was found to contain 0.004156 gram $ZrO_2$ per cc. A measured portion of this solution, together with the neodymium chloride, was diluted to 250 cc. and heated to boiling. Since zirconium oxalate is insoluble in water but is soluble in oxalic acid the precipitant was added in considerable excess. After holding at about 100° for a few minutes it was allowed to stand for some time at ordinary temperature. It was then filtered, washed with 5% oxalic acid and finally with water.

The data follow:

| No. of sample. | Gram $ZrO_2$ taken. | Gram $Nd_2O_3$ taken. | Gram $Nd_2O_3$ found. |
|---|---|---|---|
| 1 | 0.1039 | 0.1438 | 0.1448 |
| 2 | 0.2078 | 0.1438 | 0.1449 |
| 3 | 0.3117 | 0.1438 | 0.1452 |

The above results indicate that a little zirconium is carried down. They could probably be lowered by adding the mixed chlorides to the boiling solution of oxalic acid, since this would prevent the formation of the insoluble zirconium oxalate.

DURHAM, NEW HAMPSHIRE.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ALLEGHENY COLLEGE.]

# A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.

BY RICHARD EDWIN LEE, ROY H. UHLINGER AND FRANK O. AMON.

Received March 13, 1913.

CONTENTS.—Introduction: Outline of Investigation. Part I, Precipitation of Group. Part II, Analysis of Group. Part III, Summary.

## Introduction.

The investigation reported in this paper is a continuation of the work reported in a previous paper[1] in which it was pointed out that "although it is well known that many of the methods which are generally used in qualitative analysis need revision, apparently very little time has been devoted to the systematic study of their relative effectiveness. It would seem, therefore, that any investigation which comprehended a detailed study of qualitative methods with particular reference to their accuracy in detecting small amounts of the elements in the presence of large amounts of any or all of the elements, and for the purpose of developing and formulating more reliable procedures, would be of considerable value to the analytical chemist."

The purpose of this investigation, however, was the experimental survey of only those methods which are most frequently employed in the precipitation and separation of the metals of the zinc group, namely, zinc, manganese, nickel and cobalt.

As in the investigation to which reference has been made, "it was hoped that the result of such an examination would render possible the selection of the best of the proposed methods and enable the formulation of the conditions best adapted to securing the desired end. As the work progressed, however, and larger discrepancies among the recommended procedures than had been anticipated were noted, it became obvious that although some methods ought to be revised, others ought to be rejected and new ones substituted, if possible."

Although an effort has been made to formulate such methods as will enable the analyst to estimate the approximate amount of the elements present, care has been exercised in the selection of the final procedures

---

[1] "A Method for the Qualitative Analysis of the Calcium Group," Richard Edwin Lee and F. L. Mickle, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 1, 257–278; *Chem. Abstr.*, 6, 20, 3240 (1912); *Chem. Ztg.*, 36, 1302 (1912).