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Spectrophotometric Determination of Zirconium

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ABSTRACT

Development work is being continued on the use of Thoron [$\text{I}-(\text{o}-\text{arsono-phenylazo})-2\text{-naphthol-3,6-disulfonic acid}$] as a spectrophotometric reagent. Its previous use for the determination of thorium(IV), together with experimental results on its formation of complexes with tin(IV), titanium(IV), hafnium(IV) and zirconium(IV), indicates that thoron may be specific for metals which have a valence of plus four in the formation of their salts.

Thoron has been used successfully for the determination of zirconium. The method covers a range of 10 to 100 μg of zirconium with a precision of 5.7% in the 10 μg range, and 2.9% in the 100 μg range.

The method is simple, rapid and does not require a skilled analyst. The reagent, although complex, is now available commercially, and requires little preparation.

There are very few interferences which cannot be reduced to non-interfering states, or removed from the sample without loss of zirconium.

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Spectrophotometric Determination of Zirconium

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In 1938, Liebhafsky and Winslow⁽³⁾ developed a method for determining 10 to 100 μg of zirconium. This method makes use of the stable lakes formed with zirconium by alizarin, quinalizarin or purpurin.

Hayes and Jones⁽¹⁾ have developed a procedure for zirconium in steel, which is dependent upon the color produced when the zirconium salt of p-dimethyl-aminoazophenylarsonic acid is dissolved in ammonium hydroxide. This method requires 30 minutes digestion time after precipitation, plus a double filtration. This method will determine 0.02 to 1.0 mg of zirconium.

Thoron [1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid] shows promise as a reagent for the spectrophotometric determination of most metals which have a valence of plus four in the formation of their salts. It has been used previously for the determination of thorium⁽⁵⁾ and fluoride⁽²⁾, the latter made possible by its diminution of the color of the thorium-thoron complex.

EXPERIMENTAL

Aliquots of 0.25, 0.50 and 1.0 ml. of the zirconium oxide standard, which contained 100 μg of zirconium per ml., were pipetted into separate 10-ml. volumetric flasks. To each flask were added 7 drops of concentrated hydrochloric acid and 1.0 ml. of 0.2% thoron reagent. These samples were diluted to 10 ml. with distilled water. A reference was prepared by diluting 7 drops of concentrated hydrochloric acid and 1.0 ml. of 0.2% thoron reagent to 10 ml. with distilled water.

The spectral absorption curve was determined over a wavelength range of 522 to 720 m μ . When a check was made on the determination, a marked change

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was noted in the absorbancies over the entire wavelength range. The spectral absorption curve was re-determined each 30 minutes, using the same samples, until the absorbancies for all wavelengths became constant. The time required for complete color development at room temperature was 2 hours. The wavelength at maximum absorption was 555 m μ . The spectral absorption curve for the 2-hour, 100 μ g sample is shown in Figure 1. Figure 2 shows the effect of time on the development of the color of the zirconium-thoron complex. The color is stable for at least 12 hours for pure zirconium solutions containing up to 50 μ g of zirconium per 10-ml. volume. For standard solutions containing 50 to 100 μ g, per 10-ml. volume, the color is stable for at least 6 hours. There is a tendency for the complex to precipitate in a short time if the solution contains more than 100 μ g of zirconium per 10-ml. volume.

In an attempt to speed the color development of the zirconium-thoron complex, a new set of aliquots was prepared as before, and heated to 50°C, and held at 50-55°C for 5 minutes. Absorbancy readings at 555 m μ showed the development of the color to be complete for the 25 and 50 μ g samples, but slightly low for the 100 μ g sample. This experiment was repeated at a temperature of 75°C, and the development of the color was found to be complete for all three samples. When the zirconium metal standard was used for this experiment, the results were identical to those for the zirconium oxide standard.

When absorbancy readings were made immediately after heating the samples, they were slightly higher than those of the 2-hour curve. The temperature of the solution in the cells was measured, and it was found that all absorbancy readings below 40°C were constant. However, in later work with impure solutions, absorbancy readings were not constant until the samples had cooled to the temperature of the cell compartment of the Beckman spectrophotometer.

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Figure 1 Spectral Absorption Curves of the Zirconium-Thoron and Hafnium-Thoron Complexes

Figure 2 Effect of Time on the Development of the Color of the Zirconium-Thoron Complex

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A standard calibration curve for 0.25, 0.50 and 1.0 ml aliquots of the standard solution, which were heated at 75°C for 5 minutes, is shown in Figure 3. This curve is in precise agreement with the 2-hour curve shown in Figure 2. Curves prepared by both methods conform to Beer's law.

INTERFERENCES

The following interferences are listed under the method of Liebhafsky and Winslow(3): Molybdate, fluoride, sulfate, phosphate, iron(III), chromium(III), cobalt, aluminum, copper, lead, cadmium and titanium. Of these, cobalt, aluminum, copper, cadmium and sulfate do not interfere with the formation of the zirconium-thoron complex when present in a ratio of 1000 μg of the impurity to 100 μg of zirconium.

Iron(III) and chromium(III) form colored solutions which absorb light at 555 m μ , and produce positive errors if present in a ratio of 1000 μg of the impurity to 100 μg of zirconium.

Molybdate causes a positive error when present in a ratio of 10 parts of molybdenum to 1 part of zirconium. The reaction is not known. In the method of Liebhafsky and Winslow, it is stated that molybdate complexes zirconium. If this were the case, the results would be low. It is possible that a molybdenum-thoron complex is formed, but a valence of plus six for molybdenum in molybdate compounds makes it improbable.

Phosphate complexes zirconium and may be tolerated only to the extent of 10 μg of phosphate to 100 μg of zirconium.

Fluoride diminishes the color of the zirconium-thoron complex and may be tolerated only in amounts less than 1 μg per 10 ml. of solution.

Titanium(III) bleaches thoron reagent. It does not interfere if present in an amount comparable to that of zirconium.

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Figure 3 Standard Calibration Curve of the Zirconium-Thoron Complex

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Titanium(IV) forms a complex with thoron, but much greater amounts are required than is the case for zirconium. It does not interfere when present in a ratio of 100 μg of titanium(IV) to 10 μg of zirconium. Above this amount, the combined titanium and zirconium exceed the capacity of thoron to form a complex, and a precipitate is formed. The light yellow colored supernate absorbs only a small amount of light, and the absorbancy reading indicates low results.

In addition to those listed, tin(II and IV), uranium(VI), chromium(VI) and perchloric acid were tested.

Tin(II) bleaches the color if present to the extent of 1000 μg of tin(II) to 100 μg of zirconium. Tin(IV) forms a complex with thoron. When present in a ratio of 1000 μg of tin(IV) to 100 μg of zirconium, the reaction is the same as that for titanium(IV).

Uranium(VI) forms a yellow colored solution which absorbs light at 555 $\text{m}\mu$ and produces a positive error if present in a ratio of 10 parts of uranium(VI) to 1 part of zirconium.

Chromium(VI) bleaches thoron reagent and may not be present in excess of 0.5 μg per 10 ml. of solution.

Perchloric acid (70%) does not interfere if 0.1 to 0.5 ml. is present in 10 ml. of solution provided the absorbancy readings are made within 1 hour after heating. If more than 0.5 ml. of 70% perchloric acid is present per 10 ml. of solution, the zirconium-thoron complex precipitates in a short time. Although perchloric acid is used to remove fluoride from the standards, the concentration remaining after dilution is insignificant.

Tables I and II give numerical results of the deviations discussed in this section. Standards "A" and "B" refer to standards made on different

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dates from the same stock solution (zirconium oxide standard). When chromium, iron, tin or other ions are present which interfere in the oxidized state but not the reduced state, they may be reduced with hydroxylamine hydrochloride, without interfering with the formation of the zirconium-thoron complex.

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TABLE I Effect of Various Impurities on the Absorbancy of Zirconium-Thoron Complex

Volume of test solution = 10 ml.
Zirconium present in solution = 100 µg
Impurity present in solution as indicated
Wavelength - 555 mµ

Suspected Interference (X)	Absorbancy No (X) Present (Std. Zirconium)	Absorbancy 100 µg of (X) Present	Absorbancy 1.0 mg of (X) Present
Standard "A"			
Chromium(III)	0.338	0.338	0.372
Cobalt	0.340	0.340	0.343
Copper	0.338	0.340	0.338
Iron(III)	0.338	0.342	0.361
Iron(II)	0.339	0.338	0.343
Molybdenum	0.339	0.341	0.348
Standard "B"			
Aluminum	0.336	0.332	0.332
Cadmium	0.334	0.334	0.337
Chromium(VI)	0.336	- - -	0.027
Nickel	0.335	0.332	0.335
Lead	0.336	0.333	0.335
Tin(IV)	0.333	0.326	ppt.
Tin(II)	0.333	0.336	0.312
Titanium(IV)	0.333	0.330	ppt.
Titanium(III)	0.333	0.321	0.190
Uranium(VI)	0.332	0.334	0.347

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TABLE II Effect of Known Interferences on the Zirconium-Thoron Complex

Volume of test solution = 10 ml

Wavelength = 555 mμ

Sample No.	Interference		Zirconium		Deviations		
	Ion	Amount μg	Known μg	Absorbancy	Found μg	From Known μg	%
1. Chromium(VI)(a)		10	10	0.036	10.8	+ 0.8	+ 8.0
		40	40	0.137	40.8	+ 0.8	+ 2.0
		100	100	0.338	100.6	+ 0.6	+ 0.6
		100	10	0.037	11.1	+ 1.1	+11.0
		400	40	0.148	44.4	+ 4.4	+11.0
		1000	100	0.372	110.7	+10.7	+10.7
2. Iron(III)(a)		10	10	0.035	10.5	+ 0.5	+ 5.0
		40	40	0.138	41.0	+ 1.0	+ 2.5
		100	100	0.342	101.8	+ 1.8	+ 1.8
		100	10	0.036	10.8	+ 0.8	+ 8.0
		400	40	0.140	41.8	+ 1.8	+ 4.5
		1000	100	0.361	107.4	+ 7.4	+ 7.4
3. Molybdate		10	10	0.031	9.3	- 0.7	- 7.0
		40	40	0.133	39.6	- 0.4	- 1.0
		100	100	0.339	100.9	+ 0.9	+ 0.9
		100	10	0.041	12.3	+ 2.3	+23.0
		400	40	0.165	49.2	+ 9.2	+23.0
		1000	100	0.348	103.6	+ 3.6	+ 3.6
4. Tin(IV)(b)		10	10	0.035	10.5	+ 0.5	+ 5.0
		40	40	0.136	40.5	+ 0.5	+ 1.3
		100	100	0.326	97.0	- 3.0	- 3.0
		100	10	0.035	10.5	+ 0.5	+ 5.0
		400	40	0.135	40.3	+ 0.3	+ 0.8
		1000			- - -	- - -	- - -

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TABLE II Effect of Known Interferences on the Zirconium-Thoron Complex (Continued)

Sample No.	Interference		Zirconium		Deviations		
	Ion	Amount μg	Known μg	Absorbancy	Found μg	From Known μg	%
5. Tin(II)		10	10	0.036	10.8	+ 0.8	+ 8.0
		40	40	0.138	41.0	+ 1.0	+ 2.5
		100	100	0.336	100.0	0.0	0.0
		100	10	0.036	10.8	+ 0.8	+ 8.0
		400	40	0.136	40.5	+ 0.5	+ 1.3
		1000	100	0.312	92.9	- 7.1	- 7.1
6. Titanium(IV)(b)		10	10	0.031	9.3	- 0.7	- 7.0
		40	40	0.129	38.5	- 1.5	- 3.8
		100	100	0.330	98.2	- 1.8	- 1.8
		100	10	0.032	9.6	- 0.4	- 4.0
		400	40	0.100	29.9	- 10.1	- 25.2
		1000	100	ppt.	- - -	- - -	- - -
7. Titanium(III)		10	10	0.032	9.6	- 0.4	- 4.0
		40	40	0.127	37.8	- 2.3	- 5.8
		100	100	0.321	95.5	- 4.5	- 4.5
		100	10	0.027	8.1	- 1.9	- 19.0
		400	40	0.017	5.2	- 34.8	- 87.0
		1000	100	0.190	56.5	- 43.5	- 43.5
8. Uranium(VI)		10	10	0.035	10.5	+ 0.5	+ 5.0
		40	40	0.136	40.4	+ 0.4	+ 1.0
		100	100	0.334	99.4	- 0.6	- 0.6
		100	10	0.037	11.2	+ 1.2	+ 12.0
		400	40	0.143	42.5	+ 2.5	+ 6.3
		1000	100	0.347	103.3	+ 3.3	+ 3.3

(a) Reduced with 20% hydroxylamine hydrochloride.

(b) Oxidized to a valence of plus four with bromine water.

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REAGENTS AND APPARATUS

All chemicals except Thoron are "analytical reagent grade."

Hydrochloric acid, specific gravity 1.188 to 1.192

Hydroxylamine hydrochloride solution, 20%

Perchloric acid, 70%

Nitric acid, specific gravity 1.42

Sodium fluoride

Sodium tetraborate

Thoron reagent (Fine Organics, Inc., 211 E. 19th St., New York 3, N.Y.)

Dilute 0.2000 g of Thoron $\left[1-(o\text{-arsonophenylazo})-2\text{-naphthol-3,6-disulfonic acid}\right]$ to 100 ml. with distilled water.

The Beckman Model DU quartz spectrophotometer with 1-cm path length quartz cells was used for all absorbancy readings.

PROCEDURE

Preparation of Zirconium Standard from Zirconium Metal

Zirconium metal dissolves very rapidly and completely in hydrofluoric acid. However, the reaction is very vigorous, and there is a danger of loss due to splattering. A platinum vessel is required for the operation.

An improved method has been devised in which zirconium is dissolved in a solution of sodium fluoride in dilute hydrochloric acid.

A stock solution was prepared by adding 0.1000 grams of zirconium metal (99.8% pure Zr) to a beaker containing a 50 per cent stoichiometric excess of sodium fluoride and 10 ml. of 1:5 hydrochloric acid. The solution was heated until the metal dissolved, then evaporated until nearly dry. Fluoride was removed from the solution by fuming in a mixture of 5 ml. of 70% perchloric acid and 5 ml. of concentrated nitric acid until nearly dry. The residue was transferred to a 100-ml. volumetric flask and diluted to 100 ml. with 15% hydrochloric acid. A standard which contained 100 μ g of zirconium per ml. of

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solution was prepared by diluting 10 ml. of the stock solution to 100 ml. with distilled water.

Preparation of Zirconium Standard from Zirconium Oxide

The sample containing 0.1351 g. of zirconium oxide (99.8% pure ZrO_2) was fused with sodium tetraborate in a platinum crucible by the method of Lundell and Knowles⁽⁴⁾. The melt was dissolved by boiling it in 1:1 hydrochloric acid sufficient to cover the crucible in a beaker. The solution of zirconium chloride was transferred to a 100-ml. volumetric flask, and diluted to 100 ml. with distilled water. The final solution should be 15 to 20% hydrochloric acid. A standard which contained 100 μ g of zirconium per ml. was prepared by diluting 10 ml. of the stock solution to 100 ml. with distilled water.

Preparation of Hafnium Standard from Hafnium Tetramandelate

A stock solution was prepared by adding 0.7627 g. of hafnium tetramandelate [99.8% pure $Hf(C_6H_5-CHOH-CO_2)_4$] to a beaker, and fuming until nearly dry in a mixture of 5 ml. of concentrated nitric acid and 5 ml. of 70% perchloric acid. The residue was transferred to a 100-ml. volumetric flask and diluted to 100 ml. with 15% hydrochloric acid. The procedure for determining the spectral absorption curve for hafnium (Fig. 1) is identical with that for zirconium.

Procedure

Pipet a sample which contains 10 to 100 μ g of zirconium into a 10-ml. volumetric flask. If ferric, stannic or chromate ions are present, add 5 drops of 20% hydroxylamine hydrochloride solution.

Add 7 drops of concentrated hydrochloric acid and 1.0 ml. of 0.2% thoron reagent. Dilute to volume with distilled water, heat to 75°C on a water bath and maintain at 75 to 80°C for 5 minutes.

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Cool the sample to room temperature, and set the Beckman spectrophotometer at 0-0 absorbancy with a reference which contains 7 drops of concentrated hydrochloric acid and 1.0 ml. of 0.2% thoron reagent diluted to 10 ml. with distilled water.

Determine the absorbancy of the sample at a wavelength of 555 m μ .

SUMMARY

Zirconium has been determined in the range of 10 to 100 μ g with a precision of 5.7% for 10 μ g of zirconium, and 2.9% for 100 μ g of zirconium in the presence of most impurities. These percentages do not include those which were the result of obvious interference e.g., above 10% deviation from the true value. It is expected that the zirconium concentration of most samples will be large enough in proportion to the impurities, that interferences may be reduced to noninterfering valence states or diluted out of the interfering range.

The complex is stable for at least six hours for any amount of pure zirconium up to 100 μ g in a 10-ml. volume. The wavelength at the maximum absorption is 555 m μ .

Hafnium is identical with zirconium in its reaction with thoron reagent, and in its absorption characteristics. One microgram of zirconium is spectrophotometrically equivalent to 2.1 μ g of hafnium (1 mole of zirconium = 1.05 moles of hafnium).

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