

first precipitated by zinc dust, excess zinc dissolved in hydrochloric acid, the residual amalgam dissolved, and mercury determined by the iodate method.

Trials of the procedure with a variety of compounds and in presence of halogens and of sulfur showed it to be apparently of general applicability. The method has the advantage that in presence of halogens it eliminates the danger (which otherwise attends decompositions by acid agents) of loss of mercury by volatilization.

Presence of iodine prolongs the analysis, but in its absence the method is at least as rapid as others of comparable accuracy and applicability.

PHILADELPHIA, PENNSYLVANIA

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STUDIES IN THE RARE EARTHS. I. THE PREPARATION OF THE BROMATES OF CERIUM GROUP RARE EARTHS

By J. ALLEN HARRIS¹

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Historical

The method of separating the rare earth elements that proved successful in permitting of the concentration of illinium was a fractional crystallization of samarium rich fractions obtained from a double magnesium nitrate series of rare earths, as the bromates, the cerium, lanthanum and praseodymium having been removed completely prior to the conversion to the double magnesium nitrate. This latter crystallization permitted of the separation of the bulk of the neodymium from the remaining elements but experience seems to prove that in such a series the illinium concentrates with the neodymium, rendering its detection difficult, the order of solubility of these salts being such that we have an increase with increasing atomic weight.²

From such a study, then, it would appear to be most advantageous to submit the original material to a preliminary, rather than to a subsequent crystallization as the bromates. The serial order of solubilities would then become, erbium, lanthanum, yttrium, holmium, praseodymium, dysprosium, neodymium, terbium, illinium, gadolinium, samarium, and europium (least soluble), thus permitting of a more efficient separation of the illinium and neodymium.^{2,3}

Introduction

The standard method of preparing the bromate is that of James, and was used extensively by him in his classical work on the yttrium group earths.

¹ National Research Fellow.

² Harris with Hopkins, *THIS JOURNAL*, **48**, 1585 (1926).

³ James, *ibid.*, **48**, 2871 (1926).

The dried earth oxalates are mixed to the consistency of a thin paste with concentrated sulfuric acid, warmed to expel excess of acid, and finally heated strongly to convert to the anhydrous sulfates. These, on cooling, are pulverized and sifted, with constant stirring, into ice water; care being necessary to prevent the formation of a basic salt. This solution is then added a little at a time to a saturated solution of freshly precipitated barium bromate in a large steam heated evaporating dish equipped with a mechanical stirrer, care being taken to ensure the presence of excess barium in the solution. On final addition of the sulfate, the precipitated barium sulfate is removed by filtration and the solution of rare earth bromates crystallized by evaporation.

This method, while extremely annoying, in that it involves the evolution of copious fumes of oxides of sulfur over a considerable period, due to the decomposition of the acid by the oxalate radical, yields anhydrous sulfates of the yttrium group earths, even when considerable amounts of neodymium are present, which dissolve to a neutral solution, fairly readily when added slowly to large volumes of ice water.

It has been the experience of the writer, however, that when all of the members of the cerium group earths (with the exception of cerium) are present, together with certain of the yttrium group earths, it is almost impossible to remove the last traces of acid from the more basic members, without decomposing the sulfates of the less basic earths. If decomposition takes place, these basic salts will not dissolve. On the other hand, if any trace of acid is permitted to remain, although ready solution is effected, total decomposition of the bromates during final concentration of the solution invariably results.

At the suggestion of Professor Georges Urbain, of the Sorbonne, the following method was developed, and has been used extensively by the writer with excellent results, affording sulfates of the cerium group earths that are readily soluble in water, even at room temperature, yielding solutions that are neutral although considerable amounts of lanthanum be present.

Procedure

The dried earth oxalates are ignited to the oxides, weighed and the amount of sulfuric acid necessary for their conversion to the sulfates calculated, measured out and diluted considerably. After thorough moistening of the oxides with water to permit of ready penetration by the acid, the acid is added very slowly in small portions, the liquor being allowed to reach neutrality before subsequent addition. When the point is reached at which the solution shows little or no tendency to become neutral, the mixture is transferred to a hot-plate, and warmed until neutralization is again effected. The process of addition is continued until all of the acid has been added.

If upon final addition the liquor again attains neutrality, a little more dilute acid is added, so that a feebly acidic solution is maintained over the sulfate residue. The mixture is then allowed to evaporate slowly on the hot-plate and when thoroughly dry the sulfates may be removed, pulverized and then heated strongly to remove any excess acid. The evolution of fumes is thus reduced to a minimum, and when the anhydrous sulfates are obtained, as evidenced by cessation of evolution of the oxides of sulfur, they are quickly transferred to a dry and previously weighed container, roughly weighed, and transferred while still hot to a bell jar which is immediately evacuated.

From the weight of the sulfates, the amount of water necessary for their solution is calculated and measured into a large conical precipitation flask. When cool, the sulfates are taken in small portions from the bell jar and sprinkled with vigorous stirring into the water, where they dissolve very readily. In this manner it is possible to obtain a concentrated solution of the sulfates, containing no basic salts, which is neutral to litmus. The solution may now be transferred to an evaporating dish and gently evaporated until crystals begin to form at the edges of the container.

If the barium bromate solution is prepared in advance, so as to contain quantities of salt sufficient to precipitate the sulfate ion, the conversion to the bromates may be effected in the minimum of time and with small volumes of solution.

In conclusion the writer wishes to express his appreciation to the International Education Board and the National Research Council for furnishing funds to permit of the writer's working with Professor Urbain, to whom the writer is also deeply grateful.

Summary

Difficulty is experienced when attempting to prepare a neutral solution of cerium group rare earth sulfates, by igniting the oxalates with sulfuric acid, and dissolving the residue in ice water.

A method is outlined for the preparation of concentrated neutral solutions of these sulfates, by the conversion of the oxides to the sulfates and dissolving in water at room temperatures.

This method eliminates waste of sulfuric acid, annoying prolonged evolution of fumes, the use of ice water, loss of time required in conversion to the bromate and subsequent evaporation of large volumes of solution.

VANCOUVER, CANADA