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THE SELENIOUS ACID METHOD FOR THE DETERMINATION OF ZIRCONIUM

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The accurate determination of zirconium has always been a matter of considerable difficulty, especially in materials containing a variety of other metals. Many of the methods of analysis which have been proposed give good results when applied to simple zirconium compounds, but fail when certain other elements are present. The two most common methods have been the phosphate method and the cupferron method, both of which have been carefully studied by Lundell and Knowles,¹ who, in their proposed procedures, have made provision for the elimination of all interfering elements. The removal of such interfering elements in samples of moderate complexity, however, involves a very long series of manipulations.

Smith and James² have recently shown that the precipitation of zirconium by selenious acid can be applied to the quantitative determination of zirconium. They studied the effect of the presence of only a few interfering elements, however, and as J. W. Marden³ has pointed out, however promising the method may seem, the effect of such metals as are ordinarily encountered in zirconium ores and alloys must be understood before the method can be generally used.

It was the purpose of this investigation, therefore, (a) to determine the most favorable conditions for the quantitative precipitation of zirconium selenite; (b) to determine what elements other than zirconium are precipitated by selenious acid under the conditions for the most favorable precipitation of zirconium; (c) to determine what elements are adsorbed or otherwise brought down by zirconium selenite in sufficient amounts to interfere with the accuracy of the estimation of zirconium; (d) to devise a reasonably rapid and direct method for eliminating the interfering elements and quantitatively precipitating the zirconium selenite in pure form; (e) to apply the method to mixtures and natural products containing zirconium in conjunction with a wide variety of other metals, especially those which have been found to cause interference.

Previous Work.—The formula of the flocculent precipitate obtained by the addition of selenious acid to solutions of zirconium salts is, according to Nilson,⁴ $4\text{ZrO}_2 \cdot 3\text{SeO}_2 \cdot 18\text{H}_2\text{O}$. On heating the solution containing the

¹ G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, **12**, 562 (1920); *This Journal*, **41**, 1801 (1919); **42**, 1429 (1920).

² M. M. Smith and C. James, *ibid.*, **42**, 1764 (1920).

³ J. W. Marden, *Bulletin* 212, Bur. of Mines, p. 310.

⁴ A. Nilson, "Researches on Salts of Selenious Acid," University of Upsala, 1875.

suspended precipitate with excess selenious acid, the precipitate is slowly converted to the crystalline normal selenite, $Zr(SeO_3)_2$. Smith and James showed that the precipitation is quantitative and recommended that it be made from 500 cc. of solution containing 5% hydrochloric acid. Ignition of the precipitate gives zirconium dioxide and with equal amounts of original zirconium salt the weights of the dioxide are essentially the same as those obtained by the ignition of the corresponding cupferron and ammonia precipitates. Smith and James likewise found that aluminum and the rare earths do not interfere except that cerium must be in the cerous form, and also that the presence of amounts of iron usually present in zirconium ores does not affect the results. Titanium interferes but can be completely held in solution by hydrogen peroxide. Thorium also interferes but the writers state that this element is rarely a constituent of zirconium ores.

Experimental Work

Solutions Used.—A solution of c. p. selenious acid containing 100 g. per liter was prepared for use as a precipitant and several liters of zirconyl chloride solution were prepared of an approximate concentration of 12 g. of $ZrOCl_2 \cdot 8H_2O$ per liter. The zirconium from 25-cc. portions of the latter solution was precipitated (a) by cupferron from 10% sulfuric acid solution, and (b) by 20 cc. of selenious acid from 400 cc. of neutral solution.⁵ The ignited precipitates gave the following values.

Precipitation by cupferron, g. ZrO_2	Precipitation by selenious acid, g. ZrO_2
0.1200	0.1200
.1197	.1206
.1199	.1194
	.1198
	.1200
	.1200
	.1201
<hr/> Average 0.1199	<hr/> 0.1200

This zirconyl chloride solution was used throughout the entire investigation and its concentration was checked frequently.

Effect of Acid on the Precipitation of Zirconium Selenite.—Since in an ordinary analysis of zirconium it might be desirable to precipitate zirconium selenite from nitric acid or sulfuric acid solution, as well as from hydrochloric acid solution, and since considerable alkali salts might very likely be present from previous neutralizations, the effect of the presence and concentrations of these substances on the quantitative precipitation of

⁵ One-half milligram of zirconium in 500 cc. of solution acidified with hydrochloric acid gives a visible precipitate with selenious acid. This corresponds to 0.05% Zr in a one-gram sample of ore.

zirconium by selenious acid was next studied. The results are listed in Table I. In all the determinations a total volume of 400 cc. was used, 25 cc. of standard zirconyl chloride solution was present (equivalent to 0.1200 g. of ZrO_2), and the zirconium was precipitated from boiling solution with 20 cc. of 10% selenious acid solution. The precipitate was allowed to stand and was then filtered and ignited.

In these precipitations the use of hydrochloric acid or nitric acid gave immediate flocculent precipitates, which, on long standing (*e. g.*, overnight) on the hot-plate, became more crystalline. The precipitates in the presence of sulfuric acid did not appear at once and in some cases did not begin to form before an hour or more. When they did appear, they were entirely crystalline in character and had a great tendency to adhere to the scratches on the beaker, from which they were removed only with difficulty. Furthermore, the two forms of precipitates differed markedly in their ease of solubility in acids. The amorphous form (basic selenite) was readily soluble in 6 *N* mineral acids, while the crystalline form (normal selenite) was difficultly soluble.

TABLE I

Acid	ZrO ₂ present, 0.1200 g.		ZrO ₂ found, g.			
	6 <i>N</i> acid present, cc.	Acid normality of solution				
HCl	40	0.60	0.1202	} 0.1199		
			.1203			
			.1196			
			.1199			
			.1200			
			.1198			
			.1196			
		50	0.75		.1178	
		60	0.90		.1097	
		80	1.20		.0930	
HNO ₃	10	0.15	0.1201			
			25	.38	.1201	
			35	.53	.1187	
			40	.60	.1151	
			50	.75	.1040	
H ₂ SO ₄	40	.60	0.1206	} 0.1202		
			.1198			
			.1200			
			.1200			
			.1205			
		60	0.90		.0142	
		80	1.20		.0080	

It is seen from Table I that greater acidity in hydrochloric acid can be used than in nitric acid if complete precipitation is to be expected, and that with hydrochloric acid the total acidity should not much exceed 0.6 *N*

(40 cc. of 6 *N* HCl in 400 cc. of solution). Sulfuric acid is the least desirable acid medium of the three, not only because of the slowness of precipitation and greater difficulty of removing the precipitate from the beaker, but also because a slight increase in acidity over 0.6 *N* causes a very sharp decrease in the amount of zirconium precipitated.

Incidentally, the statement made by Smith and James⁶ that precipitated zirconium selenite cannot be easily redissolved for reprecipitation was found to apply only to the crystalline form. The freshly precipitated flocculent form dissolves in hot 6 *N* hydrochloric acid without much difficulty.

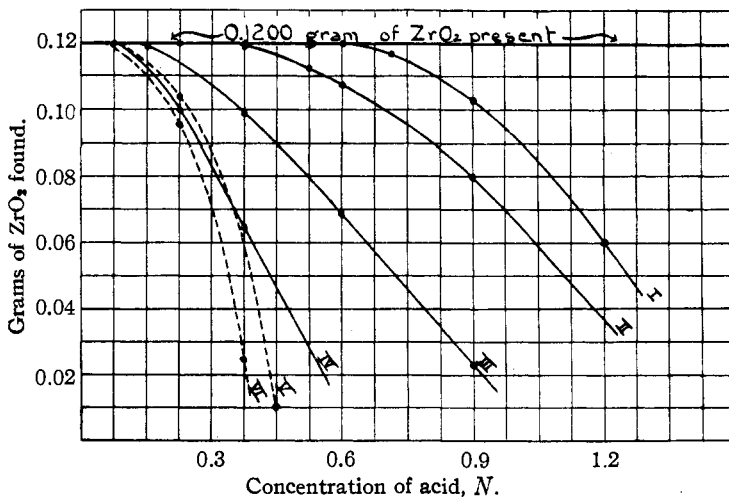


Fig. 1.—I, HCl + 0.5 g. of Na_2SO_4 ; II, HCl + 2 g. of Na_2SO_4 ; III, HCl + 5 g. of Na_2SO_4 ; IV, HCl + 10 g. of Na_2SO_4 ; V, H_2SO_4 + 0.5 g. of Na_2SO_4 ; VI, H_2SO_4 + 2 g. of Na_2SO_4 .

Effect of Alkali Salts on the Precipitation of Zirconium Selenite.—

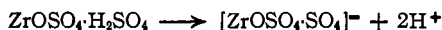
Determinations of zirconium with selenious acid in the presence of alkali salts were next made. In these experiments, 400 cc. of solution were used, 25 cc. of standard zirconyl chloride (equivalent to 0.1200 g. of ZrO_2) was present and the zirconium was precipitated from boiling solution with 20 cc. of 10% selenious acid. Varying concentrations of hydrochloric acid and of sulfuric acid were used and also varying amounts of alkali salts. Several determinations using 40 cc. of 6 *N* hydrochloric acid and amounts of sodium chloride, sodium nitrate, ammonium chloride and ammonium nitrate up to 10 g. gave precipitates of zirconium selenite producing on ignition 0.1200 ± 0.0004 g. of ZrO_2 . Similarly, the presence of alkali chloride showed no appreciable effect upon the precipitation from sulfuric acid solution. The presence of alkali *sulfate*, however, had a marked effect on the precipitation from hydrochloric acid solution, and an even

⁶ Smith and James, Ref. 2, p. 1768.

greater effect from sulfuric acid solution. These effects are shown in Fig. 1, in which grams of ZrO_2 obtained are plotted against the volume of acid in 400 cc. of solution. From this graph it is seen that *increasing amounts of sulfate require a corresponding decrease in acidity for complete precipitation of zirconium*. Conversely, with a solution of desirable acidity in hydrochloric acid (e. g., 0.6 *N*) *only a small amount of sulfate can be present if complete precipitation is desired*.

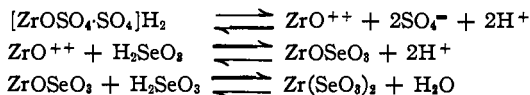
In all cases, increasing amounts of alkali sulfate caused a decrease in the rate of precipitation and gave more crystalline precipitates.

Explanation of the Effect of Sulfate.—The explanation of the peculiar effect of the presence of sulfate on the completeness of precipitation of zirconium selenite is probably analogous to that proposed by Ruer in his studies on the precipitation of zirconium oxalate.⁷ Ruer found that the addition of oxalate to zirconyl chloride solution gave a precipitate, but the addition of oxalate to zirconyl sulfate solution or to a mixture of zirconyl chloride and alkali sulfate gave no precipitate. He assumed the ionization of zirconyl sulfate to be



This assumption is borne out by the experimental fact that upon electrolysis of zirconyl sulfate the zirconium migrates to the anode, whereas with zirconyl chloride the zirconium migrates to the cathode.

Applying the same theory to the precipitation of zirconium selenite from sulfate solution, the following equilibria may be written



Application of the principle of mass action to these equilibria shows that an increase in acidity and in sulfate-ion concentration would cause a decrease in solubility of the selenite precipitate. This is borne out by the experimental data. It is likewise apparent that a considerable excess of precipitating agent is desirable.

Metals Precipitated by Selenious Acid.—Solutions of various metal ions were treated individually with selenious acid solution to determine those precipitated by that reagent. In each case, 10 mg. of metal was present in 25 cc. of solution which was also 0.6 *N* in hydrochloric acid (except that 0.6 *N* nitric acid was used where an insoluble chloride could be formed). All the common cations were tested for, as well as various members of the rare earth group and of the gold and platinum groups. Thallium, beryllium, molybdenum, vanadium, tungsten, and uranium were also included.

The only elements which precipitated with selenious acid from the acid

⁷ R. Ruer, *Z. anorg. Chem.*, **42**, 87 (1904).

solution were zirconium, titanium, thorium and ceric cerium. (Ferrous iron and stannous salts precipitated free selenium by reduction of the reagent.)

Although Berg and Teitelbaum⁸ have shown that bismuth precipitates quantitatively with selenious acid from solutions which are 0.25–0.33 *N* in nitric acid, bismuth does not precipitate from this concentration of hydrochloric acid nor from solutions which are 0.60 *N* in hydrochloric or nitric acid, the latter concentration being the one used in the finally adopted method for zirconium. Ferric iron, silver and mercuric mercury also form insoluble selenites but these are likewise soluble in 0.60 *N* acid.⁹

Although no experimental evidence has been obtained, the element hafnium undoubtedly behaves like zirconium in its reaction with selenious acid, and if present in the original sample would not be distinguished from zirconium by this method. This is, of course, equally true of all other methods in common use.

Elimination of the Effect of Titanium and Cerium.—Smith and James have claimed that the presence of hydrogen peroxide prevents the precipitation of titanium by selenious acid. Since hydrogen peroxide in acid solution also reduces ceric cerium to the cerous form, which is unprecipitated by selenious acid, it would seem that hydrogen peroxide could be used to cause precipitation of pure zirconium selenite by selenious acid even in the presence of titanium and cerium. Twenty-five cc. portions of the standard zirconyl chloride solution were mixed with solutions of ceric nitrate and titanium chloride, 20 cc. of hydrogen peroxide and 20 cc. of 6 *N* hydrochloric acid were added. The solutions were heated and diluted to 400 cc. and the zirconium precipitated with 20 cc. of 10% selenious acid. The results were as follows.

ZrO ₂ present, g.	Ce ⁺⁺⁺⁺ added, g.	Ti ⁺⁺⁺⁺ added, g.	ZrO ₂ found, g.
0.1200	0.050	...	0.1201
.1200	.0501195
.1200	...	0.050	.1338
.1200	.050	.050	.1341
.1200	.050	.050	.1331

This would indicate that zirconium selenite can be precipitated pure in the presence of cerium if hydrogen peroxide has been added to reduce the cerium to the trivalent state but that zirconium cannot be precipitated pure by one precipitation in the presence of much titanium even in the presence of hydrogen peroxide. Since basic zirconium selenite, if freshly precipitated, can be dissolved in hot 6 *N* hydrochloric acid, the above

⁸ R. Berg and M. Teitelbaum, *Z. anorg. allgem. Chem.*, **189**, 101 (1930).

⁹ Mercurous mercury precipitates with selenious acid, even from 0.6 *N* nitric acid solution, but in the adopted procedure the preparation of the solution would bring about oxidation of any mercurous mercury.

determinations were repeated, but the zirconium precipitates were washed by rough decantation, dissolved in hot 6 *N* hydrochloric acid, and the zirconium reprecipitated under the same conditions as above. The results were as follows.

ZrO ₂ present, g.	Ce ⁺⁺⁺⁺ added, g.	Ti ⁺⁺⁺⁺ added, g.	ZrO ₂ found, g.
0.1200	...	0.050	0.1203
.1200050	.1211
.1200	0.050	.050	.1207
.1200	.050	.050	.1205

Double precipitation by selenious acid in the presence of hydrogen peroxide therefore suffices to precipitate zirconium nearly completely, uncontaminated by cerium or titanium.

Elimination of the Effect of Thorium.—The presence of the element thorium gives greater difficulty in the determination of zirconium by selenious acid, since it is precipitated by the reagent and is not affected by hydrogen peroxide. Smith and James dismissed this difficulty with the statement that thorium is rarely present in zirconium ores, but Dana¹⁰ lists many zirconium ores in which thorium is present in considerable amount.

The two most common methods of separating thorium from zirconium are with hydrofluoric acid and with oxalic acid. Since the former method requires platinum ware and other special forms of apparatus, it was not experimentally applied to this case. Oxalic acid precipitates thorium oxalate from slightly acid solution and leaves zirconium in solution. Since, however, zirconium selenite will not precipitate from solutions containing oxalate, it becomes necessary in this case to remove excess oxalate after filtering off the thorium precipitate. An attempt was first made to destroy this oxalate with concentrated permanganate solution, but, besides introducing a very large amount of manganese into the solution, it was found difficult to destroy all of the oxalate by this method. It seemed best to destroy oxalate by evaporation with sulfuric acid, but since all but a small amount of sulfate must be absent from the solution from which zirconium is precipitated, an additional step is necessary, namely, that of precipitating zirconium with ammonium hydroxide and dissolving in hydrochloric acid before precipitating with selenious acid.

In the following determinations, zirconium (+thorium) was first precipitated with selenious acid from 0.6 *N* hydrochloric acid solution, the precipitate was dissolved in hot 6 *N* hydrochloric acid and 40 cc. of hot 10% oxalic acid solution. The solution was diluted to 200 cc. with hot water and made 0.36 *N* in hydrochloric acid. After standing overnight, the thorium oxalate was filtered off and the filtrate evaporated with 18 *N*

¹⁰ E. S. Dana, "System of Mineralogy."

sulfuric acid until oxalate was completely destroyed. The solution was diluted and made ammoniacal. The precipitate was filtered, washed superficially with water and dissolved in 15 cc. of hot 12 *N* hydrochloric acid. The solution was then treated with 20 cc. of 3% hydrogen peroxide, diluted to 400 cc. and the zirconium was precipitated from the hot solution with selenious acid. The results were as follows.

ZrO ₂ present, g.	Th ⁺⁺⁺⁺ added, g.	ZrO ₂ found, g.
0.1200	0.050	0.1190
.1200	.050	.1195
.1200	.050	.1191
.1200	.050	.1178

The somewhat low values seemed to indicate the probability of some zirconium precipitating with the thorium. Scott¹¹ recognizes this possibility and recommends two precipitations of thorium in its separation from zirconium. In the next series of determinations this was done by decomposing the precipitated thorium oxalate by evaporation with 18 *N* sulfuric acid. The solution was diluted, made just ammoniacal and then slightly acid. The thorium was again precipitated with oxalic acid and the filtrates were united before proceeding as above with the precipitation of the zirconium. Erratic results were obtained for the weights of zirconium dioxide, however, some being within 0.3 mg. of the correct value (*i. e.*, 0.1200 g.) while others ran as high as 0.1315 g. It seemed obvious, therefore, that thorium oxalate is incompletely precipitated in the presence of a large concentration of sulfate ion. This was substantiated by a series of determinations in which the thorium in 25-cc. portions of thorium nitrate solution was precipitated with 10% oxalic acid solution from 0.36 *N* hydrochloric acid solution in the presence of varying amounts of sulfate. The thorium oxalate precipitates were ignited to oxide and the results were as follows.

(Gram ThO₂ present = 0.1660)

Gram-equivalents of sulfate present	0.090	0.180	0.360	0.540
G. ThO ₂ obtained, g.	.1658	.1656	.1581	.1524

This effect of high sulfate concentrations in preventing the complete precipitation of thorium oxalate is therefore analogous to the effect of sulfate on the precipitation of zirconium oxalate as studied by Ruer. It also explains the erratic results obtained in the above determinations of zirconium when thorium was precipitated twice, for somewhat variable amounts of sulfate were present in the second precipitation of thorium. The obvious remedy for this error is to precipitate the thorium with ammonium hydroxide, after reprecipitating with oxalic acid. This addi-

¹¹ W. W. Scott, "Standard Methods of Chemical Analysis," 4th ed., p. 622.

tional step was therefore included in the method finally adopted and described below.

Experiments on Adsorption.—Since freshly precipitated zirconium selenite can be redissolved in hot 6 *N* hydrochloric acid and reprecipitated from the diluted solution, and since the final proposed method involves three such precipitations, it was felt that any possibility of error due to adsorption of foreign elements would be eliminated. The following experiments were made, however, to verify this conclusion.

The zirconium in 25-cc. portions of the standard zirconyl chloride solution (equivalent to 0.1200 g. of ZrO_2) was precipitated from 400 cc. of solution containing 40 cc. of 6 *N* hydrochloric acid and 0.20 g. of various metal ions. It was found that even with a single precipitation of zirconium the elements manganese, zinc, cobalt, copper, lead, bismuth, iron, aluminum, and rare earth metals are not seriously adsorbed, the maximum adsorption increasing the weight of ZrO_2 obtained to 0.1210 g. With two precipitations, the adsorption in each case was negligible, being not greater than 0.2 mg. Uranyl ions were considerably brought down by one precipitation (ZrO_2 found, 0.1225 g.) but not by two precipitations (ZrO_2 found, 0.1202 g.). Vanadium as vanadate was greatly adsorbed (0.1415 g. ZrO_2) but on dissolving the precipitate in hot hydrochloric acid, vanadate is reduced to vanadyl ions, which are not brought down by zirconium selenite, and 0.1200 g. of ZrO_2 was obtained. Since in the proposed method hydrogen peroxide is to be added to hold cerium and titanium in solution, any vanadium would be converted to pervanadic acid. Pervanadic acid, like vanadate, is greatly adsorbed by zirconium selenite (in the presence of 0.20 g. of vanadium as pervanadate 0.1294 g. of ZrO_2 was obtained), so in the proposed method of analysis one precipitation of zirconium selenite is made without the addition of hydrogen peroxide and following the addition of alcohol to reduce any vanadate to the vanadyl form.

Proposed Methods of Analysis

Proposed Method for Zirconium when Present in Solution.—To the nearly neutral solution, which should be free from phosphate, sulfate, columbium and tantalum and which should have a volume not much greater than 100 cc., add 20 cc. of 12 *N* hydrochloric acid and 20 cc. of alcohol. Heat nearly to boiling, dilute to 500 cc., again heat to boiling and add 20 cc. of 10% selenious acid solution. Allow to stand hot until the supernatant liquid is clear enough to filter (preferably not over two hours). Filter and wash superficially with hot water. Puncture the paper and thoroughly flush off the precipitate into the original beaker with a fine stream of hot water, using as little as possible and saving the paper. Add 15 cc. of 12 *N* hydrochloric acid and heat until the precipitate is dissolved (a slight turbidity sometimes persists but may be permitted to remain). Add 20 cc. of 3% hydrogen peroxide, warm, dilute to 500 cc., heat to boiling, and again precipitate with 20 cc. of 10% selenious acid. Filter and wash with hot water. Again puncture the paper and flush off the precipitate.

(A) In a small beaker digest the two filter papers with 40 cc. of hot 10% oxalic acid solution. Filter and wash the pulp, and add the filtrate and washings to the zirconium

precipitate. Dilute to 200 cc., heat to boiling and add 12 cc. of 6 *N* hydrochloric acid. Let stand at room temperature for at least ten hours. Filter and wash the precipitate with a solution containing 40 cc. of 6 *N* hydrochloric acid and 25 g. of oxalic acid per liter. To the filtrate add 30 cc. of 18 *N* sulfuric acid and start evaporating on the water-bath, covering the beaker with a large watch-glass supported on a glass triangle. (If the oxalate precipitate is large, flush it off into a 400-cc. beaker, add 5 cc. of 18 *N* sulfuric acid and evaporate on the water-bath until oxalate has been destroyed, as shown by the cessation of the evolution of gas bubbles. Dilute with water, make ammoniacal, filter and dissolve in 12 cc. of 6 *N* hydrochloric acid. Dilute to 160 cc., heat to boiling, and add 40 cc. of 10% oxalic acid. Let stand for at least ten hours and filter into the main solution.) Evaporate on the water-bath until oxalate has been destroyed as shown by the cessation of the evolution of gas bubbles. Wash down the sides of the beaker and watch-glass and filter any precipitated selenium. If a small amount of red selenium runs through the paper it may be neglected. Make the solution ammoniacal, filter and wash superficially with hot water. Puncture the paper and flush off the precipitate with as little hot water as possible. Pour 15 cc. of hot 12 *N* hydrochloric acid over the paper into the zirconium hydroxide suspension and heat until the precipitate is entirely dissolved. (B)

Add 20 cc. of 3% hydrogen peroxide and warm. Dilute to 500 cc. and heat to boiling. Add 20 cc. of 10% selenious acid and filter after the supernatant liquid is clear. Ignite over the Bunsen flame and finally for five minutes over the Méker burner. Weigh as ZrO_2 .

In the known absence of thorium, the above method may be shortened. The oxalate precipitation involved in the above directions from (A) to (B) may be omitted. In this case, dissolve the zirconium selenite precipitate obtained at (A) by adding 20 cc. of 12 *N* hydrochloric acid and heating to boiling. Continue from point (B). Ignite the two filter papers from which the first two precipitates were washed and add the weight of their ash to the final weight of ZrO_2 .

Results Obtained by Use of the Proposed Method.—The above proposed method for the determination of zirconium was applied to the following mixtures and the values obtained are shown in the last column. It may be pointed out that the mixtures used are such as to offer greater difficulty than would be encountered in an ordinary analysis.

ZrO_2 present, g.	Th ⁺⁺⁺⁺ , g.	Ce ⁺⁺⁺⁺ , g.	Ti ⁺⁺⁺⁺ , g.	V as VO_3^- , g.	U as UO_2^{++} , g.	Fe ⁺⁺⁺ , g.	ZrO_2 found, g.
0.1200	0.050	0.050	0.050	0.1202
.1200	.050	.030	.040	0.040	0.050	0.050	.1198
.1200	.050	.030	.040	.040	.050	.050	.1201
.1200	.050	.030	.040	.040	.050	.050	.1189

Decomposition of Zirconium Ores.—The most satisfactory methods for the decomposition of zirconium minerals are fusion with sodium peroxide or sodium peroxide mixtures, fusion with borax, and fusion with alkali fluorides. Of these, a strong alkaline fusion should serve best in cases where zirconium is subsequently to be determined by the selenite method, for by this fusion the interfering constituents phosphate, columbium and tantalum can be removed most easily. Hillebrand and Lundell¹² state that

¹² W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Chemistry," John Wiley and Sons, Inc., New York, p. 445.

phosphate is best removed by fusion of the original material with sodium peroxide and leaching with water. Some columbium and tantalum are removed in this way, but by fusing the residue with potassium carbonate or potassium hydroxide, columbium and tantalum can be practically completely removed. Schoeller and Powell¹³ have studied this separation and have worked out a procedure which, according to Hillebrand and Lundell, serves as probably the best method for the removal of these elements. In this connection the authors state that it is preferable to dissolve in acid the extraction residue from the first fusion, precipitate with ammonia and use the ignited precipitate for the second fusion rather than to fuse the residue directly.

Fusion with sodium peroxide is usually carried out in a nickel crucible and for ordinary zirconium ores requires about twenty minutes. A simple procedure for sodium peroxide fusions and one that is complete in a very short time is that devised by Muehlberg.¹⁴ This consists in mixing the sample with sugar carbon and sodium peroxide and igniting, the crucible being kept covered and also immersed in running water during the ignition and subsequent cooling. The melt shrinks when cooling and can be easily removed from the crucible. It has the very great advantage of introducing no nickel from the crucible into the melt. The method has been further studied by Marvin and Schumb,¹⁵ who have determined the exact conditions for the most satisfactory decomposition of refractory substances and have found that all common refractories yield to the treatment, including zircon and other zirconium ores.

The following directions serve as a rapid method not only for decomposing zirconium ores but also for removing phosphate, columbium and tantalum. The method prepares the material for the determination of the zirconium by the selenite method given above.

Proposed Method of Attack of Zirconium Ores.—Place in a 50-cc. nickel crucible about 25 g. of an intimate mixture (made by gently rolling the two constituents in a large dry bottle) of 15 parts of fine sodium peroxide with 1 part of 100-mesh pure sugar carbon. Weigh out 1 g. of the finely ground sample upon this mixture, cover with more fusion mixture and mix intimately at the surface with a spatula. Cover with a liberal layer of the fusion mixture and immerse in cold running water so that the level of the water is slightly above the level of the contents of the crucible. Cautiously start the ignition by means of the glowing tip of a piece of cotton twine and immediately cover the crucible. After fusion is complete and the crucible is cold, remove the contents to a 1-liter beaker, add 300 cc. of cold water, flush out the crucible and wash off the cover. Heat nearly to boiling until the melt has disintegrated, dilute to 900 cc. with hot water, and heat until the supernatant liquid is clear enough to filter. Filter and wash the residue with hot water. Reject the filtrate. (If much phosphate is present or if columbium or tantalum is present in small amounts, treat the residue with hydrochloric acid and without filtering

¹³ W. R. Schoeller and A. R. Powell, *J. Chem. Soc.*, 119, 1928 (1921).

¹⁴ W. F. Muehlberg, *Ind. Eng. Chem.*, 17, 690 (1925).

¹⁵ G. G. Marvin with W. C. Schumb, *THIS JOURNAL*, 52, 574 (1930).

add excess ammonia. Filter, ignite the residue and repeat the fusion and leaching as above.) Dissolve the residue in hydrochloric acid and filter off any undissolved material. This is essentially carbon but it may contain a very small amount of undecomposed original material (seldom more than one milligram), which can be separately fused with sodium peroxide-carbon mixture and the residue, after leaching with water, dissolved in hydrochloric acid and added to the main solution. To the hydrochloric acid solution add 25 cc. of 18 *N* sulfuric acid and evaporate to fuming. Cool, dilute with water and filter off any silica. Make the filtrate ammoniacal, filter, wash superficially with hot water and dissolve in 15 cc. of 12 *N* hydrochloric acid. The solution is then ready for the determination of zirconium by the method described above.

With moderate or high percentages of columbium or tantalum, treat the residue from the first peroxide-carbon fusion with hydrochloric acid and without filtering add excess ammonia. Filter and wash superficially with hot water. Ignite and fuse for five minutes in a platinum crucible with 20 parts of potassium carbonate. Leach with hot water, filter, and wash with 2% potassium carbonate solution and then with hot water. With high percentages of columbium and especially with high percentages of tantalum fuse the residue again with potassium carbonate. Leach with water; ignite the residue and fuse in the original platinum crucible with potassium pyrosulfate. Extract with 200 cc. of hot water, containing 10 cc. of 18 *N* sulfuric acid, filter, make the solution ammoniacal, filter and wash superficially with hot water. Dissolve the precipitate in 15 cc. of 12 *N* hydrochloric acid. The solution is then ready for the precipitation of zirconium as described above.

Results Obtained by the Proposed Fusion Method.—Artificial ores, made by mixing pure ZrO_2 with feldspar, apatite, and Cb_2O_6 , when fused according to the directions above and the zirconium precipitated with selenious acid, gave the following values.

ZrO_2 , g.....	0.0837	0.0973	0.1112	0.1183	0.1091	0.1034
Feldspar, ^a g.....	.66	.60	.50	.30	.50	.30
Apatite (=32% P_2O_5), ^a g.....	.13	.14	.12	.050	.050	.050
Cb_2O_6 , ^a g.....050	.050	.050
Sample, g.....	.8705	.8840	.7280	.5201	.7132	.5052
ZrO_2 found, g.....	.0830	.0950	.1109	.1184	.1100	.1040
% ZrO_2 present.....	9.62	11.66	15.28	22.75	15.30	20.46
% ZrO_2 found.....	9.54	11.39	15.23	22.77	15.43	20.58

^a Approximate weights only, as indicated.

Summary

1. Zirconium is quantitatively precipitated as basic selenite by excess selenious acid from solutions the acidity of which should not be greater than 0.6 *N*.

2. Hydrochloric acid is the best acid medium for this precipitation. Sulfuric acid causes a much slower precipitation, presumably of the crystalline normal selenite, and the precipitate is more difficult to remove from the beaker and more difficult to redissolve.

3. The presence of more than a small amount of sulfate prevents quantitative precipitation of zirconium from hydrochloric acid or sulfuric

acid solution. Increasing sulfate requires decreasing acidity for quantitative precipitation. This effect is probably due to the formation of $[\text{ZrOSO}_4 \cdot \text{SO}_4] \text{H}_2$, which provides few zirconium or zirconyl ions.

4. The elements zirconium (with hafnium), titanium, thorium and ceric cerium are the only elements which can ordinarily be present in a zirconium mineral which are precipitated either wholly or in part by selenious acid from 0.6 *N* hydrochloric acid solution.

5. The precipitate of zirconium basic selenite, if not allowed to stand suspended in hot solution long enough to become crystalline, can be redissolved in hot 6 *N* hydrochloric acid and therefore can be reprecipitated free from adsorbed elements (*e. g.*, vanadate and uranyl salts which are considerably brought down by the zirconium precipitate). Vanadium, if previously reduced to vanadyl salt, is not brought down by the zirconium precipitate.

6. The addition of hydrogen peroxide before the precipitation of zirconium causes reduction of ceric cerium, therefore prevents its precipitation, and holds up titanium sufficiently so that it is eliminated by two precipitations of zirconium selenite.

7. Quantitative separation of thorium can be effected by double precipitation of thorium oxalate in the absence of sulfate and subsequent removal of excess oxalate by evaporation with sulfuric acid.

8. A method for the analysis of zirconium by means of selenious acid is given in detail. This gives satisfactory results even when all of such elements as thorium, ceric cerium, titanium, vanadium, iron and uranium are originally present.

9. A rapid method for decomposing zirconium ores preparatory to making the above analysis is also given. By this method phosphate, columbium and tantalum can be eliminated and the selenite method as given then serves as a satisfactory method for zirconium in any zirconium ore.