2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
***ISBN:* 978-85-99141-04-5**

DETERMINATION OF URANIUM AND THORIUM BY NEUTRON ACTIVATION ANALYSIS APPLIED TO FOSSIL SAMPLES DATING

Regina B. Ticianelli[1], Ana Maria Graciano Figueiredo[1], Guilherme S. Zahn[1], Angela Kinoshita[2,3], Oswaldo Baffa[2]

[1] Instituto de Pesquisas Energéticas e Nucleares –IPEN-CNEN/SP,
C.P. 11049, 05422-970, São Paulo, SP.
ticianellli@yahoo.com.br

[2] Departamento de Física, FFCRLP- USP, Ribeirão Preto, SP

[3] Universidade Sagrado Coração, Bauru, SP

ABSTRACT

Electron Spin Resonance (ESR) dating is based on the fact that ionizing radiation can create stable free radicals in insulating materials, like tooth enamel and bones. The concentration of these radicals - determined by ESR - is a function of the dose deposed in the sample along the years. The accumulated dose of radiation, called Archeological Dose, is produced by the exposition to environmental radiation provided by U, Th, K and cosmic rays. If the environmental dose rate in the site where the fossil sample is found is known, it is possible to convert this dose into the age of the sample. The annual dose rate coming from the radioactive elements present in the soil and in the sample itself can be calculated by determining the U, Th and K concentration. Therefore, the determination of the dose rate depends on the concentration of these main radioactive elements. Neutron Activation Analysis has the sensitivity and the accuracy necessary to determine U, Th and K with this objective. Depending on the composition of the sample, the determination of U and Th can be improved irradiating the sample inside a Cd capsule, reducing the thermal neutron incidence on the sample and, therefore, diminishing the activation of possible interfering nuclides. In this study the optimal irradiation and counting conditions were established for U and Th determination in fossil teeth and soil.

1. INTRODUCTION

Electron Spin Resonance (ESR) dating is an absolute dating method adequate for the Quaternary period [1], where the age of a buried object is obtained by determining the accumulated radiation dose during the burial period. It is based on the fact that ionizing radiation can create stable free radicals in insulating materials, like tooth enamel and bones. The concentration of these radicals is determined by ESR, and it is a function of the dose deposited in the sample along the years. The accumulated dose of radiation, called Equivalent Dose (ED), is produced by the exposition to environmental radiation provided by U, Th, K and cosmic rays and by the radioisotopes present in the tooth. Thus, if the environmental dose rate (D_{ext}) in the site where the fossil sample is found is known and also the internal dose rate D_{int}, it is possible to convert this dose into the age of the sample (Eq. 1)

$$age = \frac{ED}{D_{ext} + D_{\text{int}}} \qquad (1)$$

The dose from cosmic rays is known to be about 0.25mGy per year [2] and there are well established means to correct for geographical position and depth, so the problem is reduced to the determination of the annual dose rate coming from the radioactive elements present in the soil and in the sample itself, which can be calculated by determining the concentration of the naturally-occurring radioisotopes U, Th and K [3]. The Neutron Activation Analysis Laboratory of IPEN has been analyzing U, Th in several fossil samples for many years, in a cooperation with researchers from the Department of Physics, FFCRLP- USP, Ribeirão Preto, SP, and the Universidade Sagrado Coração, Bauru, SP [3,4].

Neutron Activation Analysis (NAA) is an analytical technique that has the sensitivity and accuracy to properly determine ppm levels of both Uranium and Thorium in several different matrices, regardless of the chemical or physical form of the samples. It is based on the determination of the gamma radiation induced in a sample after it is irradiated by neutrons.

The usual NAA procedure consists in the irradiation of a sample in a neutron field with predominance of thermal neutrons, as most elements are more responsive to neutrons in this energy range; in the case of Uranium and Thorium, though, the sensitivity to epithermal neutrons is much higher than that to thermal ones, so that the irradiation of the samples inside a Cadmium capsule, to reduce the thermal neutron flux, may greatly reduce the activation of other elements without impairing the activation of U and Th. Examples of experimental difficulties that can arise by the activation of undesired elements include the bremsstrahlung continuum from pure beta emitters like phosphor and calcium, the Compton continuum from very intense high energy gamma transitions (for example, the 2754 keV and 1369 keV transitions from the activation of sodium), as well as the activation of elements which produce gamma rays with energies that are very close to the one being measured; these undesired effects will be more significant in samples where there is plenty of these elements that can interfere with the detection - dentine, for instance, is composed roughly of 25% calcium, 12% phosphor and 0.6% sodium [5], so both the bremsstrahlung and Compton continua should be a strong issue.

The *thermal cross section* and the *resonance integral*, which are the parameters that determine the sensitivity of an isotope to thermal and epithermal neutrons, respectively, are shown in Table 1 for both the interest isotopes (U and Th), as well as for some of the isotopes that may interfere in the detection. It can be seen that, while for U and Th the resonance integral is several times larger than the thermal cross section, for all other isotopes in the table this doesn’t happen; therefore, when the aim of the measurement is to determine only U and Th concentrations, the irradiation inside a cadmium capsule may greatly enhance the accuracy of the measurement [7].

Table 1. Cross section and resonance integral for some isotopes that may influence in the determination of U and Th [6].

Element and Isotope	Gamma Energy (keV)	Thermal Cross Section (barn) [6]	Resonance Integral (barn) [6]
Uranium (U-238)	228, 278	2.680	277
Thorium (Th-232)	311	7.35	85
Sodium (Na-23)	2754, 1369	0.530	0.311
Calcium (Ca-40)	Pure beta	0.41	0.22
Phosphor (P-31)	Pure beta	172	0.14
Lutetium (Lu-176)	208, **229**	2090	1087
Osmium (Os-192)	**280**, 460	3.12	4.6

Depending on the composition of the sample, the determination of U and Th can be improved by irradiating the sample inside a Cd capsule, so as to reduce the thermal neutron incidence on the sample and, therefore, diminishing the activation of possible interfering nuclides. In this study the optimal irradiation and counting conditions were established for U and Th determination in fossil teeth and soil. In the present paper, the dentine and soil data used in the study were not identified, since the objective of this study was not archeological, but to evaluate the optimal analytical conditions to improve the U and Th determination.

2. EXPERIMENTAL PROCEDURE

In order to perform the present tests, the Instrumental NAA method was used, where the samples are irradiated together with one or more comparators or standards with a well-known concentration of the elements to be analyzed, and the concentration is then determined by a simple calculation (Eq. 2), where cps are the counts per second obtained in the analysis of both the sample and the comparator, m(comp) is the mass of the element present in the comparator, M(sample) is the total mass of the sample, λ is the decay constant and dt the time interval between counting the sample and the comparator.

$$Concentration = \frac{cps(sample) \times m(comp)}{cps(comp) \times M(sample)} e^{\lambda \cdot dt} \tag{2}$$

In the present analysis, two samples of dentine and 6 samples of soil were irradiated together with three comparators:

- Uranium standard solution, SPEX, total pipetted mass 2.5 μg;
- Thorium standard solution, SPEX, total pipetted mass 25 μg; and
- BE-N reference material (multielemental basalt, 2.4 μg/g U and 10.4 μg/g Th).

For the samples and the BE-N reference material, 1cm^2 polyethylene bags containing ~100mg were prepared and weighted; the standard solutions were pipetted in filter paper and then folded and placed inside similar polyethylene bags. The samples were irradiated for 8h in a neutron flux of about 5x10^{12} neutrons cm^{-2}s^{-1} the IEA-R1 research reactor in two separate batches: in one the samples and the comparators were inserted into a regular aluminum irradiation capsule and in the other the samples and comparators were first introduced into a ~2mm thick cadmium cylindrical capsule which was then closed and placed inside an aluminum capsule for irradiation. The epithermal samples were counted after 5 days of the irradiation, in order to determine the uranium, and again after 15 days of the irradiation, for the thorium determination; the thermal samples were counted after 7 and 15 days, also. All samples were counted in a 20% HPGe detector for 1h, and the spectra were then analyzed using the VISPECT software. The concentrations were then determined taking into consideration only the statistical errors from the peak fits.

3. RESULTS AND DISCUSSION

In order to illustrate the difference between the gamma ray spectra obtained after the irradiation with and without the cadmium capsule, the spectra for the 1st acquisition for a dentine sample are shown in Fig. 1, where it can be seen that both the bremsstrahlung and Compton continua are greatly reduced, resulting in a much cleaner spectrum, with very well-defined peaks for both the transitions relative to the determination of Uranium.

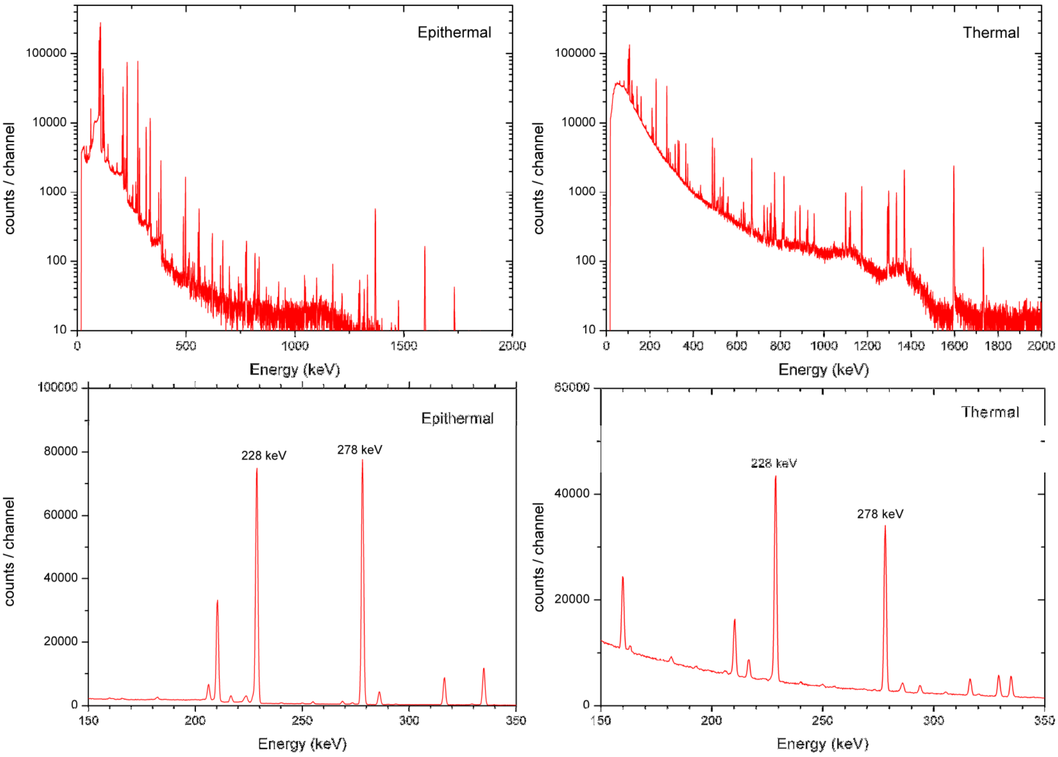

Figure 1. Gamma-ray spectra obtained for the dentine sample number 1 for the epithermal and thermal samples.

Table 2. Experimental results for the uranium concentration.

Sample		Irradiation	Comparator	Transition	U concentration (µg/g)		
Dentine	1	Thermal	U Standard	228 keV	251. 7	+/-	2.4
				278 keV	256.2	+/-	2.7
			BE-N	228 keV	211	+/-	30
				278 keV	272	+/-	55
		Epithermal	U Standard	228 keV	253.4	+/-	1.9
				278 keV	271.2	+/-	2.0
			BE-N	228 keV	207	+/-	7
				278 keV	237	+/-	8
	2	Thermal	U Standard	228 keV	89.8	+/-	0.9
				278 keV	90.1	+/-	1.0
			BE-N	228 keV	75	+/-	11
				278 keV	96	+/-	19
		Epithermal	U Standard	228 keV	94.0	+/-	0.7
				278 keV	96.2	+/-	0.7
			BE-N	228 keV	76.6	+/-	2.8
				278 keV	84.1	+/-	2.7
Soil	1A	Thermal	U Standard	228 keV	46.8	+/-	0.5
				278 keV	46.9	+/-	0.6
			BE-N	228 keV	39	+/-	6
				278 keV	50	+/-	10
		Epithermal	U Standard	228 keV	51.6	+/-	0.4
				278 keV	52. 5	+/-	0.4
			BE-N	228 keV	42.0	+/-	1.5
				278 keV	45.9	+/-	1.5
	1B	Thermal	U Standard	228 keV	52.0	+/-	0.6
				278 keV	51.8	+/-	0.7
			BE-N	228 keV	44	+/-	6
				278 keV	55	+/-	11
		Epithermal	U Standard	228 keV	55.9	+/-	0.5
				278 keV	58.3	+/-	0.4
			BE-N	228 keV	45.6	+/-	1.7
				278 keV	51.0	+/-	1.6
	1C	Thermal	U Standard	228 keV	52.7	+/-	0.6
				278 keV	54.0	+/-	0.8
			BE-N	228 keV	44	+/-	6
				278 keV	57	+/-	12
		Epithermal	U Standard	228 keV	54.4	+/-	0.4
				278 keV	58.1	+/-	0.5
			BE-N	228 keV	44.3	+/-	1.6
				278 keV	50.8	+/-	1.6
	2A	Thermal	U Standard	228 keV	12.31	+/-	0.26
				278 keV	13.0	+/-	0.3
			BE-N	228 keV	10.4	+/-	1.5
				278 keV	13.8	+/-	2.8
		Epithermal	U Standard	228 keV	13.60	+/-	0.15
				278 keV	13.89	+/-	0.14
			BE-N	228 keV	11.1	+/-	0.4
				278 keV	12.1	+/-	0.4
	2B	Thermal	U Standard	228 keV	11.25	+/-	0.21
				278 keV	11.56	+/-	0.24
			BE-N	228 keV	9.5	+/-	1.4
				278 keV	12.3	+/-	2.5
		Epithermal	U Standard	228 keV	10.78	+/-	0.10
				278 keV	11.18	+/-	0.10
			BE-N	228 keV	8.8	+/-	0.3
				278 keV	9.8	+/-	0.3
	2C	Thermal	U Standard	228 keV	12.15	+/-	0.28
				278 keV	13.3	+/-	0.3
			BE-N	228 keV	10.2	+/-	1.5
				278 keV	14.1	+/-	2.9
		Epithermal	U Standard	228 keV	16.38	+/-	0.19
				278 keV	17.59	+/-	0.19
			BE-N	228 keV	13.4	+/-	0.5
				278 keV	15.4	+/-	0.5

All the individual results obtained for uranium in all samples are shown in Table 2; indicating that the results obtained using the BE-N reference material as comparator presented much larger uncertainties, especially in the thermal irradiation; also, the results obtained using the 228 keV transition and the BE-N reference material were always quite lower than the other results, indicating a possible interference in the comparator spectra for this energy. Moreover, the results obtained in the thermal irradiation were often lower than the ones found in the epithermal one; this discrepancy may indicate that the peak fitting in the thermal spectra aren't as exact as the fits for the cleaner peaks found in the epithermal spectra.

The results obtained for thorium are presented in Table 3; in this case the results were all quite compatible, with no clear difference between the thermal and epithermal ones, or between the results obtained using the Th standard solution or the BE-N reference material. This can be due to the fact that there are no significant contaminant peaks in the vicinity of the 311 keV peak used in the determination of Th; moreover, in comparison with uranium, the thermal cross section of thorium is about 3 times larger and its resonance integral approximately 1/3, so that the advantages of the epithermal neutron irradiation will be less noticeable for thorium than for uranium.

Table 3. Experimental results for the thorium concentration.

Sample	Irradiation	Reference	Th concentration (µg/g)
1A	Thermal	Th Standard	12.22 +/- 0.11
		BE-N	11.86 +/- 0.18
	Epithermal	Th Standard	12.73 +/- 0.24
		BE-N	12.8 +/- 0.4
1B	Thermal	Th Standard	12.00 +/- 0.09
		BE-N	11.64 +/- 0.16
	Epithermal	Th Standard	11.02 +/- 0.21
		BE-N	11.0 +/- 0.3
1C	Thermal	Th Standard	11.13 +/- 0.10
		BE-N	10.80 +/- 0.16
	Epithermal	Th Standard	11.31 +/- 0.20
		BE-N	11.3 +/- 0.3
2A	Thermal	Th Standard	5.94 +/- 0.07
		BE-N	5.76 +/- 0.09
	Epithermal	Th Standard	5.91 +/- 0.15
		BE-N	5.92 +/- 0.21
2B	Thermal	Th Standard	5.86 +/- 0.06
		BE-N	5.68 +/- 0.09
	Epithermal	Th Standard	5.82 +/- 0.17
		BE-N	5.84 +/- 0.22
2C	Thermal	Th Standard	5.66 +/- 0.07
		BE-N	5.50 +/- 0.09
	Epithermal	Th Standard	5.49 +/- 0.19
		BE-N	5.50 +/- 0.23

4. CONCLUSIONS

In the present work it was observed that for the determination of uranium the results obtained using epithermal neutrons were significantly different than those obtained in the thermal irradiation, thus indicating that the use of cadmium capsules in the determination of this element is highly recommended. Also, the results obtained using the standard solution as comparator were clearly better than the ones obtained using the BE-N reference material, due to the higher presence of interfering elements in the latter, and the 278 keV peak led to more reliable results. As for the determination of thorium, no significant differences were observed between the measurements with thermal and epithermal neutrons, as well as using the standard solution or the BE-N reference material, indicating that the determination of this element can be performed either way.

REFERENCES

1. M. Jonas, "Concepts And Methods Of ESR Dating," *Radiation Measurements*, **27**, pp.943-973 (1998).
2. S. Watanabe *et. Al.*, "Some evidence of a dose of first humans to arrive in Brazil," *Journal of Archeological Science*, **30**, pp.351-354 (2003).
3. A. Kinoshita *et al..,* "ESR Dating at K and X band of northeastern Brazilian megafauna," *Applied Radiation and Isotopes*, **62**, pp.225-229 (2005).
4. R. P. Lopes *et al.*, "ESR dating of Pleistocene mammal teeth and its implications for the biostratigraphy and geological evolution of the coastal plain, Rio Grande do Sul, southern Brazil," *Quaternary International,* **212**, pp.213-222 (2010).
5. M. A. Zenobio, M. Socorro, and E. G. Zenobio, "Chemical composition of human enamel and dentine: preliminary results to determination of the effective atomic number", *Proceedings of the IRPA International Congress of the International Radiation Protection Association,* Buenos Aires, Argentina, 19-24 Oct. (2008).
6. S. F. Mughabghab, *Thermal Neutron Capture Cross Sections: Resonance Integrals And G-Factors*, IAEA INDC(NDS)-440 (2003).
7. L. T. Atalla, *Estudo Da Determinação De Urânio Por Análise Por Ativação Com Nêutrons Epitérmicos*, PhD. Thesis, IEA-USP, São Paulo (1977).