DETERMINATION OF ELEMENTAL CONTENT IN GEOLOGICAL SAMPLES*

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Concentrations of 35 major, REE and trace elements in geological samples, were determined by Epithermal Neutron Activation Analysis at the Joint Institute of Nuclear Research, Dubna, (Russia). In this paper we will present the obtained results witch were interpreted in the framework of the Upper Continental Crust model in order to determine the origin of the sediments.

Key words: activation analysis; major elements; REE, trace elements; geological samples.

1. INTRODUCTION

Neutron Activation Analysis (NAA) is a quantitative and qualitative method of high efficiency for the precise determination of a number of main-components and trace elements in different types of samples. NAA, based on the nuclear reaction between neutrons and target nuclei, is a useful method for the simultaneous determination of about 25–30 major, minor and trace elements of geological, environmental, biological samples in ppb-ppm range without or with chemical separation.

In NAA, samples are activated by neutrons. During irradiation the naturally occurring stable isotopes of most elements that constitute the rock or mineral samples, biological materials are transformed into radioactive isotopes by

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neutron capture. Then the activated nucleus decays according to a characteristic half-life; some nuclides emit β particles only, but most nuclides emit gamma-quanta, too, with specific energies. The quantity of radioactive nuclides is determined by measuring the intensity of the characteristic gamma-ray lines in the spectra. For these measurements a gamma-ray detector and special electronic equipment are necessary. As the irradiated samples contain radionuclides of different half-lives different isotopes can be determined at various time intervals.

Although the development of analytical techniques has led to the expansion of new methods (ICP-AAS, ICP-MS, etc.), which can also be widely applied in analytical chemistry, NAA is still competitive in many areas. The indisputable advantage of the method is its sensitivity and accuracy especially in respect of some trace elements. The method is of a multielement character, *i.e.* it enables the simultaneous determination of many elements without chemical separation. In the case of instrumental determination, the preparation of samples involves only the preparation of representative samples, *i.e.* pulverization or homogenization in most cases, and this reduces the danger of contamination to a minimum and accelerates the whole analytical process. If the determination of some special elements or groups of elements can be carried out only through chemical separation, it is possible to carry out after irradiation. Thus the pollution caused by the different chemicals will not get activated, the chemical yield can be measured by feeding inactive carriers and the chemical processes can be better controlled. During NAA the neutrons get into interaction with the nucleus, therefore, the chemical composition and crystal structure of the substance under analysis will have an effect on the result only in exceptional cases.

The development of the method has contributed to the elaboration of some very simple and accurate methods of standarization, which lead to a surpassingly accurate analysis [8–10].

Analysis of rock specimens by neutron activation analysis assists geochemists in research on the processes involved in the formation of different rocks through the analysis of the rare earth elements (REEs) and other trace elements [3–7]. The NAA findings support the theory that extinction of the dinosaurs occurred soon after the impact of a large meteorite with the earth.

2. MATERIAL AND METHODS

Geological samples such us: granit, basaltic lava, vacuolar basalt, basaltic microscorietes, granitoide, dacitic and porfitice tuff, were collected from Height Highis, Persani Mountain, Meridionali Carpathians, Dobrogea Table-Land.

The samples were irradiated in the IBR-2 fast pulsed reactor, the flux parameters of which are shown in Table 1.

Table 1

The main characteristics of the irradiation channels (JINR-Dubna)

Channel	Neutron fluency density (10^{12} n cm^{-2}s^{-1})			t	diameter	length
	T	R	F	[°C]	[mm]	[mm]
Ch 1 (Cd-coated)		3.31	4.32	70	28	260
Ch 2	1.23	2.96	4.10	60	28	260

T – thermal neutrons, R – resonant neutrons, F – fast neutrons

Quantitative determinations were done using both short and long term epithermal neutrons irradiation. In order to be analyzed the samples were prepared (grinded and homogenized) at Geological Institute of Russian Academy of Sciences, Moscow, Russia.

For short term irradiation the samples were heat-sealed in polyethylene foil and irradiated together with standards for 60s in the unscreened Channel 2 at the Joint Institute of Nuclear Research-Dubna (Russia) IBR-2 reactor, by using all energy spectrum of neutrons.

After irradiation the samples were measured twice, after 2 and 10 minutes for about 5 and 12 minutes, respectively, using a Ge (Li) detector with the energy resolution of 2.2 keV for ^{60}Co 1332.4 keV line and a relative efficiency of 18%.

For the long term irradiation samples were packed in aluminum foil together with internal standard, placed in an aluminum container and irradiated for 44 hours in the Cd-screened Channel 1. Spectra of induced gamma activity were recorded after 4 and 14 days of cooling, respectively. Software developed at FLPN-JINR was used for acquisition and processing of experimental gamma ray spectra.

3. RESULTS AND DISCUSSION

The method allowed us to obtain the concentration of the following elements: 7 major (Na, Al, Cl, K, Ca, Ti and Fe) and 28 trace (Sc, V, Cr, Mn, Co, Ni, Zn, As, Cu, Br, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Hf, Ta, W, Th and U).

All the experimental data have been processed by using MS ExcelTM XP, Origin5.0 and StatSoft StatisticaTM 6. programs.

In the Fig. 1, the ternary diagram of La, Th and Sc is presented As it can be observed in this diagram, the distribution of La, Th and Sc, has confirmed the continental origin of the investigated samples.

A tree-diagram designed of the investigated elements in the geological samples collected from different area of Romania suggests that these elements can be grouped into several main clusters (see Fig. 2) in accordance with their chemical affinity.

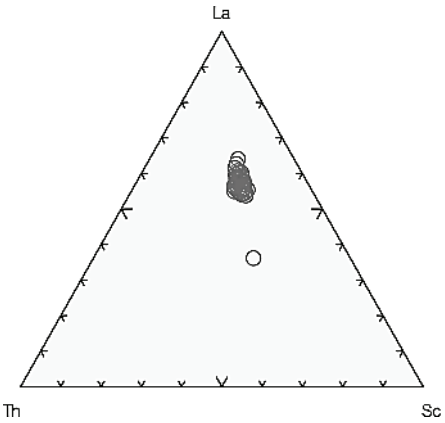

Fig. 1 – Ternary diagram of La, Th and Sc.

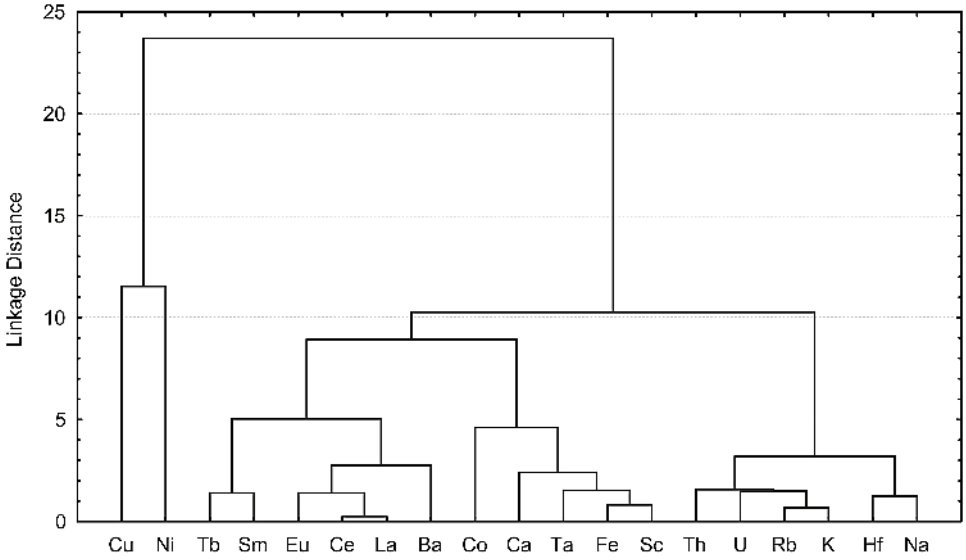

Fig. 2 – Tree diagram for cluster analysis (Word's method of linkage) of the investigated elements concentration.

4. CONCLUSION

Neutron Activation Analysis several important advantages over other techniques like Atomic Absorption, X-Ray Resonance Fluorescence, Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Couples Plasma Mass Spectrometry:

1. Nuclear technique that measures the intensity of gamma rays of "characteristic" energy using gamma spectroscopy.
2. Multielement Analysis.

3. Rapid analyses of multiple samples.

4. Sample size can be variable (typically 1 mg to 1 gm).

5. Analysis of Reference Standards:

Neutron Activation Analysis is very useful for analysis of materials for the purpose of preparing the reference standards.

6. Nondestructive – that is valuable and safe, samples are not destroyed.

7. No Chemical processing; therefore samples are not contaminated during sample preparation, no uncertainty about total dissolution of sample, no need for dilutions of solutions, making the technique valuable and safe. Samples are not destroyed.

8. No need for repeated blank measurements because no memory effects.

9. Gamma ray spectroscopy is largely free from matrix interferences.

10. Depending on the sample matrix, elemental concentrations can be determined at parts per million (ppm), parts per billion (ppb) and parts per trillion (ppt) level.

The work is in progress.

REFERENCES

1. W. C. Krumbein, F. A. Graybill, *An Introduction to Statistical Models in Geology*, McGraw-Hill, New York, 1965.
2. S. R. Taylor, S. M. McLennan, *The Continental Crust its Composition and Evolution*; Geoscience Texts. Blackwell: Oxford, 312 p., 1985
3. B. Anders, W. Junge, J. Knoth, W. Michaelis, J. R. Vogt (Ed.), Nuclear Methods in Environmental Research. US-DOE, CONF-840408, p. 202, 1984.
4. L. Fodor, L. Csontos, G. Bada, I. Györfi, L. Benkovics, Geol. Soc., London, Spec. Publ., 156 (1999) 295, in: The Mediterranean Basins: Tertiary Extension within the Alpine Orogen.
5. B. Durand, L. Jolivet, F. Horváth, M. Séranne (Eds), H. W. Nesbitt, Mobility and fractionation of rare earth elements during weathering of a granodiorite, Nature 279, 206–210, 1979.
6. A. B. Ronov, Y. A. Balashov, A. A. Migdisov, Geochemistry of the rare-earth's in the sedimentary cycle. Geochemistry International 4, 1–17, 1967.
7. R. A. Zielinski, The mobility of Uranium and other elements during alteration of rhyolite ash to montmorillonite: a case study in the Troublesome Formation, Colorado, U.S.A. Chemical Geology 35, 185–204, 1982.
8. V. F. Peresedov, A. D. Rogov, Simulation and analysis of neutron energy spectra from irradiation channels of the IBR-2 reactor, J. of Radioanal. Nucl. Chem., Letters, 214(4), 277–283 (1996).
9. V. M. Nazarov, S. S. Pavlov, E. Herrera, M. V. Frontasyeva, Recent developments of radioanalytical methods at the IBR-2 pulsed fast reactor. J.of Radioanal. Nucl. Chem.,167, 11–21 (1993).
10. T. M. Ostrovnaya, L. S. Nefedyeva, V. M. Nazarov, S. V. Borzakov, L. P. Strelkova, Software for INAA on the basis of relative and absolute methods using nuclear data base, Proc. Activation Analysis in Environment Protection, D14-93-325, JINR, Dubna, p. 319–325, 1993.