Test Report T65-9-1

DETERMINATION OF ZIRCONIUM IN ZIRCONIUM METAL AND ZIRCONIUM POWDER

by

GEORGE NORWITZ

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REVIEWED BY: Samuel Sitelman
SAMUEL SITELMAN
Acting Chief, Basic
Materials Evaluation Laboratory

APPROVED BY: L H Adam
L. H. ADAM
Acting Chief, Test and
Evaluation Division

QUALITY ASSURANCE DIRECTORATE
FRANKFORD ARSENAL
Philadelphia, Pa. 19137

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I. SUMMARY

An accurate method is proposed for the determination of zirconium in zirconium metal and zirconium powder. The sample is dissolved in a mixture of hydrofluoric, nitric, perchloric, and sulfuric acids, the solution is evaporated to dryness, the salts are dissolved in dilute hydrochloric acid, mandelic acid is added, the solution is heated at 80° C. for 40 minutes, the zirconium mandelate is filtered off, the residual zirconium in the filtrate is recovered by heating at 80° C. overnight, and the combined precipitates are ignited over a blast burner to zirconium dioxide. An investigation was made of the factors involved in the dissolution of the sample, precipitation with mandelic acid, ignition of the precipitate, and size of the sample. The effect of hafnium and possible interferences was considered.

II. RECOMMENDATIONS

It is recommended that the proposed method for the determination of zirconium be incorporated into the military specifications for zirconium powder (JAN-Z-399A and PA-PD-MI-2364).

III. INTRODUCTION

There is presently no satisfactory method for the determination of zirconium in zirconium metal or zirconium powder. The comprehensive works on the analysis of zirconium metal by Elwell and Wood (4) and Goward and Jacobs (6) do not give a method for the determination of zirconium. A method for the determination of zirconium in zirconium powder by use of selenious acid (15) is inaccurate according to the experiences of this and other laboratories. A method for the determination of zirconium in zirconium powder whereby the zirconium is separated with cupferron and is ignited to the oxide (13) is troublesome because corrections must be made for iron, titanium other elements precipitated by cupferron. A method for zirconium in zirconium powder whereby the zirconium is precipitated with ammonium hydroxide and is ignited to the oxide (5) has the disadvantage that corrections must be made for iron, titanium, aluminum, and other elements precipitated by ammonium hydroxide.

In view of the need for a method for the determination of zirconium in zirconium metal and zirconium powder this laboratory undertook the development of a satisfactory method.

Various approaches to the problem were considered. The EDTA titration method (8) was not found sufficiently accurate for the determination of zirconium in zirconium metal and zirconium powder, since the end point is not sharp and there are many interferences. The zirconium phosphate method (8) was also found to be unsatisfactory. The use of mandelic acid or its derivatives seemed to offer the best possibilities.

The use of mandelic acid for the determination of zirconium was first proposed by Kumins in 1947 (12). Since that time it has been used for the analysis of all kinds of materials, containing traces to fairly large amounts of zirconium (1,2,3,7,8,9,10,11,14,16,17,18,19). No study has been made of the use of mandelic acid or its derivatives for the determination of zirconium in zirconium metal or zirconium powder.

Previous investigators have generally agreed that the acidity for the precipitation of zirconium by mandelic acid or its derivatives is not critical (acidities of 0.1 to 8 M have been used). Hydrochloric acid is the preferred medium although small amounts of sulfuric acid have been found not to interfere. The precipitation is usually made from a hot solution. The use of p-bromomandelic acid or p-chloromandelic acid rather than mandelic acid has been considered advantageous because zirconium p-bromomandelate and zirconium p-chloromandelate are somewhat less soluble than zirconium mandelate. Zirconium mandelate is usually washed with a solution containing hydrochloric acid and mandelic acid. Zirconium p-bromomandelate and zirconium p-chloromandelate are usually washed with water. The precipitates are ordinarily ignited to the oxide. The technique of weighing as zirconium mandelate, zirconium p-bromomandelate, or zirconium p-chloromandelate, after washing with ethyl alcohol and drying at 110° to 120° C, is troublesome because the composition of the precipitate is not exactly stoichiometric.

IV. STUDY

A. DEVELOPMENT OF METHOD

1. Dissolution of the Sample

Zirconium can only be dissolved by treatment with media containing hydrofluoric acid or by fuming with a mixture of sulfuric acid and a sulfate. The latter method of attack gave erratic results for the mandelic acid precipitation, hence a hydrofluoric acid medium was selected.

At first, the sample was dissolved in a mixture of hydrofluoric and sulfuric acids and the solution evaporated to fumes of sulfuric acid. Subsequently, in order to destroy organic matter (carbides), perchloric and nitric acids were added and the solution was evaporated to low volume in order to drive off the perchloric and nitric acids. Later it was found that more complete precipitation of the zirconium was obtained if the sulfuric acid solution was evaporated to dryness and the residue dissolved in dilute hydrochloric acid (10 ml of hydrochloric acid and 50 ml of wate-). The barest trace of fluoride caused low results, hence to ensure complete removal of fluoride the sides of the platinum dish were washed down after an initial fuming and the solution was again evaporated to fumes. Dissolution of the sample in a mixture of hydrofluoric and perchloric acids, followed by evaporation to fumes of perchloric acid, caused low results in the mandelic acid precipitation for reasons that were not clear.

2. Precipitation with Mandelic Acid

The manner of adding the mandelic acid was not critical. The same results were obtained whether the mandelic acid solution was added dropwise from a buret, slowly from a graduate over a period of 15 to 30 seconds, or at one stroke from a graduate. The addition from a graduate over a period of 15 to 30 seconds is recommended. Seventy-five milliliters of 15% mandelic acid solution were used.

The temperature used for the precipitation was 80° C. The digestion time was 40 minutes. Allowing the solution to stand for 1-1/2, 3, and 7 hours at 80° C. did not give better recovery. In fact, the recovery was less, since prolonged heating caused the precipitate to adhere to the sides of the beaker. Allowing to stand for several hours at room temperature did not give better recovery. Acidity had no significant effect on recovery.

Regardless of the method of precipitation used or whether p-bromomandelic acid or p-chloromandelic acid were used in place of the mandelic acid, complete precipitation of the zirconium could not be obtained (1 to 3 mg. of zirconium was always found in the filtrate). The probable reason for incomplete precipitation is that a portion of the large amount of precipitate always dissolved during the transferring and washing operation, particularly since many treatments with a policeman were necessary to remove the precipitate from the beaker.

Attempts were made to determine the unprecipitated zirconium in the filtrate spectrophotometrically after the mandelic acid precipitation with the intention of determining the total zirconium. The technique was not feasible since sensitive colorimetric reagents for zirconium require a prior separation of zirconium from interfering metals (20). In addition, before the zirconium could be determined spectrophotometrically it was necessary to destroy the mandelic acid. This could only be done by the tedious procedure of fuming with sulfuric acid and repeatedly adding nitric acid. Attempts to destroy the mandelic acid by treatment with nitric and perchloric acids and evaporation to fumes of perchloric acid caused a mild explosion.

In view of the failure of the spectrophotometric technique it was decided to recover the residual zirconium by other means. It was found that the zirconium in the filtrate could be completely recovered by allowing the filtrate to stand overnight at about 80° C. (this was conveniently done by placing an inverted 1-liter beaker over the 400-ml beaker containing the filtrate and heating in an oven at the indicated temperature). Heating at 80° C. for 6 hours or allowing to stand overnight at room temperature did not give complete recovery of the zirconium.

The solution used to wash the zirconium mandelate precipitate was a 5% mandelic acid solution containing 2% hydrochloric acid. An excessive hydrochloric acid concentration increased solubility losses on washing.

3. Ignition of the Precipitate

The manner of charring and burning off the organic matter presented problems. At first, the filter paper and precipitate were charred and the organic matter was burned off by heating over the low flame of a Meker burner. However, it was found that low results were obtained by this technique, probably because of mechanical expulsion of some of the precipitate by the cloud of carbon produced. It was found that the losses could be eliminated by heating the platinum crucible containing the paper and precipitate on a hot plate (gas type) at highest heat for 1 hour so as to decompose the zirconium mandelate. The organic material that was left then readily burned off over a Meker burner without the formation of a cloud of carbon. It is believed that the reason for the effectiveness of the hot plate technique is that it controls the decomposition of the zirconium mandelate over the temperature range at which the decomposition is vigorous.

The final ignition temperature for the zirconium dioxide precipitate also presented problems. Previous investigators have recommended a temperature of 800° to 1000° C., although some do not specify a temperature. The findings from thermogravimetric studies of previous investigators are not necessarily applicable to the present problem since in thermogravimetric studies much less zirconium dioxide is handled than in the proposed method. According to the thermogravimetric studies of Stachtchenko and Duval (21) on zirconium mandelate, there is an extremely rapid decrease in weight from 200° to 300° C., then a moderately rapid decrease to 550° C., then a slower decrease to 700° C., and finally a slow increase to 959° C., at which point constant weight is obtained. The thermogravimetric studies of Adams and Holness (1) on zirconium mandelate show an extremely rapid decrease from 200° to 350° C., then a moderately rapid decrease to 600° C., and finally a very slight decrease to 1000° C., at which point constant weight is obtained.

According to experiences in this laboratory it is necessary when working with larger amounts of zirconium to ignite over a blast burner (temperature approximately 1100° to 1200° C.) to obtain constant weight. If the precipitate obtained in the determination of zirconium in zirconium metal or zirconium powder is first ignited at 1000° C. for 60 minutes and then over a blast burner for 20 minutes, there will be a decrease in weight between the two ignitions of approximately 1 mg. This amount of zirconium dioxide represents 0.3% zirconium (on a 0.25 gram sample).

Twenty minutes is an adequate length of time for the ignition over the blast burner. Heating for an additional 30 minutes caused an insignificant loss of 0.1 mg.

Oesper and Klingenberg (16) and Hill and Miles (10) recommended filtering the zirconium mandelate through a Selas filtering crucible, drying in an oven, and then igniting at 1000° C. This technique cannot advantageously be applied to the method described in the present paper since two different crucibles would have to be used, thus doubling the error due to weighing. Also, Selas crucibles lose a significant amount of weight when heated in a blast burner.

Ignited zirconium dioxide can be considered non-hygroscopic; however, the usual precautions for handling an ignited precipitate should be observed.

4. Size of Sample

A 0.23 to 0.25-gram sample was found to be ideal for obtaining maximum accuracy. If a sample much larger than 0.25 gram were used, the zirconium sometimes hydrolyzed before the mandelic acid was added.

5. Effect of Hafnium and Other Elements

Hafnium, the sister element of zirconium, is quantitatively precipitated by the mandelic acid and is included with the zirconium. There is an error caused by the determination of zirconium plus hafnium since the factor for converting zirconium dioxide to zirconium is 0.7403, whereas the factor for converting hafnium dioxide to hafnium is 0.8481. The amount of hafnium found in ordinary commercial zirconium is about 2%. This amount of hafnium will cause a negative error in the result of zirconium plus hafnium of about 0.25%. There is a considerable amount of zirconium containing less than 0.02% hafnium being produced for atomic energy purposes. Much of the scrap from this purified metal is available for producing zirconium powder for ordinary civilian use.

Ordinarily, it will suffice to determine the total of zirconium plus hafnium calculated as zirconium. This is especially true of zirconium powders which have a minimum requirement for zirconium plus hafnium calculated as zirconium (usually 95% or 96%). For materials for which separate results for zirconium and hafnium are desirable, this laboratory determines the percent of hafnium in the sample spectrographically (4) on the ignited and weighed mixed oxides from the mandelic acid precipitation. The amount of hafnium dioxide in the precipitate is then deducted and the percent of zirconium is calculated.

No other elements found in zirconium metal or zirconium powder interfere with the method.

B. RECOMMENDED METHOD

1. Reagents

Mandelic acid solution (15%). Dissolve 75 grams of mandelic acid in water and dilute to 500 ml.

Mandelic acid wash solution. Dissolve 25 grams of mandelic acid in 400 ml of water, add 10 ml of hydrochloric acid, and dilute to 500 ml.

2. Procedure

If the sample is a powder, wash a portion of it with water, acetone, and ether on a Buchner funnel, dry in an oven at 70° C., and store in a stoppered bottle.

Transfer a 0.23 to 0.25-gram sample (weighed to 0.1 mg) to a large platinum dish. Add 15 ml of water, 10 ml of sulfuric acid (1 to 1), 5 ml of nitric acid, and 2 ml of perchloric acid. Cover with a plastic (or wax-covered) watch glass. Add 5 ml of hydrofluoric acid in 0.5-ml portions from a plastic medicine dropper, while swirling the platinum dish and allowing about 1 minute between additions. After the final addition, allow to stand for 5 minutes to complete solution, then wash down the watch glass with water. Evaporate to fumes of sulfuric acid at gentle heat without the watch glass, remove the dish from the hot plate, cool it in water, wash down the sides with water, and swirl. Again evaporate to fumes of sulfuric acid at gentle heat, then raise the temperature of the hot plate to moderate heat, and evaporate to dryness and the disappearance of fumes. Cool somewhat, add 50 ml of water and 10 ml of hydrochloric acid, swirl, and heat on the hot plate at gentle heat for 5 to 10 minutes until the solution is clear. Wash into a 400-ml beaker and police the platinum dish.

Dilute to approximately 120 ml, put in a stirring rod, and heat to about 80° C. on the hot plate. Add 75 ml of mandelic acid solution (15%) from a graduate over a period of 15 to 30 seconds while stirring the solution with the stirring rod. Stir frequently during the next 5 minutes. Cover with a watch glass and allow to stand at about 80° C. for 40 minutes while stirring occasionally. Wash down the cover lid with water, filter through a Whatman No. 40 filter paper, and collect the filtrate in a clean 400-ml beaker. Police the stirring rod and beaker, and wash the filter paper and precipitate with mandelic acid wash solution. Place the filter paper and precipitate into a tared platinum crucible and heat on the hot plate at highest heat for 1 hour or more.

Within 30 minutes after the filtration, wash the filtrate into the original 400-ml beaker, cover with a watch glass (but do not insert a stirring rod), and heat to about 80° C. on the hot plate. Place the beaker in an oven at about 80° C., cover with an inverted 1-liter beaker, and allow to stand overnight. Filter through a Whatman No. 40 filter paper and transfer and wash with mandelic acid wash solution. Place the filter paper into the crucible containing the first precipitate and heat on the hot plate at highest heat for 1 hour or more. Burn off the carbonaceous material over the low flame of a Meker burner and then heat over the full flame of the Meker burner until the precipitate is white. Ignite over a blast burner for 20 minutes, cool in a desiccator, and weigh.

Calculate as follows:

$$\% \text{ Zr } (+\text{Hf}) = \frac{74.03 \times \text{grams of precipitate}}{\text{grams of sample}}$$

C. RESULTS

The results obtained for zirconium on typical samples of zirconium metal and powder are shown in Table I. The results show good precision and are in satisfactory agreement with the results obtained for zirconium (plus hafnium) calculated by difference after analyzing for impurities.

V. ACKNOWLEDGMENT

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VII. TABLES

Table I. Results for Zirconium (Plus Hafnium) in Samples of Zirconium Metal and Zirconium Powder

Sample	Contains (%)	% Zr (+Hf) by Difference	% Zr (+Hf) Found
Zr Wire	0.01 Hf; <0.1 impurities	>99.9	99.86, 99.96, 99.92 Ave. 99.91
Zr Powder 1	0.01 Hf; 0.63 O, 0.01 H, 0.03 C, 0.01 Fe, 0.07 N, 0.00 Si, 0.02 Cl, 0.01 Ti, 0.00 Mo, 0.00 Al	99.22	99.32, 99.36, 99.39 Ave. 99.35
Zr Powder 2	0.01 Hf; 1.09 O, 0.05 H, 0.03 C, 0.11 Fe, 0.04 N, 0.01 Si, 0.02 Cl, 0.04 Ti, 0.00 Mo, 0.00 Al	98.61	98.60, 98.50, 98.58 Ave. 98.56
Zr Powder 3 (Zircaloy)	0.01 Hf; 1.43 O, 0.46 H, 0.13 C, 0.26 Fe, 0.04 N, 0.00 Si, 0.01 Cl, 0.01 Ti, 0.00 Mo, 0.00 Al, 0.02 Ni, 0.05 Cr, 1.10 Sn	96.49	96.46, 96.33, 96.39 Ave. 96.39
Zr Powder 4	2.0 Hf; 0.82 O, 0.05 H, 0.16 C, 0.44 Fe, 0.03 N, 0.22 Si, 0.03 Cl, 0.06 Ti, 0.21 Mo, 0.5 Al	97.5	97.24, 97.29, 97.19 Ave. 97.24
Zr Powder 5	1.8 Hf; 0.77 O, 0.08 H, 0.19 C, 1.00 Fe, 0.52 H, 0.08 Si, 0.02 Cl, 0.06 Ti, 0.31 Mo, 0.00 Al	97.0	96.91, 96.86, 96.79 Ave. 96.85
Granular Zr	1.9 Hf; 0.84 O, 0.08 H, 0.26 C, 0.70 Fe, 0.55 N, 0.65 Si, 0.12 Cl, 0.06 Ti, 0.49 Mo, 0.2 Al	96.0	95.94, 95.90, 95.71 Ave. 95.85