

Several hydrates of the camphorsulfonates appear to exist.

Neodymium 1,3,4-Metaxylenesulfonate, $(C_6H_3(CH_3)_2SO_3)_6Nd_2 \cdot 2H_2O$.—This sulfonate separated out, during the evaporation on a water bath, in crystalline form. It was of a very pale amethyst color, insoluble in acetone, slightly soluble in alcohol and soluble in water.

Calculated: Nd_2O_3 , 22.46. Found: Nd_2O_3 , 22.35.

Neodymium Metasulfobenzoate, $(C_6H_4 \begin{matrix} \diagup SO_3 \\ \diagdown COO \end{matrix})_3Nd_2 \cdot 9H_2O$, formed pale colored crystals soluble in alcohol and acetone, and very soluble in water.

Calculated: Nd_2O_3 , 32.03. Found: Nd_2O_3 , 32.19.

Neodymium Quinate, $(C_6H_7(OH)_4COO)_6Nd_2 \cdot 11H_2O$.—Neodymium hydroxide was boiled with quinic acid; the solution filtered and evaporated. The quinate crystallized out upon cooling. Pale amethyst colored powder, slightly soluble in cold water.

Calculated: Nd_2O_3 , 20.62. Found: Nd_2O_3 , 20.61.

Neodymium Anisate, $(C_6H_4.CH_3O.COO)_6Nd_2$.—This compound was precipitated when a slightly acid solution of sodium anisate was added to a nearly neutral solution of neodymium chloride. Free anisic acid was removed from the precipitate by means of hot acetone. The pale colored precipitate was insoluble in water.

Calculated: Nd_2O_3 , 28.16; H, 3.54; C, 48.19. Found: Nd_2O_3 , 28.17; H, 3.31; C, 48.29.

Neodymium Oxanilate, $(C_6H_5NHOC(=O))_6Nd_2 \cdot 5H_2O$.—When neodymium chloride was added to a hot, slightly acid solution of sodium oxanilate, a thick sticky mass separated, which rapidly became hard and crystalline upon cooling. The compound was insoluble.

Calculated: Nd_2O_3 , 24.70. Found: Nd_2O_3 , 24.69.

Neodymium Cacodylate, $((CH_3)_2AsO_2)_6Nd_2$.—Cacodylic acid was saturated with neodymium hydroxide. The liquid was filtered and evaporated. Upon cooling, the salt separated in very soft asbestos-like crystals. It was insoluble in alcohol and acetone, slightly soluble in cold water, and soluble in hot water.

Calculated: Nd_2O_3 , 30.31. Found: Nd_2O_3 , 30.40.

Neodymium Hydroxyethanesulfonate.—A solution containing this compound would not crystallize, so as to be workable.

DURHAM, NEW HAMPSHIRE.

A NEW METHOD FOR THE SEPARATION OF THORIUM.

By T. O. SMITH AND C. JAMES.

Received January 13, 1912.

While working upon the separation of thorium from the rare earths the authors observed that sebacic acid gave a precipitate in a neutral solution which appeared to be quantitative.

Thorium sebacate is a voluminous, granular precipitate which settles

readily and is easily filtered. Solutions of cerium, lanthanum, yttrium, etc., give no precipitate with sebacic acid even upon boiling.

In order to determine whether or not the above observations were correct, the following work was carried out.

A thorium nitrate solution was prepared, carefully standardized by the oxalic acid and hydrogen peroxide methods, and was found to contain 0.005572 gram of thorium dioxide per cc.

The precipitant was used in the form of a boiling solution practically saturated at that temperature.

Fifty cc. portions of the standard thorium nitrate solution were measured into a 250 cc. beaker and raised to the boiling point. A slight excess of the hot solution of sebacic acid was added slowly with continuous stirring. The precipitate which formed at once was immediately filtered and thoroughly washed with boiling water. The sebacate washes readily and the operation may be performed with ease in a very short time. The precipitate was rapidly dried, ignited and weighed as thorium dioxide:

The following data show a good agreement with the standardization by oxalic acid:

No. of cc. of standard thorium solution.	Grams ThO ₂ precipitated by oxalic acid.	Grams ThO ₂ precipitated by sebacic acid.
50	0.2791	0.2787
50	0.2786	0.2785
50	0.2780	0.2786
50	0.2783	0.2790
50	0.2787	0.2792
50	0.2790	0.2790
	Average, 0.2786	0.2788

The next step was to ascertain the effect of the presence of rare earths upon the thorium precipitate. Accordingly a solution consisting chiefly of cerium, together with fair amounts of lanthanum, praseodymium, neodymium and traces of samarium, gadolinium, etc., was prepared. Varying quantities of this solution which contained 0.005516 gram of the combined oxides per cc. were added to the standard thorium solution. The thorium dioxide was determined as above.

Results are given below:

No. of cc. of standard thorium solution.	Grams of rare earth oxides present.	ThO ₂ present by average of oxalic and sebacic standardization.	ThO ₂ found.
50	0.05516	0.2787	0.2789
50	0.11032	0.2787	0.2786
50	0.16548	0.2787	0.2789
10	0.5516	0.05574	0.0562
10	0.5516	0.05574	0.0565
10	0.5516	0.05574	0.0564

The authors did not test the action of salts such as dysprosium, erbium, thulium, etc., upon the thorium precipitate, as these elements occur only in small amounts in the ordinary thorium minerals.

Separation of Thorium from the Rare Earths.

The reaction between sebacic acid and neutral thorium solutions would appear to be valuable for the separation and purification of thorium materials.

Sebacic acid can probably be prepared more cheaply than the reagents ordinarily used for the more rapid purification of thorium. It is formed when castor-oil soap is heated with sodium hydroxide. It dissolves in 1000 parts of water at 17°, 40 parts per liter at 65° and at the boiling point becomes fairly soluble. Owing to its slight solubility in cold water it can readily be recovered; hence, it could be used in the separation of thorium on a large scale.

Qualitative Tests with Other Acids.

Phenoxyacetic acid, $\text{CH}_2(\text{OC}_6\text{H}_5)\text{COOH}$, precipitated thorium from a neutral solution almost quantitatively. The addition of aniline did not aid in the separation. It was therefore considered that thorium phenoxyacetate was very slightly soluble in water.

The ortho-nitro-phenoxyacetic acid did not give satisfactory results.

Mucic acid, $(\text{CHOH})_4(\text{COOH})_2$, gave a precipitate which filtered slowly and was not quantitative.

Anisic acid, $\text{C}_6\text{H}_4(\text{OCH}_3)\text{COOH}$, only partially precipitated thorium from a neutral solution.

Aspartic acid, $\begin{array}{c} \text{CH}_2\text{CONH}_2 \\ | \\ \text{CH}_2\text{COOH} \end{array}$, when boiled with a neutral solution of thorium nitrate gave a precipitate which could not be separated by filtration.

Pyrotartaric acid, $\begin{array}{c} \text{CH}_3\text{CHCOOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$.—The addition of this acid to a cold neutral solution of thorium nitrate caused no precipitation. However, upon boiling, a curdy precipitate rapidly formed and after filtering no thorium was found in the solution. From the above facts it would seem that pyrotartaric acid could be used for the quantitative determination of thorium.

Since the cost of pyrotartaric acid is considerably greater than that of sebacic acid, and since the former cannot be regained so readily, no further work was done with it.

Oxanilic acid, $\text{C}_6\text{H}_5\text{NHCOCOOH}$, precipitates both the rare earths and thorium from neutral solutions. From slightly acid solutions thorium

only is precipitated. By increasing the concentration of the acid the precipitate redissolves.

All the above acids, with the exception of oxanilic, give no precipitate with the rare earths in cold or hot neutral solutions.

NEW HAMPSHIRE COLLEGE AND EXPERIMENT STATION.
DURHAM, NEW HAMPSHIRE.

NOTES.

A Modification of the Modified Winkler Method for the Determination of Sulphates in Water.—The Modified Winkler Method for the determination of sulphates in water colorimetrically consists in adding to the sample a small amount of barium chromate, acidifying with a few drops of concentrated hydrochloric acid, bringing to a boil, cooling, then adding sodium hydroxide solution (1 : 10) carefully until a tiny drop of the liquid placed upon red litmus paper produces a blue color; a greater excess of alkali must be avoided as the solubility of barium chromate varies greatly with the degree of alkalinity. After filtering, the color is compared in a colorimeter with that of a standard solution of potassium chromate. A correction must be made for the solubility of barium chromate. The SO_4 is equivalent to the CrO_4 found. It is a more or less tedious step in the procedure to neutralize the hydrochloric acid to just the right point. It occurred to the writer to modify the method at this point by changing the acidity from hydrochloric acid to acetic acid by the addition of sodium acetate. This seems to give good results and is easily carried out.

The process as modified is as follows: Measure into an Erlenmeyer flask 150 cc. of the sample. Add 10 drops of concentrated hydrochloric acid and sprinkle in 0.1 to 0.2 g. of pure barium chromate. Rapidly bring the contents of the flask just to a brisk boil. Cool at once and to the cooled liquid add 5 g. of sodium acetate. Filter, transfer 100 cc. of the clear filtrate to a colorimeter cylinder and make alkaline with sodium hydroxide. The standard for comparison should be made slightly stronger than this solution and should be made up to 100 cc. after adding sodium hydroxide to alkaline reaction. A blank determination must be made, using distilled water, to determine the correction to apply for the solubility of the barium chromate under the conditions of the experiment.

It requires but a moment to weigh out the sodium acetate (a close approximation is sufficient). This method gives duplicate results agreeing perfectly within one's ability to read the colors.

The following determinations were made by the method as described.

Different amounts of potassium sulphate were added to separate portions of distilled water and the SO_4 determined.