

## X-RAY SPECTROGRAPHIC DETERMINATION OF HAFNIUM-ZIRCONIUM RATIO IN ZIRCONIUM MINERALS

A. M. ABDEL-GAWAD, *Department of Geology and Raw  
Materials, U.A.R. Atomic Energy Establishment,  
Cairo, U.A.R.*

### ABSTRACT

Variations of zirconium and hafnium in zirconium minerals are highly significant in geochemical studies. Many methods described in the literature deal with analyzing the two elements individually by  $x$ -ray emission spectrography. Many more needed data on their relative abundance would be obtained if the ratio could be determined directly on mineral concentrates. This paper contributes a rapid method applied indestructively on zirconium mineral grains. It is based on calibrating peak intensity ratios against elemental ratios in standard samples.

Analytical lines used are the first order  $L_{\beta_{1,6}}$  doublet of hafnium and the second order doublet  $K_{\beta_{1,3}}$  of zirconium. For intensity measurements the flow counter was found to be superior to the scintillation counter in reducing serious interference caused by Zr  $K_{\beta_2}$  (second order) line. Optimum operating conditions required for maximum long-term reproducibility of ratios were determined. Stability of analytical line intensity ratios is attained at 44–48 Kv tungsten tube potential and a flow counter high voltage 1500–1700 v.

Examples of Hf/Zr ratios determined for a number of zircon varieties from the U.A.R. are given. Values were found to be reproducible within 5 per cent over a three month period without any need for recalibration.

### INTRODUCTION

The significance of the coherent pair of elements zirconium and hafnium in geochemical studies and in problems of petrogenesis has been recognized by many workers. Having the same charge and comparable ionic radii (Zr<sup>4+</sup> 0.87 KX; Hf<sup>4+</sup> 0.86 KX), they are so similar in crystallochemical properties that they always occur together in nature and show little tendency for fractionation during minor geochemical cycles. However, this strong association is somewhat disturbed during major phases of magmatic differentiation. Variations in Hf/Zr ratio were found to reflect basic petrogenetic differences. For instance, the Hf/Zr ratio in zircons from granitic rocks is higher than that of zirconium minerals from nepheline syenites (Barth, 1927; Rankama and Sahama, 1949.) The early figures on the average hafnium in zirconium minerals (von Hevesy and Würstlin, 1928) and maximum hafnium contents quoted by Rankama and Sahama from von Hevesy *et al.* (1928) are modified in more recent studies. The high hafnium content, which reaches 16–17 per cent HfO<sub>2</sub> in alvite, cyrtolite and other altered zircons (von Hevesy and Jantzen, 1924; Fleischer, 1955) was exceeded in "proper" zircons from Norway. Levinson and Borup (1960) reported

two types containing 22 and 24 per cent  $\text{HfO}_2$  with up to 0.65 Hf/Zr ratio. The highest ratio reported so far is 1.9 in thortveitite from Norway (Fleischer, 1955.) Greater hafnium contents are likely to be found and more data would accumulate, relating the Hf/Zr ratio to petrogenetic trends, if a relatively rapid method to determine this ratio is developed.

Several spectrographic and  $x$ -ray emission methods for hafnium and zirconium determination in minerals and rocks are described in the literature. Most of the  $x$ -ray methods, since the early work of von Hevesy and Jantzen (1923) to the more recent (Birks and Brooks, 1950; Mortimore and Roman, 1952; Parks *et al.*, 1960, and others), deal with quantitative determination of one or both Hf-Zr pair and problems involved. The difficulty in hafnium determination is that the strongest Hf lines,  $L_\alpha$  and  $L_{\beta_{1,6}}$ , are seriously interfered with by the second order  $K_{\alpha_1}$  and  $K_{\beta_2}$  of zirconium. Lublin (1960) reported that silicon and germanium analyzing crystals, cut parallel to their (111) planes, substantially eliminate second order reflections. They are, therefore, suitable for Hf determination in the presence of zirconium; and Ta in the presence of niobium. The silicon crystal was found to give finer resolution and lower background but has a somewhat lower reflectivity than germanium.

Due to not having these crystals available, an alternative procedure was used in this study, which can be applied directly and indestructively to zirconium mineral concentrates. Since samples need not be powdered, those obtained for mineralogic or petrologic and age determination studies could be analyzed without any loss. The advantages of the flow counter over scintillation counter in obtaining more accurate results are discussed. The paper also gives some values determined for a number of zircon varieties from the United Arab Republic.

The author wishes to thank the following members of the Department of Geology and Raw Materials, U.A.R. Atomic Energy Establishment: Mr. Nasr Hammoud for providing zircon fractions concentrated from the black sands near Rosetta; Mr. Muhammad Attawia for laboratory assistance.

#### APPARATUS

This study was made on a Philips Vacuum Chamber  $X$ -Ray Spectrograph. The tungsten target  $x$ -ray tube (type 25714/60) was operated at 44 Kv and 20 mA, for Hf/Zr ratio calibration. In the sample chamber an inverted optics arrangement is used for sample irradiation. Sample cups with thin polyester film bottoms allow the sample to be irradiated from below for better geometry. A nickel foil collimator with 160  $\mu$  spacings and a lithium fluoride analyzing crystal were used. The 7  $\mu$  mylar window flow proportional counter (PW 1965/10) was operated at

1700 volts, with methane-argon (P 10) gas mixture flow of 3 liters per hour. Counting rates were measured 5 minutes after starting the vacuum pump, at 1 mm. Hg. Otherwise indicated, the same conditions were used with the scintillation counter (PW 1964/10) operated at 1000 volts.

#### STANDARDS

*Rosetta Zircon.* Standard zircon samples with Hf/Zr ratio ranging from 0.011 to 0.074 were prepared by spiking a zircon sample with specpure HfO<sub>2</sub> or ZrO<sub>2</sub>. The base sample

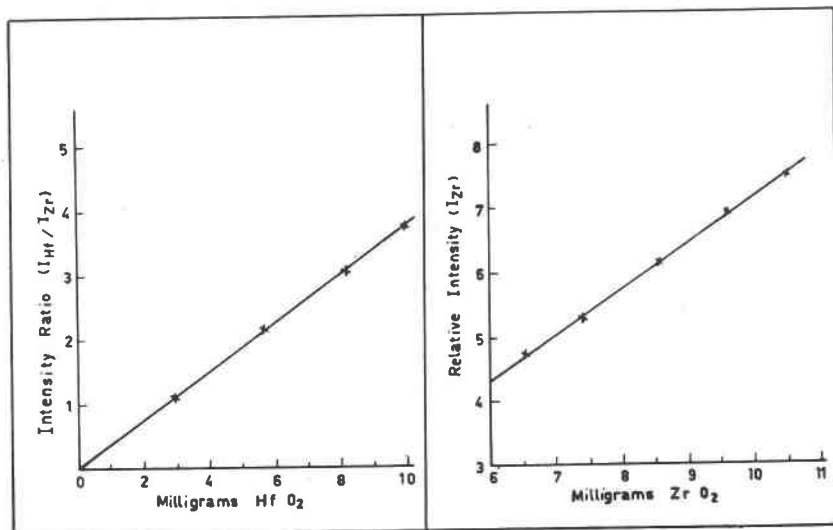


FIG. 1. Calibration curves for Hf and Zr in Rosetta zircon

consisted of pure diamagnetic zircon from the black sands of the Mediterranean sea coast near Rosetta. The spiked samples served to determine the zirconium and hafnium contents in the base zircon, and were used as standards for calibration.

a) *Zirconium content:* Four of five powdered samples containing 0.99 grams borax glass and 0.01 grams zircon were spiked with 0.9, 2.0, 3.1 and 4.0 milligrams of specpure zirconium oxide. The five samples were fused in platinum crucibles at 1000° C. for 20 minutes, and the chilled glass was powdered to -300 mesh and briquetted. In order to equalize precision of analysis, the time required to accumulate 128,000 counts by the scintillation counter was determined for the Zr K<sub>α</sub> analytical line as well as the background reading. Intensity differences show linearity in the concentration range of the five samples (Fig. 1). The zirconium content of the Rosetta zircon was found to be  $48.34 \pm .05$  per cent Zr.

b) *Hafnium content:* The four briquettes used for hafnium determination represented an unspiked sample containing 0.765 grams borax glass and 0.235 grams base zircon and three samples spiked with 2.7, 5.1, and 7.0 milligrams specpure hafnium oxide. The proper amount of dilution and HfO<sub>2</sub> were determined by a pilot briquette which gave the approximate hafnium content in Rosetta zircon. Analysis was made by the flow counter using the first order Hf L<sub>β1,6</sub> line, while the second order Zr K<sub>β1,3</sub> line served as a convenient internal standard. Correction for emission enhancement of the analytical line by the second order

Zr  $K_{\beta_2}$  line was made. Details of necessary corrections for flow and scintillation counter measurements are discussed later in the text. The hafnium content of Rosetta zircon was found to be  $1.06 \pm .02$  per cent Hf. A plot of the total hafnium vs. line intensity ratio ( $I_{Hf}/I_{Zr}$ ) is shown in Fig. 1.

## INSTRUMENTATION

*Line Intensities and Tube Potential.* Analytical lines used for Hf/Zr ratio determination are the first order  $L_{\beta_{1,6}}$  doublet of hafnium and second order  $K_{\beta_{1,3}}$  doublet of zirconium. This selection is based on their proxi-

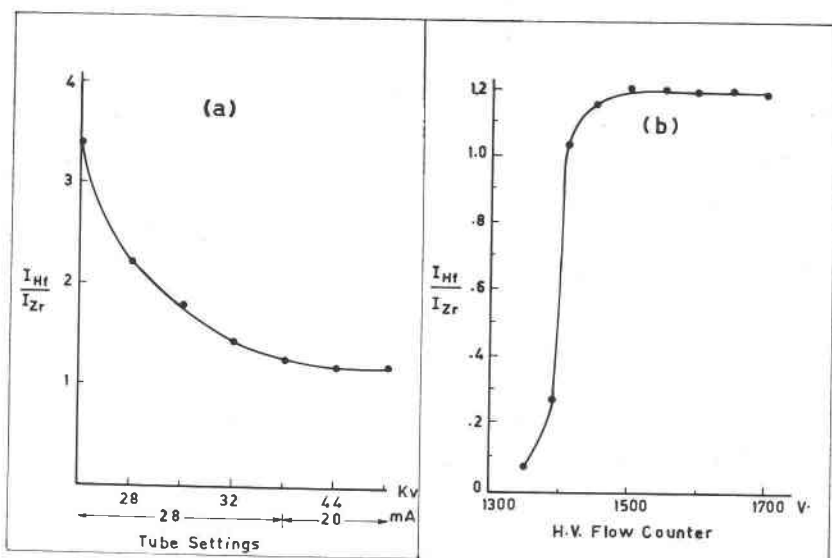


FIG. 2. Peak ratio variation with tube potential and flow counter voltage.

mity (for LiF crystal  $39.89^\circ$  and  $40.74^\circ 2\theta$ ), and sufficient resolution by the commonly used crystal. In addition, for most common Hf/Zr ratios, the two lines have suitable peak ratios when measured on the flow counter.

Due to the large difference in atomic numbers and consequent difference in excitation potentials, the hafnium and zirconium lines will show considerable intensity variations depending on the kilovoltage of the x-ray tube. In order to determine the most suitable voltage the  $I_{Hf}/I_{Zr}$  peak ratio of a pure zircon sample was obtained at increasing voltage values from 20 to 48 Kv. In order not to exceed the power tolerance of the x-ray tube the filament current was reduced from 28 mA to 20 mA at voltages higher than 40 Kv. The plot (Fig. 2a) shows that the peak ratio decreases rapidly and becomes constant from 44 to 48 Kv.

*Peak Ratios and Flow Counter Voltage.* The flow proportional counter has some disadvantages in comparing peak ratios of hard and soft radiations. These result (Jones *et al.*, 1960) from the fact that the amplitudes of its output pulses are proportional to the energy of the quanta causing the pulses. Consequently, in this case, pulses generated by the harder zirconium peak (Zr  $K_{\beta_{1,3}}$ ,  $\lambda = .701 \text{ \AA}$ ) are large compared to the softer hafnium peak (Hf  $L_{\beta_{1,6}}$ ,  $\lambda = 1.374 \text{ \AA}$ ). Converting the flow proportional counter to a flow Geiger counter, the output current per pulse is increased by several orders of magnitude, but the pulse size is independent of the energy of radiation.

In this study, the peak ratio of hafnium and zirconium lines was obtained for increasing counter voltage covering the proportional and Geiger regions of the flow counter. The curve showing this relation, (Fig. 2b) which was made on a Rosetta zircon sample shows a rapid increase in the peak ratio from 1350 to 1450 volts. Beyond that it becomes constant up to 1700 v. Although the voltage range of peak ratio slope is considerably lower than that of the proportional region, the curve shows that above 1450 v rather large variations in counter voltage have no effect on peak ratios for a given sample.

*Zirconium Line Interference.* The determination of Hf/Zr ratio is subject to higher errors using the scintillation than the flow counter when the Hf  $L_{\beta_{1,6}}$  (1st) and Zr  $K_{\beta_{1,3}}$  (2nd) lines are considered. The relative sensitivities of both counters to these lines could be judged by comparing relative intensities in the same zircon sample, (Fig. 3c). It is obvious that the hafnium line is more efficiently measured by the flow counter than the much harder zirconium line. On the other hand, the scintillation counter is extremely efficient in detecting zirconium. The performance of various counters used in *x*-ray analysis was discussed by Dowling *et al.* (1957), Birks (1959), Lambert (1959) and others.

Since the hafnium content is generally much lower than zirconium in minerals, it is desirable in ratio determinations to use the flow counter. This is particularly true since the interference of the second order Zr  $K_{\beta_2}$  line, which is adjacent to the hafnium line would be considerably reduced. In order to demonstrate this fact, specpure  $\text{HfO}_2$  and  $\text{ZrO}_2$  samples were scanned in the  $2\theta$  range between 38 and 42 degrees. Operating the *x*-ray tube at 44 Kv and 20 mA, and using a LiF analyzing crystal, the following line relationships were observed. Hafnium oxide: Does not show any peak at  $40.8^\circ$  (Fig. 3e), indicating the absence of zirconium impurities. The relative intensity of the Hf  $L_{\beta_{1,6}}$  line, measured for the same sample by scintillation and flow counter, is 73 and 49.5 respectively. The relative efficiency of the flow counter is thus 68 per cent that of the scintillation counter.

*Zirconium oxide*: Shows a peak at  $40.7^\circ$  (Fig. 3f), corresponding to the second order reflection of Zr  $K_{\beta_2}$  line. The relative intensity of this peak to the Zr  $K_{\beta_{1,3}}$  (2nd) is 16 per cent and 15.5 per cent on the scintillation

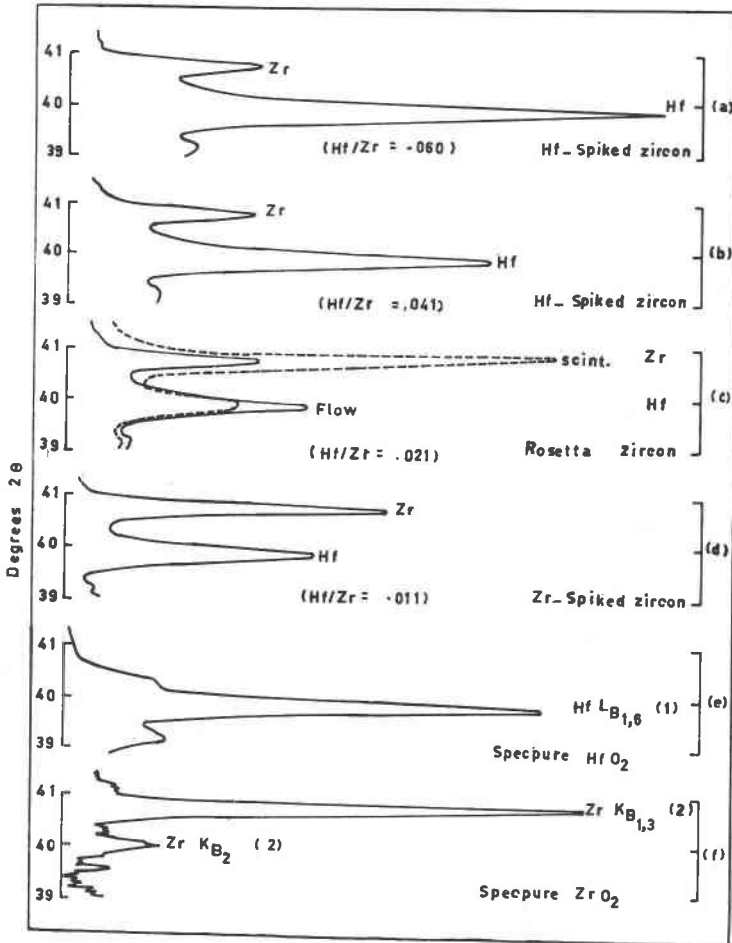


Fig. 3. Chart recordings of Hf and Zr analytical lines.

and flow counter respectively. The relative intensity of Zr  $K_{\beta_{1,3}}$  (2nd), determined for the same sample, is 53 (scint.) and 3.2 (flow); *i.e.*, the flow counter efficiency is 6 per cent that of the scintillation counter. At  $39.89^\circ 2\theta$ , where the Hf line is situated, the interfering Zr  $K_{\beta_2}$  line is only 30 per cent its peak intensity at  $40.07^\circ$ , and therefore the enhancement of the Hf line amounts to 4.7 per cent of the Zr  $K_{\beta_{1,3}}$  (2nd) peak. The effect

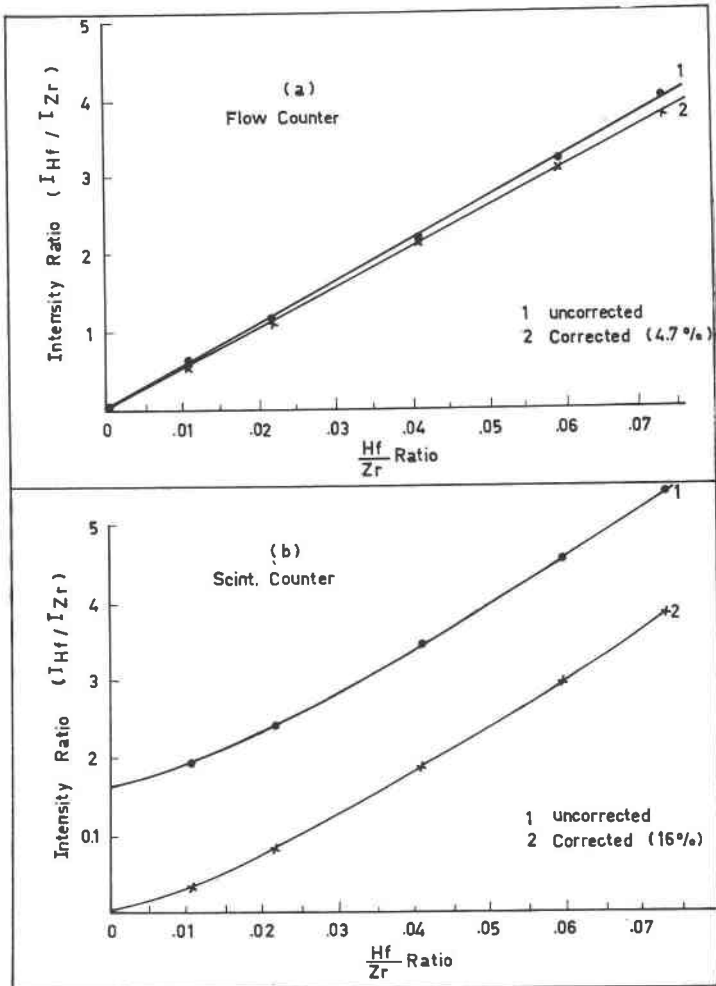


FIG. 4. Calibration curves for flow and scintillation counters.

of this correction on the Hf/Zr calibration curve is shown in Fig. 4a. The scintillation counter, on the other hand, was found to require the full correction of 16 per cent—of the Zr  $K_{\beta_{1,3}}$  peak—in order to bring the calibration curve to pass through the origin point of the plot (Fig. 4b). This is probably due to the broader amplitude distribution and consequent poorer resolution of the scintillation as compared to the flow counter.

In order to emphasize the superiority of the flow counter, taking the Hf and Zr lines of Rosetta zircon as an example, 55.3 per cent of the Hf

TABLE 1. Hf/Zr RATIOS IN SOME ZIRCONS FROM U.A.R.

Locality	Rock Type	Hf/Zr	Remarks
		0.022	Representative zircon sample.
		0.020	Diamagnetic zircon, free from brown magnetic varieties.
		0.019	Colorless zircon, with fine magnetic inclusions.
Mediterr. Sea Coast at Rosetta	Black sands	0.035 0.029 0.027 0.024 0.021 0.024 0.024 0.025 0.033 0.026 0.025 0.022	Rare varieties of brown magnetic zircons; arranged in descending magnetic susceptibilities.
Um Saafi, Eastern- Desert.	Sodic felsite	0.048 0.047 0.043	Radioactive zircons from different samples of same locality.
Abu Garadi, Eastern- Desert.	Pink granite (sodic)	0.075	Radioactive zircon associated with uranothorite, columbite.
El Atshan, Eastern- Desert.	Bostonite	0.021	"Atshanite"; a zirconium bearing uranium mineraloid.

line intensity on the scintillation counter is contributed by zirconium, compared to 3.7 per cent on the flow counter.

#### CALIBRATION

Six standard samples were used for calibration in the most common Hf/Zr ratio range up to 0.074. The two curves, obtained by measuring the intensities by the flow counter (Fig. 4a) show a linear relationship between the Hf/Zr ratios and intensity ratios of their peaks. Curve (1) represents the uncorrected peak ratios. In Curve (2), intensities of the Hf line are corrected for the small enhancement by the Zr  $K_{\beta_2}$  second order line. In Fig. (3), chart recording scans over the  $2\theta$  range of the Hf and Zr lines are shown for selected ratios, (Curves a-d); and for



specpure oxides (Curves e,f). Line intensities of Rosetta zircon are compared for flow and scintillation counters (Curve c).

#### Hf-Zr RATIOS IN SOME EGYPTIAN ZIRCONS

The method described has been applied successfully to the determination of Hf/Zr ratios in zircon concentrates obtained in the course of mineralogic and petrologic studies at the laboratories of the Department of Geology and Raw Materials, U.A.R. Atomic Energy Establishment. Sample preparation requires only obtaining about 10 milligrams of purified mineral grains or about 20 mg of concentrate. The sample is spread thinly in the sample holder for maximum exposure to  $\alpha$ -rays. An approximate ratio could be obtained in a 5-minutes scan, over the appropriate  $2\theta$  range, by measuring the peak height ratio and finding the corresponding elemental ratio on the calibration curve. Accurate determinations require precise counting of analytical line intensities and the background.

In order to illustrate the usefulness of the method, selected ratios in zircons are given in Table 1. Applied to zircon fractions from Rosetta black sands, separated according to differences in magnetic susceptibilities, a Hf/Zr range from .019 to .035 was found. Determinations repeated at different times within three months were found to be reproducible within an error of about 5 per cent.

#### REFERENCES

- BARTH, T. (1927) Die Pegmatitgänge der Kaledonischen Intrusivgesteine im Seiland-Gebiete. *Norske Videnskaps-Akad. Oslo Skrifter. I. Mat.-Naturv. Kl. 8.*
- BIRKS, L. S. (1959) *X-ray Spectrochemical Analysis*. Interscience Publishers, Inc., New York.
- AND E. J. BROOKS (1950) Hf/Zr and Ta/Nb systems-quantitative analysis by  $x$ -ray fluorescence. *Anal. Chem.* **22**, 1017.
- DOWLING, P. H., C. F. HENDEE, T. R. KOHLER AND W. PARRISH (1957) Counters for  $x$ -ray analysis. *Norelco Reporter* **4**(2), 23-33.
- FLEISCHER, M. (1955) Hafnium content and Hf/Zr ratio in minerals and rocks. *U.S. Geol. Survey Bull.* **1021-A**.
- JONES, J. L., K. W. PASCHEN, H. H. SWAIN AND G. ANDERMAN (1960) Components for  $x$ -ray polychromators: In, *Advances in X-Ray Analysis*, v. 1, Plenum Press, 471-482.
- LAMBERT, M. C. (1959) Some practical aspects of  $x$ -ray spectroscopy. *U.S. Atomic Energy Comm. Report HW-58956*.
- LEE, O. I. (1928) The mineralogy of hafnium. *Chem. Rev.* **5**, 17.
- LEVINSON, A. A. AND R. A. BORUP (1960) High hafnium zircon from Norway. *Am. Mineral.* **45**, 562-565.
- LUBLIN, P. (1960) A novel approach to discrimination in  $x$ -ray spectrographic analysis. In, *Advances in X-Ray Analysis*, v.2, Plenum Press, New York, 229-237.
- MORTIMORE, D. M. AND P. A. ROMANS (1952) *Jour. Am. Optical Soc.* **42**, 673.
- PARKS, J. C., JR., D. G. PLACKMANN AND G. H. BEYER (1960) Fluorescence analysis of

- trace amounts of hafnium in zirconium using a silicon crystal. In, *Advances in X-Ray Analysis*, v. 4, Plenum Press, New York, 488-94.
- RANKAMA, K. AND TH. G. SAHAMA (1949) *Geochemistry*. The University of Chicago Press.
- VON HEVESY, G. (1925) Recherches sur les propriétés du hafnium. *Kgl. Danske Videnskab. Selskab; Mat. Fys. Medd.* VI, 7.
- AND V. T. JANTZEN (1923) Der Hafniumgehalt von Zirkonmineralien. *Zeit. anorg. allgem. Chem.* 113-118.
- AND K. WÜRSTLIN (1928) Über das Häufigkeitsverhältnis Zirkonium/Hafnium und Niob/Tantal. *Zeit. physik. Chem. A*, Haber-Band, 605.

*Manuscript received, August 7, 1965; accepted for publication, December 9, 1965.*