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Spectrofluorimetric Determination of Zirconium in Hafnium Metal with Salicylic Acid and Rhodamine B after Its Separation Using Chloroacetic Acid and Salicylic Acid

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A spectrofluorimetric method is described for the determination of 2 to 16 μg of zirconium based on the formation of an ion-association complex with salicylic acid and Rhodamine B. Hafnium behaved similarly to zirconium, but the interference can be overcome by selective extraction of zirconium at pH 1.4—1.6 from 1 mol dm^{-3} chloroacetic acid medium into 0.3 mol dm^{-3} solution of salicylic acid in 2:3 mixture of isobutyl methyl ketone (IBMK) and chloroform. The spectrofluorimetric method in conjunction with the separation procedure has been used for the determination of 4.4 to 14.5% of zirconium in hafnium metal.

Methods have been described for the spectrophotometric determination of zirconium based on the ion-association between its anionic chelates with cationic dyes.[1,2] These complexes were not fluorescent and were extracted into organic solvents prior to determination. In the present work it was found that the ion-association complex involving zirconium(IV), salicylic acid and Rhodamine B can form the basis of an extractive spectrofluorimetric procedure as the presence of traces of zirconium with salicylic acid caused the nonfluorescent Rhodamine B in benzene to intensely fluoresce. However, hafnium behaved very similarly to zirconium and therefore necessitated their separation to be realised beforehand.

Methods have been described for the extractive separation of zirconium from various carboxylic acid solutions. Zirconium was shown to be preferentially extracted in the presence of H_2O_2 at pH 3.2 to 3.6 into organic phase containing 0.5 mol dm^{-3} solution of mixed C_7 to C_9 fatty acids.[3] Cole and Brown[4] achieved a separation factor of 22 for zirconium by using a saturated solution of salicylic acid (1.115 mol dm^{-3}) in furfural. Quantitative extraction of zirconium from 33% trichloroacetic acid solution into 1-butanol[5] and from 0.01 mol dm^{-3} malonic acid at pH 3.0 into a 4% solution of Amberlite LA-1 or LA-2 in xylene[6] have been reported, but the use of these methods for the separation of zirconium from hafnium has not been demonstrated. The preferential extraction of zirconium to the extent of 80% from solutions at pH 1.4± 0.1 into a chloroform solution containing 0.05 mol dm^{-3} salicylic acid and 0.37 mol dm^{-3} collidine has also been described.[7] In the course of our study, it was found that zirconium can be selectively extracted from hafnium, rapidly and quantitatively, from 1 mol dm^{-3} chloroacetic acid at pH 1.4—1.6 into IBMK and chloroform mixture containing salicylic acid. The organic phase upon equilibration with dilute hydrochloric acid returned the zirconium quantitatively into the aqueous phase thus making it available for fluorimetric determination. In conjunction with the extractionprocedure the fluorimetric method developed was found useful for application to samples containing high concentration of hafnium.

Experimental

Reagents. *Standard Zirconium Solution*: Dissolve 0.3532 g of $ZrOCl_2\cdot8H_2O$ in 20 cm^3 of 1:1 perchloric acid and dilute to 100 cm^3 with distilled water to provide a 1000 ppm Zr stock solution. Dilute appropriate volume of the stock solution with water, just before use, to obtain 100 ppm and 4 ppm solution.

Salicylic Acid Extraction Solution (0.3 mol dm^{-3}): Dissolve 4.14 g of salicylic acid in 1000 cm^3 of 2:3 mixture of IBMK and chloroform.

Chloroacetic Acid (3 mol dm^{-3}):

Hydrochloric Acid (2.5 mol dm^{-3}):

Salicylic Acid Solution (2%): Dissolve 2 g of salicylic acid in 100 cm^3 methanol and store in a stoppered bottle.

Rhodamine B Solution (0.03%):

Acetate Buffer (pH 4.0):

Apparatus. A Carl Zeiss PMQ II spectrophotometer with a ZFM fluorescent attachment provided with a 250 VA mercury vapour lamp was used. Slit widths of 5 mm for excitation filter and 0.03 mm for emission monochromator were employed for the fluorescence measurements with 10 mm×10 mm×45 mm quartz cells with polished bottoms. The instrument was standardised using standard glass fluorescer F53 supplied by the manufacturer.

Procedure. To an aliquot of the sample containing not more than 1000 μg of zirconium, add 5 cm^3 of 3 mol dm^{-3} chloroacetic acid and adjust the pH of the solution to 1.4 to 1.6 using dilute sodium hydroxide and hydrochloric acid. Transfer the solution to 60 cm^3 separatory funnel and dilute to 15 cm^3 with water. Equilibrate the solution for 1 min with 10 cm^3 of salicylic acid extraction solution. Drain the organic phase into another separatory funnel and strip twice with 5 cm^3 portions of 2.5 mol dm^{-3} hydrochloric acid. Boil the solution over a hot plate for 5 min, cool and make up to a suitable volume with water.

Determination of Zirconium: Transfer an aliquot of the stripped phase containing not more than 16 μg of zirconium into a 25 cm^3 beaker. Add 1 cm^3 each of salicylic acid and Rhodamine B solution followed by 5 cm^3 of 0.5 mol dm^{-3} solution of sodium acetate. Adjust the pH to 4.0 and transfer to a 60 cm^3 separatory funnel. Dilute the solution to about 15 cm^3 with water and shake for 1 min with 5 cm^3 benzene. After separating the benzene phase and centrifuging off the water droplets measure the fluorescence intensity of the extracts at 575 nm using 546 nm excitation filter. Subtract the blank reading and establish the concentration of zirconium by reference to a calibration graph prepared by applying the procedure to 0.5 cm^3 to 4 cm^3 of 4 ppm zirconium solution in place of sample solution.

Results and Discussion

The fluorimetric method resulted from an investiga-

TABLE 1. EFFECT OF DIFFERENT PARAMETERS ON THE EXTRACTION OF THE COMPLEX
(Salicylic acid (2.0%) and Rhodamine B (0.03%) solutions 1 cm^3 each at pH 4.0 except when varied as shown) (Zr : 10 μg).

pH	3.4	3.6	3.7	3.9	4.1	4.3	4.4
Fluorescence intensity	19	32	40	40	40	30	25
Salicylic acid solution (%)	0.25	0.5	1.0	2.0	3.0	4.0	5.0
Fluorescence intensity	20	30	40	40	40	37	20
Rhodamine B solution 0.01% (cm^3)	0.5	1.0	2.0	3.0	4.0	4.5	5.0
Fluorescence intensity	20	28	40	41	40	37	35
Extraction time/min	0.5	1	2	3	4	5	
Fluorescence intensity	40	41	41	39	40	40	
Aqueous phase volume (cm^3)	10	12	15	17	20	25	30
Fluorescence intensity	41	40	41	40	40	30	26

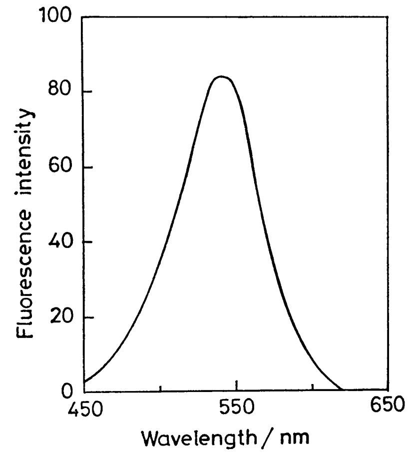

Fig. 1. Excitation spectra (uncorrected) 10 μg of zirconium treated as in determination.

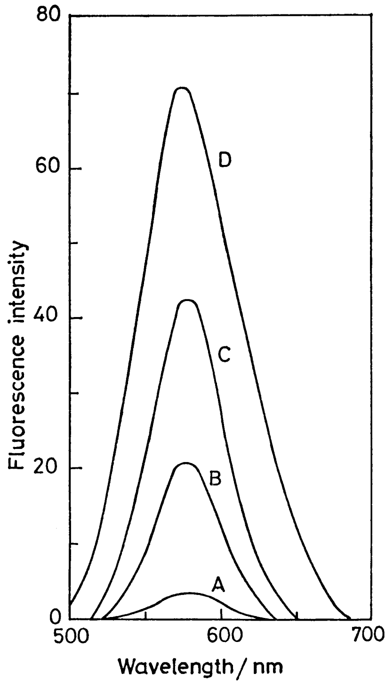

Fig. 2. Emission spectra. (A) 0 μg, (B) 5 μg, (C) 10 μg, and (D) 15 μg of zirconium treated as in determination.

tion of the interaction of Rhodamine B with zirconium after the addition of various carboxylic acids over the pH range 1 to 5. The carboxylic acids examined included mandelic acid, cinnamic acid, anthranilic acid, salicylic acid, and *N*-phenylanthranilic acid. Amongst these, salicylic acid was found to be the best as in its presence the benzene extract was found to be strongly fluorescent with excitation and emission maximum at 546 nm and 575 nm respectively (Figs. 1 and 2). The blank was found to fluoresce only feebly under similar conditions. Using 5 cm^3 benzene for extraction purposes and maintaining an equeous phase volume of 15 cm^3, optimum analytical conditions were established and the results are summarised in Table 1.

The fluorescent intensity of the benzene extract remained stable for at least 4 h and the calibration graph was linear in the range 2 to 16 μg of zirconium.

Ten replicate standard solution containing 10 μg of zirconium gave an average recovery of 101% with a relative standard deviation of 3.9%.

Composition of the Complex. The ratio of zirconium to Rhodamine B in the complex was found to be 1:1 by both mole ratio and continuous variation methods. However the ratio of zirconium to salicylic acid in the complex could not be found out since the extraction of the ion-association complex into benzene was found to be negligible when the salicylic acid concentration was present in molar proportions.

Interference Studies. Besides hafnium many ions were found to interfere in the determination of 10 μg of zirconium when present in excess of the amounts shown in parantheses. The ions that caused enhancement of fluorescent intensity included UO_2^{2+} (10 μg), Th^{4+} (50 μg) and Sb^{5+} (50 μg), while the presence of Al^{3+} (200 μg), Fe^{3+} or Fe^{2+} (50 μg), Cr^{3+} (50 μg), Ce^{4+} (50 μg), VO_3^- (500 μg), Ti^{4+} (100 μg), MoO_4^{2-} (500 μg), WO_4^{2-} (500 μg), Pd^{2-} (500 μg), Pt^{4+} (500 μg), Bi^{3+} (200 μg), and Sn^{2+} (100 μg) caused a decrease in fluorescent intensity. No interference was encountered from one milligram amounts of Ag^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, rare earths, CrO_4^{2-}, AsO_4^{3-}, $S_2O_3^{2-}$, SO_4^{2-}, and SCN^-.

Extractive Separation of Zirconium. Initial studies were made using 1 mol dm^{-3} solution of chloroacetic acid and trichloroacetic acid and 100 μg of zirconium or hafnium. Extractions were made from 15 cm^3 aque-

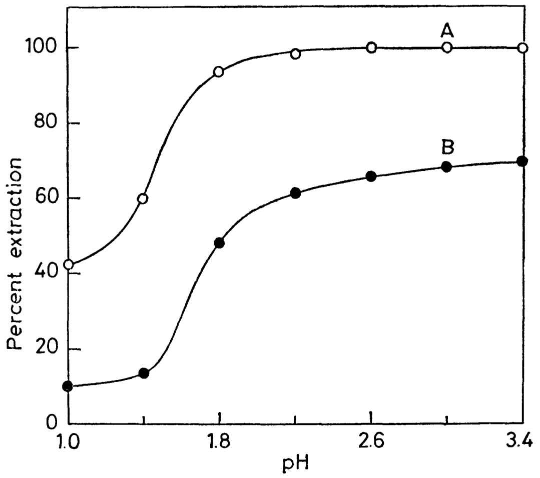

Fig. 3. Percentage extraction of (A) 100 μg of zirconium (B) 100 μg of hafnium as a function of pH. Chloroacetic acid: 1 mol dm^{-3}, IBMK solvent.

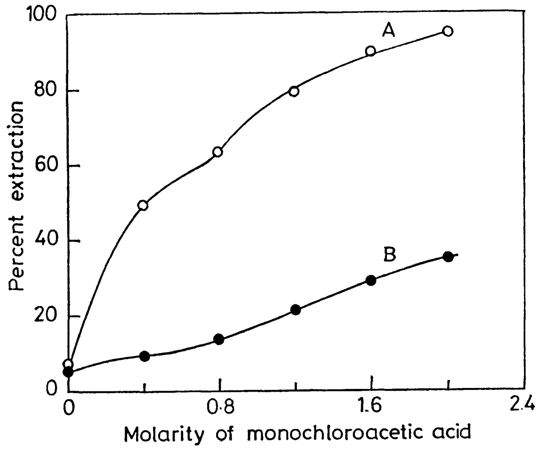

Fig. 4. Percentage extraction of (A) 100 μg of zirconium and (B) 100 μg of hafnium as a function of chloroacetic acid concentration. pH: 1.5, IBMK solvent.

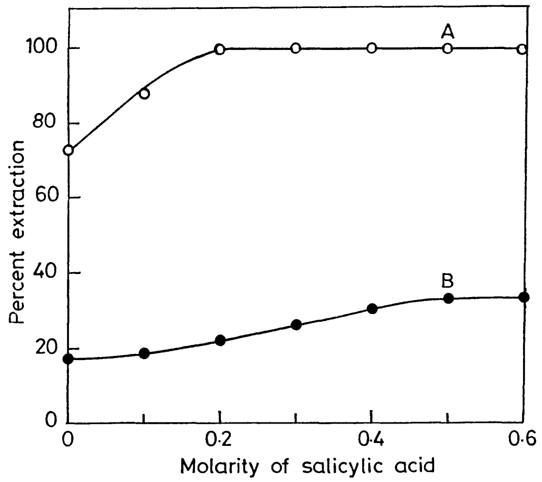

Fig. 5. Effect of salicylic acid concentration on the extraction of (A) 100 μg of zirconium and (B) 100 μg of hafnium into IBMK from 1 mol dm^{-3} chloroacetic acid at pH 1.5.

ous phase maintained at pH 0.5, 1.5, and 2.5 into 10 cm^3 IBMK for 5 min. The percentage of zirconium or hafnium extracted was established after stripping the organic phase twice with 5 cm^3 of 2.5 mol dm^{-3} of hydrochloric acid and applying the quercetin procedure.[8] The results showed that zirconium and hafnium extract to varying extent from each of these aqueous systems. Chloroacetic acid at pH 2.5 was found to quantitatively extract zirconium and 60% of hafnium while under similar conditions trichloroacetic acid extracted 82% of zirconium and 40% of hafnium. At other pH conditions, zirconium and hafnium were found to extract to a lesser extent from both systems. Extraction from chloroacetic acid was therefore chosen for further study.

The extraction of zirconium or hafnium as a function of pH is shown in Fig. 3. It is evident that the extraction of zirconium (curve A) is quantitative at pH's greater than 2.5. Hafnium (curve B), though did not extract quantitatively, showed a trend which was very similar to zirconium. The separation factor for zirconium was maximum (13.8) at pH 1.5, where zirconium extraction was incomplete (75%) and hafnium coextracted to a significant extent (18%).

Figure 4 shows the effect of chloroacetic acid concentration maintained at pH 1.5 on the extraction of zirconium (curve A) and hafnium (curve B) into IBMK. It is clear that zirconium extraction does not reach a quantitative value even upon raising the concentration of chloroacetic acid to 2 mol dm^{-3}. In addition, as evident from curve B, the presence of higher concentration of chloroacetic acid also increased the coextraction of hafnium and therefore it was decided to confine the investigation using 1 mol dm^{-3} solution.

Other solvents examined included chloroform butyl acetate, cyclohexanone, benzene, cyclohexane, 1-butanol, and carbon tetrachloride to ascertain the most suitable solvent for the quantitative extraction of zirconium from hafnium. Amongst these chloroform and carbon tetrachloride did not extract either zirconium or hafnium. Cyclohexanone, 1-butanol, cyclohexane, and benzene gave very low separation factor for zirconium. Butyl acetate behaved almost similar to IBMK, but the extraction of hafnium into this solvent was slightly more (22%) than into IBMK (18%).

Studies to improve the extraction of zirconium revealed that the addition of salicylic acid to be effective, as its presence in IBMK was found to quantitatively extract zirconium from 1 mol dm^{-3} chloroacetic acid at pH 1.5. Figure 5 shows the effect of variation of salicylic acid concentration on the extraction of these elements. It is evident that the salicyclic acid concentration should be at least 0.2 mol dm^{-3} for the quantitative extraction of zirconium and that its presence in excess of this amount also increases the extraction of hafnium. To ensure quantitative extraction of zirconium, it was decided to use a 0.3 mol dm^{-3} solution of salicyclic acid in IBMK, though this resulted in the coextraction of hafnium to an extent of 25%.

Attempts to render the organic extract free from hafnium revealed that retrograde extraction with a fresh aqueous phase of 1 mol dm^{-3} chloroacetic acid at pH 1.5 is ineffective as it caused 5% decrease in the recovery of zirconium. As chloroform did not extract zirconium or hafnium the use of 0.3 mol dm^{-3} salicyclic acid in IBMK–chloroform mixture for extraction was considered. Detailed examination showed that the presence of 5.5 to 6.5 cm^3 of chloroform in 10 cm^3 of the solvent mixture was sufficient for the quantitative extraction of zirconium without the coextraction of hafnium. The presence of chloroform in excess of the volume indicated, resulted in the lower recovery of zirconium.

A shaking time of 1 min was found to be sufficient for the quantitative extraction of zirconium and the extraction remained unaffected up to an aqueous to organic phase volume ratio of 3:2. After extraction, equilibration for 1 min with 10 cm^3 of hydrochloric acid of acidity 1.25 mol dm^{-3} was found to be sufficient for stripping the zirconium quantitatively from the organic phase. However, the use of 2.5 mol dm^{-3} hydrochloric acid was preferred for back-extraction as polymerization of zirconium in this medium has been shown to be minimum.[9]

The results of extraction and back-extraction of 5 to 1000 μg of zirconium showed quantitative recovery over the concentration range examined. In the presence of hafnium there was no evidence of its extraction up to 500 μg. However, when hafnium was present at 1 mg level a slight enhancement in the recovery of zirconium (to the extent of 4%) was noticed.

Nature of the Extracted Species. The plots of log *D* *vs.* log[chloroacetic acid] when extractions were carried out using IBMK containing 0.3 mol dm^{-3} salicyclic acid at pH 1.5 gave straight lines for both zirconium and hafnium with slopes of 0.80 and 0.98 respectively indicating that chloroacetic acid forms 1:1 species with both zirconium and hafnium. Similarly plot of log *D* *vs.* log[salicylic acid] when extractions were carried in the presence of 1 mol dm^{-3} chloroacetic acid, gave slopes of 1.2 and 0.84 for zirconium and hafnium, thus showing that both zirconium and hafnium form 1:1 complexes with both chloroacetic acid and salicylic acid.

Attempts to establish the molar ratio of solvent to metal using benzene as diluent were unsuccessful probably due to the existence of many species with varying number of solvent molecules occupying the coordination positions.

Under the optimal conditions for zirconium, the behaviour of aluminium, titanium, iron(III), thorium, uranium(VI), and vanadium(V) were ascertained using 1 mg amounts of the respective metal ions. After the organic phase was stripped twice with 5 cm^3 portions of 2.5 mol dm^{-3} hydrochloric acid, the concentration of the metal ion in the strippings and in the aqueous phase first subjected to extraction were spectrophotometrically determined using arsenazo III for thorium and uranium,[10] hydrogen peroxide for titanium,[11] 1,10-phenanthroline for iron,[12] Eriochrome cyanine R for aluminium[13] and tungstophosphoric acid for vanadium.[14] The results showed that uranium was not detected in the strippings but 5% of titanium, aluminium, and vanadium, 2.5% of iron and 2% of thorium were found to accompany zirconium.

Table 2. Recovery of zirconium in synthetic mixture

Mixture compositions (μg)	Amount of Zr found μg
Zr(100)+Hf(100)+Ti(1000)+SO$_4^{2-}$(1000)	101
Zr(500)+Hf(5)+La(1000)+Fe(III)(1000)	495
Zr(5)+Hf(500)+U(VI)(1000)+Al(1000)	5.0
Zr(10)+Hf(10)+Th(1000)+U(VI)(1000)	10.2
Zr(20)+Hf(200)+La(1000)+Ti(1000)	19.8

Table 3. Determination of zirconium in hafnium metal[a]

Weight of the sample taken (mg/100 cm^3)	Zr added (wt%)	Zr found (wt%)	Average concentration %
50	—	4.40	4.60
50	—	4.60	
50	2.5	7.20	
50	5.0	9.75	
50	10.0	14.50	

a) The sample containing 4.55% zirconium was supplied by Bhabha Atomic Research Centre, Bombay.

The results of the study of the anions revealed that the presence of one milligram amounts of fluoride and phosphate caused a low recovery and sulfate up to 2 mg does not affect the extraction of zirconium.

The method developed was applied in conjunction with the fluorimetric procedure for the determination of 2 to 16 μg of zirconium. After back-extraction into two 5 cm^3 portions of 2.5 mol dm^{-3} hydrochloric acid, the combined strippings in each instance was heated on a hot plate to reduce the volume to 5 cm^3. The solutions were then subjected to determination as described under experimental. A linear relationship was obtained over the whole range and the slope was identical to that obtained for aliquots of standard zirconium solutions that were not subjected to extraction and back-extraction step.

Recovery Studies. The method developed was applied in conjunction with spectrofluorimetry for the determination of zirconium in synthetic mixtures. After back-extraction, the strippings were subjected to the determination as described under determination. The results shown in Table 2 indicate satisfactory recovery in all instances.

Analysis of Hafnium Metal. The zirconium content of a hafnium metal sample was determined by the method developed. 50 mg of the impure hafnium metal was initially brought into solution by dissolving in 3 to 4 drops of hydrofluoric acid in a platinum crucible. Then 10 cm^3 of perchloric acid was added and the solution was evaporated to fumes of perchloric acid. The solution was cooled and made up to 100 cm^3 with water. A suitable aliquot of the solution was pipetted out and the zirconium content was determined by the method described under procedure. Samples to which known amounts of zirconium were added prior to dissolution were also analysed. The results are shown in Table 3. The close agreement of the results obtained with the reported value suggests that the method developed is useful for the determination of zirconium in hafnium-containing samples.

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