

ON THE PREPARATION OF ZIRCONIA.

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WHEN the new system of artificial illumination, based on Tessié du Motay's process of manufacturing oxygen at commercial rates, was inaugurated at the Paris Exhibition of 1867 pencils of compressed magnesia were made incandescent by the oxy-hydrogen flame. Afterwards zirconia was used instead of magnesia, either to coat a magnesia pencil or to form the entire cylinder. In 1868 a company was organized in this city to exploit the oxygen process and a large number of zirconia pencils were imported from France. The demand thus created for this material led to the collection of zircon crystals in North Carolina. Subsequent experiments with the new light led, however, to the employment of highly carburetted coal gas and oxygen. The incandescent pencils were discarded and a smokeless flame of great brilliancy was obtained by the use of a burner through the central portion of which oxygen escaped to mingle with the coal gas delivered at the circumference. This system of illumination was operated in New York and Buffalo.

Since that time there has been little demand for zirconia except for use instead of lime in lantern projection. The zirconia pencils 8 m. m. long and 5 m. m. in diameter yield a brilliant point of light especially well adapted for experiments in projection, as with the microscope attachment to the lantern, were great definition is necessary.

Some of the cylinders imported in 1869 are still perfect notwithstanding the frequent and not over-careful use to which they have been subjected.

In 1881 and again in 1885, at the request of parties interested in experiments on electric lighting, the preparation of several ounces of zirconia was undertaken. As the experience gained in the first work was sufficient to show that the method then followed was objectionable for many reasons, preliminary experiments were made to improve it before attempting the preparation of the second quantity.

As the result of these, the following method of procedure was devised.

North Carolina zircons, containing some iron, were heated to redness, quenched in water and pulverized in an iron mortar. The powder was passed through a sieve of 100 meshes to the inch.

A proportion of sodium hydrate three times as great as that of zircon to be disintegrated, was heated to fusion in a wrought-iron dish over a common laboratory gas stove and the zircon powder sprinkled in.¹ The silicate seemed to undergo decomposition at once, though to insure this the fusion was continued at dull red heat for half an hour.

The melt was next lixiviated. An insoluble residue consisting of zirconia, ferric oxide and some silica remained. This was washed with water.

To separate iron this residue was suspended in water and sulphur dioxide gas was passed through the mixture. What was left undissolved by this treatment was allowed to settle, the liquid above decanted and the residue treated with fresh water and gas till only silica remained. The silica was removed by filtration and the clear solution of sulphite boiled as long as sulphur dioxide escaped.²

The granular precipitate of zirconium sulphite thus obtained was washed with dilute sulphurous acid water, at first by decantation, then on a filter.

The sulphite was white and granular and not like that obtained when a solution of the chloride is precipitated by the same reagent. Unless a chloride solution is largely diluted, the sulphite precipitated on boiling is gelatinous and utterly unmanageable.³

It has been found objectionable to use sodium sulphite or hyposulphite on account of the retention of sodium by the precipitate.⁴ When much ferric chloride is present, as will be the case when the fusion is made in an iron dish, then the hydrochloric acid set free through its conversion into ferrous salt adds another source of trouble. Ammonium hydrate⁵ may be added in small quantities

¹ While the use of sodium hydrate is given as in Watt's Dictionary (Vol. V., p. 1083) a silver crucible is recommended. F. Stolba (Chem. News, 49, 174) speaks of nickel crucibles. Graham Otto (Vol. III., p. 884) quotes Hermann as using iron vessels as well as charcoal crucibles.

² Berthier, Graham Otto, III., p. 895.

³ J. C. Draper, Am. Jour. Science, Art. III., Ser., Vol. XIV., p. 212.

⁴ J. C. Draper, loc. cit.

⁵ Hermann, Jour. f. prakt. Chem., Ed. xcvi., s. 331 and Graham Otto, III., p. 895.

at a time, to neutralize the free acid, but since the zirconium is thoroughly dissolved and separated from iron by sulphurous acid alone, after boiling, there is no necessity for converting the residue left after fusion successively into chloride and sulphite.

To free the sulphite from any traces of silica it was dissolved in hydrochloric acid and the solution evaporated on a water bath to dryness. Prolonged heating at 100° C., or at a higher temperature, renders some of the zirconium insoluble.

Where much iron is present it is advisable to remove it before trying to separate silica.

The trace of silica was removed by filtration and the zirconia precipitated by ammonium hydrate from the clear solution.

When washed, dried and ignited the zirconium hydrate left a flinty, semitransparent, slightly yellow mass which became a white powder when pulverized in an agate mortar. It was found best to precipitate the hydrate from a cold solution since it then dissolved readily in acids.⁶ Pure sulphite yields zirconia directly by ignition. To separate the zirconia from all elements of the same group the final precipitation may be accomplished by hydrogen peroxide instead of ammonium hydrate.⁷

Hydrogen peroxide is now commercially available and, if strong, produces a precipitate of zirconium peroxide, $Zr_2 O_5$, in a solution of either chloride or sulphate.

Processes requiring the use of platinum vessels for fusion were discarded because of their limited size and the bulkiness of the fusion mixtures. This was the case with⁸ potassium fluoride, the carbonates of the alkalis and calcium carbonate with ammonium chloride.⁹ The latter mixture was found to resolve the silicate most thoroughly and to be well adapted for analytical purposes. The process could be conducted in an iron crucible without seriously contaminating the residue with iron. The crucible could only be used twice however.

Fusion with acid potassium sulphate¹⁰ converts zircon into a basic sulphate and separates iron and silica, but the basic sulphate

⁶ J. B. Hannay, Jour. Chem. Soc., 1873, p. 703.

⁷ G. H. Bailey, Jour. Chem. Soc., 1886, p. 149.

⁸ Marignac and others, Watt's V., 1083 and 4.

⁹ Rose Anal. Chem., 1871, II., 699. et. seq.

¹⁰ Bruno Franz Ber. d. d. Chem. Gesell., III., 58.

must be fused with sodium hydrate to render it soluble. It is more convenient to fuse directly with sodium hydrate and separate iron by sulphurous acid and boiling.

While the process above outlined is not intended to replace those given for analytical research it requires less material, less skill to conduct it, less time, less costly apparatus and less expensive chemicals where zirconia is to be prepared in quantity than any we have found described or have experimented with.

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ABSTRACTS.

GENERAL CHEMISTRY.

Action of Aluminium Chloride upon Bromo-, Chloro- and Iodo-Naphthol. L. ROUX.

Friedel and Crafts have studied the action of aluminium chloride on naphthalene; the author has extended the study to the action of this salt (anhydrous) upon the derivatives of naphthalene.

α Monobromonaphthol.—This last body is prepared by the action of bromine on naphthalene dissolved in carbon disulphide. The action of the chloride is too violent if a temperature of 100° is reached; this is avoided by dissolving the monobromonaphthol in carbon disulphide, and heating slowly on the water bath. The product of the reaction is poured into cold water, and the products are separated by fractional distillation. The reaction gave: 1° Naphthalene.—2° *α* monobromonaphthol not decomposed.—3° *β* monobromonaphthol.—4° small quantities of dibromonaphthols.—5° black tar-like bodies not distillible. The author gives the results of the study of *β* monobromonaphthol. He was unable to obtain the *β* derivative directly by the action of bromine on naphthalene in the presence of aluminium chloride.

α Monochloronaphthol.—This last body has been prepared by the action of chlorine on naphthalene slightly heated. This body is dissolved in carbon disulphide, then boiled for two hours with aluminium chloride. The product is heated with water and frac-