

DETERMINATION OF SMALL AMOUNTS OF ZIRCONIUM—II*

ANALYSIS OF REFRACTORY SAMPLES

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(Received 23 October 1962. Accepted 29 January 1963)

Summary—In connection with the determination of small amounts of zirconium in complex samples, procedures have been developed for bringing various types of sample into solution and removing possible interferences, which procedures allow *p*-bromomandelic acid to be used as a precipitant for the final recovery of zirconium for gravimetric measurement. The applicability of these procedures, which are described in detail, has been investigated by the analysis for zirconium of a variety of refractory mineral and metallurgical samples.

A PREVIOUS paper¹ described an investigation of the optimum and limiting conditions for the gravimetric determination of small amounts of zirconium using mandelic acid and its *p*-bromo and *m*-nitro derivatives as precipitants. The procedure employing *p*-bromomandelic acid has been applied with gratifying results to the determination of zirconium in a variety of refractory mineral and metallurgical samples, including several National Bureau of Standards analysed samples.

The procedures used in the dissolution of the various samples are given in the following sections. They were developed from the results of the previous paper¹ and other papers on the determination of zirconium.²⁻⁶ The results obtained are given in Table I; as an indication of the selectivity of the zirconium precipitation, the compositions of the National Bureau of Standards samples analysed are given in Tables II and III.

EXPERIMENTAL

Minerals

Flint clay (National Bureau of Standards Sample No. 97)

A 0.500-g sample, dried for 2 hr at 140°, was mixed with 2 g of Na₂CO₃ and 2 g of Na₂B₄O₇ in a platinum crucible, which was covered and slowly heated with a Meker burner. After 5–6 min the heat was gradually increased, and the crucible was finally strongly heated for 35–40 min with occasional stirring. The cooled crucible and cover were then placed in a 400-ml beaker and the melt digested with 100 ml of hydrochloric acid (1 + 3). After removing crucible and cover with necessary washing, the solution was evaporated to dryness on a steam bath. The residue was dissolved with 50 ml of 10% HCl, filtered through a No. 40 Whatman paper (with suction) and washed with 10% HCl. The filtrate was saved.

The residue was ignited in a platinum crucible and fused with 2 g of Na₂CO₃. The cool melt was treated with 70–80 ml of HCl (1 + 3), and slowly evaporated on a sand bath; the residue was treated with 40–50 ml of 25% HCl, boiled to expel CO₂, filtered through a No. 40 Whatman paper (suction) and carefully washed with dilute HCl. The resulting filtrate, combined with the original filtrate, was evaporated on a steam bath in a 150-ml beaker. The residue obtained was taken up with 30 ml of

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15–20% HCl and filtered. The filtrate was heated to 50–60° and 30–35 ml of 1.5% *p*-bromomandelic acid added dropwise with constant stirring. The mixture was digested for 15 min at 80–85°, filtered after 3–4 hr through a No. 40 Whatman paper and washed with 20–25 ml of hot distilled water. The precipitate and paper were slowly charred in a platinum crucible, ignited at 900–1000° and weighed as ZrO₂.

Burnt refractory (National Bureau of Standards Samples No. 78)

A 0.500-g sample, dried for 1 hr at 110°, was mixed with 4 g of Na₂CO₃ in a platinum crucible, covered and heated very slowly with a Meker burner for a few min, then with gradually increasing heat and finally at full capacity of the burner for about 40 min; the melt was occasionally stirred. The cooled crucible and cover were placed in a 400-ml beaker, and treated with 100 ml of H₂SO₄ (1 + 4). The resulting solution was boiled to remove CO₂, evaporated nearly to dryness, diluted to about 50 ml with 10% HCl, boiled, filtered through a No. 40 Whatman paper and washed with 10 ml of dilute HCl. The filtrate was saved.

The filter paper and residue were ignited in a platinum crucible; 1 ml of H₂SO₄ (1 + 1) and 5 ml of HF were then added, and the contents thoroughly mixed with a piece of thick platinum wire (left in the crucible for further stirring). The crucible contents were evaporated on an electric hot plate in a hood with the aid of an infrared heating lamp; the heat was gradually increased until all free acids were driven off; the crucible was then ignited at dull redness, cooled and weighed. Treatment with HF–H₂SO₄, evaporation and ignition were repeated to constant weight.

The cold and weighed residue from HF–H₂SO₄ treatment was fused with 2 g of K₂S₂O₇, the melt leached with distilled water and added to the main filtrate. The latter was slowly concentrated on a sand bath to 20–30 ml and cooled; 5–8 ml of HCl (1 + 1) were added. If the solution was not clear, it was filtered after 4–5 hr, treated with about 25–30 ml of 1.5% *p*-bromomandelic acid reagent as described before but filtered after 24 hr.

The above procedure gave 0.114% of ZrO₂. Application of a decomposition procedure involving Na₂CO₃–Na₂B₄O₇, followed by Na₂CO₃, as described for Flint Clay, gave 0.10% of ZrO₂.

Bauxite (National Bureau of Standards Sample No. 69A)

A 0.500-g sample, dried at 140° for 2 hr was fused with 4 g of K₂S₂O₇ in a platinum crucible, gradually increasing the temperature to 600–700° and stirring the melt from time to time for 10–15 min. The cool crucible and cover were placed in a 400-ml beaker and digested with 50 ml of HCl (1 + 10). After removal and washing of crucible and cover, the mixture was evaporated on a sand bath, then digested with 50–55 ml of 10% HCl and filtered through a No. 40 Whatman paper. This filtrate was saved.

The residue was ignited, then mixed with 3 ml of H₂SO₄ (1 + 1) and 5 ml of HF. This mixture was evaporated on an electric hot plate with the aid of an infrared heating lamp. When all free acid was driven off, the crucible was ignited at dull redness and weighed. The silica removal procedure was repeated until constant weight was obtained.

The weighed residue was fused with 2 g of K₂S₂O₇, dissolved in hot water and added to the main filtrate. The latter was diluted to about 150 ml, treated with a slight excess of aqueous NH₃, boiled, filtered through a No. 40 Whatman paper with suction and washed with 2% aqueous NH₃. The precipitate was transferred to a beaker; the paper was washed with 40 ml of hot HCl (1 + 1), which was also added to the beaker; the resulting solution was digested for 10 min, diluted to 150 ml, evaporated to near dryness, and digested with 30–35 ml of 1.5% *p*-bromomandelic acid added dropwise with constant stirring, then digested for 15 min at 80–85°. After 4–5 hr, the precipitate was filtered, washed with hot water and ignited to ZrO₂.

Alloys

Electrical-heating alloy (National Bureau of Standards Sample No. 169)

A 2-g sample was treated in a 150 ml beaker with 14 ml of HCl and 7 ml of HNO₃, then evaporated to about 5 ml on an electric hot plate; 15 ml of HCl were added and the solution evaporated to near dryness; on addition of 10 ml of HCl, the alloy was completely dissolved. The solution was evaporated to dryness; the residue was treated with 20 ml of HCl (1 + 2) and evaporated to dryness; the HCl addition and evaporation were repeated. The cooled residue was treated with 50–55 ml of HCl (1 + 4), filtered through a No. 40 Whatman paper using suction and washed with the same dilute acid.

The filtrate was evaporated to about 10 ml, diluted with distilled water to 120–150 ml, treated with a slight excess (few drops beyond neutrality) of aqueous NH₃, boiled for 1–2 min, filtered through a No. 40 Whatman paper (suction) and washed with 2–3% aqueous NH₃.

The precipitate was dissolved with about 50 ml of HCl (1 + 1), evaporated to dryness and taken

up with 30–35 ml of 10% HCl, then heated to 50–60°; 30–35 ml of 1.5% *p*-bromomandelic acid were added dropwise with constant stirring; the mixture was digested for 15 min at 80–85°, filtered after 4–5 hr and washed with 20–25 ml of hot water. The precipitate was ignited and weighed as ZrO₂. Because the residue was green in colour, it was fused with a small amount of Na₂CO₃ in a platinum crucible; the cooled melt was dissolved in dilute HCl and heated to expel CO₂; the zirconium was then precipitated and ignited as before.

High-temperature alloy (National Bureau of Standards Sample Nos. 1203–4–5)

A 0.5-g sample (obtained by turning, washing with acetone and EtOH, and drying) was treated in a 150-ml beaker with 20 ml of HCl and evaporated to about 5 ml on an electric hot plate. After two or three repetitions of the HCl addition and evaporation, the sample was completely dissolved. The resulting solution was evaporated to dryness; the residue was dissolved with 20–25 ml of HCl (1 + 1) and the solution again evaporated to dryness. This residue was treated with 35–40 ml of HCl (1 + 5), filtered through a No. 40 Whatman paper and washed with the dilute acid. The filtrate was boiled to about 30–35 ml; 30–35 ml of 1.5% *p*-bromomandelic acid were added dropwise with constant stirring; the mixture was digested for 15 min at 80–85°, filtered after 4–5 hr and washed with 20–25 ml of hot water; the precipitate was ignited to ZrO₂. Because the ignited residue had a slight green colour, it was fused with a small amount of Na₂CO₃ in a platinum crucible; the cooled melt was treated with 30–35 ml of HCl (1 + 3) and the crucible washed with dilute HCl. The resulting solution was evaporated on a steam bath to 30 ml and zirconium precipitated as usual.

Magnesium alloys

The nature and zirconium content of the two high temperature magnesium alloys analysed have been discussed by Elving and Olson.³ The following procedures were used to determine total zirconium content.

A 0.170-g sample of Alloy EK30 was dissolved with 7 ml of 10% H₂SO₄ in a platinum crucible, evaporated to dryness on an electric hot plate, ignited, treated with 2.5 ml of HF and 0.5 ml of H₂SO₄, and evaporated on the hot plate with the aid of an infrared heating lamp (stirring with a platinum rod); the HF–H₂SO₄ evaporation was repeated. To ensure removal of silica, the following procedure, which is probably unnecessary, was used: Na₂CO₃ was added; the crucible and its contents heated; the cooled crucible placed in a 150 ml beaker, treated with HCl (1 + 1), heated to expel CO₂, and filtered through a No. 40 Whatman paper; the residue was fused with *ca.* 1.5 g of Na₂CO₃, the cool melt dissolved with dilute HCl and warmed to expel CO₂; this solution was added to the main solution. The latter was evaporated to 20–25 ml; 20–25 ml of 1.5% *p*-bromomandelic acid were added dropwise with constant stirring, the mixture digested for 15 min at 80–85°, filtered after 3–4 hr and washed with 15–20 ml of hot water; the precipitate was ignited as usual.

A 0.5-g sample of Alloy ZK60 was treated in a covered 150-ml beaker at room temperature with 10 ml of 10% H₂SO₄. When dissolution was complete, 1.5 ml of H₂SO₄ (1 + 1) were added; the solution was evaporated to the appearance of fumes of H₂SO₄, cooled, diluted to 20 ml and heated to 50–60°. Then 20 ml of 1.5% *p*-bromomandelic acid were added dropwise, stirring constantly; the mixture was digested for 15 min at 80–85°, filtered after 3–4 hr and washed with 10–15 ml of hot water; the precipitate was ignited as usual.

A 0.5-g sample of EK30 treated by the procedure described for ZK60 gave 0.377% of zirconium.

DISCUSSION

The determination of zirconium, present as a relatively minor constituent, in mineral, metallurgical and other types of sample, is a difficult problem, especially when relatively accurate results are required. The high degree of selectivity and the sensitivity of *p*-bromomandelic acid as a precipitant for zirconium provide ample support for the use of this reagent as a pivotal means of isolating zirconium for gravimetric measurement, especially when combined with the classical methods of effecting solution and removing matrix constituents such as silica, *e.g.*, high temperature Lewis acid-base attack involving fusion with carbonate and borate, and lower temperature attack involving hydrofluoric and sulphuric acids.

The procedures developed, which are given in sufficient detail so that they can be used with a minimum of difficulty regarding conditions, amounts of reagents and operations, were applied to the determination of zirconium in nine standard mineral

TABLE I.—DETERMINATION OF ZIRCONIUM IN MINERAL AND METALLURGICAL SAMPLES

Sample nature and source	Zirconium content	
	Specified, ^a %	Found, %
Flint Clay, N.B.S. No. 97	0.25 ZrO ₂	0.244 ZrO ₂
Burnt Refractory, N.B.S. No. 78	0.12 ZrO ₂ (0.09–0.13)	0.10 ZrO ₂ 0.10 ZrO ₂ ^b
Bauxite, N.B.S. No. 69A	0.18 ZrO ₂	0.174 ZrO ₂
Electrical-Heating Alloy, N.B.S. No. 169	0.042 Zr (0.035–0.048)	0.043 Zr
High-Temperature Alloys:		
N.B.S. No. 1203	0.05 ₅ Zr	0.043 Zr
N.B.S. No. 1204	0.12 Zr	0.114 Zr
N.B.S. No. 1205	0.46 Zr	0.469 Zr
Magnesium Alloys:		
EK30	0.346 Zr	0.377 Zr
		0.621 Zr ^b
ZK60	0.608 Zr	0.625 Zr

^a Range of values on N.B.S. certificate is given in parentheses beneath average value.

^b Use of an alternate procedure as indicated in the text.

TABLE II.—ANALYSES GIVEN FOR NATIONAL BUREAU OF STANDARDS SAMPLES IN WHICH ZIRCONIUM WAS DETERMINED (VALUES GIVEN AS PERCENTAGES)

Constituents	No. 97 Flint Clay	No. 78 Burnt Refractory	69A Bauxite
MoO ₃	0.0002	—	—
CuO	0.003	—	—
MnO	0.003	—	<0.01
Total S as SO ₃	0.04	—	0.04
BaO	0.015	—	0.01
MgO	0.26	0.5	0.02
CaO	0.10	0.36	0.29
Na ₂ O	0.32	0.53	<0.01
K ₂ O	0.55	2.83	<0.01
Cr ₂ O ₃	0.085	—	0.05
Total V as V ₂ O ₅	0.04	0.047	0.03
P ₂ O ₅	0.07	0.62	0.08
Total Fe as Fe ₂ O ₃	0.98	0.79	5.82
ZrO ₂	0.25	0.12	0.18
TiO ₂	2.35	3.37	7.78
Al ₂ O ₃	38.80	69.97	55.0
SiO ₂	42.85	20.69	6.01
Loss on ignition	13.34	0.26	29.55

TABLE III.—ANALYSIS GIVEN FOR NATIONAL BUREAU OF STANDARDS SAMPLES IN WHICH ZIRCONIUM WAS DETERMINED (VALUES GIVEN AS PERCENTAGES)

Constituent	No. 169 Electrical Heating Alloy (77Ni-20 Cr)	High-Temperature Alloy		
		No. 1203	No. 1204	No. 1205
N	0.031			
C	0.043	(0.01)	(0.03)	(0.19)
Co	0.19			
Cu	0.015	0.19	0.12	0.056
Mn	0.073	0.31	0.41	0.29
S	0.002			
Ca	0.015			
Cr	20.26	11.90	12.75	13.82
V	0.018			
Fe	0.54	(1.4)	(3.1)	(1.55)
Zr	0.042	0.05 _g	0.12	0.46
Ti	0.006	1.09	0.63	0.36
Al	0.095	4.34	5.60	6.68
Si	1.42	0.86	0.56	0.63
Ni	(77)	75.5	70.6	67.5
Mo		3.01	4.28	5.75
W		<0.01	0.028	0.019
Nb		1.00	1.31	1.95
Ta		0.34	0.46	0.67

and metallurgical samples, seven of which were analysed National Bureau of Standards standard samples. The results obtained were eminently satisfactory as indicated by the data of Table I.

Obviously the dissolution and fusion procedures described can be modified as the nature of the sample may indicate. Consequently, in some cases alternate procedures are indicated; other possible ways of shortening the procedures will be apparent.

Acknowledgment—One of the authors (M. R.) wishes to thank the International Atomic Energy Agency for a fellowship, upon which the work described was done.

Zusammenfassung—Im Zusammenhang mit der Bestimmung kleiner Mengen von Zirkonium in Komplexverbindungen wurden Methoden entwickelt, um verschiedene Arten von Proben in Lösung zu bringen und Störungen auszuschalten, damit die Fällung mit p-Brommandelsäure zur gravimetrischen Bestimmung von Zirkonium möglich wird. Die Anwendbarkeit dieser im einzelnen beschriebenen Verfahren wurde bei der Bestimmung von Zirkonium in verschiedenen feuerfesten Mineralien und Metallproben geprüft.

Résumé—En relation avec la détermination de micro-quantités de zirconium dans les composés complexes, certains procédés ont été développés comme convenant à des types variés d'échantillons en solution, et éliminant les influences gênantes possibles; à ces procédés, se rattache l'emploi de l'acide p-bromomandélique comme agent précipitant du zirconium dans la récupération finale pour les mesures gravimétriques. L'application de ces procédés qui ont été décrits en détail a été essayé pour l'analyse du zirconium contenu dans une variété de minéral réfractaire et dans certains échantillons métallurgiques.

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