

## Determination of Rare Earth Elements, U and Th in the Standard Rock GS-N by Neutron Activation Analysis\*

A. M. G. FIGUEIREDO<sup>†</sup>, M. SAIKI

*Instituto de Pesquisas Energéticas e Nucleares, C.N.E.N/S.P.,  
Divisão de Radioquímica, Caixa Postal 11049,  
01000 São Paulo-SP, Brazil*

and L. S. MARQUES

*Instituto Astronômico e Geofísico, Universidade de São  
Paulo, Departamento de Geofísica, Caixa Postal 30627,  
01000 São Paulo-SP, Brazil*

The analysis of U, Th and rare earth elements in rocks is of great interest, since these elements can provide important petrogenetic information. Therefore, the utilization of geological standards with recommended concentration values is of great importance.

Neutron activation analysis of the French geological standard GS-N, provided by C.R.P.G. (Centre de Recherches Petrographiques et Geochemiques), has been carried out and the concentration values of the elements uranium, thorium and nine other rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Yb and Lu) have been determined.

Some data for the concentration values in the GS-N standard have already been reported in the literature [1–7]. Nevertheless, there are recommended values only for the elements U, Th, La, Ce, Sm, Eu and Yb. Even for these elements, there are considerable discrepancies between different authors.

The aim of this work was to provide results in order to compare them with literature data and give a contribution to the concentration values proposed for this standard.

### Experimental

The procedure adopted was of irradiating aliquots of the GS-N rock for 8 to 72 h with thermal and epithermal neutrons (flux of  $10^{12}$ – $10^{13}$  n cm<sup>-2</sup> s<sup>-1</sup>), followed by counting the induced gamma radiation in a Ge(Li) detector (resolution of 2.8 KeV for the 1332 KeV peak of <sup>60</sup>Co) and a hyperpure Ge detector (resolution of 0.58 KeV for the 122 KeV peak of <sup>57</sup>Co).

\*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

<sup>†</sup> Author to whom correspondence should be addressed.

The standards used were those provided by the United States Geological Survey (U.S.G.S.) (AGV-1, BCR-1 and G-2) because of their recommended concentration values [8–10]. Also standards consisting of aliquots of lanthanide solutions of known concentrations were used.

The assignment of the energies of the several peaks in the gamma spectrum and the calculation of the corresponding activities were performed by means of a PDP-11/04 minicomputer using the 'Geligam' program in ORACL language, developed by EG & G ORTEC.

The concentrations of the elements were determined by comparing the activities obtained in each peak of the sample (GS-N rock) and of the standard spectra.

Table I shows the radioisotopes used to calculate the concentration of the analysed elements as well as their nuclear data and the irradiation and counting conditions. An asterisk denotes the conditions that provided the best values. The absence of notation means that similar results were obtained.

In the cases where spectral interferences were found, such as gadolinium, a radiochemical process was employed. The method used was the retention of the interfering elements Pa and Ta in a hydrated antimony pentoxide (HAP) column [11]. Also a pre-irradiation separation step was developed to eliminate interferences, including those from uranium fission products, by solvent extraction with a solution of tetracycline in benzyl alcohol. The interfering elements U, Th, Mo, Ta, Sc and Fe were extracted into the organic phase. Lanthanides remaining in the aqueous phase were coprecipitated either in ferric hydroxide or in calcium oxalate.

### Results and Discussion

The results obtained for the GS-N standard are shown in Table II, together with some literature concentration values. The data determined for most of the analysed elements agree with those reported by Govindaraju [1] to within 1 to 7% and are situated in the range of literature values [1–7]. It can be seen that the results present a good precision, with relative standard deviations lower than 15%.

In the case of Gd, few data have been so far reported in the literature, which enhances the contribution of this work. The radiochemical procedure adopted for Gd determination was satisfactory in eliminating the interfering elements.

The proposed pre-irradiation separation method allowed the separation of lanthanide elements as a group, and there was no chemical fractionation of the individual elements. Chemical yield values of

TABLE I. Radioisotopes Used and Main Energies Corresponding to the Analysed Elements. Irradiation and Counting Conditions

| Element | Radioisotope      | Energy (KeV)                       | Type of irradiation | Decay interval (days) | Detector       |
|---------|-------------------|------------------------------------|---------------------|-----------------------|----------------|
| La      | $^{140}\text{La}$ | 815.5, 1595.4                      | T, E*               | ≈5                    | Ge(Li)         |
| Ce      | $^{141}\text{Ce}$ | 145.4                              | T                   | 15–30                 | Ge*            |
|         |                   | 145.4                              | E                   | 15–30                 | Ge(Li)         |
| Nd      | $^{147}\text{Nd}$ | 91.4                               | T                   | 5–15                  | Ge             |
|         |                   | 531.0                              | T, E                | 5–15                  | Ge(Li)         |
| Sm      | $^{153}\text{Sm}$ | 47.0 ( $K\beta_1$ Eu), 69.6, 103.0 | T                   | ≈5                    | Ge*            |
|         |                   | 103.0                              | E                   | ≈5                    | Ge(Li)         |
| Eu      | $^{152}\text{Eu}$ | 45.4 ( $K\beta_1$ Sm), 121.8       | T                   | 15–30                 | Ge             |
|         |                   | 1407.5                             | T                   | 15–30                 | Ge(Li)         |
| Gd      | $^{153}\text{Gd}$ | 97.5, 103.2                        | T                   | 30–60                 | Ge(Li)         |
| Tb      | $^{160}\text{Tb}$ | 298.6, 879.4                       | T, E*               | 15–30                 | Ge(Li)         |
| Yb      | $^{169}\text{Yb}$ | 50.7 ( $K\alpha_1$ Tm), 63.0       | T                   | 15–30                 | Ge*            |
|         |                   | 177.0, 197.8                       | T                   | 15–30                 | Ge(Li)         |
| Lu      | $^{177}\text{Lu}$ | 113.0, 208.4                       | T                   | ≈15                   | Ge,<br>Ge(Li)* |
| U       | $^{239}\text{Np}$ | 277.5                              | E                   | ≈5                    | Ge(Li)         |
| Th      | $^{233}\text{Pa}$ | 311.8                              | E                   | 15–30                 | Ge(Li)         |

\*Irradiation and counting conditions that provided the best results. E = epithermal activation; T = thermal activation.

TABLE II. Results for the Geological Standard GS-N Compared with Literature Values<sup>a</sup>

| Element | Concentration (ppm) |                     |             | Range of reported data [1–7] |
|---------|---------------------|---------------------|-------------|------------------------------|
|         | This work           |                     | From ref. 1 |                              |
|         | Instrumental        | Chemical separation |             |                              |
| La      | 71 ± 4 (5.3)        | 71 ± 5 (5.6)        | 75          | 66.5–76                      |
| Ce      | 138 ± 15 (1.4)      | 133 ± 12 (5.0)      | 140         | 112–155                      |
| Nd      | 48 ± 6 (4.0)        | 54 ± 6 (7.4)        | 50          | 47–51.2                      |
| Sm      | 7.6 ± 0.7 (7.3)     | 7.8 ± 0.4 (4.9)     | 8.2         | 6.7–8.24                     |
| Eu      | 1.6 ± 0.1 (5.9)     | 1.7 ± 0.2 (2.9)     | 1.7         | 1.6–1.8                      |
| Gd      |                     | 5.6 ± 0.3           |             | 3.4–5.6                      |
| Tb      | 0.63 ± 0.07 (5.0)   | 0.68 ± 0.04 (14.1)  | 0.6         | 0.51–0.76                    |
| Yb      | 1.8 ± 0.2 (5.9)     | 1.8 ± 0.2 (5.9)     | 1.7         | 1.3–1.9                      |
| Lu      | 0.25 ± 0.02 (25.0)  | 0.19 ± 0.03 (4.0)   | 0.2         | 0.17–0.24                    |
| U       | 7.7 ± 0.6 (3.8)     |                     | 8           | 7.7–8.2                      |
| Th      | 41 ± 1 (6.8)        |                     | 44          | 32–45                        |

<sup>a</sup>Numbers in parentheses are the relative errors (%) compared to Govindaraju's [1] values. Numbers in italics are recommended values.

85 ± 3% and 80 ± 6% were obtained with  $\text{Fe}(\text{OH})_3$  and  $\text{CaC}_2\text{O}_4$ , respectively. The pre-separation method is relatively simple and rapid. Since the procedure is applied before irradiation, there are no problems of radiation exposure, therefore many samples can be processed at the same time. This method is particularly useful in the analysis of uraniferous rocks.

Except for Gd, significant differences were not observed between the results obtained by the instrumental method and by the chemical procedure. This fact may be explained by the low uranium concentration (8 ppm) in the GS-N rock.

The highest relative errors were obtained for the elements Lu (instrumental analysis) and Tb (pre-separation procedure). In both cases it must be considered that these errors do not show significant differences compared to the proposed values, considering their low concentration (<1 ppm) in the GS-N rock.

The results obtained in this work for the French Geological Standard GS-N confirm the already published values, giving some more recent data and contributing an improvement in the proposed concentration values for this standard.

### Acknowledgements

The authors are grateful to Dr Marina B. A. Vasconcellos for helpful reviews of this paper. This work was partially supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (F.A.P.E.S.P.).

### References

- 1 K. Govindaraju, *Geostand. Newsl.*, **8**, 173 (1984).
- 2 S. Pal and D. J. Terrel, *Geostand. Newsl.*, **2**, 187 (1978).
- 3 P. J. Potts, O. W. Thorpe and J. S. Watson, *Chem. Geol.*, **34**, 331 (1981).
- 4 S. E. Church, *Geostand. Newsl.*, **5**, 133 (1981).
- 5 S. May and G. Pinte, *J. Radioanal. Nucl. Chem.*, **81**, 273 (1984).
- 6 S. J. Barnes and M. P. Gorton, *Geostand. Newsl.*, **8**, 17 (1984).
- 7 I. Roelandts and G. Michel, *Geostand. Newsl.*, **10**, 135 (1986).
- 8 S. Abbey, *Geostand. Newsl.*, **4**, 163 (1980).
- 9 E. S. Gladney, C. E. Burns and I. Roelandts, *Geostand. Newsl.*, **7**, 3 (1983).
- 10 K. Govindaraju, *Geostand. Newsl.*, **8**, (Special issue) (1984).
- 11 L. T. Atalla, M. S. M. Mantovani, L. S. Marques and M. A. Sousa, *An. Acad. Brasil. Ciênc.*, **57**, 19 (1985).