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Quantitative Analysis of Mixtures of Metal Ions by the Ring-Oven Method: Uranium–Thorium–Zirconium–Titanium and Thorium–Cerium–Zirconium–Titanium

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Summary

Successful schemes for the separation of the constituents in the mixtures U–Th–Zr–Ti and Ce–Th–Zr–Ti have been worked out, using the ring-oven method. The constituents are first separated in the form of thin rings. The rings are then developed with selective organic reagents. For the determinations, the intensities of these rings are then compared visually with standard rings, similarly prepared with known amounts. The time required for complete separation and determination of the constituents is about 60–70 min, excluding the time required for the preparation of the standard scales. Separations are possible down to the following concentrations. Ce, 2.1 μg; Th, 3.5 μg; Ti, 0.36 μg; U, 1.8 μg; Zr, 2.7 μg.

In connection with the work on the analytical chemistry of less familiar elements, the analyses of the following mixtures have been attempted by the ring-oven method, using suitable solvents for washing:

A. Uranium–thorium–zirconium–titanium
B. Thorium–cerium–zirconium–titanium

After separation, the rings containing the individual metal ions have been developed with organic reagents and determined by ring colorimetry (*1*). It may be mentioned that the separation of the above metal ions in combination is difficult, particularly when

small amounts are present. The procedures described here permit the separations of exceedingly small amounts of these.

EXPERIMENTAL

Apparatus

A Weisz Ring Oven (National Appliance Co., Portland, Oregon) was used with a suitable power unit yielding 25 V from 220 V/50 cycles a.c. mains. The same self-filling capillary pipet (ca. 1.5 μl) was employed in every case.

Filter Paper

Circles of Whatman No. 1 filter paper of 55 mm diameter (chromatography grade) were employed throughout and are referred to as "paper" in the procedures.

Solvents for Washing

The following solvents were used for washing:

1. *n*-Butanol (BDH AnalaR)
2. 30 volumes of hydrogen peroxide (E. Merck)
3. 0.5 *N* HNO_3 (BDH AnalaR)

Precipitant

The precipitant used was 10% aqueous w/v ammonium oxalate.

Developing Reagents

The following developing reagents were used:

Alizarin: 0.1% w/v in ethanol
Benzidine: 0.05% w/v in 4 *M* acetic acid
Chromotropic acid: 5% w/v aqueous solution
Potassium ferrocyanide: 1 *M* aqueous solution
Thoron: 0.1% aqueous w/v solution

Metal Solutions

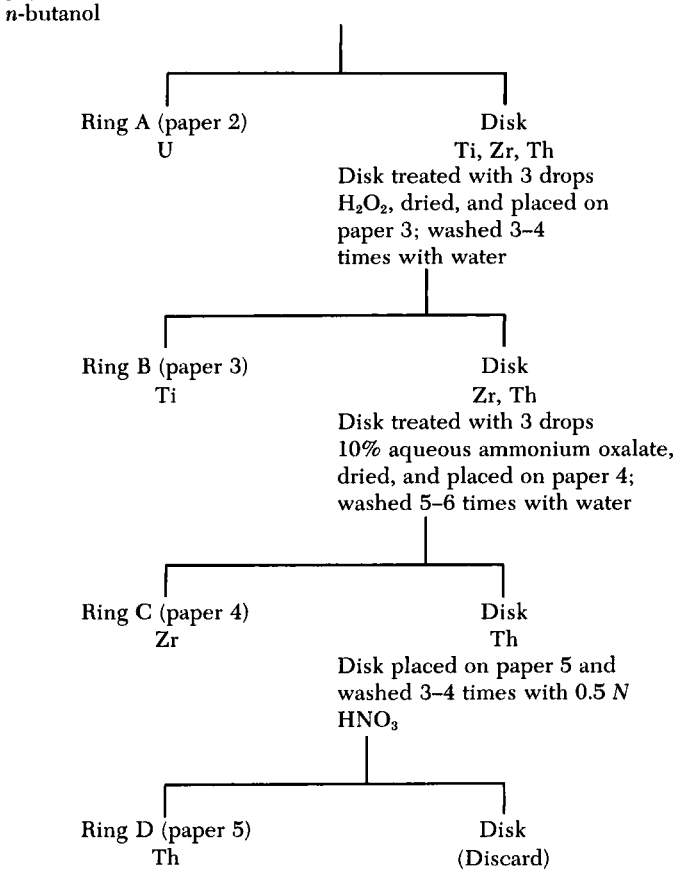
0.1 *M* solutions of thorium nitrate, titanium tetrachloride, zirconyl chloride, ceric sulfate, and uranyl acetate were prepared and

standardized as usual. Suitable mixtures were prepared by mixing varying volumes of metal solutions.

Procedure

Separation and Determination of Uranium–Thorium–Zirconium–Titanium. The mixture was spotted on the marked center of filter-paper circle 1 with the self-filling pipet, dried, and the spot was punched out (disk). The disk was placed on paper 2, 1 drop of 1 *N* HNO_3 was added, and the moist disk was washed 5 times with *n*-butanol.

Chart 1. Separation of uranium–titanium–zirconium–thorium.

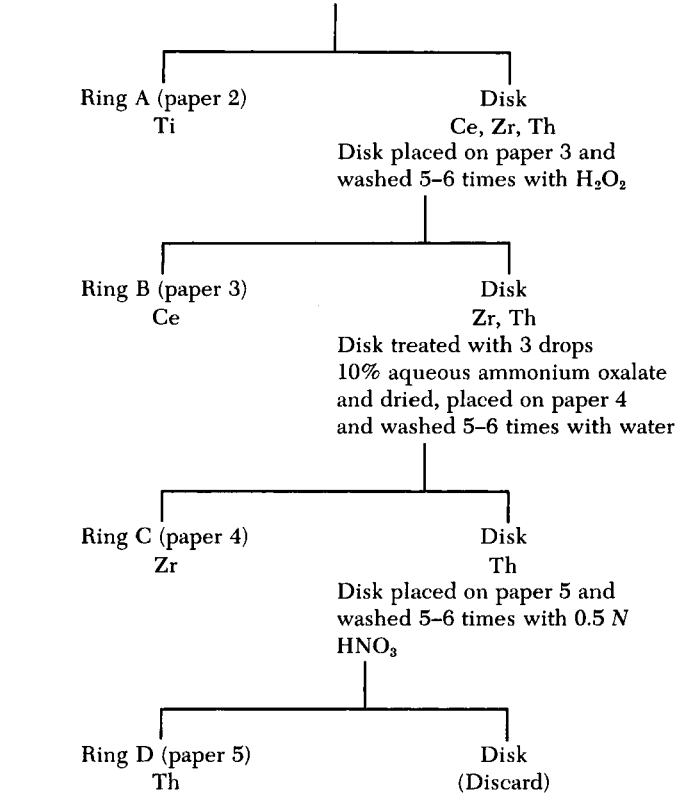


Uranium(VI) was thus transported to ring zone A. The disk containing the remaining metal ions was taken in the holder and treated with 3 drops of hydrogen peroxide. At first, 1 drop was applied and heated in the ring oven; then the next drop was applied and again heated. The alternate application of the reagent and heating is necessary, otherwise the metal ions may flow with the reagent. After the treatment, the disk was placed on paper 3, and washed 3–4 times with water. Thus titanium(IV) was washed to ring zone B. The disk then containing Zr(IV) and Th(IV) was taken again into the disk holder and it was treated with 3 drops of 10% ammonium oxalate. The disk was kept on paper 4 and washed with water 5–6 times. Thus zirconium(IV) migrated to ring zone C. The disk now contained only Th(IV). The disk was placed on paper 5 and washed 5 times with 0.5 *N* HNO_3 to carry thorium(IV) to ring zone D. The disk was then discarded. Papers 2, 3, 4, and 5 containing uranium, titanium, zirconium, and thorium, respectively, were developed in ring zones with the reagents described in the Table 1. The entire procedure is described in Chart 1.

Separation and Determination of Thorium–Cerium–Zirconium–Titanium. The mixture was spotted on the marked center of circular filter paper 1, dried, and the spot punched out (disk). The disk was then taken into the holder, treated with 2 drops of hydrogen peroxide, and dried in the ring oven. After the treatment, the disk was placed on paper 2 and washed 3–4 times with water. Thus titanium(IV) migrated to ring zone A. The disk containing the remaining metal ions was placed on paper 3 and washed 3–4 times with hydrogen peroxide. Cerium(IV) was thus transported to ring zone B. The disk now contained Th(IV) and Zr(IV). The disk was taken into the holder, treated with 3 drops of 10% aqueous ammonium oxalate, dried, placed on paper 4, and washed 5–6 times with water. Thus zirconium(IV) moved to ring zone C. The disk now containing Th(IV) only was placed on paper 5 and 5–6 washings were applied with 0.5 *N* HNO_3 to transfer thorium(IV) to ring zone D. The disk was then discarded. Papers 2, 3, 4, and 5 containing titanium, cerium, zirconium, and thorium, respectively, were developed in the ring zones with the reagents described in the Table 1. The entire procedure is described in the Chart 2.

For the quantitative determinations, appropriate standard scales were prepared with each of the individual cations separately. The

Chart 2. Separation of thorium–cerium–zirconium–titanium.



standard rings (3,5) were prepared with even numbers of drops of the standard solutions by using the self-filling micropipet (1.5 μl) and were numbered II, IV, VI, VIII, and X and contained 2, 4, 6, 8, and 10 drops of solution, respectively. The test rings were prepared with 1, 3, 5, 7, and 9 drops and were numbered I, III, V, VII, and IX, respectively. The total number of test rings were compared with the total number of standard rings. The amounts of Ce, U, Th, Zr, and Ti were determined by visual comparison of the intensities of the rings formed from the test drops with those formed from

TABLE 1

Developing Reagents Employed (2)

Metal ion	Reagent	Color
Cerium(IV)	Treated the ring with (dil) NaOH + benzidine	Blue
Thorium(IV)	Thoron	Crimson red
Titanium(IV)	Chromotropic acid	Red-brown
Uranium(VI)	Potassium ferrocyanide	Dark-brown
Zirconium(IV)	Alizarin	Red to dark violet

the standard drops (3,4). The amount of each constituent in the rings is given by

$$C_a = C_s(n_s/n_a)$$

where C_s is the concentration of the standard solution, n_a the volume of the sample solution, and n_s the volume of the standard solution used in the matching ring.

A large number of artificial mixtures were analyzed. It has been found that determinations are possible down to the following limits when present in a drop of the solutions: Ce, 2.1 μg; Th, 3.5 μg; Ti, 0.36 μg; U, 1.8 μg; Zr, 2.7 μg. Some of the typical results for the separation of mixture A are shown in Table 2 and those of for mixture B are shown in Table 3.

TABLE 2

Results of the Determinations, A

No.	Ion	Taken, mg/ml	Found, mg/ml	% Error
I	U	1.50	1.43	−4.6
	Ti	0.25	0.24	−4.0
	Zr	1.00	0.96	−4.0
	Th	2.30	2.32	+0.87
II	U	2.00	1.90	−5.0
	Ti	0.30	0.29	−3.3
	Zr	1.50	1.46	−2.7
	Th	3.20	3.25	+1.56
III	U	2.50	2.38	−4.8
	Ti	0.40	0.42	+5.0
	Zr	2.00	2.01	+0.5
	Th	4.10	4.17	+1.7

TABLE 3

Results of the Determinations, B

No.	Ion	Taken, mg/ml	Found, mg/ml	% Error
I	Ti	0.25	0.24	−4.0
	Ce	1.50	1.40	−6.6
	Zr	1.00	0.96	−4.0
	Th	2.30	2.32	+0.87
II	Ti	0.30	0.29	−3.3
	Ce	2.00	1.96	−2.0
	Zr	1.50	1.46	−2.7
	Th	3.20	3.25	+1.56
III	Ti	0.40	0.42	+5.0
	Ce	2.50	2.52	+0.8
	Zr	2.00	2.01	+0.5
	Th	4.10	4.17	+1.7

The time required for separation and determination of the constituents of the above combinations was about 60–70 min, excluding the time required for the preparation of the standard scales.

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