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The Spectrochemical Determination of Hafnium-Zirconium Ratios

Cyrus Feldman

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THE SPECTROCHEMICAL DETERMINATION OF HAFNIUM-ZIRCONIUM RATIOS

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Abstract

A spectrochemical technique is presented for determining hafnium-zirconium ratios in the range (Hf x 100)/Zr = 0.073-9.28 by weight, with and without the aid of hafnium-free zirconium preparations. The sample is brought into solution in 10% H_2SO_4, and sparked by the porous cup technique. The intensity ratio Hf II 2641.406/Zr II 2761.911 is measured, and the Hf/Zr ratio read from a standard curve.

The determination of hafnium in zirconiferous materials has always been a singularly difficult task by traditional analytical methods. No colorimetric reagent is known which is specific for one of these elements in the presence of the other. Those methods based on the effect of the Hf/Zr ratio on various gravimetric conversion factors rapidly lose accuracy at low Hf/Zr values because of the relatively large effect of errors in weighing and other chemical operations. Those based on selective precipitation of either constituent are liable to relatively large errors caused by coprecipitation.

In addition to these difficulties, it has heretofore been almost impossible to obtain zirconium preparations which were completely free of hafnium. Consequently, any comparison of mixtures with "pure" zirconium rested on an insecure foundation.

As an analytical technique, X-ray emission spectrography (1) enjoys certain inherent advantages over the methods mentioned. The analytical data are produced specifically by the inner electrons of hafnium, and are

not affected by the presence of zirconium. This, in turn, enables one to dispense with a pure zirconium matrix. As a result, much of the analytical work on hafnium-zirconium mixtures has been performed by this method. X-ray emission analysis is rather time-consuming, however, and the necessary apparatus is not commonly available.

The success of the X-ray emission method and the comparative unavailability of pure zirconium and hafnium preparations are probably responsible for the almost total lack of published material on the determination of hafnium-zirconium ratios by optical emission spectrochemical methods. The few papers which mention the subject (2,3) are semi-quantitative in treatment, and give no working curves or detailed analytical procedures.

Spectrochemical methods for the construction of working curves usually require the use of standards which resemble the sample in gross composition, and which contain known amounts of the element to be determined. It is not necessary for this purpose, however, that compounds of either the matrix element (Zr, in this case) or the element to be determined (Hf) be available in the pure state. If the concentration of hafnium in the hafnium preparation is known, its concentration in the zirconium preparation can be determined.

Two spectrochemical procedures for estimating the concentration of residual impurities have been described by A. Gatterer (10). Although these methods make no assumptions as to the shape of the working curve, they involve a fair amount of calculation. It was therefore decided to adopt the empirical, but reliable method of trial additions.

This method is based on the assumption that a plot of log intensity ratio vs. log (true) concentration is always a straight line. No exceptions

to this have been found so far in the writer's experience. The method is in common use; it has been described as follows by W. C. Pierce and N. H. Nachtrieb (4):

"First, a working curve plot is made of log intensity ratio vs. log apparent concentration. When a residuum is present, the line will tend to become parallel to the concentration axis at low concentrations. A straight line is drawn through the points for the higher concentrations, and the amount of the residuum is estimated by the magnitude of the departure of the lower concentration points from this line. Next, all concentrations are corrected by adding the estimated residual value, and the process is repeated. Usually, two or three approximations will suffice to give a value which will bring all points onto a straight line. Finally, the correctness of the estimation is tested by using the working curve so obtained to determine spectrographically the amount of residuum in the pure matrix material."

Before one can use this procedure, however, the precision and accuracy of the data must be sufficient to give a rather narrow range of residuum concentration values which will bring all points onto a straight line. The original points must be rather close to the best smooth curve drawn through them, so that it will be possible to judge accurately when the best "straight line" has been achieved.

Several factors will combine, in this case, to affect the precision and accuracy of the results obtained:

(1) Accuracy of standards: The composition of the hafnium preparation mixed into the zirconium matrix must be accurately known. In this analysis, we are confronted by the fact that hafnium compounds free of zirconium are

almost as difficult to obtain as are their opposite numbers. For instance, the first sample of hafnium oxide used in the present investigation was stated by the supplier to contain less than 1% zirconium. Spectrochemical analysis (see section on purity of hafnium oxide, below) showed it to contain 25.0% Zr as the oxide. This condition will, of course, be harmless if known about and corrected for in the calculation of standard compositions when the curve is plotted.

(2) Background correction: The success of the abovementioned procedure for constructing a working curve with the use of impure matrix material depends largely on the accuracy and precision of the intensity ratios obtained for the lower concentration points. The use of an accurate background correction is therefore a matter of major importance. In view of this fact, it was desired to have an intensity scale which was as accurate as possible at low intensities.

The flatness of the density - log intensity and density-intensity curves at low intensity values tends to make the calibration marks on an intensity scale rather inaccurate in this region.

Prefogging the film is sufficient in itself to enable one to avoid working in the flattest regions of the density curves, but it shortens the useful range of intensities if used to the extent necessary to reach the linear portion of the H and D curve. If an intensity scale accurate in the lower intensities is available, however, a slight prefogging is useful in drawing attention to weak backgrounds for which corrections might not

otherwise be made.*

A suitable film calibration function was found in the Seidel function W, which is defined for a given line (or background) reading by the equation

$$W = \log \left(\frac{T_o}{T} - 1\right)$$

where T_o is the "clear plate" galvanometer deflection and T is the deflection for the background or line (+ background) under consideration.

This function has been discussed by H. Kaiser and M. Honerjager-Sohm (8).

With SAl film, at 2600Å, the Seidel function gives an almost perfectly straight line between 5% and 97% transmission when plotted against log intensity. The slope of the line is moderate, usually lying between 0.9 and 1.8. If the ordinates are made proportional to W, but the ordinate scale is calibrated in terms of T/T_o, percent transmission values and relative intensity values can be interpolated from this curve rather accurately over a wide range. This property substantially increases the accuracy of the low intensity calibrations.

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* The advisability of prefogging is illustrated by the following hypothetical situation, which is typical of those encountered in spectrochemical photometry.
A line having an intensity of 1.5 (arbitrary) units is situated in a region having a background intensity of 0.3 units. A spectrogram of this region is developed without prefogging; the intensity of the line (+ background) is registered and measured as 1.8, but the adjacent background intensity appears to be zero, due to the inertia of the emulsion. The intensity read for the line is thus in error by 20%.
However, if the emulsion is prefogged sufficiently to give a "clear plate" intensity reading of 1.0, the line (+ background) will give an intensity reading of 2.8, and the spectrum background will read 1.3. Subtraction will then give the correct value for the line intensity.

(3) Conditions in the light source: A stable light source is one of the main prerequisites for obtaining precise and accurate intensity ratios. The difficultly of controlling arc conditions where zirconium and hafnium are concerned makes it advisable to convert samples and standards to some uniform chemical state for analysis. Even when this is done, however, zirconium is notoriously sensitive to variations in arc conditions, as is evident from eloquent complaints registered against this element by L. W. Strock and S. Drexler (5,6).

Any attempt to volatilize hafnium in an arc, with or without zirconium, appeared certain to involve high-and sometimes difficultly controllable - arc temperatures.

When it became necessary for this laboratory to determine hafnium-zirconium ratios spectrochemically it therefore seemed advisable to use a spark-solution method. The porous cup technique (7), in which a solution slowly soaks through the bottom of a graphite cup used as the upper electrode, seemed well suited for this analysis. In addition to being able to handle the rather viscous and highly acid solutions likely to be encountered, this technique offered the possibility of using uniformly controlled spark excitation, and of having the composition of the radiating vapor vary in a reproducible manner, if at all, during the exposure.

Experimental

1. Preparation of Stock and Sample Solutions: Stock solutions of zirconium and hafnium were prepared as follows: the appropriate oxide was fused with potassium pyrosulfate, and the melt dissolved in approximately 200 ml of hot 1% sulfuric acid. The hydroxide was then precipitated with alkali. In order to reduce buffering action as much as possible, the

neutralization was performed with 10% NaOH solution until a precipitate began to form; the precipitation was then continued with NH_4OH. The precipitate was allowed to settle, the bulk of the supernate decanted, and the remaining slurry centrifuged. The supernate was again decanted, and the residue washed twice with water containing a few drops of ammonia. The hydroxide was next dissolved in the smallest possible volume of 1-to-1 sulfuric acid and the solution diluted with 10% sulfuric acid until it contained approximately 1% of the metal.

The metallic concentration of stock solutions was determined by assaying with cupferron. (The hydroxide could not be quantitatively precipitated with ammonia, because of the complexing action of the large amounts of sulfuric acid present (11).) Stock solutions were then diluted to the desired strength with 10% sulfuric acid.

2. Purity of Hafnium Oxide: A preliminary qualitative spectrographic analysis of the purest hafnium available at the time failed to show any impurities ether than minor amounts of zirconium and traces of silicon and titanium.* Chemical determinations carried out by F. J. Miller showed the two latter elements to be present in concentrations of about 0.15% and 0.1% as the oxides, respectively.

The zirconium content of this hafnium oxide was determined as follows: a solution of this material containing approximately 1 mg/ml of Hf was prepared and assayed as above. The proper amount of 1% thorium nitrate solution (calculated as the metal) was added to make the solution 200 ppm in thorium.

A spectrogram of this solution was then obtained by the porous cup method, and the intensity ratio Zr II 3273.047/Th 3324.754 measured. The

*This material was obtained from the Chemical Commerce. Corp., Newark 8, N.J.

zirconium concentration of the solution was read from a standard curve, and the Zr/Hf ratio calculated to be 0.022 by weight. (Control experiments had shown the presence of 1 mg/ml of hafnium to have no measureable effect on this intensity ratio.) The zirconium content of this material was, of course, taken into account in calculating standard concentrations.

3. Choice of Optimum Working Conditions:

a. Choice of lines: In view of the abundance of zirconium lines, it was decided that a minor zirconium line could be used as an intensity reference line. This was a definite advantage, since it eliminated both the need for the exact concentration of the sample solution and the need for adding an internal standard element.

(1) Hf lines: To find the hafnium lines showing the greatest sensitivity by the porous cup technique, a spectrogram was obtained of a solution containing 25 ppm Hf as the metal in 10% sulfuric acid. Of the nine hafnium lines visible at that concentration between 2300 and 4300Å, those listed in Table I were the most prominent:

Table I

Most Sensitive Lines of Hafnium

Wavelength		Possible Interferences
Hf II 2641.406	Th 2641.49	(Would not interfere under conditions of experiment unless sample contained ~5% Th)
	C II 2641.44	(Has never been observed in porous cup exposures
Hf II 2773.357	None Pertinent	Proximity of several Zr and Hf lines makes accurate background correction difficult.
Hf II 2820.224	Th 2820.337	(Would not interfere under conditions of experiment unless sample contained ~ 20% Th) Proximity of Zr II 2818.739 makes accurate background correction somewhat difficult.

Since the material dealt with was believed to be essentially free of thorium, Hf II 2641.406 and Hf 2820.224 were the first and second choices, respectively.

(2) Zr lines: In order to cover the maximum range of hafnium concentrations with the least variation in sample concentration, it was desirable that the line selected be in the middle density range under standard operating conditions. Zr 2761.911 suited the requirements best; Zr II 2583.405, although somewhat too intense to give maximum accuracy over the entire range of sample concentrations, appeared satisfactory for use with the more dilute solutions.

It was suggested by A. Gatterer and J. Junkes (9) that the sum of two line ratios be used as an analytical dependent variable in order to even out inequalities in excitation. In accordance with this suggestion, and in view of the characteristics of the lines mentioned, the three following ratios were selected for further investigation:

(A) $\frac{\text{Hf II } 2641.406}{\text{Zr } 2761.911}$

(B) $\frac{\text{Hf II } 2641.406 + \text{Hf II } 2820.224}{\text{Zr } 2761.911}$

(C) $\frac{\text{Hf II } 2641.406 + \text{Hf II } 2820.224}{\text{Zr } 2761.911 + \text{Zr II } 2583.405}$

4. Choice of Sample Concentration: It was desirable to know to what extent, if any, a given hafnium-zirconium intensity ratio varied with the concentration of the sample. This was important in two connections:

(a) It determined whether the concentration level of a given solution could be adjusted to suit its hafnium content without affecting the Hf/Zr intensity ratio obtained. (It would naturally be desirable to vary the sample concentration inversely with the expected hafnium concentration in order to keep the hafnium line at a moderate density level.)

(b) It determined to what extent it was necessary to control the (Zr + Hf) concentration of a sample solution. Such control, if necessary, would involve gravimetric or colorimetric assaying, and would be very time-consuming.

The effect of sample concentration was therefore investigated as follows: A zirconium preparation in which the Hf/Zr ratio was ~ 1.9%* by weight was made up in three dilutions covering the range Zr = 2.3 - 9.4 mg/ml. Four samples of each solution were sparked for 180 seconds apiece, and the abovementioned ratios measured at each concentration. The results of this set of measurements are given in Table II.

Table II

Intensity Ratio	Value of Ratio at Indicated Zr Concn. in mg/ml			Average	Precision as between Concns.
	2.3	4.7	9.4		
A	0.98 ± .06	1.02 ± .03	0.93 ± .05	0.977 ± .037	± 3.7%
B	1.75 ± .070	1.81 ± .10	1.65 ± .05	1.75 ± .04	± 2.5%
C	0.639 ± .020	0.639 ± .020	0.639 ± .015	0.647 ± .010	± 1.7%

These results do not show any clear-cut variation of a given ratio with sample concentration. It therefore appeared permissible to increase or decrease the sample concentration within this range if hafnium lines proved too light or too dense, respectively, for accurate photometry. Unless there was reason to expect an extremely high or extremely low Hf/Zr ratio, solutions were therefore made up to a concentration of approximately 5 mg Zr/ml.

* i.e., $\frac{Hf \times 100}{Zr} = \sim 1.9$

Since the results of this study were intended to apply to routine determinations, it was felt that the superior performance of ratios B and C was not worth the additional time necessary to measure the additional lines. Attention was therefore concentrated on ratio A.

5. Choice of Length of Exposure: It was desired to use as long an exposure as possible, in order to bring out weak hafnium lines, if present. The longest exposure period normally obtainable with a single filling of the porous cup is 180 sec. Experience with this technique has shown that it is safest to use a single uniform exposure period when dealing with some concentrated solutions; all exposures were therefore made for 180 seconds.

6. Exposure, Development, and Photometry: All exposures were made on an ARL-Dietert 1.5 meter grating instrument having a dispersion of 7 Å/mm, using SA1 film. The slit-width was 20 microns. Excitation was provided by a Baird high voltage spark source.

Films were prefogged by a 7 second exposure to the light of a 25 watt Mazda lamp operated at 40 volts, situated 3 feet from the film. A three-inch section of film not in the region of interest was kept covered during the prefogging.

The films were next developed 3 minutes in Du Pont X-ray developer at 18°, and fixed for 3 minutes in Eastman F-5 fixer.

The film was then sandwiched between two thin glass plates and mounted on the plateholder of a Leeds and Northrup microphotometer. A "clear plate" reading was taken on unexposed position of the unfogged portion of the film, and photometer tracings made of Hf II 2641.406 and Zr 2761.911 and the adjacent regions. The intensities of these lines and

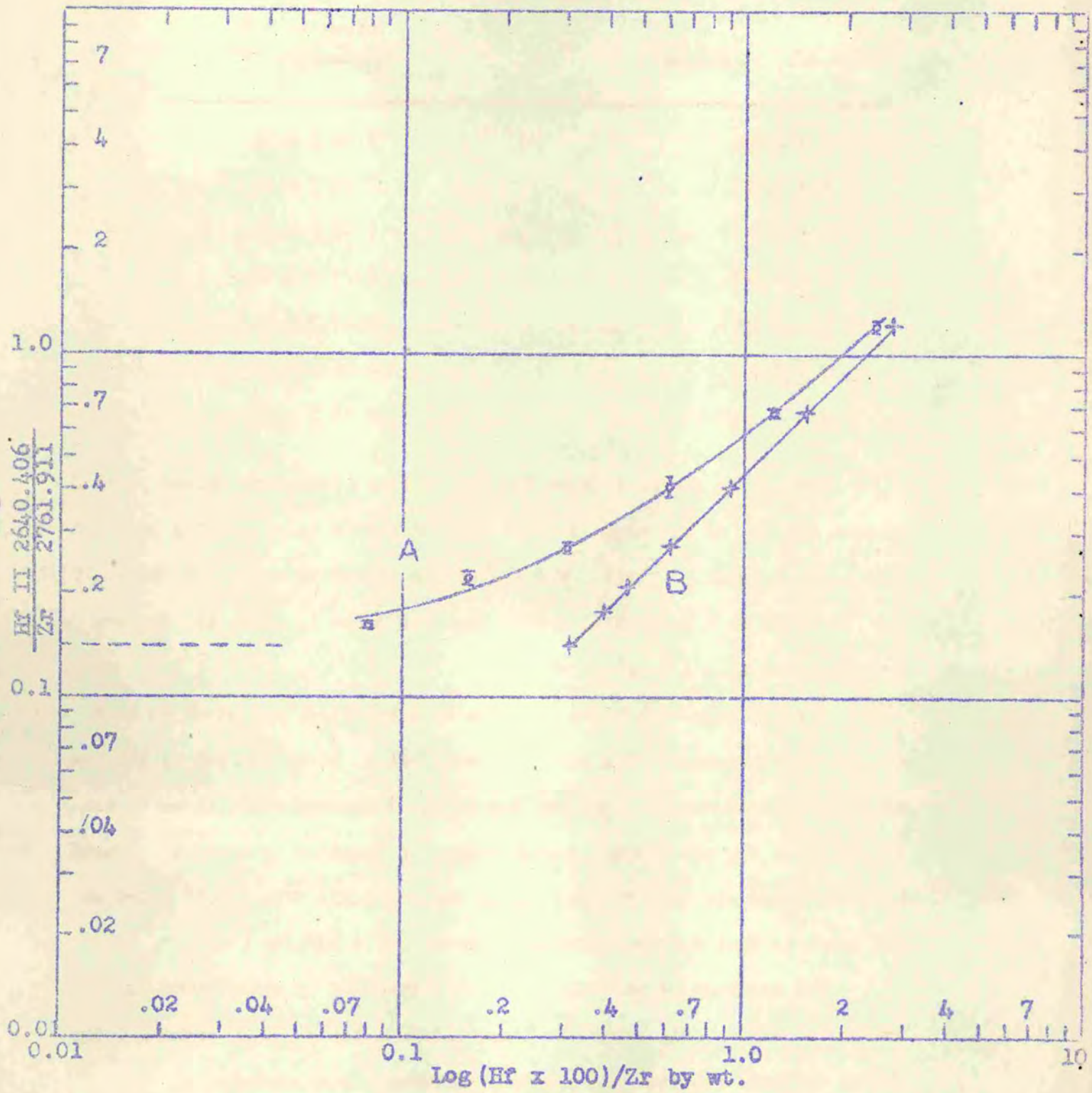

Figure 1
Base material: Foote ZrO_2
(Uncorrected and corrected curves)

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their respective backgrounds were measured on the tracing with an intensity scale prepared for 2600Å using the Seidel function. The background intensity was subtracted from the line + background intensity, and the appropriate ratio calculated.

7. Construction of Working Curve:

(a) With impure base material: A sample of zirconium oxide obtained from the Foote Mineral Co., of Paoli, Pa., was used as base material. A stock solution containing 5.12 mg/ml of Zr, calculated as the metal, was prepared as described above. A 2 ml. aliquot of this material (aliquot A) was taken, and 50 λ of a 4.98% solution of the abovementioned hafnium added to it.

The stock zirconium solution was then diluted to 0.952 times its original strength to compensate for the decrease in the zirconium concentration in aliquot A caused by addition of the hafnium solution. Five successive 1 + 1 dilutions of aliquout A were then made with the diluted stock zirconium solution. These six solutions, plus a sample of the stock zirconium solution, were exposed in quadruplicate as described above, and the intensity ratio Hf II 2641.406/Zr 2761.911 (ratio A) measured. The hafnium-zirconium ratios and observed intensity ratios, corrected for background, are given in Table III. In the left-hand column, r represents the residual amount of Hf present in the Zr base material.

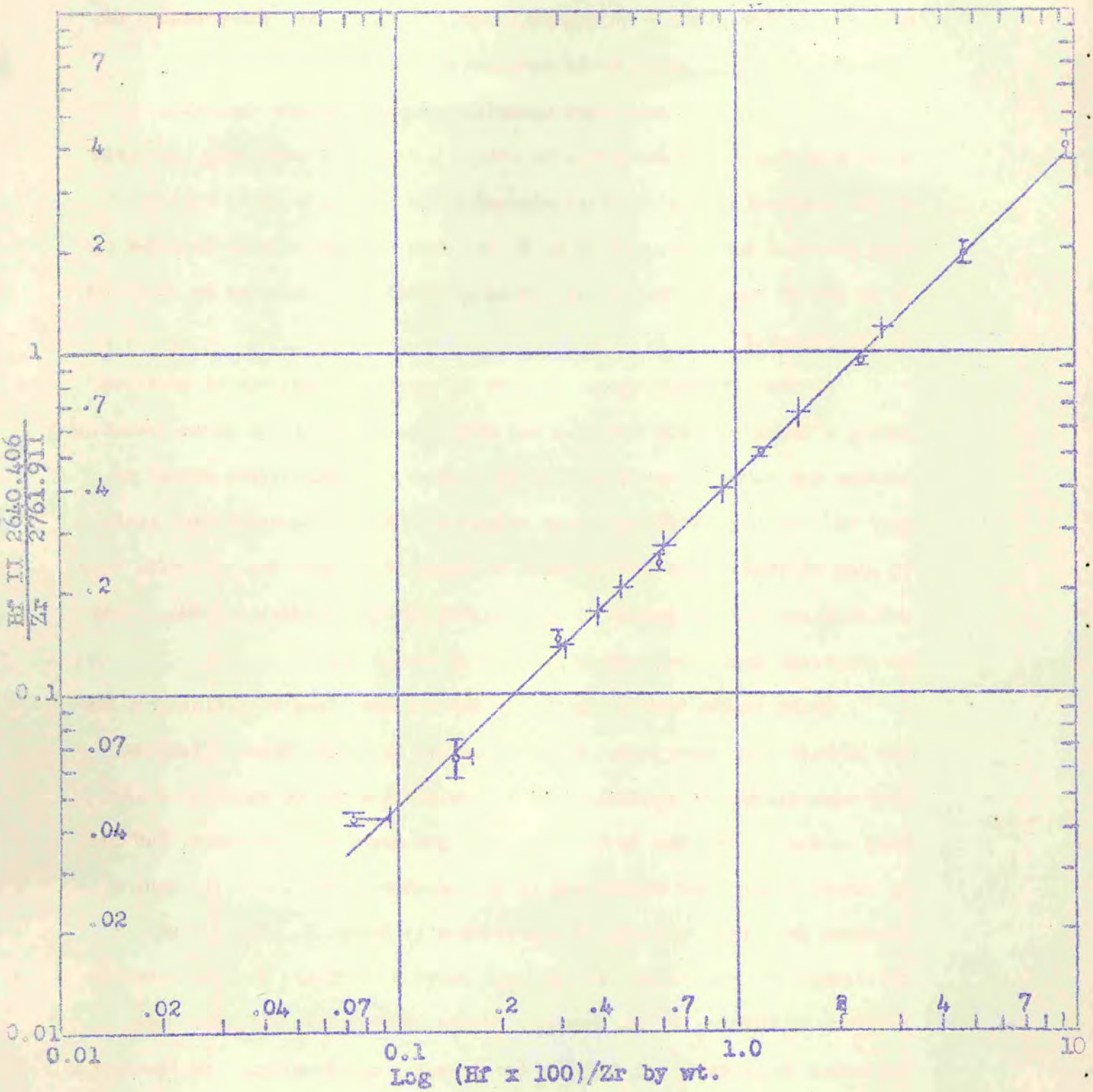

Figure 2
Base material: NBS ZrO_2

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Table III

$\frac{Hf \times 100}{Zr}$, by weight	Intensity Ratio $\frac{Hf\ II\ 2641.406}{Zr\ \ 2761.911}$
r + 2.43	1.20 ± 0.03
r + 1.22	0.67 ± 0.02
r + 0.607	0.41 ± 0.03
r + 0.304	0.27 ± 0.01
r + 0.157	0.22 ± 0.01
r + 0.079	0.16 ± 0.00
r	0.14 ± 0.01

Curve A in figure 1 shows the log of these intensity ratios plotted against the log of the nominal (Hf x 100)/Zr ratios (i.e., ratios in which r is assumed equal to zero). The log of the intensity ratio for (Hf x 100)/Zr = r is shown as a horizontal dotted line for curve A, since the abcissa corresponding to r = 0 is $-\infty$.

A trial value for r was selected by inspection, and added to each nominal concentration. The curve was re-plotted, using the log of the new concentration as abcissa, and the log of the intensity ratio shown by the smooth curve for the nominal concentration in question as ordinate. Curve B is the curve obtained in this manner for r = 0.31. The lowest point on the curve is that for the solution in which (Hf x 100)/Zr = r.

The accuracy of the value of r as determined by this method is estimated as $\pm \sim 0.01$, since the lines obtained for r = 0.29 and r = 0.33 showed definite negative and positive curvature, respectively.

As a method of constructing working curves, however, this procedure has the weakness that the hafnium concentration range lying below the

hafnium content of the base material must be reached by extrapolating the corrected curve, if it is to be reached at all.

(b) With pure base material: Several months ago, this laboratory was fortunate enough to obtain a sample of pure ZrO_2, prepared at the National Bureau of Standards under the direction of E. Wichers. This material was estimated by B. F. Scribner to contain less than 200 ppm of Hf (No Hf was detected in it spectrographically, either by Dr. Scribner or the author.)

As this afforded an opportunity to check the accuracy of previous curve, a stock solution was prepared from this material. A known amount of hafnium was added to an aliquot of this stock, and successive dilutions were made as above with the stock solution. The hafnium-zirconium ratio in each of these solutions is given in Table IV. Since the zirconium base material may have contained as much as 200 ppm of residual hafnium, r may be different from zero, but is no greater than 0.02%.

Owing to the high intensity of the hafnium lines resulting from the two highest concentrations, it was necessary to dilute these solutions. They were diluted to approximately 1.3 mg Zr/ml with 10% sulfuric acid. This proved to make the Zr line too weak for accurate photometry, but lack of material prevented repetition of the exposure. The intensity ratios obtained are given in Table IV and plotted in figure 2. The + marks on this curve are the points used to plot curve B of figure 1. The possible residuum of hafnium in the National Bureau of Standards ZrO_2 has been neglected in plotting all but the two lowest concentrations. In the latter two cases, its possible presence is indicated by concentration limit marks placed at log 0.094 and log 0.165, respectively.

Table IV

$\frac{Hf \times 100}{Zr}$ by weight	Intensity Ratio $\frac{Hf\ II\ 2641.406}{Zr\ \ 2761.911}$
r + 9.28	4.05 ± 0.35
r + 4.64	1.95 ± 0.16
r + 2.32	0.938 ± 0.007
r + 1.16	0.504 ± 0.020
r + 0.580	0.242 ± 0.017
r + 0.290	0.145 ± 0.008
r + 0.145	0.065 ± 0.009
r + 0.073	0.043 ± 0.002
r	- - - - -

Curve B of figure 1 agrees with the curve obtained with the National Bureau of Standards material to well within the limits of experimental error over the concentration range common to both.

(c) Accuracy: H. S. Pomerance, of the Physics Division of Oak Ridge National Laboratory, has determined the cross sections of the abovementioned National Bureau of Standards preparation and of a piece of metallic zirconium for the absorption of thermal neutrons.
The values obtained are shown in Table V.

Table V

Material	Cross-section for capture of thermal neutrons in barns ($cm^2 \times 10^{-24}$)
Zr	1.35 ± 0.02
ZrO_2 (N.B.S.)	0.40 ± 0.04

Dr. Scribner's spectrographic examination of the oxide indicated that undetected foreign elements could be contributing no more than 0.04 barn to the cross-section of the oxide. Spectrographic examination of the metallic sample in this laboratory indicated a similar degree of freedom from high cross-section impurities other than hafnium. The contribution of hafnium to the cross-section of the metallic sample was therefore taken as 0.95 $\pm$ 0.04 barn. This indicates a hafnium-zirconium ratio of 1.90 $\pm$ 0.08% by weight.

Spectrochemical analysis of this sample by the present method gave a value of 1.94 $\pm$ 0.04%.

This is in conjunction with the agreement between the curves obtained with the two base materials, indicates the curve to be accurate to within $\pm \sim 2.5\%$ over the range (Hf x 100)/Zr = 0.31 - 2.70. Its accuracy below this range is somewhat uncertain, owing to the possible hafnium residuum referred to above. No check has as yet been made on its accuracy above this range.

Acknowledgement

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