

## Determination of hafnium and zirconium in geological materials by neutron activation analysis

J. P. Lins, M. Saiki

*Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Radiochemistry Division,  
P.O. Box 11 049, CEP 05422-970, São Paulo, SP, Brazil*

(Received June 20, 1996)

In this work, neutron activation analysis was applied to analyze the geological standard materials: GSP-1 and W-1 from USGS, GB-1 and BB-1 from the University of Bahia, Brazil and a sample of uraniferous rock. Hf was determined by instrumental method and the obtained results was shown with relative standard deviations varying from 1.1 to 14%. In the case of Zr analyses, both instrumental and radiochemical neutron activation analyses were used. The interference of  $^{154}\text{Eu}$  radioisotope that emits  $\gamma$ -rays too close to those emitted by  $^{95}\text{Zr}$  was eliminated by retention of Zr in an anionic exchange resin column. The contribution of uranium fission product was considered in the Zr determination by using an interference factor. Results of Zr were presented with relative standard deviations varying from 2.0 to 25.7%. More precise results were obtained by using radiochemical separation. The concentration obtained for Hf and Zr in reference materials agreed well with respective certified values or information values.

### Introduction

The determination of Zr and Hf in geological materials is of great interest for geochemical and cosmochemical studies as well as in evaluating their economic potential in ore prospecting programs. The knowledge on the concentrations of these two elements and their relations help to predict the source and the evolutionary history of those rocks containing them. Zr and Hf are also widely used in several areas of the modern technology because of their excellent properties like resistance to corrosion, mechanical strength and thermal stability. Particularly Zr alloys are generally used for fuel cladding and other components of nuclear reactors because of their low thermal neutron cross section.

Reliable determinations of Zr and Hf have been a challenge for the analytical chemists since these elements present a great analytical problem due to their similar chemical behavior, and not many techniques are sufficiently sensitive to determine their trace concentrations. In this work, neutron activation analysis was applied to determine Zr and Hf in geological standard materials and a sample of uraniferous rock. Hf was analyzed by purely instrumental method and in the case of Zr both instrumental and destructive techniques were applied. Rocks containing large amounts of uranium in relation to Zr present interferences due to the contribution of fission product of  $^{235}\text{U}$ . The radioisotope  $^{95}\text{Zr}$ , commonly used in activation analysis of the corresponding element, is also produced as a fission product. This contribution of uranium fission product was considered in Zr analyses by using an interference factor which was experimentally determined. Besides

this a radiochemical procedure was applied in the analysis of some samples in order to eliminate  $^{154}\text{Eu}$  interference that emits  $\gamma$ -rays with energies of 723.30 and 756.86 keV too close to those emitted by  $^{95}\text{Zr}$  radioisotope.

### Experimental

#### Samples

Zr and Hf were analyzed in the following samples: GSP-1 (granodiorite) and W-1 (diabase) geological standard rocks from the United States Geological Survey (USGS), the Brazilian geological standards GB-1 (granite) and BB-1 (basalt) from Instituto de Geociências of the University of Bahia and P-1, an uraniferous volcanic rock from Poços de Caldas, MG, Brazil. The volcanic rock was previously ground in a manual agate mortar to obtain a fine powder form.

#### Standards

The synthetic standards of Zr (25  $\mu\text{g}$ ), Hf (5  $\mu\text{g}$ ) and U (5  $\mu\text{g}$ ) were prepared by pipetting appropriate volumes of the standard solution onto a small sheet of Whatman filter paper and drying under an infrared lamp. Standard solutions of Zr and Hf were prepared by dissolving specure oxides of these elements obtained from Johnson Mattheys & Co. A mixture of  $\text{HNO}_3$  and HF was used for heating. Standard solution of uranium was prepared by dissolving  $\text{U}_3\text{O}_8$  No. 6 from Compagnie Générale des Matières Nucléaires (COGEMA), France with  $\text{HNO}_3$ .

*Instrumental neutron activation analysis (INAA)*

Aliquots of about 100 mg of each material were weighed and heat sealed in clean polyethylene envelopes. It was irradiated together with the synthetic standards at the IEA-R1 research nuclear reactor. Two kinds of irradiations were carried out for each sample: thermal neutron irradiations for 8 hours in a thermal neutron flux of  $9.7 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  and epithermal irradiations for 8 or 16 hours in an epithermal neutron flux of  $2.3 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ . In the case of epithermal irradiation, the thermal component of the flux was suppressed by using a cadmium sheet as shield. The irradiated samples and standards were fixed in stainless steel planchets and after about 10 days of decay time they were counted using a hyperpure Ge or Ge(Li) detector connected to a 4096 channel pulse-height analyzer. The counting system had a resolution (FWHM) better than 1.35 keV for the 122.1-keV  $\gamma$ -ray of  $^{57}\text{Co}$  and 2.7 keV for the 1332.5-keV  $\gamma$ -ray of  $^{60}\text{Co}$ . The spectral data were processed using an appropriate computer program and the elemental concentrations were calculated by comparative method. Hf was analyzed using 482.18 keV  $\gamma$ -ray of  $^{181}\text{Hf}$  with a half-life of 42.39 days. Zr was determined using either the 724.20 or 756.73 keV peak of  $^{95}\text{Zr}$  with half-life of 64.02 days.

*Radiochemical neutron activation analysis (RNAA)*

The radiochemical procedure applied for the W-1 and BB-1 samples was based on the work presented by MIGNONSEN and ROELANDTS.<sup>1</sup> About 100 mg of the sample were irradiated together with the synthetic standards for 32 hours at a thermal neutron flux of about  $10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ . After approximately one week of decay time, the sample was transferred to a Teflon beaker, to which 5 mg of Zr carrier, 3 ml of conc.  $\text{HNO}_3$  and 6 ml of conc. HF were added. The dissolution was carried out in a closed system

(Teflon bomb) in an oven at 80 °C for 8 hours. The Teflon beaker was opened for cooling and the sample solution was evaporated to dryness on a heated sand bath. The residue was taken up with distilled water and heating, and then 2 ml of 8N HCl were added to the solution. The sample solution was again evaporated to eliminate the acid. After this step the resulting solution was diluted with distilled water up to 30 ml and its pH was adjusted between the values 1 and 2 using a solution of 1.0M NaOH. Subsequently 2 ml of 0.6M NaF solution with pH 7.0 were added to the solution to obtain anionic species of Zr complex.

The resin column of 15 cm long and 1 cm in diameter was prepared by using IRA Amberlite resin (100–200 mesh) conditioned by using firstly a solution of 1.0M NaOH then 1.0N HCl. The sample solution was passed through the column at a flow rate of about 0.5 ml/min. After this step of percolation, the resin column was washed with 120 ml of distilled water in order to completely eliminate  $^{154}\text{Eu}$  radioisotope. The resin with  $^{95}\text{Zr}$  was transferred to a penicillin vial for counting by using a hyperpure Ge detector.

The standard of Zr was prepared by dissolving the synthetic standard, and by transferring directly the solution into a penicillin vial.

In this separation procedure a recovery of  $(93.1 \pm 4.4)\%$  of Zr was obtained using  $^{95}\text{Zr}$  tracer whereas the activities of  $^{154}\text{Eu}$  and  $^{152}\text{Eu}$  radioisotopes were found in the effluent solution.

*Determination of interference factors*

The interference factors due to the contribution of uranium fission product in the Zr analysis were determined experimentally, using the same irradiation conditions described for the rock analysis. The experimental correction factor was used because of a difficulty in getting the accurate energy spectrum of the neutrons at the irradiation position that affects the activation cross section utilized in the theoretical determination of this factor.

Table 1. Hafnium determinations (in ppm) in geological materials by INAA

Samples	This work		Literature value
	Thermal neutron activation	Epithermal neutron activation	
GSP-1	15.30 ± 0.30 (1.9)*	15.22 ± 0.29 (1.90)	15.0 ± 1.3 <sup>2</sup>
W-1	2.40 ± 0.17 (7.1)	2.47 ± 0.10 (4.0)	2.6 ± 0.3 <sup>2</sup>
GB-1	5.18 ± 0.06 (1.1)	5.65 ± 0.59 (10.4)	5.6 ± 0.2 <sup>3</sup>
BB-1	4.50 ± 0.50 (1.1)	4.77 ± 0.67 (14.0)	5.58 <sup>4</sup> 4.83 ± 0.08 <sup>3</sup>
P-1	17.40 ± 0.50 (2.9)	18.30 ± 2.00 (10.9)	5.63 <sup>4</sup> -

\*Mean and standard deviation at least four determinations. Numbers in parentheses are relative standard deviations.

Table 2. Interference factors for Zr determinations (ppm Zr/ppm U)

Reference	Thermal neutron activation	Epithermal neutron activation
This work	10.8 ± 0.5	2.0 ± 0.4
KUMAR et al. <sup>5</sup>	10.8 ± 0.7	-
GLASCOCK et al. <sup>6</sup>	11.3 ± 0.2	-
LANDSBERGER <sup>7</sup>	10.9 ± 0.9	3.95 ± 0.2
VOBECKY <sup>8</sup>	9.6	2.6
KOROTEV and LINDSTROM <sup>9</sup>	8.4	-
POTS et al. <sup>10</sup>	9.8	-
MEYER <sup>11</sup>	9.77	1.66
GOUVEIA et al. <sup>12</sup>	10.5 ± 0.4	-
PARK et al. <sup>13</sup>	11.7 ± 0.1	-

applied and their results were more precise and accurate when compared with those obtained by INAA.

INAA and RNAA methods applied in this work allowed the reliable determination of Zr and Hf in geological samples, and the results obtained for GB-1 and BB-1 rocks contributed to certify these reference materials.

The authors are grateful to CNPq and FAPESP from Brazil for financial support.

Table 3. Zirconium determinations (in ppm) in geological materials by INAA and RNAA

Sample	Thermal INAA	Epithermal INAA	RNAA	Literature value
GSP-1	626 ± 20 (3.2)	614 ± 56 (9.1)	-	530 ± 70 <sup>2</sup>
W-1	127 ± 13 (10.2)	132 ± 34 (25.7)	97.2 ± 2.1 (2.2)	100 ± 9 <sup>2</sup>
GB-1	208 ± 13 (6.2)	217 ± 9 (4.1)	-	130 and 171 <sup>14</sup> 165 and 211 <sup>4</sup>
BB-1	231 ± 55 (23.8)	237 ± 40 (16.9)	223.5 ± 7.5 (3.3)	186 and 255 <sup>14</sup> 186 and 229 <sup>4</sup>
P-1	975 ± 20 (2.0)	1035 ± 145 (14.0)	-	-

## Results and discussion

Accuracy and precision of INAA used for the determination of Hf in the geological reference materials were good, as shown in Table 1. The relative standard deviations varied from 1.1 to 14.0% and with the published data a good agreement was noted. The relative errors for GSP-1 and W-1 results were lower than 7.7%.

Table 2 shows that uranium interference correction factors obtained for Zr analysis agree with those reported in the previous papers. To obtain the correct Zr concentrations in the presence of uranium in the rock, firstly the amount of U was determined and multiplied by the interference factor. This interference contribution was then subtracted from the concentration of Zr measured.

Table 3 shows the results for Zr obtained by INAA using thermal and epithermal irradiations and by RNAA. The relative standard deviations of these results varied from 2.0 to 25.7% depending on the sample. By comparing these results with those appeared in the literature, it can be concluded that there is, generally, a good agreement. Less precise and accurate results were obtained by INAA for W-1 and BB-1 samples. For these samples RNAA was

## References

1. E. P. MIGNONSON, I. ROELANDTS, *Radiochem. Radioanal. Letters*, 25 (1976) 41.
2. E. S. GLADNEY, C. E. BURNS, I. ROELANDTS, *Geostand. Newsl.*, 7 (1983) 3.
3. A. M. G. FIGUEREDO, L. S. MARQUES, *Geochim. Brasiliensis*, 3 (1989) 1.
4. P. S. LINHARES, Resumos do 3º. Congresso Brasileiro de Geoquímica e 1º. Congresso dos Países de Língua Portuguesa. São Paulo, v. 2, 1991, p. 430.
5. P. A. KUMAR, A. N. GARG, W. D. EHMANN, *J. Radioanal. Nucl. Chem.*, 40 (1977) 51.
6. M. D. GLASCOCK, P. I. NABELEK, D. D. WEINRICH, D. D. CONVENY JR., *J. Radioanal. Nucl. Chem.*, 99 (1986) 121.
7. S. LANDSBERGER, *Chem. Geol.*, 57 (1986) 415.
8. M. VOBECKY, *Radiochem. Radioanal. Letters*, 52 (1979) 231.
9. R. L. KOROTEV, D. J. LINDSTROM, *Transactions ANS*, 49 (1985) 177.
10. P. J. POTTS, O. W. THORPE, C. ISAACS, N. W. ROGERS, *Geostand. Newsl.*, 9 (1986) 173.
11. G. MEYER, *Radiochem. Radioanal. Letters*, 52 (1982) 233.
12. M. A. GOUVEIA, M. I. PRUDENCIO, M. C. FREITAS, E. MARTINHO, J. M. P. CABRAL, *J. Radioanal. Nucl. Chem.*, 114 (1987) 309.
13. K. S. PARK, N. B. KIM, H. J. WOO, K. Y. LEE, Y. Y. YOON, J. H. LEE, *J. Radioanal. Nucl. Chem.*, 168 (1993) 153.
14. P. S. LINHARES, *Anais do 1º. Congresso Brasileiro de Geoquímica*, v. 1, 1987, p. 327.