

and all may be dried over sulfuric acid; malic and fumaric acids may be dried for 2 hours at temperatures from 90° to 120°; because of the formation of the anhydride, samples of maleic acid should not be dried above 100°. As standards in alkalimetry and acidimetry these acids, in the pure state, are as accurate as hydrochloric acid determined gravimetrically as silver chloride. The most serviceable of these organic acids are those most soluble in water—malic and maleic acids—although they are no more accurate than fumaric acid. Although maleic and fumaric acids may be used as standards for potassium permanganate solutions, they are neither as accurate nor as convenient as sodium oxalate for this purpose. Succinic, malic, maleic and fumaric acids cannot be used as standards for ammonium hydroxide solutions; the last 2 acids cannot be used for iodine titrations.

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[CONTRIBUTION FROM THE CERAMIC EXPERIMENT STATION, UNITED STATES BUREAU OF MINES]

## THE PURIFICATION AND ANALYSIS OF ZIRCONIUM DIOXIDE<sup>1</sup>

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In preparation for an investigation of refractories to be later conducted at this Station, 1 or 2 kg. of very pure zirconium dioxide was needed. Low-melting impurities were especially undesirable. The subject of purification was, therefore, investigated.

Marden and Rich<sup>4</sup> have covered the subject of zirconium oxide very thoroughly and give a variety of methods of both dissolving and purifying the ores and oxide. They recommend fusion, either with caustic soda or with soda ash. Washburn<sup>5</sup> has approached the complete removal of impurities from the commercial oxide by heating in a current of carbonyl chloride. Venable's new book, "Zirconium and Its Compounds," has appeared since this work was completed.

Zirconium oxide, which has been ignited, resists attack of fusion mixtures more strongly, the higher the previous ignition temperature. The commercially purified sample obtained as a starting point for this work was very resistant. Neither caustic soda, nor soda ash, nor borax, alone, attacked it markedly; hence the method of Marden and Rich would not serve. However, an equal mixture of borax and soda ash proved more

<sup>1</sup> Published with the permission of the Director of the U. S. Bureau of Mines.

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<sup>4</sup> Marden and Rich, "Investigations of Zirconium with Especial Reference to the Metal and Oxide," *U. S. Bur. Mines Bull.*, **186** (1921).

<sup>5</sup> Washburn and Libman, *J. Am. Ceramic Soc.*, **3**, 634 (1920).

effective, a mixture of 4 parts of this to 1 of oxide dissolving 60 to 70% in an hour's fusion.

It is known that a basic sulfate of zirconium is formed in the cold on adding the calculated amount of sulfuric acid to a concentrated chloride solution containing but little excess of acid. This was the compound selected for separating zirconium from its impurities.

When a fusion with hydrochloric acid was extracted, the unattacked zirconia was so fine that it would pass through any filter paper, and also would not settle well. Crystallization of boric acid on cooling also interfered with filtration. These difficulties were surmounted by adding ammonia, thus precipitating the gelatinous hydroxide along with the oxide and entangling it in this jelly. The mixed precipitate is then filtered on a Büchner funnel and washed with hot water until free from borates and chlorides. All iron, alumina, titania and much of the silica present are included in this jelly. On repeatedly pouring a slight excess of warm hydrochloric acid through the precipitate, the hydroxides are dissolved and removed. At first the liquid that runs through is cloudy with zirconium dioxide, which later, or upon repetition of filtration, forms a mat on the paper, and the filtrate then runs clear or very nearly so. Last traces can be removed by decantation after settling.

The clear chloride solution is then diluted and the calculated amount of sulfuric acid is added. Zirconium, with most of the titanium, is precipitated as a transparent, extremely gelatinous precipitate of basic sulfate, while iron, aluminum, silicon and titanium remain in solution. Complete precipitation is impossible because of the acid formed in the reaction. In order to obtain a precipitate which can be washed, the mixture must be heated, with constant stirring or on a water-bath to avoid bumping, but it should not be boiled, as this would precipitate a basic titanium sulfate.

The basic sulfate is washed until the washings give no test for iron with thiocyanate solution; all aluminum will by this time also have been removed. After drying at 110°, which causes the precipitate to shrink greatly, it is ignited to oxide at a dull red heat for several hours in a covered crucible to avoid loss by decrepitation.

A second yield can be obtained either by diluting and heating the filtrate from the basic sulfate precipitate or by precipitating the hydroxide with ammonia, washing, dissolving in the minimum amount of hydrochloric acid and precipitating the basic sulfate by the addition of sulfuric acid as before.

Analysis of the crude material and of the purified product was performed by a method based on that used by Marden and Rich.<sup>4</sup> About 0.5 g. of material was ignited to constant weight and then mixed with 2.5 g. of c. p. sodium carbonate and 2.5 g. of borax, and fused for 12 hours over

a Meker burner. On dissolving in dil. hydrochloric acid, there was no residue. The solution was made up to 250 cc. Silicon was determined in the customary way—iron and titanium colorimetrically. The determination of zirconium by precipitation as phosphate or otherwise, presents, according to Marden and Rich, so many uncertainties as to be unreliable for a sample of high purity. An attempt was made, therefore, to determine zirconium by volatilization of the fluoride in the absence of sulfuric acid. This volatilization, however, proved to be only partial. By 12 successive treatments with hydrofluoric acid solution, the residue was reduced progressively to 2%. This determination was, therefore, not made. Analysis showed 0.36% of ferric oxide, 0.70% of silica and 1.00% of titania; after purification, the percentages were 0.00, 0.00 and 0.92, respectively.

### Summary

Zirconia is best dissolved by fusion with a mixture of borax and soda. The fusion, when taken up in dil. hydrochloric acid, cannot be separated from insoluble residue by direct filtration. It was found that by precipitating the hydroxide, the residue is entangled and can then be filtered and washed. The hydroxide can then be dissolved on the filter and filtered clear by repeatedly pouring the filtrate through the precipitate. A very little sulfuric acid added to this filtrate precipitated very gelatinous, zirconium basic sulfate which, however, could be coagulated by heating nearly to boiling and then filtered and washed free from iron and aluminum. Titanium was also precipitated as basic sulfate and could not be removed to any great extent.

The process, while complicated and slow, seems to be efficient in removing iron, alumina and silica.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 21]

## THE MOLECULAR WEIGHT OF THE SODIUM-TELLURIUM COMPLEX IN LIQUID AMMONIA AS DERIVED FROM VAPOR-PRESSURE MEASUREMENTS

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### Introduction

As a result of the investigations of Kraus,<sup>1</sup> Posnjak,<sup>2</sup> Smyth,<sup>2</sup> and Kraus and Chiu,<sup>3</sup> the atomic proportions in which sodium appears combined with lead and with tellurium in liquid ammonia solution have been definitely established.

<sup>1</sup> Kraus, *THIS JOURNAL*, **29**, 1556 (1907).

<sup>2</sup> Posnjak, see Smyth, *ibid.*, **39**, 1299 (1917).

<sup>3</sup> Kraus and Chiu, *ibid.*, **44**, 1999 (1922).