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THE VOLUMETRIC DETERMINATION OF CERIUM IN CERITE AND MONAZITE.

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In a previous number of THIS JOURNAL[1] it was shown by one of us that cerium could be accurately and rapidly determined in the presence of other rare earths by oxidation of the sulphate in sulphuric acid solution with sodium bismuthate, reduction of the ceric salt with an excess of ferrous sulphate, and titration of the excess of ferrous sulphate with potassium permanganate. This method has now been applied with excellent results to the analysis of cerite and monazite sands, and has also been used, with certain modifications, for the determination of cerium in mantle ash, in connection with a colorimetric method for the latter now being worked out in this laboratory. The results on mantle ash are withheld until the completion of this method.

The solutions required for the determination of cerium in cerite and monazite are: (1) A potassium permanganate solution, approximately $N/40$. It was found necessary to standardize this solution at least every two weeks, as it deteriorated slowly in spite of all precautions, presumably owing to the extent of dilution. (2) A solution containing 10 grams of Mohr's salt and 50 cc. of concentrated sulphuric acid per liter. This solution should be standardized every time it is used. The value of the permanganate in terms of iron, multiplied by 3.08415, gives its value in terms of CeO_2 (1910 at. wts.).

In the case of the cerite, 0.5 gram of the finely powdered mineral was fused with potassium bisulphate, and the melt dissolved in about 350 cc. of cold water acidulated with not more than 5 cc. of concentrated sulphuric acid. Care must be taken, in making the fusion, not to allow a ring of finely divided, undecomposed cerite to form on the side of the crucible around the top of the fused mass, otherwise fusion of the residue may be necessary. The solution must also be left in contact with the residue overnight, or until all basic salts which may have formed are dissolved.[2]

The monazites (0.6 gram samples) were decomposed in the usual manner, by heating on a hot plate in small porcelain dishes with concentrated sulphuric acid for at least six hours, the mixtures being stirred occasionally. They were then carefully poured into about 350 cc. of ice-cold water and allowed to stand overnight, or until all basic salts had dissolved.

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[1] THIS JOURNAL, 31, 523.

[2] When these conditions have been carefully followed, further treatment of the residue is unnecessary.

The cerite and monazite solutions were then filtered, heated to boiling, and the rare earths precipitated by the addition of a large excess (100 cc. or more) of a saturated solution of oxalic acid. After standing overnight, the precipitated oxalates were filtered off and washed with a 1 per cent. solution of oxalic acid. It had been expected that the sulphuric acid solution of the sample could be treated directly wth sodium bismuthate without removal of impurities, but the separation of the rare earths as oxalates was found necessary owing to the discovery that manganese interfered, giving high results. Experiments now under way in this laboratory indicate that the manganese is held in solution apparently in the quadrivalent form, and a volumetric method for its determination is now being worked out.

Three general methods suggested themselves for the treatment of the oxalate precipitate:

1. It may be washed off the filter paper with water, dissolved with 20 cc. of concentrated sulphuric acid, and, after the addition of 5 grams of ammonium sulphate and dilution to 100 cc., oxidized by means of 2 grams of sodium bismuthate. This method was successfully used in analysis 5*a*, but could not be applied to 1, as it was found in one case that enough basic salts were precipitated to hold back some cerium, while in another case an excessive amount of bismuthate had to be used, resulting in a very heavy precipitation of basic salts. While this method cannot, in general, be recommended, it is believed that it will give satisfactory results when the precipitate of oxalates is small, and care is taken to avoid the introduction of organic matter from the filter paper, preferably by the use of hardened papers.

2. The precipitate and paper may be transferred to a platinum crucible and ignited, finally with a blast lamp. The mixed oxides are then warmed in the crucible for several hours with 10 cc. of concentrated sulphuric acid, allowed to cool, and carefully poured into about 100 cc. of cold water. It was found that incomplete solution results, even on long standing, but on the addition of 10 cc. more of concentrated sulphuric acid, and subsequent evaporation on a hot plate, a clear, yellow solution is obtained. This is diluted to 100 cc., 2 grams of ammonium sulphate added, and oxidation effected by means of 1 gram of sodium bismuthate. This method was used with good results in analysis 9.

3. The oxalates may be washed off the filter with hot water and converted to hydroxides by boiling with sodium hydroxide. The precipitate is filtered off, washed well with hot water, and dissolved through the filter by means of dilute sulphuric acid. The filtrate is diluted to 100 cc. after adding enough sulphuric acid to bring the amount up to 20 grams of the concentrated acid. Ammonium sulphate and sodium bismuthate are then added as in method 2. Method 3 was used for

all the analyses except those mentioned above. While not as rapid as method 1, it was found to be entirely trustworthy, and in addition proved itself far more convenient and rapid than 2. It is therefore recommended as the best of the three methods.

In all the determinations, after adding the sodium bismuthate, the solution was slowly brought to the boiling point, allowed to settle a moment, and then decanted from the residue through a gooch. The residue must be thoroughly washed with 2 per cent. sulphuric acid in order to remove all the cerium. The filtrate is then titrated with the ferrous sulphate solution until an excess has been run in, the excess being titrated back with the permanganate solution.

Duplicate determinations were made on each sample with the following results:

No.	Material.	Source.	Per cent. CeO_2.
1*a* 1*b*	Cerite	Unknown	22.08 21.97
2*a* 2*b*	Monazite	Brazil	28.60 28.74
3*a* 3*b*	Monazite	Brazil	22.84 22.56
4*a* 4*b*	Monazite	Brazil	23.13 23.16
5*a* 5*b*	Monazite	Brazil	23.93 24.01
6*a* 6*b*	Monazite	Brazil	27.25 27.09
7*a* 7*b*	Monazite	Brazil	24.31 24.28
8*a* 8*b*	Monazite	North Carolina	22.19 21.99
9*a* 9*b*	Monazite	North Carolina	22.54 22.49
10*a* 10*b*	Monazite	North Carolina	20.47 20.55

The above results show that the new volumetric method for cerium yields accurate results when applied to monazite and cerite. In addition to its accuracy, the method recommends itself on account of its ease of manipulation and its rapidity.

QUANTITATIVE LABORATORY.

THE REACTION BETWEEN HYDRIODIC ACID AND BROMIC ACID IN THE PRESENCE OF A LARGE AMOUNT OF HYDROCHLORIC ACID.

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Andrews[1] has shown that when a solution of potassium iodide, strongly

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[1] THIS JOURNAL, 25, 756.