

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

**SCANDIUM IN AMERICAN WOLFRAMITE.**

BY HIRAM STANHOPE LUKENS.

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The occurrence of scandium in wolframite was first noticed by G. Eberhard.<sup>1</sup> He found the wolframite and tinstone from some places in the mountains of Saxony and Bohemia to contain such quantities of scandium that these minerals might be profitably used as a source of supply. Further, they had an advantage over other sources of this element in that scandium was the only member of the rare earths present in any considerable quantity.

R. J. Meyer<sup>2</sup> confirmed the above observations in his early work on the study of scandium and its compounds. He further observed that after decomposing wolframite by fusion with sodium carbonate and subsequently extracting the mass with water, all of the scandium remained in the insoluble residue. That the scandium did not enter solution in combination with the sodium carbonate as a soluble salt was explained later when it was found "that solutions of scandium salts in soda, when diluted with water and boiled, undergo a hydrolytic decomposition with the complete separation of the carbonate." Accordingly, some wolframite residues from the Zinnwald were examined and found to contain sufficient scandium to make this a productive source of this element. Only certain specimens, however, were found to be worth working up and, in general, those ores which contained large quantities of gangue were not rich in scandium.

The method pursued by Meyer for the recovery of pure scandium oxide from these residues was adopted in this investigation.

The material employed was supplied by Dr. W. R. Whitney, of the General Electric Company. It consisted of residues from American wolframite from Colorado and was of a light buff color. Three and two-tenths kilos were used.

The residues were dissolved in boiling hydrochloric acid, using three liters of concentrated acid for each kilo, the powder being introduced in small quantities. The boiling was continued for 30 minutes. After filtering, the residue was boiled with dilute hydrochloric acid and washed. The combined filtrates were then brought to boiling and 40 grams of solid sodium silicofluoride introduced in small portions, for each kilo of residues treated. Upon boiling for one-half hour longer, all of the scandium separated as scandium fluoride, a "salve-like precipitate." This was then washed with very dilute hydrochloric acid—1 liter of water to 300 cc. of dilute hydrochloric acid. The colorless fluoride, in this case con-

<sup>1</sup> *Sitzungsber. Kgl. Preuss. Akad. Wissensch.*, **38**, 851 (1908).

<sup>2</sup> *Z. anorg. Chem.*, **60**, 134 (1908); *Chem. News*, **99**, 85-97 (1909).

taining some silicic acid from the decomposition of the silicofluoride, was decomposed with strong sulfuric acid, diluted, filtered, and the scandium precipitated as hydroxide with ammonia. This hydroxide was then transposed to chloride by solution in pure dilute hydrochloric acid. The excess of hydrochloric acid was removed by evaporation to dryness on a water bath.

The neutral chloride so obtained was dissolved in a small amount of water and the solution treated with a solution of sodium carbonate, containing 20% of the anhydrous salt. The chloride was equivalent to that which would be obtained from about 1.6 grams of scandium oxide. One hundred and sixty cc. of the carbonate solution were therefore used in order to maintain the concentration of one liter of carbonate solution to each 10 grams of oxide as recommended by Meyer and Winter.<sup>1</sup> At first a white precipitate of scandium carbonate was produced which dissolved, on stirring, to a perfectly clear solution. This solution was then boiled for one-half hour with constant stirring, during which time the scandium was precipitated as carbonate,  $\text{Sc}_2(\text{CO}_3)_3$ , in the form of small white crystals. The solution was decanted from the precipitate while hot and the carbonate again boiled with sodium carbonate. The precipitate so obtained was dissolved in pure hydrochloric acid, the excess of acid removed by evaporation and the resultant neutral scandium chloride dissolved in water. Scandium oxalate was then precipitated from this solution by the addition of a slight excess of oxalic acid. This salt was ignited to oxide and used for the determination of the atomic weight.

*Determination of the Atomic Weight.*—The purified oxide of scandium was dissolved in a small amount of pure sulfuric acid on boiling. This solution was carefully evaporated to dryness in a weighed platinum crucible and heated in an electrically heated resistance oven to  $440^\circ$ , until the weight was constant. This treatment should yield anhydrous scandium sulfate as demonstrated by Herbert Winter.<sup>2</sup> To convert the sulfate to oxide, the crucible was then heated over a large Meeker burner to constant weight. Two determinations of the ratio  $\text{R}_2\text{O}_3 : (\text{SO}_3)_3$  were made in this manner with the following results:

| Wt. of $\text{Sc}_2(\text{SO}_4)_3$ . | Wt. $\text{Sc}_2\text{O}_3$ . | At. wt. Sc. |
|---------------------------------------|-------------------------------|-------------|
| 0.30636                               | 0.11134                       | 44.59       |
| 1.14140                               | 0.41553                       | 44.77       |

A determination of the atomic weight, using material obtained in the first precipitation of the scandium as fluoride, gave the value  $\text{Sc} = 46.26$ . This would indicate that thorium was probably present in the first precipitate, although the material was not examined for thorium.

<sup>1</sup> *Z. anorg. Chem.*, 67–398 (1910); *Chem. News*, 102, 163 (1910).

<sup>2</sup> Inaugural Dissertation, Friedrich-Wilhelms-Universität zu Berlin, Über Vorkommen und Reindarstellung des Scandiums, p. 36.

To determine the purity of the material finally obtained, a photograph of the spark spectrum was made. No lines other than those characteristic of scandium were found.

As a still further test of the purity of the material, about 1 gram of the oxide was tested by means of a very delicate electrometer. It gave no evidence of radioactivity. The instrument was then tested quantitatively and it was found possible to have detected easily as little as 0.05% of thorium in the sample used.

The tests of radioactivity of the oxide were very kindly performed by Dr. Dicran Hadjy Kabakjian, of the Department of Physics.

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## THE ELECTROLYSIS OF POTASSIUM CHLORIDE.

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A number of papers<sup>1</sup> have appeared from this laboratory treating of the determination of anions by the electrolysis of salts in the so-called "double cup." For the most part, small quantities of salt have been the subject of investigation. The simplicity of the process and the accuracy of the results obtained make it appear an attractive method for the analysis of larger quantities of material. The purpose of this investigation has been to determine the accuracy of the results that might be expected from the electrolysis of solutions of potassium chloride containing from 1 to 2 grams of the salt.

### Preparation of Pure Materials.

The water, nitric acid, ammonia water, ammonium oxalate, silver nitrate and mercury, used in this study were prepared and purified with the utmost care. The potassium chloride was obtained by the method of Richards and Staehler<sup>2</sup> with halides.

The purest potassium nitrate prepared by a German factory was dissolved in pure water and recrystallized six times in platinum, using a hand-power centrifuge of high velocity to free the crystals from the mother liquor. The spark spectrum of this material was quite free of lines other than those of potassium. A portion of the salt so purified was dissolved in water in a platinum dish and transposed to chloride by exposing the liquid to the action of pure hydrochloric acid gas. The gas was prepared by the well-known method devised by Robert Hare, and used so often in this laboratory for the preparation of hydrochloric acid. Purest commercial sulfuric acid was allowed to drop from a tap-funnel into pure concentrated hydro-

<sup>1</sup> THIS JOURNAL, 29, 447; 29, 1445; 29, 1455; 29, 1460; *Proc. Am. Philos. Soc.*, 46, 341; THIS JOURNAL, 30, 1705; 31, 900; 32, 1468; 33, 35.

<sup>2</sup> THIS JOURNAL, 29, 623.