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Determination of the Elements Concentration in Egyptian Black Sand Using the Neutron Activation Analysis Technique

Eman Salem

Physics Department, Faculty of Women for Arts, Science and Education, Ain Shams University, 11577, Cairo, Egypt.

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ABSTRACT

The neutron activation analysis (NAA) technique was used for the investigation of the elements present in black sand from beach of Rosetta area. After irradiation the data was analyzed using the hyper pure germanium detector system. The analysis of such complex sample using the neutron activation analysis technique causes difficulties such as elemental interferences which produces the masking effects in the spectra, and in turn affects the efficiency of the analysis. Therefore, the measurements were repeated, after a period long enough for the short and medium lived isotopes to decay, to estimate accurately the concentration of the low content long lived isotopes.

In the present work the elemental interference were taking in consideration. Hence the nineteen elements La, Sm, Gd, Nd, Tb, Eu, Hf, Ce, Lu, Yb, Zr, U, Th, Te, Sc, Cr, Fe, Co, and Ta were detected and their concentration values were estimated.

Keywords: NAA, the Egyptian black sand, rare earth elements

Introduction

The Egyptian black sands (Mahmoud *et al.,* 2013; Dawod *et al.,* 2007) are the end products of the disintegrated materials from the igneous and metamorphic rocks. It deposits comprise huge reserves of the six common economic minerals (Mahmoud *et al.,* 2013; El-Hadry, 1988; Ibrahim, 1995) that include ilmenite, magnetite, garnet, zircon, rutile and monazite.

The extensive black sands placer deposits are disconsolately distributed along the northern Mediterranean castle plain of the Nile Delta and Sinai Peninsula. The sediments of Nile Delta were studied by neutron activation analysis; (Wafaa *et al.,* 2015) contain strategic and economic heavy minerals which are required for the industrial exportation whether for nuclear industry or other metallurgical and engineering industries. These contain a monazite which contains Uranium, Thorium, rare earths and other elements. Neutron activation analysis is a non-destructive method is considered as a technique of high accuracy and an effective tool, especially useful in qualitative and quantitative analyses of heavy metals and rare –earth elements. The neutron activation is considered as precise technique used in many branches for life science (Nekhoroshkov *et al.,* 2014; Frontasyeva, 2011; Allan *et al.,* 2006; Ismail, 2000).

In the present work the Egyptian black sand provided by the Nuclear Material Authority of Egypt from Rosetta area as shown in Fig.1. The black sand was studied using the neutron activation analysis technique to detect the different elements present and to estimate their concentrations using the absolute method. However, the analysis using the NAA may cause some difficulties such as elemental interferences which produces the masking effects in the spectra, and in turn will affect the efficiency of the analysis especially for gamma rays of long lived isotopes, of low content, in presence of other strong short lived ones. In order to overcome such a problem the sample was left for a cooling period long enough for all the short and medium lived isotopes to decay, then the measurements were repeated to study and estimate accurately the concentrations of the unresolved long lived elements or masked elements in the black sand sample.

Experimental procedure and measurements:

An Egyptian black sand sample from beach sands which provided by the Nuclear Material Authority of Egypt was prepared, wrapped in an aluminum foil of known weight and together with a similar aluminum empty foil were irradiated for a period of 48 hours in the core of the Egyptian Research Reactor.

Corresponding Author: Eman Salem, Physics Department, Faculty of Women for Arts, Science and Education, Ain Shams University, 11577, Cairo, Egypt.
E-mail: eman_salem2011@yahoo.com

A coaxial hyper pure Ge detector of volume 76.11 cm^3 and of energy resolution 1.9 keV at the 1332.5 keV gamma ray transition of ^{60}Co was used together with the other measuring components in a singles spectrometer and a Maestro, EG&G ORTEC MCA card mounted on an IBM compatible PC together with simple programs, using the equations given below, to estimate quantitatively the elements present in the samples under investigation.

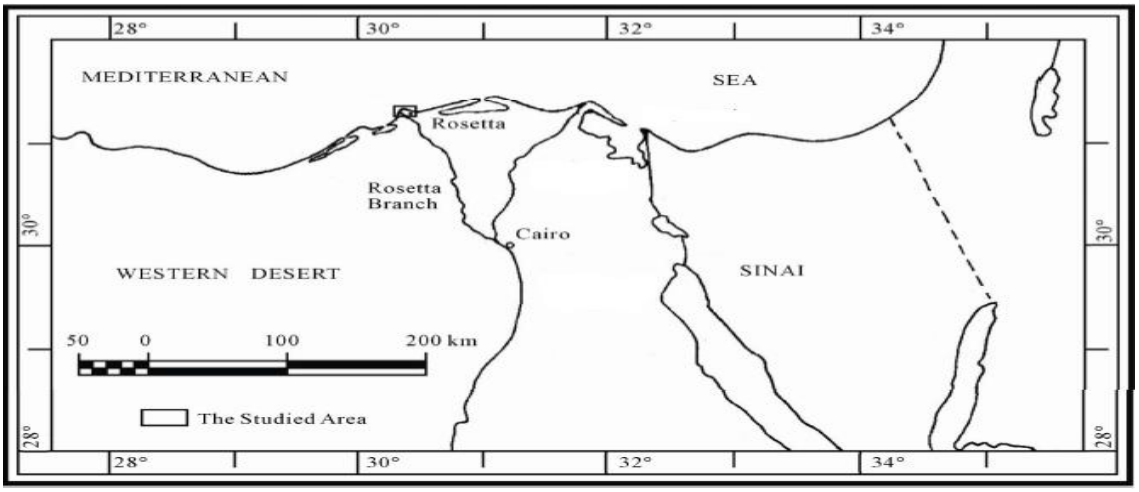

Fig. 1: The map of studied region after (Mahmoud *et al.,* 2013).

The absolute efficiency calibration carried out earlier using a standard multi gamma source MGS-4A was used in this work. The irradiated sample was placed at a distance of 10 cm, energy calibration was performed before and after each run. The accumulation time was 7200 sec for each spectrum and was repeated many times.

The concentration was calculated using the different gamma transitions of each isotope present after the correction for the transportation times and masses of the aluminum wraps and aluminum foil and back ground were made.

The samples were left for two years for all medium and short lived isotopes to decay and the measurements were repeated to estimate the concentration for the long lived isotopes with high accuracy.

Table (1) shows the nuclear parameters (Lilley, 2014; Lederer and Shirley, 1978) which used for the quantitative analysis in the present work.

Table 1: Nuclear Parameters for (n,γ) reaction for the detected elements (Lilley, 2014; Lederer and Shirley, 1978) [10& 11].

Target isotope	Abundance %	Cross section (barn)	Product isotope (parent)	Half life time of product isotope	Daughter isotope
La-139	99.9098	9.23	La-140	1.68 d	Ce-140
Sm-152	26.7	2045	Sm-153	46.27 h	Eu-153
Gd-152	0.20	$1.11*10^3$	Gd-153	241.6 d	Eu-153
Nd-146	17.19	1.31	Nd-147	10.98 d	Pm-147
Tb-159	100	232	Tb-160	72.3 d	Dy-160
Eu-151	47.8	$5.82*10^3$	Eu-152	13.54 Y	Sm-152,Gd-152
Hf-180	35. 100	142	Hf-181	42.39 d	Ta-181
Ce-140	88.48	0.564	Ce-141	32.50d	Pr-141
Lu-176	2.59	7	Lu-177m	160.1 d	Hf-177
Yb-174	31.8	196	Yb-175	4.19 d	Lu-175
Zr-94	17.38	0.055	Zr-95	64.02d	Nb-95
U-238	99.2745	2.71	U-239➔ Np-239	2.36 d	Pu-239
Te122	2.603	31	Te123m	119.7 d	Te-123
Sc-45	100	173	Sc-46	83.79d	Ti-46
Cr-50	4.345	15.94	Cr-51	27.74d	V-51
Fe-58	0.282	1.142	Fe-59	44.50d	Co-59
Co-59	100	18	Co-60	5.27Y	Ni-60
Ta-181	99.988	21	Ta-182	115 d	W-182

From the spectrum analysis the net area under the photo peak was calculated then correct with respect to the wrapping Al back ground

The corrected area A_{corr} was calculated as follows (Abdel Malak, 2000).

$$A_{corr} = A_{sample}\, e^{\lambda t_{trans}} - \frac{m_{wrap}}{m_{Al}} A_{Al}\, e^{\lambda t_{trans}}$$

Where

A_{sample} : Pure area under the gamma photo peak for A1 wrap and sample.

λ : Decay constant = ln2/ half life time.

$e^{\lambda t_{trans}}$: Correction for transportation time.

A_{Al} : Pure area under the gamma photo peak for empty A1 and back ground,

m_{wrap} : Al wrap mass,

m_{Al} : Mass of empty Al foil.

A_{corr} value was used in the following equation to estimate the concentration values.

$$\mathbf{m} = \frac{\mathbf{A_{corr}\, M \lambda}}{\mathbf{I_\gamma\, \varepsilon f \sigma \varphi N_A (1 - e^{\lambda t_{irr}})(1 - e^{\lambda t_{coll}})}}$$

$$\text{Concentration \%} = \frac{\text{m} \times 1000}{\text{m}_{\text{sample}}}$$

$$\text{ppm (mg/kg)} = \text{concentration\%} \times 10000$$

Where

M : The mass number.

I_γ : Absolute gamma ray intensity %.

ε : Detector absolute efficiency for certain gamma energy .

f : Abundance %.

σ : The (n, γ) reaction cross section.

φ : neutron flux.

N_A : Avogadro's number

$(1 - e^{\lambda t_{irr}})$: Correction for irradiation time.

$(1 - e^{\lambda t_{coll}})$: Correction for collection' time.

m_{sample} : Sample mass

Results and Discussion

From the present results, the La, Sm, Gd, Nd, Tb, Eu, Hf, Ce, Lu, Yb, Zr, U, Th, Te, Sc, Cr, Fe, Co, and Ta were detected and their concentration values were estimated according to the intense gamma energies as shown in table (2).

Lanthanum (La)

The La element was detected due to the decay of La-140 with half life time (H.L.T) 1.67d from the observation of the gamma transitions at 328.8,, 487.1, 815.7, 867.9.,919.8, 925.2 and 1596.5 keV. The concentration values of La-140 were estimated for each of the gamma transitions, and the average value is 1942 ppm.

Table 2: The elements detected in black sand and their concentration values

Isotope & it's H.L.T	Energy (keV) *	Iγ % *	Element concentration (ppm)	Average concentration (ppm)
La -140 (1.68 d)	328.8	19.9	2082.83	1942
	487.1	49	1724.54	
	815.7	22	2007.61	
	867.9	5.6	2096.07	
	919.8+925.2	3.08 + 7.84	1863.61	
	1596.5	100	1874.82	
Sm-153 (1.93d)	69.67	48.8	393	437
	103[a]	28.2	762 neglected	
Eu-155 (4.76 y)	86.54	32.88	481	
Gd-153(241.60d)	97.5	100	570	570
	103.2[a]	71	570	
Nd-147(10.98d)	91.11	227	1015.42	1040
	531.01	100	1063.76	
Tb-160(72.30d)	197.04	17.48	41.52	40
	215.65	13.37	39.06	
	879.37	100	38.85	
	962.36+966.17	31+83	39.72	
Eu-152(13.54y)	121.78	112.79	12.51	13
	344	100	13.97	
	778.90	48.80	12.55	
	964.01	52.7	12.5	
Hf-181(42.39d)	133.02+136.25[b]	40+6	235.32	225
	482.0	81	215.06	
Ce- 141(32.50d)	145.43	48.4	1023	1023
Lu177m(160.10d)	208.4+Np	510	3241.69	3259
	228.4+Np	310	3275	
Yb- 175(4.19d)	396.32	100	124	124
Zr- 95(64.02d) Nb[c] -95(34.97d)	724.18	78.9	11373	9259
	756.72	100	8204.25	
	765.78	100	8201	
U-239(23.45m) Np[c]-239(2.36d)	209.73	3.47	31.20	32
	228.14	11.46	33.48	
	277.63	15	32.59	
Te-123m(119.70d)	159.0	100	11889	11889
Sc-46(83.79d)	889.25	100	92.03	91
	1120.54	100	89.39	
Cr- 51(27.74d)	320.03	10	2096	2096
Fe-59(44.50d)	1099.0	55.5	597648.7	600277
	1292.0	44.1	602905.9	
Co- 60(5.27y)	1173.21	100	195.12	205
	1332.47	100	215.48	
Ta-182(115d)	1189.05	47.05	69.26	63
	1221.418	78.3	58.58	
	1230.97	33.14	62.12	

**: elements (Lilley, 2014; Lederer and Shirley, 1978), a:Interference for two difference isotopes. b:The two lines unresolved. c: Nb is a Zr daughter.*

Samarium, Gadolinium, and Europium contributions (Sm, Gd & Eu):

In the first measurements the Sm-153 with H.L.T 1.93d was identified in the studied sample due to the observation of the 69.67 and 103keV gamma transitions in the different spectra, these transitions were used to estimate the Sm concentration which was found to be 393and 762 ppm respectively. These differences may be due to the interference between some transitions of other elements have long half life time.

Therefore the measurements were repeated after a long time. The concentration of Sm was determined again as a result of the observation of gamma transitions at 86.54,105 keV with intensity 32.88, 21.8 % respectively, which belong to Eu-155 (4.76 y) as beta decay of Sm-155 which produced from Sm-154(n,γ) Sm-155 with cross section of this reaction σ =51 barn, the abundance of Sm-154 equal 22.6 % and H.L.T.of Sm155 equal 22.43 m (Lilley, 2014; Lederer and Shirley, 1978). The concentration value of Sm

was also estimated and was found to be 481 ppm using 86.54 keV. Hence the gamma energy 105 keV was neglected; the reason will be discussed in the following section.

Gd-153 (241.6 d) was identified in the studied sample due to the observation at 97.5 and 103.2 keV, it was found that the 103.2 keV for Gd-153 and 105 keV from Eu-155 were not resolved. Therefore the net area of 103.2 keV calculated after correction from 105 keV. After this correction the concentration of Gd element was determined from 97.5, 103.2 keV which found to be 570, 570 ppm respectively.

This may indicated that the value obtained in our first measurements a 762 ppm for Sm- 153 have a contribution from the 103keV of Gd observed in our repeated measurements and which was masked due to the presence of other strong short lived isotope.

Neodymium (Nd)

Nd-147 (10.98 d) was also detected in the studied sample due to the presence of 91.11 and 531.01 keV gamma transitions were used to estimate the Nd concentration in the samples and which is l040 ppm.

Terbium (Tb)

The Tb element was detected due to the observation of the 197.04, 215.65, 298.58,765, 879.37, 962.36, 966.17, 1178 and 1272 keV gamma transitions belonging to Tb-160 with H.L.T_2 =72.3 d. The Tb concentration determined from gamma energies at 197.04, 215.65 and 879.37 keV and the other energies were neglected because their interference with Zr-95 (64.02 d) and it daughter Nb-95(35 d), Eu-152(13.537Y). Hence the average concentration value of Tb was 40 ppm.

Europium (Eu):

The Eu element was detected by the presence of the different gamma rays due to the Eu-152 decay yet they were either very weak or not resolved from other strong gamma transitions, or submerged in the spectra, in the repeated measurements after all the medium and short lived isotopes have decayed the gamma transitions due to the decay of Eu-152 as well as those due to the Eu-154 decay were much more pronounced and resolved. The gamma transitions at 121.78, 344, 778.90 and 964.01 keV of Eu-152 were used to estimate the concentration of the Eu element in the sample, and the average value is given 13 ppm.

Hafnium (Hf)

The concentration value of Hf element was found to be 225 ppm. The Hf element was identified by the presence of Hf-175 (70 d) and Hf-181(42.39 d) yet only the gamma energies 136.25 and 482.0 keV of Hf-181 were used to estimate the Hf concentration. While the 343, 344 and 345 keV of Hf-175, Eu-152 and Hf-181 respectively were not resolved.

Cerium (Ce)

The Ce-141 (32.50 d) was identified for the present sample due to the observation of the 145.43 keV gamma transition in the different spectra and which was used to estimate an average Ce concentration value of 1023 ppm in the black sand sample.

Lutetium (Lu)

The Lu was detected in the present investigation due to the observation of the 208.4 and 228.4 keV transitions of Lu-175m (160.1d) as shown in table 2 which after the correction for the interference of the Neptunium (Np) gamma energies. The Lu concentration was estimated to be 3259 ppm.

Ytterbium (Yb)

The Yb was estimated to have a concentration of 124 ppm due to the observation of the 396.32 keV of Yb-175 (4.19 d).

Zirconium and Niobium contributions (Zr, Nb)

The Zr element has an isotope Zr-95 which is produced as the result of Zr-94 (n , γ) Zr-95 reaction, it decays to Nb-95 and the 724.18 and 756.72 keV are two characteristic transitions. The areas were estimated and the concentration value of Zr-95 was found to equal 11373 using the 724.18 keV transition and 8204 using the 756.72 keV. Since Nb-95, is a daughter of Zr-95 with (34.97 d) decays emitting a gamma transition which was observed at 765.78 keV, the concentration value for the Zr was estimated using the 765.78 keV transition to equal 8201 ppm in agreement with the value calculated using the Zr-95 transitions. The concentration value was found to be 9259 ppm.

Uranium (U)

The U was estimated to have a concentration of 32 ppm due to the observation of the due to the observation of the characteristic gamma transitions at 209.73, 228.14 and 277.63 keV which belong to Np-239 (2.36 d) as beta decay of U-239 which produced from U-238(n,γ) U-239 with H.L. T. 23.45m.

Tellurium (Te)

Tellurium element was calculated due to the observation of 159.0 keV gamma transition of Te-123m to indicate the presence of Te with a concentration of 11890 ppm.

Scandium (Sc)

The scandium concentration was estimated using the 889.25 and 1120.54 keV gamma transitions of Sc-46 with (83.79 d) and the average value was 91 ppm.

Chromium (Cr)

Chromium was detected in the sample due to the observation of the 320.03 keV line of Cr-51 with (27.74 d) and its concentration was found to be 2096 ppm.

Iron (Fe)

Iron was detected with the highest concentration 60.029% due to the observation of the 1099.0 and 1292.0 keV gamma transitions of Fe-59 as a result of Fe-58(n,γ)Fe-59-reaction.The concentration according to these gamma transitions was found to be 600277 ppm.

Cobalt (Co)

Co-60 (5.27 y) was determined due to the observation of the two gamma transitions of Co-60 at 1173.21 and 1332.47 keV with an average concentration of 205 ppm .

Tantalum (Ta)

Tantalum concentration was estimated due to the observation of 1189.05, 1221.42, and 1230.97 keV gamma transitions of Ta-182 with (115 d), and the average value of 63ppm was given. Table 3 shows the average elemental concentration of the investigated black sand in ppm.

Table 3: The elemental average concentration for the investigated black sand.

groups	No.	The element symbol	The average concentration ppm
The first group	1	Eu	13
	2	U	32
	3	Tb	40
	4	Ta	63
	5	Sc	91
	6	Yb	124
	7	Co	205
	8	Hf	225
The second group	9	Sm	437
	10	Gd	570
	11	Ce	1023
	12	Nd	1040
	13	La	1942
	14	Lu	3259
The second group	15	Zr	9256
	16	Te	11889
	17	Fe	600277

Conclusion

From this study, it was concluded that the elemental concentration can be grouped to 3 groups: Firstly the lowest concentration ranged from 13 to 225 ppm for Eu, U, Tb, Ta, Sc, Yb, Co and Hf elements, respectively. Secondly, the concentration less than 3300 ppm concern six elements Sm, Gd , Ce, Nd, La and Lu which ranged between 393 to 3259 ppm. The third group has the highest concentration 9259, 11889 and 600277 ppm for Zr, Te and Fe, respectively.

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