Spectrographic Estimation of Zirconium and Niobium in Rocks and its Significance

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Summary: A reliable spectral analysis method for quantitative determination of zirconium and niobium content in rock samples has been developed. A chemical enrichment procedure was adopted as the concentration of these elements in rocks was very low. Histograms showing the frequency distributions of the estimated elements were drawn.

Introduction

Many elements occur in rocks, minerals, soils and plants in concentrations often below the limit of the their detection. Enrichment procedures are therefore necessary if a spectrographic method is attempted for quantitative estimation of such elements. Various enrichment procedures have been employed such as the carrier distillation method[1] and the evaporation technique[2]. In the present work an enrichment procedure depending on chemical extraction of the elements followed by their precipitation on spectroscopically pure carbon powder was applied. Such procedure helped in reducing the interelement effect to a great extent[3]. Preparation of matrices similar to the composition of the rocks to construct the working curves was then unnecessary. Determination of zirconium and niobium in rocks of different origin, i.e. of different chemical composition was possible using the same working curves.

Experimental

Preparation of samples

The prospected areas from which the samples were collected are located in the southern part of the eastern desert of Egypt called Wadi Sikait. Sixty three rock samples were collected in a square grid pattern of 50 m and to a depth of 30 cm. Rock samples were broken down before grinding to pass through 2 mm sieve. Each sample was ignited at 450°C to destroy any organic matter present and to remove the humidity. The samples were then quartered and ground in a mechanical agate mortar to pass through a 100 mesh sieve.

0.5 gm of each sample was digested with aliquot of 20 ml aqua regia till a cake was obtained. The process of addition of aqua regia and disgestion was repeated ten times to secure complete dissolution of zirconium content and its separation from the sample. The solution was filtered and the filterate containing zirconium salt was concentrated till its volume reached about 5 ml. A 0.25 gm of spec. pure carbon powder containing molybdenum as an internal standard element with concentration of 1000 ppm was added to the zirconium salt solution. It was then heated to complete dryness.

Due to the insolubility of niobium in aqua regia, it remains in the residue on the filter paper. The residue was transfered to a beaker and a portion of 20 ml concentrated sulphuric acid was added. The same treatment applied to zirconium was followed for niobium using sulphuric acid instead of aqua regia.

The spec. pure carbon powder containing both sample and internal standard was used to fill the craters of spec. pure graphite electrodes while pressing with stainless steel needle to attain compact filling[4]. The amount of sample was 28±1 mgm. The lower electrode used as anode has a crater with dimentions 1.5 x 9.5 mm while the wall thickness is 0.65 mm. The counter electrode used as cathode is tapered at an angle of 60°.

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Table 1. The Distribution of Nb and Zr in Rocks.

Rock Type	No. of samples analysed	Nb-range (ppm)	Nb-average (ppm)	Zr-range (ppm)	Zr-average (ppm)
Psammitic gneiss	18	4.1-50.2	18.2	1.1-15.8	4.4
Schists	17	5.0-89.1	39.6	1.1-32.1	6.6
Hornblende gneiss	6	10.1-44.7	17.7	1.2- 4.2	2.8
Amphibolites	2	11.2-25.1	18.2	4.7- 8.7	6.7
Serpentines	6	25.2-68.7	44.4	4.0-17.8	5.1
White Grantie	4	8.9-44.7	25.6	16.1-31.7	20.6
Pink Granite	2	24.4-28.1	26.3	8.0-20.0	14.0
Pegmatites	6	8.6-56.2	26.8	6.7-28.2	13.3
Quartz veins	2	5.6- 7.1	6.4	4.9- 7.9	6.4

Preparation of standards

Two sets of standards were prepared by incorporating separately zirconium dioxide and niobium pentoxide in carbon powder containing 1000 ppm Mo used as an internal standard element. The main standard for each set contains 100 ppm Zr or Nb. Further dilutions were made from this main standard using carbon powder containing 100 ppm Mo Standard samples of Zr and Nb with concentrations of 1, 5, 10, 25 and 50 ppm were prepared.

Working curves and their characteristics

A 3.4 m Ebert-Plane grating spectrograph (Jarrel-Ash) of 5.05 $A^°$/mm dispersion and 10 mμ slit width was used for construction of the working curves. Spectral line pairs Zr II 2571.4/Mo 2572.3 $A^°$ and Nb 2578.7/ Mo 2572.3 $A^°$ were selected for determination of Zr and Nb respectively. Excitation of samples was made by anode d.c. arc supplied from Jaco Custom Varisource using an analytical gap of 5 mm.

Two linear working curves covering the range from 1 to 100 ppm were constructed for Zr and Nb. Their slopes were found to be 0.35 and 0.39 while the index values ere 1 and 758.6 ppm respectively. The two analytical curves can be represented by the following equations:

$$\log \frac{I_{Zr} \text{ II } 2571.4}{I_{Mo} \quad 2572.3} = 0.35 \log C_{Zr} - 0.37$$

$$\log \frac{I_{Nb} \quad 2578.7}{I_{Mo} \quad 2572.3} = 0.39 \log C_{Nb} - 1.50$$

The coefficient of variation for determination of Zr and Nb in rock samples were found to be ± 5.02 and ± 5.72 respectively.

Distribution of Nb and Zr in rocks and its significance:

The collected samples were analysed for Zr and Nb content. The ranges of Zr and Nb concentrations and their averages for the various types of rocks encountered in the area from which the samples were collected are summarized in Table 1. The average content of zirconium in all rock samples was found to be 7.7 ppm, while that of niobium is 27.6 ppm.

To illustrate the behaviour of Zr and Nb in rock samples, the samples were classified into two main groups. The first contains 15 psammitic gneiss samples, while the second contains 39 different rock types. Some anomolies from each group were excluded. Figs. (1 to 8)
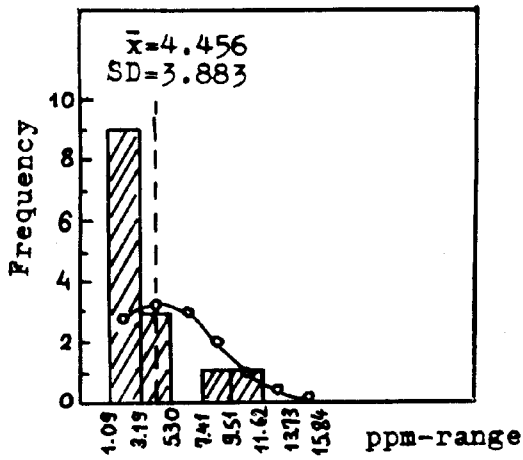
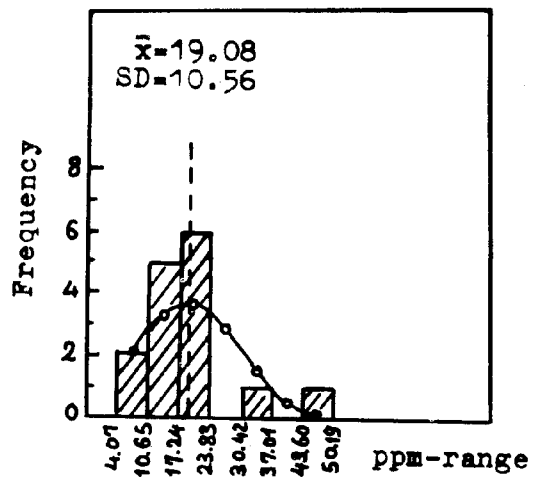Fig.1 Histogram of Zr in psammitic gneiss using arithmetic values.

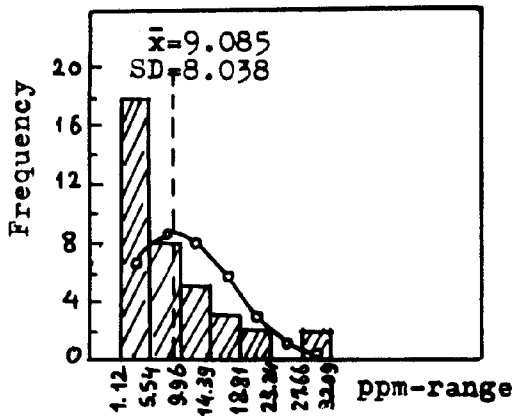Fig.2 Histogram of Nb in psammitic gneiss using arithmetic values.

Fig.3 Histogram of Zr in different rock types using arithmetic values.
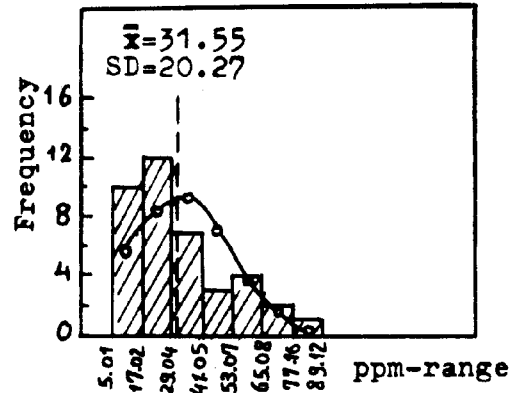

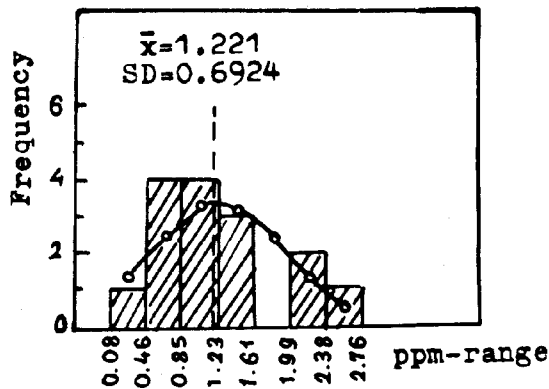Fig.4 Histogram of Nb in different rock types using arithmetic values.

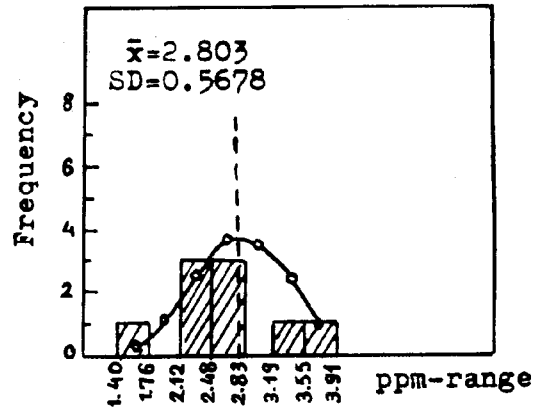Fig. 5 Histogram of Zr in Psammitic gneiss using logarithmic values.

Fig.6 Histogram of Nb in psammitic gneiss using psammitic gneiss logarithmic.
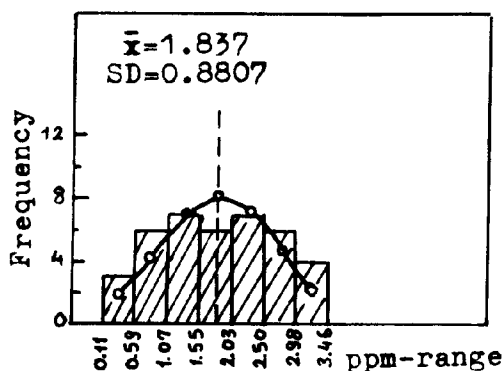
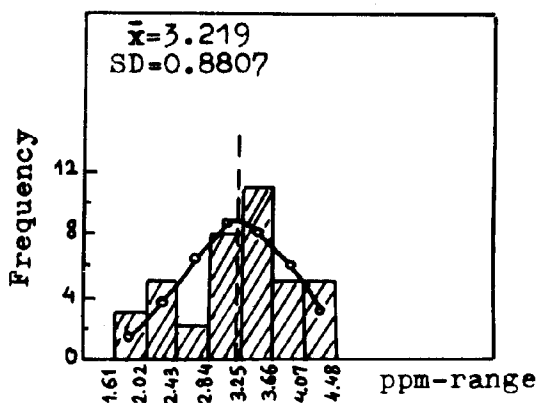Fig.7 Histogram of Zr in different rock types using logarithmic values.

Fig.8 Histogram of Nb in different rock types using logarithmic values.

demonstrate the obtained histograms (frequency distribution diagrams) using arithmatic and logarithmic values.* The theoretical distribution curves were drawn in each histogram, which indicate that the distribution of the mentioned elements is more or less of logarithmic type. The experimental results give an arithmatic mean for zirconium content in psammitic gneiss of 4.4 ppm and that for the rest of the samples of 9.1 ppm. The mean niobium content in psammitic gneiss is 19.1 ppm and for the rest of the samples is 27.6 ppm. Our experimental values for Zr are lower than that reported by Rankama[5]. The results obtained for Nb are in agreement with those given in reference 5. The difference between our data for Zr and some of the published data may be due to the difference in local conditions of the area in which the samples were collected.

Conclusion:

Profound variations in the constituents of the matrices affect the slopes and index values of the working curves established using the same line pairs. Extraction of the elements to be estimated reduces the matrix effect to the minimum and cancels the necessity of preparing matrices indentical in composition, strucure and physical properties to the different analysed samples. Consequently a single working curve for each element to be estimated will be satisfactory.

References:

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2. S.L. Mandel' Shtam, N.N. Semenov and Z.M. Turovtseva, Zhm. Anal. Khim., 2, 9 (1956).
3. N. Barakat, F. Abou El-Nour and F. Khatab, Zeitschrift fur Analytische Chemie, 289, 367 (1978).
4. R.L. Mitchell, Technical Communication No. 44 A of the Commenwealth Bur. Soil Science, U.K. (1964).
5. K. Rankama, Isotope Geology, Table 9.1, 135 (1945).

*The values of arithmatic mean ($\bar{x}$) and standard eviation (SD) are included with each Fig.