

INVESTIGATION OF AN EGYPTIAN ALABASTER ORE BY MEASURING ITS NATURAL RADIOACTIVITY AND BY NAA USING K_0 STANDARDIZATION AND COMPARATOR METHODS.

N. F. Soliman

*Reactor Physics Department, Reactors Division, Nuclear Research Center,
Atomic Energy Authority, Cairo, Egypt
E-mail: nabihfrg@yahoo.com*

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Passive gamma-ray spectrometry and neutron activation analyses (NAA) were applied in investigating an alabaster ore sample. In the passive measurement 273.4 g of standard monazite sand (with uranium and thorium concentrations of 2860 and 39400 mg/kg, respectively) was used in finding the energy dependence on the efficiency of the used HPGe detection system. An alabaster ore sample weighing 172.9g of identical volume and geometry as the monazite sample was used in the passive measurement. The concentration of the radioactive series parent in mg/kg of the sample and dose rate in mSv/hr at 1 meter was calculated. In the long time irradiation NAA, a thermal to epithermal neutron flux ratio of 77.68 and a cadmium ratio of 5.94 for gold were measured by the cadmium difference method using thin gold foils. This was done by locating 269.1 mg of the alabaster sample wrapped in a thin aluminum foil together with a bare and cadmium covered thin gold foils weighing 5.4 and 6.4 mg respectively, in the same irradiation can. The can was irradiated in one of the vertical wet channels of the ET-RR-1 for 48 h. at power 1.6 MW. In the short irradiation NAA, 373.5 mg alabaster sample and 295.0 mg standard geological sample (JB-1) as a comparator were irradiated separately for 50 sec. by using the pneumatic irradiation rabbit system (PIRS) in the vertical tangential thermal column of the ET-RR-2. The power was 18 MW and the thermal neutron flux was of the order of 10^{11} n / cm². s.

Keywords: *Natural Radioactivity; NAA; k_0 Standardization; Comparator Method; Passive Measurements.*

INTRODUCTION

Alabaster, varieties name is applied to two different minerals. The ancient Egyptians extensively used one oriental alabaster. It is a variety of calcite usually white and translucent, but is often banded with dark or colored streaks. The other one, true alabaster, is a variety of gypsum, usually snow-white in color with a uniform, fine grain. True alabaster is softer than oriental alabaster and is easily carved into intricate shapes. Egyptian alabaster is also known as travertine. Travertine is a massive, finely crystalline rock of calcite formed by secondary chemical precipitation from ground water solutions in limestone formations. The Egyptian deposits of this rock occur in veins and pods. They frequently exhibit alternating bands of fine-grained white and coarse-grained brown calcite, and occasionally as massive fine-grained amber-brown calcite. The ancient Egyptians at numerous locations in the Eastern Desert and the Nile Valley quarried travertine. Throughout the ancient Egyptians entire history of their civilization used travertine, the extensive use of this material was undoubtedly due to the fact that it is a very soft material in terms of indentation hardness and is easily worked. Travertine being made almost entirely of the mineral calcite can almost be carved with a fingernail, and it is easily taken on a good polish by hand lapping. The rock travertine also exhibits a high rock hardness, which allows it to be finely detailed when carved. The ancient Egyptians used it as a subsidiary building material, chiefly for the lining of passages and rooms, particularly in Shrines, one of the more common and earliest usage was for vases and mace-heads.

On the other hand alabaster contains some radioactive materials that emit a constant stream of gamma rays. Passive detection systems measure these spontaneous emissions without applying any external radiation or particle beams. Generally speaking the radiological hazard connected to natural radioactivity is not so important; however some radiation protection problems can occur in industrial processes involving the treatment of large quantities of slightly radioactive materials [1-4]. At Luxor, children are widely used in industrialization of some status, vases and else where large amounts of alabaster ore sample are used, also construction of the most famous Egyptian mosque such as Amro Ebn El-ass which includes large alabaster volumes. Since we deal with external radiation, passive gamma ray measurement to determine the elemental concentration and the dose rate are required. The gamma-ray spectroscopy by HPGe technique has many advantages for nearly complete elemental analysis of complex samples [5-10]. The precise k_0 standardization method [11-13] was used in the elemental analysis of the alabaster sample by neutron activation analysis. Two high-resolution spectroscopic systems (one for the long time irradiation and the other for the short time irradiation) are used for measurement of the gamma-ray spectra.

EXPERIMENTAL

The sample was crushed, pulverized to a fine powder and homogenized in preparation and handled in clean containers to avoiding any contamination. For passive measurement, a quantity of the dry powdered sample weighing 172.93g was put in a plastic cup of the same geometry and volume as that containing 273.4 g of a standard monazite sample. The monazite sample was used for measuring the energy dependence of gamma-ray efficiency. Cups were sealed and left to stand-alone for a month to let the standard and the sample reach secular equilibrium.

In long time irradiation a 269.0mg of the alabaster sample was wrapped in an aluminum foil and placed in an irradiation can. A previously cleaned bare thin gold foil of 5.6 mg was wrapped in an aluminum foil and another weighing 6.5 mg was covered by 0.5mm thick cadmium foil were placed in the same irradiation can. This was located in one of the vertical wet channels at the core periphery of the ET-RR-1 and irradiated for 48 h. at 1.6 MW power. After cooling time 25.9 days for the alabaster sample, its aluminum foil cover was removed and the sample was weighed again and γ -ray measurements were started. The data were corrected for cooling, decay during measurement and dead times. A thermal to epithermal neutron flux ratio of 77.68 and a cadmium ratio of 5.94 for gold were measured by the cadmium difference method.

The detection system used in the passive and long irradiation time consists mainly of a vertical dipstick P-type HPGe detector with 40% relative efficiency with 1.9keV FWHM, and 60:1 peak to Compton ratio at 1.33MeV of ^{60}Co . This is in addition to Canberra spectroscopy amplifier model 2026 and high voltage power supply. A low background chamber model 747E consisting of lead shield surrounding the HPGe detector and sample area. Software Genie-2000 was used for analysis of the obtained gamma -spectra.

The short time irradiation was performed at a thermal neutron flux of the order 10^{11} n/cm².s. by the (PIRS) in the vertical thermal column of the ET-RR-2 at a power of 18 MW. An alabaster sample weighing 373.5 mg and 295.0 mg of the (JB-1) standard were irradiated separately for 50 seconds. The cooling time for alabaster and JB-1 were 2 and 20 minutes, respectively. The gamma-ray spectra were measured for 600 s.. The accrued counts under the gamma-ray peaks were corrected for cooling, decay during measurement and dead times. The detection system used in (PIRS) consists mainly of p-type coaxial HPGe detector and its associating electronic equipment and PCA.

RESULTS AND DISCUSSION

The elements were identified according to the energies of the well-resolved characteristic gamma rays of the naturally active or activated radioisotopes. The elemental concentrations of the samples under investigation in this work were estimated by means of the specific activities of the radioisotopes.

Results of Passive Measurement

Table 1. shows qualitative and quantitative analysis of the sample where ^{208}Tl , ^{212}Pb and ^{228}Ac indicate the decay products of the thorium chain. Also ^{214}Pb , ^{214}Bi were indicate the decay of the uranium chain.

Results of Long Time Irradiation Measurement

This was done by locating 269.1 mg of the alabaster sample wrapped in a thin aluminum foil together with a bare and cadmium covered thin gold foils weighing 5.4 and 6.4 mg respectively, in the same irradiation can. The can was irradiated in one of the tangential vertical wet channels of the ET-RR-1 for T= 48 h. at 1.6 MW. The cadmium ratio was found by the cadmium difference method using thin gold foils as follows:

$$R_{cd} = \frac{\text{Specific activity of bare thin gold foil Ab}}{\text{Specific activity of cadmium covered thin gold foil Acd}} \quad (1)$$

Table 1. Qualitative and quantitative investigation of the alabaster sample by means of passive measurement.

Radio-nuclides	Parent of Decay Chain	Photon Energy in keV	Sample Parent Concentration in mg/kg	Error	Sample Dose Rate at 1.0 m in mSv/hr
$^{208}\text{Tl}_{81}$	Th-232	510.72	.23059E+02	.54948E+00	.20671E-04
$^{212}\text{Pb}_{82}$	Th-232	238.60	.19590E+02	.81517E+00	.26765E-06
$^{214}\text{Pb}_{82}$	U-238	295.22	.21506E+01	.60305E-01	..19399E-05
		351.99	.20664E+01	.43128E-01	.21970E-05
$^{214}\text{Bi}_{83}$	U-238	609.32	.20882E+01	.46841E-01	.63238E-05
		665.45	.21779E+01	.27464E+00	.62028E-05
		768.36	.20672E+01	.15329E+00	.61410E-05
		1120.30	.22213E+01	.99474E-01	.64099E-05
		1238.10	.20241E+01	.16101E+00	.54224E-05
		1729.60	.20644E+01	.24139E+00	.60423E-05
		1746.50	.23226E+01	.11553E+00	.64997E-05
2204.10	.19161E+01	.20831E+00	.52589E-05		

where

$$A_b = \frac{(N_b / W_b t_b') \cdot \lambda_{Au} t_b}{\varepsilon \cdot [1 - \exp(-\lambda_{Au} t_b)] \cdot \exp(-\lambda_{Au} \cdot \tau_b) (1 - \exp(-\lambda_{Au} T))} \quad (2)$$

$$A_{Cd} = \frac{(N_{Cd} / W_{Cd} t_{Cd}') \cdot \lambda_{Au} t_{Cd}}{\varepsilon \cdot [1 - \exp(-\lambda_{Au} t_b)] \cdot \exp(-\lambda_{Au} \cdot \tau_{Cd}) (1 - \exp(-\lambda_{Au} T))} \quad (3)$$

where ε is the γ -ray absolute efficiency for the full-energy peak (FEP) of the detection system. N_b and N_{Cd} are the net counts accrued under the 411.8 keV γ - ray peak of the bare and cadmium covered gold foils during real and live times in each measurements t_b , t'_b and t_{Cd} , t'_{Cd} , respectively. Corrections for the dead and cooling times as well as the decay of the foils during the measurements are included in equations (2) and (3). τ_b , τ_{Cd} are the relevant decay times of each foil post irradiation for time periods T and λ_{Au} is ^{198}Au decay constant. By assuming an ideal 1/E epithermal neutron spectrum, a thermal to epithermal neutron flux ratio F of 77.68 was obtained from the measured cadmium ratio 5.94 for gold by using the equation:

$$F = Q_{Au}(0) (R_{Cd} - 1) \quad (4)$$

where $Q_{Au}(0)$ is 15.71 which is the ratio of the thermal neutron cross-section σ_{th} to the resonance integral I_0 for gold.

Similarly, the gamma-ray specific activity A_{si} of a characteristic gamma ray identifying an isotope i of an element in the sample s can be written as:

$$A_{si} = \frac{(N_s / W_s t_s') \cdot \lambda_{si} t_s}{\varepsilon_{si} \cdot [1 - \exp(-\lambda_{si} t_s)] \cdot \exp(-\lambda_{si} \cdot \tau_s) (1 - \exp(-\lambda_{si} T))} \quad (5)$$

The elemental concentration C_{si} can be calculated relative to the bare gold foil by the k_0 standardization:

$$C_{si} = \frac{A_{si}}{k_0 (1 + Q_{si}(0)) / F} \frac{(1 + Q_{Au}(0) / F)}{A_b} 1.0E+06 \quad (6)$$

where $Q_{si}(0)$ is the ratio of the thermal neutron cross-section σ_{th} to the resonance integral I_0 for an isotope in the sample. Table 2. shows qualitative and quantitative analysis in NAA for long irradiation time where the results indicate that the major element is calcium (21.13%) and iron(293 mg/kg), there are some traces of scandium chromium, cobalt, zinc, bromine, rubidium, zinc, bromine, rubidium, strontium, zirconium, ruthenium, silver, cadmium, antimony, barium, europium, ytterbium, lutetium, hafnium, tantalum, rhenium, gold, osmium, mercury and terbium also there are some rare earths lanthanum, cerium, samarium and gadolinium.

Neutron radiative capture by the uranium isotopes forms what is called transuranic elements in the periodic table. In case of ^{238}U , ^{239}U is created. ^{239}U quickly

emits a beta particle to become ^{239}Np , which in turn emits a beta particle to form ^{239}Pu , which is relatively stable. Table 3. shows the results of elemental_uranium concentration of parent product by means of active measurement.

Results of Short Time Irradiation Measurement

In short irradiation measurement, ^{24}Na , ^{22}Mg , ^{28}Al , ^{31}Si , ^{51}Ti , ^{52}V , ^{56}Mn and ^{239}U which are short-lived isotopes, were measured by irradiation rabbit system. Table 4. shows qualitative and quantitative analysis of some selected isotopes using pneumatic irradiation rabbit system (PIRS) for short irradiation time. The analysis was obtained by using the comparator method where a reference standard JB-1 was used.

Table 2. Qualitative and quantitative investigation of the alabaster sample by means of k_0 standardization method.

Element	Identifying Isotope symbol	Characteristic Gamma-ray Energy in keV	Concentration	Error
Calcium	^{47}Ca	1296.8 807.90 489.20	21.13%	0.06330
Scandium	^{46}Sc	889.30 1120.5	0.028325 mg/kg	1.4161E-5
Chromium	^{51}Cr	320.10	0.027650 mg/kg	1.3831E-3
Iron	^{59}Fe	1099.2 1291.6 192.30 142.60	293 mg/kg	4.541
Cobalt	^{60}Co	1173.2 1332.5	0.026 mg/kg	0.0001
Zinc	^{65}Zn	1115.5	7.975 mg/kg	0.0560
Bromine	^{82}Br	776.50 619.10	19.64 mg/kg	0.2100
Rubidium	^{86}Rb	1076.6	0.1912 mg/kg	0.0090
Strontium	^{85}Sr	514.00	30.71 mg/kg	0.433
Zirconium	^{95}Zr	756.70 724.20	102 mg/kg	1.795
Ruthenium	^{97}Ru & ^{103}Ru	215.70 497.10 610.30	10.12 mg/kg	1.471
Silver	$^{110\text{m}}\text{Ag}$	657.70	0.0164 mg/kg	0.002
Cadmium	^{115}Cd	335.3 527.90	70.31 mg/kg	18.527

Continued Table 2.

Antimony	¹²² Sb & ¹²⁴ Sb	564.10 602.70 1691.0 722.80 645.90 2090.9	31 mg/kg	0.403
Barium	¹³¹ Ba	496.30 373.20	5.48 mg/kg	0.138
Lanthanum	¹⁴⁰ La	1596.5 487.00 815.80 328.80	52.39 mg/kg	0.0796
Cerium	¹⁴¹ Ce	145.40	0.2965 mg/kg	0.013
Samarium	¹⁵³ Sm	103.20	4.6270 mg/kg	0.075
Europium	¹⁵² Eu	121.80 344.30 1408.0 964.40 .111200 778.90	0.00419 mg/kg	0.0002
Gadolinium	¹⁵³ Gd	97.400 103.20	2.658 mg/kg	0.018
Terbium	¹⁶⁰ Tb	879.40 965.10 1178.0 966.20	0.13359 mg/kg	0.041
Ytterbium	¹⁶⁹ Yb	197.90 177.20 109.77 307.70	0.01456 mg/kg	0.0009
Lutetium	¹⁷⁷ Lu	208.40	0.00172 mg/kg	0.0007
Hafnium	¹⁷⁵ Hf ¹⁸¹ Hf	343.60 482.20 133.40 345.90 136.30 7	0.35785 mg/kg	0.005
Tantalum	¹⁸² Ta	1121.3 1221.4	0.01872 mg/kg	0.0001
Rhenium	¹⁸⁶ Re	137.20 122.30	0.5068 mg/kg	0.01
Osmium	¹⁸⁵ Os	646.10	2.0610 mg/kg	0.021
Gold	¹⁹⁸ Au	411.80	0.0047 mg/kg	0.001
Mercury	²⁰³ Hg	279.20	0.0078 mg/kg	0.003

Table 3. Elemental concentration of parent product by means of active measurement.

Element	Identifying product isotope symbol	Characteristic Gamma-ray Energy in keV	Elemental Concentration In mg/kg
Uranium	^{239}Pu	277.60	2.2
		228.20	
		334.30	
		285.40	

Table 4. Elemental concentration from short irradiation time by (PIRS).

Element	Identifying product isotope symbol	Characteristic Gamma-ray Energy in keV	Elemental Concentration In mg/kg using JB-1
Sodium	^{24}Na	.1368E+04	600.9
Aluminum	^{28}Al	.17789E+04	181.8
Silicon	^{31}Si	.12662E+04	1403
Titanium	^{51}Ti	.32010E+03	1368
Vanadium	^{52}V	.14340E+04	0.599
Manganese	^{56}Mn	.84680E+03 .18107E+04	4.98
Uranium	^{239}U	.74700E+02	2.191

CONCLUSION

One can conclude the following points:

- The natural radioactivity of the alabaster sample is due to the thorium, actinide and uranium series. The dose rates are in the permissible range.
- The computer program used in these studies is useful for radioactively environmental measurement.
- Using NAA techniques applied in this work make it possible to determine the elemental concentrations of its constituents Sc., Cr, Fe, Co, Zn, Sr, Zr, Ru, Ag, , Sb , Cd., La, Ba, Ce, Yb, Lu,Hf,Ta,Re,Au,Os and Hg with high accuracy.

REFERENCES

- [1] Panakkal, J.P., Vrinda Devi, K.V., Mukherjee, D., Wadhvani, R.S. and Kamath, H.S., " Passive gamma scanning (PGS) AND gamma autoradiography (GAR) of MOX fuel pins for boiling water reactors "A comparative study Advanced Fuel Fabrication Facility, Bhabha Atomic Research Centre, Tarapur - 401 502 .Bibliography of 14 th conference on non destructive testing (14 th WCNDT) 8-13 decembre 1996, New Delhi.
- [2] Testa, C., *et al.*, *Journal radioanalytical and Nucl. Chem.* **107**(3), p. 165(1986).
- [3] Testa, C., *et al.*, *Journal radioanalytical and Nucl. Chem.* **107**(1), p. 439(1993).
- [4] Ajayi, *et al.*, "Natural radioactivity measurement in rock samples of Undo and Ekiti states in Nigeria. *Radiat. Meas.* **33**, 13-16(2001).
- [5] Nir-El, Y., *Applied Radiation and Isotopes* **52**, pp. 753-757(2000).
- [6] Korob, R.O., *Radiochim. Acta.* **77**, p. 161(1997).
- [7] English, G.A., Firestone, R.B., Perry, D.L., Reijnen, J., Ludewigt, B., Leung, K.N., Garabedian, G., Molnr, G., Révay, Zs, *Nucl. Instr. & Methods* **213**, pp. 410-413(2004)
- [8] Molnr, G.L., Révay, Zs., Belgya, T., *Nucl. Instr. & Methods* **213**, pp. 389-393(2004).
- [9] English, G.A., *et al.*, *Nucl. Instr. and Methods* **213**, pp. 406-409(2004).
- [10] De Corte, F., "The K_0 -standardization method: a move to the optimization of neutron activation analysis", *Agrege Thesis*(1987).464
- [11] Popescu, I., Badica, T., Olariw, A., Besliu, C., Ene, A., Ivanescu, A., J. radioanal. Nucl. Chem, Letters **213**, No. 5, pp. 364-376(1996).
- [12] De Corte, F.A., De Wispelaere, Van Sluijs, R., Bossus, D., Simonits, A.P., Ku era, J., Frana, J., Smodis, B., ja Imovi, R., J. Radioanal. Nucl. Chem., **215**(1), p. 31(1997).
- [13] Geostandards Newsletter Vol. XVIII, Special Issue, July 1994. ISSN:0150-

دراسة خام المرمر المصري عن طريق قياس النشاط الإشعاع الطبيعي و إشعاع التنشيط بالنيوترونات بطريقة k_0 العيارية وكذلك بطريقة المقارنة بعينات عيارية

د.نبيلة فرج سليمان

قسم طبيعة المفاعلات - شعبة المفاعلات - مركز البحوث النووية - هيئة الطاقة الذرية

تم في هذا البحث دراسة خام المرمر المصري بالطرق النووية المختلفة حيث تم قياس طيف أشعة جاما الناتج عن النشاط الإشعاعي الطبيعي لعينة تزن ١٧٢,٩ جرام ومقارنته بتلك الناتجة عن عينة عيارية من المونازايت تزن ٢٧٣,٤ جرام لها نفس الحجم ونفس الشكل الهندسي لعينة المرمر. وبمعلومية نسب تركيز كل من اليورانيوم (٢٨٦٠ مجم/كج) و الثوريوم (٣٩٤٠٠ مجم/كج) في المونازايت أمكن تعيين الكفاءة المطلقة لكاشف الجرمانيوم الفائق النقاوة. ويعمل برنامج للحاسب

الآلي بلغة الفورتران تم حساب النشاط الإشعاعي النوعي لهذين العنصرين في عينة المرمر وكذلك حساب الجرعات الإشعاعية على بعد 1 متر من العينة.

كما تم أيضا استخدام المفاعل المصري البحثي الأول عند قدرة 1,6 ميغاوات في فحص الخام بطريقة التنشيط بالنيوترونات حيث تم تشعيع 269,1 مللي جرام من الخام مع عينتان من الذهب العيارى إحداها مغلقة بالكادميوم والأخرى بدون كادميوم لمدة 48 ساعة حيث وجد ان نسبة فيض النيوترونات الحرارية إلى فوق الحرارية 77,68 وأن نسبة الكادميوم للذهب هي 0,94 وهذا وقد تم تشعيع 373,5 مجم من خام المرمر لمدة 50 ثانية بالمفاعل المصري البحثي الثاني عند قدرة 18 ميغا وات وفيض نيوترونات حرارية 10¹¹ نيوترون/سم² ثانية وذلك لتعيين تركيز العناصر من النظائر القصيرة العمر باستخدام جهاز التنشيط السريع الملحق بالمفاعل. وقد تم تعيين التركيزات مقارنة خطوط طيف الجاما لعينة المرمر مع ما يناظرها من خطوط في عينة عيارية تزن 295,0 مجم شععت لمدة 50 ثانية على نفس النحو كعينة المرمر. وباستخدام طريقة التنشيط بالنيوترونات أمكن التعرف على العناصر التالية وتعيين نسب تركيزها:

Ca, Sc, Cr, Fe, Co, Zn, Br, Rb, Sr, Zr, Ru, Ag, Cd, Sb, Ba, La, Ce, Sm, Eu, Gd, Tb, Yb, Hf, Ta, Re, Os, Au, Hg, Na, Al, Si, Ti, V and Mn.