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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	11
page range	383-392
year	1959
URL	http://doi.org/10.50974/00042022

Studies on Analytical Methods for Trace Elements in
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Determination of Hafnium in Zirconium by Means of
Isotope Dilution Method*

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(Received August 13, 1959)

Synopsis

A method for the determination of hafnium in zirconium metal was studied. Hafnium was enriched from hydrochloric acid solution of zirconium sample with four steps of thiocyanate-hexone extraction-stripping method. After the several steps of extraction, pure hafnium fraction was obtained by passing the solution through the cation exchanger resin column, and eluting with the mixture of 0.45 M nitric acid and 0.095 M citric acid as an eluent. Combining the isotope dilution method and the above mentioned method, hafnium which existed from 0.025 to 0.1 per cent in zirconium was determined.

I. Introduction

The contents of hafnium in zirconium metals are determined by the indirect gravimetric method⁽¹⁾, the X-ray fluorescent method^{(2) (3)}, the spectrochemical method^{(4) (5)} and the spectrophotometric method⁽⁶⁾.

Recently zirconium was separated from hafnium effectively by the organic solvent extraction method^{(7) (8) (9) (10)} or by the ion exchange in order to produce pure zirconium metal^{(11) (12) (13)}. But it seems that there are some difficulties in applying these methods to analytical problem, especially to the analysis for low hafnium content in zirconium.

In present case, the isotope dilution method, combining with the ion exchange method and organic solvent extraction method, were studied for the purpose of

* The 950th report of the Research Institute for Iron, Steel and Other Metals. Published in Japanese in the Journal of Japan Institute of Metals, **23** (1959), 367.

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the determination of hafnium content in zirconium.

II. Apparatus and reagents

1. Radioactive tracer solution

(i) Hafnium-181 tracer solution

The hydrochloric acid solution of hafnium-181 was added to the hafnium carrier solution containing the mixture of sulfuric acid and oxalic acid, and the hafnium was precipitated as hydroxide by adding ammonium hydroxide solution. The precipitate was dissolved in the mixture of sulfuric acid and oxalic acid, and again hafnium was precipitated as its hydroxide. Repeating above mentioned process two or three times, hafnium was purified radiochemically.

Finally hafnium solution was prepared as the solution of 3 N in sulfuric acid and 1 per cent in oxalic acid. The amount and radioactivity of hafnium in 1 ml of solution were measured. In present case, 1 ml of solution contained 0.62 mg of hafnium and the radioactivities of solution were changed from 1424 cpm to 4250 cpm per ml.

(ii) Zirconium-95 tracer solution

Zirconium-95 tracer was purified by the method mentioned in the 1st report^{(14) (15)} from the zirconium-95 and niobium-95 solution which was separated from the fission products solution by means of cation exchange method. The solution was made to contain 1.05 mg of zirconium in 1 ml of solution. The measured radioactivity was 415 cpm per ml.

2. Standard solution

(i) Hafnium standard solution

The hafnium metal of 99.8 per cent purity was dissolved in the mixture of hydrofluoric acid and sulfuric acid, and was heated to dense fume. After the expelling of hydrofluoric acid, the solution was diluted to the fixed volume with the mixture of sulfuric acid and oxalic acid, and the acidity of solution was made to 3 N in sulfuric acid and 1 per cent in oxalic acid. In present case, 1 ml of this solution had contained 0.31 mg of hafnium.

(ii) Zirconium standard solution

Zirconium standard solution was prepared from the zirconium metal of 99.9 per cent purity by the method as same as the preparation of hafnium standard solution. In the present experiment, this solution was made to contain 1.03 mg of zirconium in 1 ml of solution.

3. Ion exchange resin

The cation exchanger resin, Dowex-50 ($\times 8$, 40~100 mesh), was used. The resin which was soaked in water was packed in the glass tube (10 mm in diameter and 300 mm in length). The flow rate of the effluent and eluent were controlled by the glass stopcock settled at the bottom of glass tube.

(14) H. Amano, *J. Japan Inst. of Metals*, **21** (1957), 260.

(15) G. W. Willkinson and W. E. Grummitt, *Nucleonics*, **9** (1951), 52.

4. Scaler and counter

The radioactivities of samples were measured by the decimal scaler combined with β -counting Geiger-Müller tube.

5. Reagents

All reagents used were chemically pure or analytically pure grades.

III. Experiments and results

1. Separation of zirconium and hafnium by cation exchanger

Zirconium and hafnium are separated by eluting the cation exchanger column which absorb both elements using suitable eluent, because of the difference of equilibrium constant between the cation exchanger and these two elements. Bennedict et al.⁽¹¹⁾ have separated these two elements with the cation exchanger by the use of a mixture of 0.45 M nitric acid and 0.095 M citric acid as an eluent, and Kraus et al.⁽¹³⁾ have reported on the separation of zirconium and hafnium by using the anion exchanger.

In the present paper, the author had tried to separate hafnium from various amounts of zirconium.

The experiments were carried out as follows; the sample solution which contained zirconium, hafnium or the mixture of them was treated with ammonium hydroxide, After the filtration of produced precipitate, it was returned into original beaker dissolving with the small volume of 6N hydrochloric acid. The solution, adjusting the acidity of 0.1~0.5 N hydrochloric acid, was then passed through the acid type cation exchanger column. After the washing by the water, zirconium and hafnium were eluted from the column by a mixed solution of 0.45 M nitric acid and 0.095 M citric acid which was passed through the column with the velocity of 2ml per minute. Every one drop of each 1 ml of eluent was dried up, and was counted. To ascertain the elution curve of zirconium or hafnium separately, the solution which contained only one of them was used. When mutual effect on the elution of two elements was studied, two sample solution containing two elements was taken, to the one of them zirconium tracer was added, to the other hafnium-181 tracer, and these two solution were treated above mentioned procedure.

As shown in Curve I and II of Fig. 1, when zirconium or hafnium existed in the solution separately, the elution of zirconium occurred immediately and completed by the 40 ml of eluent, but hafnium was eluted from the 50 ml of eluent. This fact was considered by the reason of the difference of equilibrium constant of each element. So the elution of hafnium was carried out by the column which was half of the one used in the first experiment in length. As shown in Curve III of Fig. 1, the beginning of elution of hafnium transferred to earlier part of elute. From this, it is evident that zirconium and hafnium will be separated finely by long column, but to shorten the time required to the separation the length of column was fixed in 15 cm length. Fig. 2 shows the

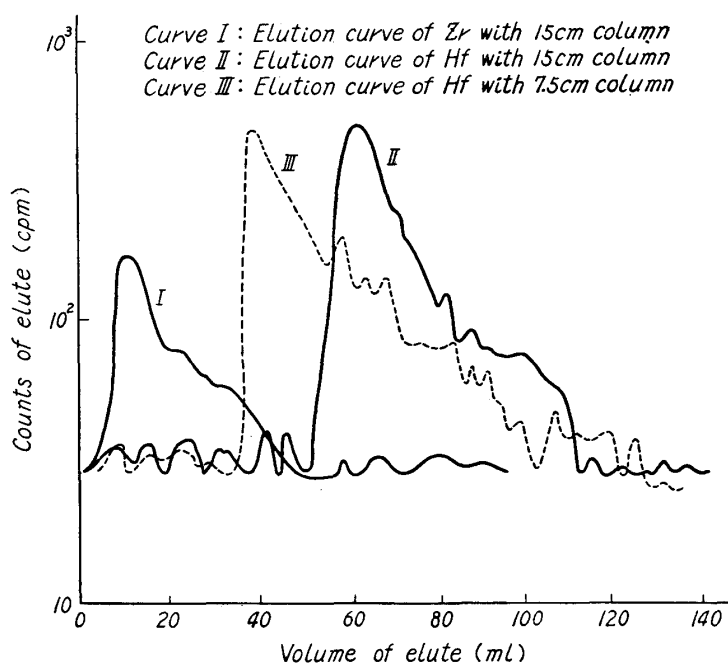


Fig. 1. Elution curves of Zr or Hf.

eluting curves for the various mixture of zirconium and hafnium. The pure hafnium fraction could be obtained up to the zirconium amounts of 100 times of hafnium, but it was contaminated with zirconium when zirconium existed

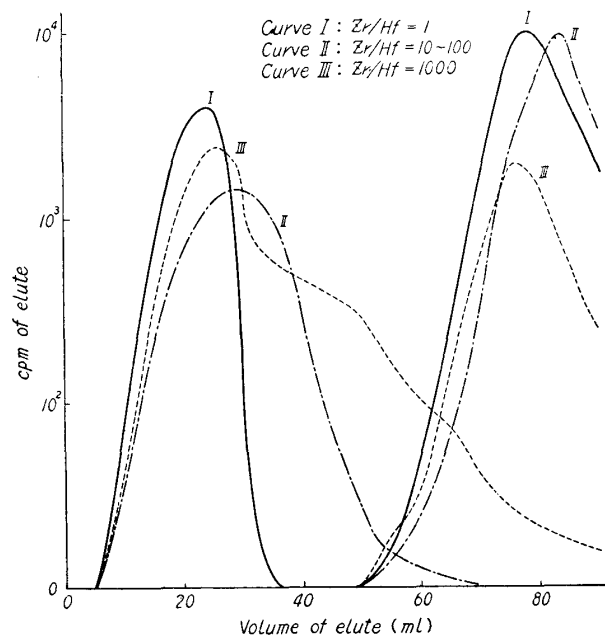


Fig. 2. The elution curves for various Zr-Hf mixture.

1000 times of hafnium. In the latter case, the eluent from 50 ml to 140 ml of first elution was collected, the citric acid was decomposed with nitric acid, and hafnium and zirconium were precipitated as hydroxide. This precipitate was dissolved with hydrochloric acid, and was treated again with cation exchanger as mentioned above. As shown in Fig. 3, when zirconium existed 1000 times of hafnium, double separation of two elements was not yet perfected.

Even though the solutions were prepared as 0.1 N hydrochloric acid solution in the above mentioned experiments, the effects of various acid to the cation exchanger method were examined. The results are

shown in Table 1, and it is found that hydrochloric acid medium is most available. Table 2 shows the effects of time interval from the dissolution of hydroxide to the beginning of efflution, and it is found that efflution has to begin immediately.

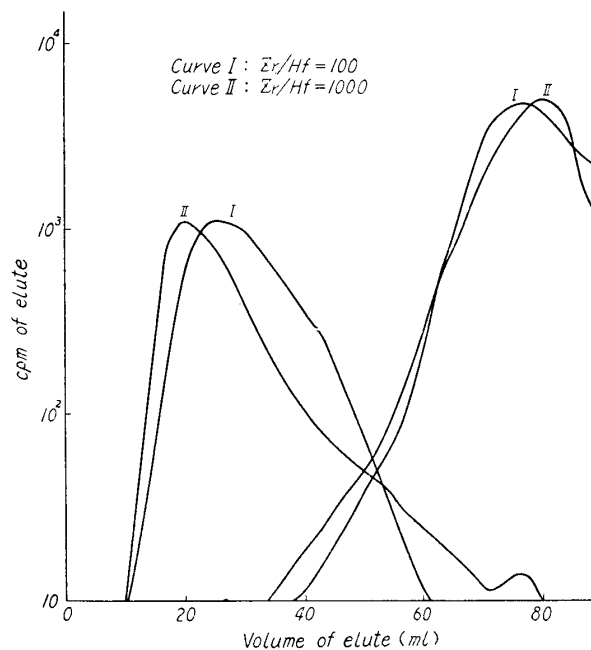


Fig. 3. The elution curves of second elute of double elution of Zr-Hf mixture.

Table 1. The effects of various acid to the recovery of Hf in the ion exchange method.

Acidity of sample solution	Recovery of Hf (%)			
	Effluent	Eluent	The fraction eluted with 3N-HC	
HCl	0.1 N	0.02	99.47	0.49
	0.5 N	0.02	99.40	0.57
HNO ₃	0.1 N	3.52	74.88	22.60
	0.5 N	1.25	78.66	21.09
HClO ₄	0.1 N	0.02	92.83	7.15
	0.5 N	0.03	96.80	3.17
H ₂ SO ₄	0.1 N	15.85	83.82	1.33
	0.5 N	22.31	77.67	0.02

Table 2. The effect of time interval from dissolving of hydroxide precipitate to beginning of ion exchange on the recovery of Hf.

Acidity of sample solution	Recovery of Hf in eluent (%)		
	Immediately after	1hr. after	5hrs. after
0.1 N-HCl	99.8	99.9	94.5
0.1 N-HNO ₃	92.5	85.3	82.6
0.1 N-HClO ₄	99.5	98.3	91.5

From the experiments, it was decided to use hydrochloric acid medium and to begin efflution as fast as possible.

2. Enrichment of hafnium from zirconium by using organic solvent extraction

From the above mentioned experiments, it is found that hafnium must be concentrated preliminarily before treating with cation exchanger when zirconium exist over 1000 times of hafnium.

So zirconium solution and hafnium solution were treated by three kinds of organic extraction method separately, and the per cent extraction of each element was examined.

As seen in Table 3, 93.57 per cent of original hafnium and 21.07 per cent of

Table 3. The comparison of three extraction method for Zr and Hf.

Composition of organic phase	Acidity of aqueous phase	Volume ratio of org. phase to aq. phase	Recovery of Zr (%)	Recovery of Hf (%)
Tributyl phosphate 80 % <i>n</i> -heptane 20 %	5.6 N HNO ₃	1 : 1	79.97	77.91
Thenoyl trifluoro acetone 5g per 1l benzene	3.0 N HNO ₃	1 : 1	40.59	23.46
Hexone	1 N HCl with 2 g NH ₄ SCN + 0.5g(NH ₄) ₂ SO ₄ /5ml	3 : 1	21.07	93.57

original zirconium was extracted to organic phase by using ammonium-thiocyanate hexone method, but other two methods showed poor per cent extraction with hafnium. When hexone phase which extracted hafnium from aqueous phase treated with 1 N hydrochloric acid, 92.14 per cent of original hafnium and 20.06 per cent of original zirconium were stripped into aqueous layer. Repeating the extraction-stripping procedure for four times, the amounts of hafnium remained

Table 4. The recovery of Zr and Hf in each step of extraction and stripping with thiocyanate-hexone and HCl.

Step number	Reagent	Recovery of Zr (%)	Recovery of Hf (%)
1	extraction : org. phase-hexone aq. phase-0.1N HCl contained 5g NH ₄ SCN and 0.5 g (NH ₄) ₂ SO ₄ per 5 ml.	20.94	93.41
		20.06	92.14
2	Stripping : org. phase-hexone aq. phase-0.1 N HCl	5.38	82.26
		5.26	80.03
3		1.15	80.06
		1.20	70.98
4		0.30	70.92
		0.28	70.93

in final step was 70.93 per cent of original amounts, and zirconium remained only 0.28 per cent of original amounts (Table 4). To the mixed solution of zirconium and hafnium (10.30 mg of zirconium and 1.24 mg of hafnium) hafnium-181 tracer was added, and hafnium was concentrated by four steps extraction-stripping procedure. The specific activities of mixed oxide obtained from each step were examined. As shown in Table 5, original specific activity, 325 cpm per mg,

Table 5. The change of specific activity of mixed oxide of Zr+Hf in each step of thiocyanate-hexone extraction-stripping method.

Step number	0	1	2	3	4
Specific activity of mixed oxide (cpm/mg)	325	783	1425	1735	1924

finally changed to preferably high value, 1924 cpm per mg. And it seems reasonable to think that hafnium was concentrated from zirconium by extraction-stripping method.

3. Examination on the isotope dilution method for hafnium

It was found from above mentioned experiments that pure hafnium fraction could be obtained by treating with cation exchanger after the concentration of hafnium by means of organic solvent extraction method. So it seems possible to determine hafnium with isotope dilution method by adding hafnium-181 solution in first step of sample preparation. But in this case the amount of hafnium became so small that it was difficult to determine hafnium amount by gravimetric or volumetric method in order to measure specific activity. So the method determining hafnium amount by using colorimetric method⁽¹⁶⁾ in order to calculate specific activity was studied.

After the treatment of the hafnium enriched sample solution by the cation exchanger, the eluted fraction from 100 ml to 140 ml was collected, citric acid in the elute was decomposed by boiling with 10 ml of aqua regia, and then the solution was evaporated nearly to dryness. The residue in the beaker was exactly filled to 50 ml after transferring to measuring flask by using 1.5 N hydrochloric acid. 2 ml portion of this solution was pipetted out, was dried on the porcelain dish, and the radioactivity was measured. Another 2 ml portion was taken into Ukena's colorimetric tube, 2 ml of 0.15 per cent alizarin red-S solution was added, then the solution was diluted to 10 ml by adding 1.5 N hydrochloric acid, and was shaken well. The developed color of sample solution was compared with the color of standard hafnium solution, and the sample solution was diluted with 1.5 N hydrochloric acid until the color intensity of sample became equal to that of standard. Then the amount of hafnium was calculated from the dilution factor. From the amount of hafnium obtained by colorimetric method and radioactivity, the specific activity of hafnium sample was calculated. The reciprocal

(16) A. Mayer and G. Bradshaw, *Analyst*, **72** (1952), 476.

of specific activity of sample was plotted on the calibration curve⁽¹⁷⁾, and original hafnium amount was determined.

To obtain calibration curve, 1 ml of hafnium-181 solution (0.62 mg/ml, 4250 cpm/ml in this case) was added to various amounts of hafnium solution. These mixture was diluted exactly to 200 ml by adding 1.5 N hydrochloric acid. Every 2 ml portion of each solution was dried up in porcelain dish, and radioactivity was measured. Beside this, hafnium amount was determined with 5 ml portion of each solution by means of colorimetric method. The specific activity of hafnium in each solution was calculated, and the reciprocal of it was plotted versus hafnium amounts. As shown in Fig. 4, hafnium amounts and reciprocal of specific activities show good linear relation from 0 to 1.0 mg.

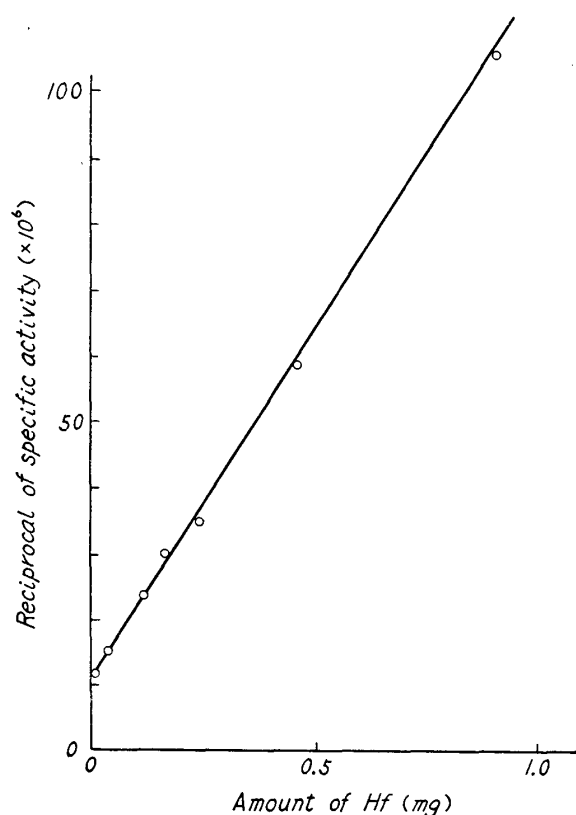


Fig. 4. Calibration curve for Hf.

zirconium, ammonium sulfate and ammonium thiocyanate are added so as to contain 0.5 g of sulfate and 5g of thiocyanate in 5 ml of the solution, and hafnium is extracted with hexone, which is three times of the volume of aqueous phase and is treated with mixture of hydrochloric acid, ammonium thiocyanate and ammonium sulfate. The aqueous layer is discarded, and hexone layer is treated with 1N hydrochloric acid which is one third volume of hexone. To the aqueous layer, again is added the mixture of ammonium thiocyanate and ammonium sulfate, and hafnium is extracted with hexone as before. This extraction-stripping procedure is repeated for four times, and the hydrochloric acid solution

4. Method for determination of hafnium in zirconium metal

From the experimental results mentioned above, the isotope dilution method for hafnium in zirconium metal is recommended as follows:

i) Decomposition of sample: 3~5 g of sample is dissolved in platinum dish with the mixture of 10 ml of hydrochloric acid and 3 ml of hydrofluoric acid. After the completion of dissolution, suitable amount of hafnium-181 solution is added. The solution is evaporated twice adding hydrochloric acid, and finally the solution is adjusted to 1 N hydrochloric acid medium.

ii) Enrichment of hafnium: To the hydrochloric acid solution of

(17) H. Amano, Jour. Japan Inst. Metals, 22 (1958), 625.

finally obtained is transferred to the beaker.

iii) Separation and determination of hafnium: The hydrochloric acid solution after the extraction is boiled in order to expell the remained hexone, ammonium hydroxide is added drop by drop, and zirconium and hafnium are precipitated as hydroxide. The precipitate is first washed with 3 per cent ammonium nitrate solution for three times, and then with 5 ml of hot water. After the washing, the precipitate is returned into the original beaker dissolving with 2 ml of 6 N-hydrochloric acid, and the filter paper is washed well with hot water. The solution and washing are evaporated nearly to dryness, and is dissolved with 40 ml of 0.1 N hydrochloric acid. This solution is passed through acid-type cation exchanger (Dowex-50, $\times 8$, 40~100 mesh, 1 cm dia. and 15 cm leng.) with the flow rate of 2 ml per minute to absorb zirconium and hafnium on the resin. The column is washed with water, and then these two elements are eluted by the mixture of 0.45 M nitric acid and 0.095 M citric acid with the flow rate of 1 ml per minute. The eluted fraction from 100 ml to 140 ml is boiled with aqua regia in order to decompose citric acid, and is evaporated nearly to dryness. The residual content of the beaker is diluted accurately to 50 ml with 1.5 N hydrochloric acid. One 2 ml portion of the solution is dried in porcelein dish, and radioactivity is measured. From the other 2 ml portion, hafnium amount present in the solution is determined by means of alizarin red-S colorimetric method. The reciprocal of specific activity is calculated from these values, and hafnium amount is determined plotting the value on the calibration curve.

iv) Analytical results of synthetic sample: Table 6 shows the actual results

Table 6. The analytical results of sythetic sample.

Zr taken (g)	Hf added (mg)	Hf found (mg)	Hf % to Zr (calculated)	Hf % to Zr (found)	error (%)
3	0	0.33	0.008	0.014	+0.006
"	0.5	0.83	0.023	0.028	+0.005
"	1.0	1.36	0.041	0.045	+0.004
"	2.0	2.38	0.074	0.079	+0.005
"	4.0	4.29	0.141	0.143	+0.002

of synthetic sample consisting of 3 g of zirconium (hafnium content, 80 ppm) and various amounts of hafnium could be determined accurately provided the hafnium content higher than 0.025 per cent.

Summary

- (1) Hafnium content in zirconium metal was determined by using isotope dilution method combined with organic solvent extraction and ion exchange method.
- (2) Low content hafnium in large amounts of zirconium was enriched by repeating ammonium thocyanate-hexone extraction and stripping to hydrochloric acid medium.

(3) After the enrichment of hafnium, pure hafnium fraction could be obtained by means of cation exchange method eluting with the mixed solution of 0.45 M nitric acid and 0.095 M citric acid.

(4) In calculating specific activity, the amount of hafnium was determined by colorimetric method. And the reciprocal of specific activity thus obtained and the amount of hafnium showed good linear relation.

(5) From the experiences, isotope dilution method for hafnium in zirconium was recommended and the method was applied to the analysis of synthetic sample. It was found that hafnium amount of not less than 0.025 per cent in zirconium could be determined by this method.

The author wishes to thank to Prof. Hidehiro Gotô for his kind guidance through this experiment.