Observations on the Rare Earths
OBSERVATIONS ON THE RARE EARTHS

BY

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THESIS

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UNIVERSITY OF ILLINOIS
THE GRADUATE SCHOOL

May 28, 1945.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Harry Cleveland Kremers

ENTITLED OBSERVATIONS ON THE RARE EARTHS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

Clarence W. Balke
In Charge of Major Work

W. A. Bond
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Recommendation concurred in:

Committee on Final Examination
OBSERVATIONS ON THE RARE EARTHS

The primary object in view in all work done upon the rare earths, has been to obtain better methods for their separation. Methods in use at present are laborious and incomplete. For this reason the majority of the rare earths have found very little technical use. Their mineral resources are quite abundant and it is very desirable that more rapid and quantitative methods of separation be obtained. The amount of work done upon the rare earths is quite limited. Very little is known of their properties. Chemical houses can supply very little material and even that is very expensive and impure. The methods of separation in use, are fractional crystallization and fractional precipitation. The former of the two methods is mostly used since it involves less manipulation and small loss of material. The working up of the minerals and residues described in this paper has been done in order to become better acquainted with the properties of the earths and to obtain suitable material for further investigation. Many difficulties have been encountered and some of them overcome by devising proper methods of manipulation. The preparation of the double salts has been done in the hope of obtaining better methods of separation.

THE WORKING UP OF SAMARSKITE

In November 1913 work was begun upon 21 pounds of Samarskite. This mineral was crushed and ground in a disc mill and then placed in a ball mill and ground until it all passed a 100 mesh sieve. The mineral was decomposed by fusion with potassium hydrox-
ide. Three parts of potassium hydroxide to two parts of mineral were taken. The potassium hydroxide was fused to a red heat in four inch iron crucibles. When all the water was expelled, the mineral was stirred in and the charge heated to 800°C. in a muffle furnace.

This fusion left the earths in the form of hydroxides and the tantalum and columbium in the form of tantalates and columbates. The fused mass was heated with water and the potassium tantalates and columbates were dissolved out, the earths remaining as insoluble hydroxides. The water solution was acidified with sulphuric acid precipitating out the tantalum and columbium hydroxides. The latter were washed by decantation, until free from sulphates, dried and bottled. About four kilos were obtained. The water insoluble residue was treated with aqua regia and heated. When the earths were all dissolved, the solution was evaporated to dryness and the silica dehydrated. The earths were again dissolved in 10% hydrochloric acid, filtered and precipitated from this solution by means of oxalic acid. The oxalates were washed until free from chlorides.

The Thorium (Zirconium being absent) was separated by boiling the oxalates with concentrated ammonium oxalate solution. By the addition of hydrochloric acid to the filtrate, the thorium oxalate was again precipitated. The latter was washed free from chlorides, ignited and bottled. About 100 grams of the oxide was obtained.

The remaining oxalates were dissolved in concentrated nitric acid, the excess of acid evaporated off and the earths again precipitated as oxalates, washed and dried. The dried material was moistened with concentrated sulphuric acid until a thick paste was formed and then heated to 400° centigrade in a muffle until all
excess of sulphuric acid was driven off. The resulting anhydrous sulphates were dissolved in ice water and converted to bromates by the barium bromate method. Due to the low solubility of the two reacting substances, the operation was carried out in a 50 liter porcelain evaporating dish, with the aid of heat and continual mechanical stirring. This conversion took about six weeks. Four kilos of yttrium group bromates were obtained and these were fractionated for six weeks. In this short time very little separation had taken place.

WORK DONE ON WELSBACH MATERIAL

The material for this investigation consisted of cerium group residues from a quantity of Welsbach material. A ten-gallon jar of residue, composed of double sodium sulphates, hydroxides, oxides, silica and various residues had been left from former work done on some 400 pounds of double sodium sulphates. This material had been obtained through the courtesy of the Welsbach Company.

The hydroxides and oxides of the earths were dissolved out by means of nitric acid and the acid insoluble residues were boiled with a 50% solution of sodium hydroxide until completely decomposed. The resulting hydroxides were washed by decantation to remove the excess of sodium sulphate and sodium hydroxide, and then dissolved in 30% hydrochloric acid, dehydrated to remove silica, and again taken up with 10% acid. The earths were precipitated as oxalates and washed. To insure the removal of all impurities, the earth was again dissolved in concentrated nitric acid and again precipitated as oxalates and washed completely. The dried oxalates were decomposed with nitric acid and the resulting solution made nearly neutral with ammonium hydroxide. To neutralize the remaining acid, a lump of marble was left in the solution over night.
The cerium was separated as ceric basic nitrate by oxidation with potassium bromate from the neutral nitrate solution. After many attempts, the best method of procedure was found to be as follows:

The neutral nitrate solution was boiled very vigorously in 8 quart granite pails and potassium bromate added from time to time. To keep the solution neutral a few lumps of marble were left in the solution all the time. It was found that the cerium separated best in a rather concentrated solution. In order to maintain the proper concentration, constant water levels were fitted up by supporting over the pails inverted five liter jena flasks, fitted with rubber stoppers and short pieces of combustion tubing. In this way any desired concentration could be maintained very easily. In some instances it required several days of continual boiling to remove the last traces of cerium. The cerium could be removed quantitatively up to about 1%. At this point it was filtered off and washed and the washings added to the next separation. The last portion of cerium that came down contained some earth in it. It was thus also added to the next separation. In all cases the hydrogen peroxide test was used for a qualitative test for cerium. The cerium free earths were precipitated as oxalates, washed, dried and bottled for further investigations.

THE RECOVERY OF OTHER RESIDUES

About fifteen kilos of yttrium group residues in the form of double potassium sulphates and containing about 10% thorium, were also recovered. The sulphates were decomposed by boiling with 50% sodium hydroxide, washed and dissolved in hydrochloric acid. The
earths were precipitated as oxalates, washed and about one kilo of thorium separated out by the ammonium oxalate method described above. The oxalate was then converted to anhydrous sulphates, dissolved in ice water and converted to bromates by the barium bromate method.

DOUBLE SELENATES OF LANTHANUM, NEODYMIUM AND SAMARiUM.

GOLD NEODYMIUM CHLORIDE.

The preparation of Lanthanum and Neodymium material:

The purest lanthanum fraction was taken from a series of double ammonium nitrates. The earth was precipitated by the addition of ammonium hydroxide. The hydroxides were washed free from all dissolved salts by decantation. It was found that considerable magnesium was still present from a former series of double magnesium nitrates. It was found very difficult to remove the last traces of magnesium and only by keeping an excess of ammonium salts in solution and by repeated re-precipitation, could they be removed. The washed hydroxides were finally dissolved in nitric acid, precipitated as oxalates, dried and ignited to the oxides. The neodymium was taken from the best fraction of a double magnesium nitrate series. The same method of purification as described was used and the same difficulty in separating out the magnesium was experienced.

THE PREPARATION OF SELENIC ACID AND THALLIUM SELENATE

Selenic acid was prepared as follows: Selenium was dissolved in nitric acid to form selenious acid, and the selenium re-precipitated by using sulphur dioxide. The resulting selenium was again dissolved in nitric acid and evaporated to dryness. The sel-
enium dioxide obtained was re-sublimed to remove the last traces of impurities. This was dissolved in nitric acid and precipitated as silver selinite and washed. This silver selinite was oxidized to selenic acid and the silver precipitated as silver bromide with bromine. The excess of bromine was driven out of the solution by bubbling air through the solution. The selenic acid was evaporated to about 3.5 normal and its strength roughly determined.

Thallium selenate was prepared thus: Thallium was dissolved in sulphuric acid and the sulphate recrystallized once. Enough barium hydroxide was added to precipitate out all the sulphate as barium sulphate. The slight excess of barium hydroxide was removed by means of carbon dioxide. The resulting thallium hydroxide and carbonate was neutralized with selenic acid, and the salt crystallized out by slow evaporation of the solution.

**THALLIUM SAMARIUM DOUBLE SELENATE**

\[ 5 \text{Tl}_2 \text{SeO}_4 \cdot \text{Sa}_2 (\text{SeO}_4)_3 \cdot 10 \text{H}_2\text{O} \]

Assuming that this complex would unite in equal molecular proportions, the required amount of samarium oxide, to prepare ten grams of the complex, was weighed out and dissolved in a slight excess of selenic acid. An equi-molecular proportion of thallium selenate was added. The double salt precipitated out in a few minutes and upon cooling the solution, some more of the salt came down. This was washed upon a filter, centrifuged and air dried. Upon analysis it was found that the compound had the formula indicated above. The analysis was as follows:

The sample was dissolved by the aid of a little hydrochloric acid and the samarium was precipitated with ammonium hydroxide. The
hydroxide was washed on a filter and weighed as the oxide. The filtrate was boiled to remove the excess of ammonium hydroxide and a little more than the calculated amount of potassium iodide added. The thallium iodide formed was washed on an alundum filter cone, with very dilute potassium iodide, water, alcohol and ether. It was dried at 150°C. and weighed. The filtrate from this precipitation was acidified with hydrochloric acid and evaporated to a small volume. The selenium was quantitatively reduced by the hydriodic acid present in the solution. The selenium was washed on a Gooch crucible, dried at 150°C. and weighed. The following analytical results were obtained:

<table>
<thead>
<tr>
<th>Found</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.61%</td>
<td>55.67%</td>
</tr>
<tr>
<td>9.02</td>
<td>8.23</td>
</tr>
<tr>
<td>31.20</td>
<td>31.17</td>
</tr>
<tr>
<td>5.17</td>
<td>4.93</td>
</tr>
</tbody>
</table>

**THALLIUM NEODYMIUM DOUBLE SELENATE**

5 Tl₂ Se O₄ · Na₂ (Se O₄)₃

This double salt was prepared in the same manner as described under the preparation of the samarium compound. The method of analysis was the same as above and the following analytical results were found:

<table>
<thead>
<tr>
<th>Found</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.88%</td>
<td>8.30%</td>
</tr>
<tr>
<td>32.25</td>
<td>32.97</td>
</tr>
<tr>
<td>58.21</td>
<td>58.73</td>
</tr>
</tbody>
</table>
THALLIUM LANTHANUM DOUBLE SELENATE

5 Tl₂ Se O₄ • La₂ (Se O₄)₃

The preparation and analysis of this compound was carried out as described above. The following data was obtained:

<table>
<thead>
<tr>
<th>Found</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.76%</td>
<td>Tl</td>
</tr>
<tr>
<td>8.09</td>
<td>La</td>
</tr>
<tr>
<td>32.70</td>
<td>Se O₄</td>
</tr>
</tbody>
</table>

It was found that the ratio of the three thallium compounds is 5 to 1, quite different than that expected. In the case of the alkali bases, the ratio is 1 to 1.

GOLD NEODYMIUM DOUBLE CHLORIDE

Au Cl₃ • Nd Cl₃ • 10 H₂O

Solutions of gold chloride and neodymium chloride were united in equi-molecular proportion. The compound was found to be very soluble and was crystallized over sulphuric acid in a vacuum dessicator. The mother liquor was removed in a centrifuge and the crystals air dried. The analysis was as follows: The solution was made alkaline with potassium hydroxide, heated to boiling and some formaldehyde added. The gold was quantitatively precipitated as metallic gold. The gold was digested over night on a steam bath and then made slightly acid to dissolve the neodymium hydroxide, filtered, ignited and weighed. The neodymium was precipitated as the hydroxide, ignited and weighed. Chlorine was determined as silver chloride. Water was determined by difference since the compound decomposed at 115°c. The following data was obtained:
<table>
<thead>
<tr>
<th>Found</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.18% -- Nd</td>
<td>19.64</td>
</tr>
<tr>
<td>26.30 -- Au</td>
<td>26.84</td>
</tr>
<tr>
<td>29.20 -- Cl</td>
<td>28.99</td>
</tr>
<tr>
<td>24.32 -- H₂O</td>
<td>24.53</td>
</tr>
</tbody>
</table>

An attempt was also made to prepare some of the double strychnine selenates of the earths, but upon analysis it was found that no combination had taken place. A possible explanation of the failure seemed to be that the strychnine selenate is too insoluble.

In conclusion, I wish to say that work is under way to prepare the double selenates of all the earths. With a few exceptions, the earths have been separated with a high grade of purity and it is hoped that by preparing the double selenates with various bases, a more rapid method of separation may be obtained.

I wish to take this opportunity to express my thanks to Professor C. W. Balke for his valuable suggestions and patience throughout the progress of this work.