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# Neutron Activation Analysis of Surface Sediments From Dardanelles

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Some surface sediments, collected from 7 sampling sides of the Dardanelles and 13 sampling sited of creeks in the area of surrounding of the Dardanelles were analyzed quantitatively by neutron activation analysis (NAA) and concentrations of Na, Al, K, Ca, Sc, Fe, Co, As, Rb, Sr, Y, Sb, Cs, Hf, U, Th and rare earth elements (La, Ce, Sm, Eu, Dy, Yb, Lu) were determined. Uranium and thorium results were found to be compatible with those given in the literature for marine sediments. Results indicated correlations between Rb and Sr (r = 0.8542), Th and Ce (r = 0.8131), Th and La (r = 6371), Th and Sm (r = 4756) in the creek sediments. These correlations were find to be r = 0.5361 (Rb and Sr), r = 0.8571 (Th and Ce), r = 7397 (Th and La), r = 0.9045 (Th and Sm), respectively, in the marine sediments.

**Key Words: Neutron activation analysis, Rare earth elements, Sediments, Thorium, Uranium.**

## INTRODUCTION

The strait of Canakkale, Dardanelles, is a narrow strait in northwestern Turkey, connecting the Aegean sea to the Marmara sea. It is located at *ca.* 40º13'N, 26º26'E. It separates the Gallipoli peninsula (Thrace) from Biga peninsula (Anatolia). The strait is 61 kilometres long and 1.2-6.0 km wide, averaging 55 m deep with a maximum depth of 82 m. It has two layer flow system; sea water flows from the Sea of Marmara to the Aegean *via* a surface current and in the opposite direction *via* an undercurrent. The strait of Canakkale, Dardanelles, is affected by two tectonically active regimes; the active tensional regime in the Aegean Sea[1,2] and the transpressional and transtensional regimes of the North Anatolian Fault[2,3]. There are a number of creeks, carrying water from Gallipoli peninsula to Dardanelle (namely Munibey, Sutluce, Cumali, Ilgar, Kayaalti, Bigali and Eceabat) and carrying water from Anatolian side, Biga peninsula, to Dardanelle (namely Kepez, Saricay, Musakoy, Yapildak, Umurbey, Lapseki). One of the most useful approaches to long term monitoring of aquatic systems is the analysis of marine/river sediments[4-9].

In this study surficial sediments obtained from 7 sampling sides at the northern and southern parts of the Dardanelles, together with the 13 sampling sites of creeks mouths in the area surrounding the Dardanelles were analyzed. In the previous study Al, Cu, Fe, Mn, Ni, Pb, Zn concentrations of these sediment samples were analyzed by atomic absorption spectroscopy[10]. Now in this study the distributions of Na, Al, K, Ca, Sc, Fe, Co, As, Y, Sb, Cs, U, Th, La, Ce, Sm, Eu, Dy, Yb, Lu, Hf were investigated in these surficial sediments. The data of U, Th and rare earth elements composition in sediments from the strait of Dardanelles have not been reported in literature until now. This study will represent a baseline dataset in U, Th and rare earth elements concentrations in marine and creek sediments from the zone of Dardanelles, the Strait between Aegean Sea and The Sea of Marmara.

## EXPERIMENTAL

The surface sediment samples (0-1 cm) were collected from 20 stations, 7 sampling sides at the northern and southern parts of the Dardanelles and 13 sampling sites at small creeks mounts in the area surrounding the Dardanelles[10] (Fig. 1). Sediment samples were dried at 105 ºC and ground in a mortar.

For neutron activation analysis, the samples were irradiated simultaneously with reference materials from IAEA (SL-1, soil-7) for 70 h at thermal neutron flux density of $6.5 \times 10^{10}$ $cm^{-2}$ $s^{-1}$ in the nuclear reactor of Institute of Nuclear Physics, Tashkent, Uzbekistan. Condition of cooling and measuring were chosen taking into account the half-life of basic elements and impurities. The parameters of irradiation and measurement for determined elements in sediments were given in Table-1. For measurement and treatment of the sample spectrum,

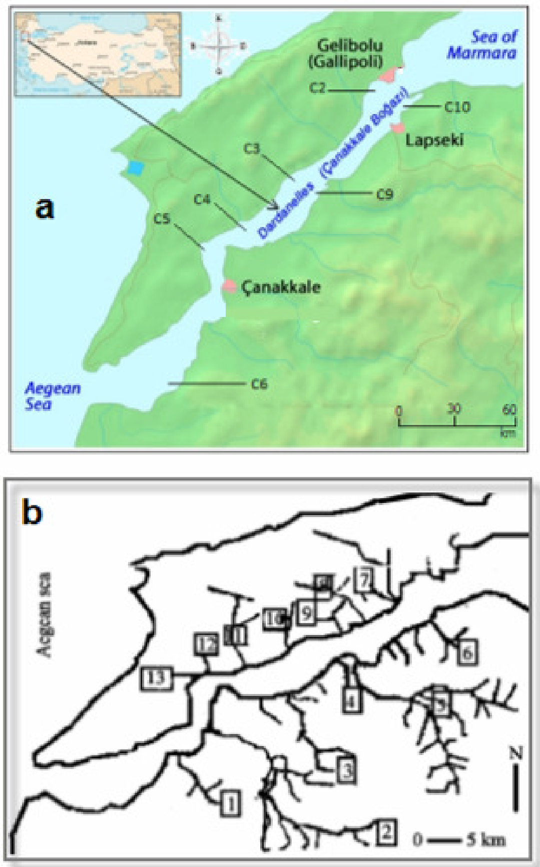


Fig. 1. Map of the Dardanelles region showing the sample locations. Sampling stations of marine sediments (a) and sampling stations of creek sediments: 1 = Kepez, 2 = Saricay, 3 = Musakoy, 4 = Yapildak, 5 = Umurbey, 6 = Lapseki, 7 = Munipbey, 8 = Sutluce, 9 = Cumali, 10 = Ilgar, 11 = Kayaalti, 12 = Bigali, 13 = Eceabat

γ-spectrometer was used with HPGe coaxial γ-ray detector (the resolution 1.8 keV at 1332.5 keV, relative efficiency 15 %), charge sensitive preamplifier and multichannel analyzer DSA-1000 with software Genie-2000 (Canberra industries).

The contents of Th and U were calculated from the γ-line intensities of radionuclide $^{233}$Pa ($T_{1/2}$ = 27.1 d, Eγ = 299.9; 311.8 keV) and $^{239}$Np ($T_{1/2}$ = 2.35 d, Eγ = 228.3; 277.8 keV). The detection limit for Th and U was 0.01 and 0.03 mg/kg, respectively and the relative standard deviation was 0.1[11].

Principle component analysis was performed using The Unscrambler CAMO software.

## RESULTS AND DISCUSSION

The analytical results of some elements of the investigated sediments are given in Table-2. The concentration of U increases from 1.9 mg/kg up to 3.8 mg/kg, whereas Th concentration alters from 4.7 to 11 mg/kg on the sediment samples around Dardanelles. The U and Th concentrations of the surficial sediments of the east Black Sea were reported in the 1.4-2.3 and 4.9-10.7 mg/kg ranges, respectively[12,13]. On the other hand, U content of the organic rich-mud components of the Black Sea sediment cores[14] was found to be in 3-19 mg/kg. Thus present U and Th results are compatible with those given in the literature for marine sediments.

A linear regression correlation test was performed to investigate the correlation between the elemental concentrations of our sediment samples. Correlation analysis revealed close relationships between Rb and Sr (r = 0.8513), Ce and La (r =0.8965), Th and La (r = 0.740), Th and Ce (r = 0.846), Th and Sm (r = 0.476), U and Th (r = 0.57) concentration pairs of creek sediments. The corresponding correlations were found to be r = 0.6267 (Rb and Sr), r =0.8642 (Ce and La), r = 7397

TABLE-1
PARAMETERS OF IRRADIATION AND MEASUREMENT FOR DETERMINED ELEMENTS IN SEDIMENTS

| Determined elements | Sample mass (g) | Neutron flux and spectra ($cm^{-2}$ $s^{-1}$) | Irradiation (h) | Time of cooling | Measuring (m) |
|---|---|---|---|---|---|
| Na, Sr | 0.1 | $6.5 \times 10^{10}$, thermal | 2-5 | 2-3 h | 5-7 |
| As, La, Sm, U | 0.1 | $5.7 \times 10^{13}$ fission spectra | 1.0 | 5-7 d | 5 |
| Ca, Sc, Fe, Co, Sb, Cs, Ce, Hf | 0.15-0.2 | $5.7\text{-}6.5 \times 10^{13}$ fission spectra | 5-10 | 10-15 d | 10-15 |
| Others | 0.1 | $5.7 \times 10^{13}$ (fission spectra) | 1.0 | 5-10 d | 3-5 |

TABLE-2
NEUTRON ACTIVATION ANALYSIS (mg/kg) OF THE SEDIMENT SAMPLES*

| Sample No | Station name | Na (%) | Al (%) | K (%) | Ca (%) | Fe (%) | Sc | Co | As | Rb | Sr | Y | Sb | Cs | U | Th | La | Ce | Sm | Eu | Dy | Yb | Lu | Hf |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Kepez | 1.5 | 3.3 | 1.6 | 4.5 | 1.6 | 6.2 | 10 | 7.1 | 146 | 108 | 13 | 0.7 | 1.7 | 2.4 | 6.2 | 19 | 40 | 3.1 | 0.65 | 0.25 | 1.8 | 0.3 | 2.6 |
| 2 | Saricay | 1.1 | 5.0 | 1.8 | 5.4 | 2.8 | 14 | 18 | 11 | 151 | 136 | 18 | 0.9 | 3.8 | 2.6 | 8.9 | 31 | 60 | 5.8 | 0.90 | 7.70 | 2.0 | 0.34 | 5.2 |
| 3 | Musakoy | 2.0 | 3.8 | 1.8 | 3.4 | 1.4 | 4.9 | 5.0 | 4.0 | 130 | 95 | 11 | 0.7 | 3 | 2.0 | 9.0 | 20 | 48 | 3.7 | 0.74 | 4.2 | 1.9 | 0.24 | 3.1 |
| 4 | Yap?ldak | 1.7 | 3.3 | 2.1 | 4.7 | 1.8 | 14 | 22 | 21.5 | 148 | 110 | 12 | 0.7 | 6.4 | 2.7 | 8.6 | 26 | 55 | 4.9 | 0.81 | 7.1 | 2.0 | 0.37 | 3.6 |
| 5 | Umurbey | 1.7 | 3.2 | 1.5 | 5.4 | 1.2 | 5.1 | 7.8 | 6.1 | 125 | 56 | 9 | 0.5 | 6.8 | 2.2 | 4.8 | 17 | 35 | 2.8 | 0.56 | 3.2 | 1.6 | 0.33 | 2.6 |
| 6 | Lapseki | 1.6 | 4.4 | 1.7 | 4.4 | 1.4 | 7.2 | 12 | 9.2 | 135 | 52 | 11 | 0.5 | 5.0 | 2.4 | 5.4 | 19 | 35 | 3.4 | 0.65 | 5.2 | 1.4 | 0.23 | 2.3 |
| 7 | Munipbey | 0.6 | 4.6 | 5.3 | 1.1 | 1.6 | 4.2 | 5.5 | 20.0 | 155 | 145 | 9 | 0.8 | 5 | 3.8 | 11 | 23 | 49 | 3.2 | 0.51 | 4.6 | 1.0 | 0.35 | 2.6 |
| 8 | Sutluce | 1.0 | 3.4 | 1.2 | 1.9 | 2.0 | 6.0 | 12 | 9.4 | 144 | 130 | 8 | 0.9 | 5.1 | 2.9 | 5.0 | 14 | 30 | 2.3 | 0.45 | 3.2 | 1.0 | 0.27 | 3.3 |
| 9 | Cumali | 1.9 | 4.1 | 2.2 | 2.0 | 1.1 | 6.0 | 4.5 | 2.3 | 127 | 55 | 8 | 0.7 | 2.7 | 1.9 | 4.7 | 18 | 29 | 3.1 | 0.65 | 4.3 | 2.0 | 0.18 | 3.3 |
| 10 | Ilgar | 1.7 | 3.3 | 2.2 | 1.0 | 1.8 | 8.8 | 14 | 18.5 | 155 | 112 | 11 | 2.3 | 2.9 | 3.5 | 8.9 | 23 | 52 | 3.5 | 0.72 | 5.3 | 1.4 | 0.41 | 3.5 |
| 11 | Kayaalti | 0.7 | 5.2 | 2.1 | 7.1 | 2.7 | 8.4 | 8.0 | 22 | 150 | 125 | 14 | 1.3 | 6.5 | 3.1 | 8.6 | 22 | 40 | 3.4 | 0.64 | 3.1 | 1.1 | 0.45 | 2.5 |
| 12 | Bigali | 1.5 | 4.1 | 2 | 6.2 | 2.5 | 6.4 | 6.9 | 16 | 146 | 130 | 12 | 1.9 | 5.5 | 2.9 | 8.5 | 22 | 50 | 3.6 | 0.44 | 4.4 | 2.0 | 0.50 | 4.6 |
| 13 | Eceabat | 1.9 | 4.0 | 2.5 | 10.0 | 1.4 | 7.0 | 9.5 | 12 | 149 | 120 | 13 | 1.2 | 5 | 2.7 | 11 | 26 | 55 | 3.8 | 0.42 | 4.1 | 2.0 | 0.54 | 3.8 |
| 14 | C2 | 2.8 | 4.3 | 2.1 | 6.6 | 3.5 | 15 | 15 | 14 | 132 | 65 | 19 | 0.9 | 1 | 1.9 | 10 | 28 | 55 | 4.8 | 0.91 | 4.8 | 2.5 | 0.30 | 4.9 |
| 15 | C3 | 2.6 | 3.6 | 2.1 | 5.4 | 2.0 | 10 | 13 | 8.5 | 130 | 61 | 12 | 0.6 | 5.2 | 2.5 | 7.1 | 24 | 48 | 4.0 | 0.69 | 5.0 | 2.4 | 0.35 | 5.6 |
| 16 | C4 | 2.8 | 3.5 | 1.5 | 7.2 | 1.5 | 6.5 | 11 | 5.8 | 129 | 46 | 13 | 0.8 | 5.4 | 2.5 | 6.2 | 20 | 43 | 3.4 | 0.70 | 2.6 | 2.2 | 0.19 | 3.9 |
| 17 | C5 | 2.6 | 3.9 | 1.6 | 4.6 | 1.5 | 8.0 | 7.5 | 7.5 | 128 | 42 | 11 | 0.7 | 2.8 | 2.2 | 7.0 | 22 | 52 | 3.8 | 0.72 | 3.6 | 2.2 | 0.35 | 4.8 |
| 18 | C6 | 2.5 | 3.3 | 2 | 6.0 | 1.6 | 6.6 | 10 | 8.8 | 138 | 55 | 11 | 0.6 | 5 | 2.8 | 8.0 | 22 | 45 | 3.5 | 0.80 | 4.0 | 2.8 | 0.24 | 3.2 |
| 19 | C9 | 2.3 | 4.5 | 2.1 | 1.8 | 2.4 | 10.5 | 11 | 16 | 107 | 54 | 13 | 2.5 | 11 | 2.2 | 8.6 | 27 | 57 | 4.5 | 0.91 | 3.7 | 2.0 | 0.40 | 3.5 |
| 20 | C10 | 2.5 | 4.8 | 1.9 | 2.2 | 2.7 | 11.5 | 14 | 18 | 100 | 46 | 12 | 0.7 | 15 | 2.9 | 10 | 27 | 61 | 4.6 | 0.82 | 4.8 | 2.2 | 0.34 | 4.3 |

*Results in mg/kg unless where indicated. Sediment samples 1-13 were obtained from small creeks mouths and samples 14-20 were obtained from Dardanelles.

(Th and La), r = 0.8571 (Th and Ce), r = 0.9045 (Th and Sm) and r = 0.32 (U and Th), respectively, in the marine sediments.

A typical graph of the rare earth elements concentration distribution of the sediment samples studied depending on their atomic numbers is given in Fig. 2. The result indicates that lanthanides have a natural origin.

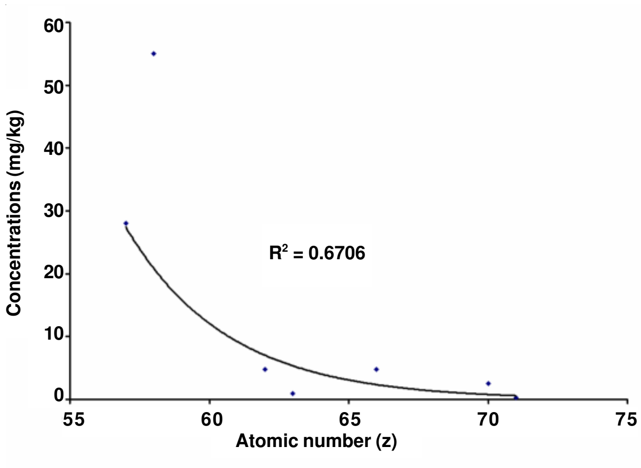


Fig. 2. A typical graph of the rare earth elements concentrations in the sediments of the Dardanelles depending on their atomic numbers

The higher arsenic concentration was observed at the sediments of Yapildak (sample No. 4 in Fig. 1b), Ilgar (sample No. 10 in Fig. 1b) and Kayaalti (sample No. 11 in Fig. 1b), which was higher than the arsenic level of the surface sediments of the Gulf of Saros (northeastern Aegean Sea, Turkey), which was found to be in the interval 4-6 mg/kg[15]. The main source of high concentration of arsenic is the erosion products of mineralized zones of these areas. Arsenic levels of these creek sediments, however, were found to be lower than to those of Gulp of Naples[16], which were in the interval of 33-66 mg/kg and that of the surface sediments of the Johor Strait[17], Malasia (27 mg/kg). Fe levels were found to be compatible to those of surface sediments of the Gulf of Saros[15] (1.5-3.5 %).

In order to reveal the data embedded in the chemical composition of sediment samples, we performed a chemometric method, principle component analysis (PCA). Principle component analysis is a multivare analysis technique that reduces data matrix to their lowest orthogonal space and found to be very informative to obtain hidden data structures[18]. Mathematically, principle component analysis is based on an eigenvector decomposition of the covariance matrix of the variables in a data set. Given a data matrix X with m rows of samples and n columns of variables, the covariance matrix of X is defined as:

$$\{\text{cov}\}(X) = \frac{X^T X}{m-1} \quad (1)$$

here $X^T$ is transpose matrix of data matrix X and m is the number of samples. The result of the PCA procedure is a decomposition of the data matrix X into principal components called score and loading vectors. As matrix notation we can write data matrix X:

$$X = TP^T + E \quad (2)$$

here T is the score matrix, $P^T$ is the transpose of P loading matrix and E is the residual matrix. The matrix related to the sample contributions (T) is called score matrix and the matrix related to the variables contributions (P) is called loadings matrix. The score and loading matrixes contain information on how the samples and variables, respectively, relate to each other. Firstly we investigated all the minor elements of marine and creek sediments (Sc, Co, As, Rb, Sr, Y, Sb, Cs, U, Th, La, Ce, Sm, Eu, Dy, Yb, Lu, Hf), therefore X matrix contains chemical compositions of 20 sediment samples and thus it has 20 rows (corresponding to the number of samples) and 18 columns (corresponding to chemical elemental compositions see Table-2). Score matrix provides information about the samples distribution and grouping, while the loading matrix gives information about the most relevant chemical elements used to obtain this distribution and grouping. The result of the PCA projection of our data (creek and marine sediments) from the original 20-dimensional space into the plane of the first two principal components is shown in Fig. 3, where each sample is presented as a point. The components PC1 and PC2 (Fig. 3) show the greatest contribution to the variance in concentrations (PC1 = 85 %, PC2 = 8%). Since the first two principal components (PCs) represent 93 % of the total variance, these two components were sufficient to provide effective clustering of the samples origin with clear separation between the groups. The PC1 *versus* PC2 plot is dominated by Sr (high weight to PC1) and Ce, (high weight to PC2) (Fig. 3b), indicating that the variance in the concentration data can be explained mainly by the concentration variations in Sr and

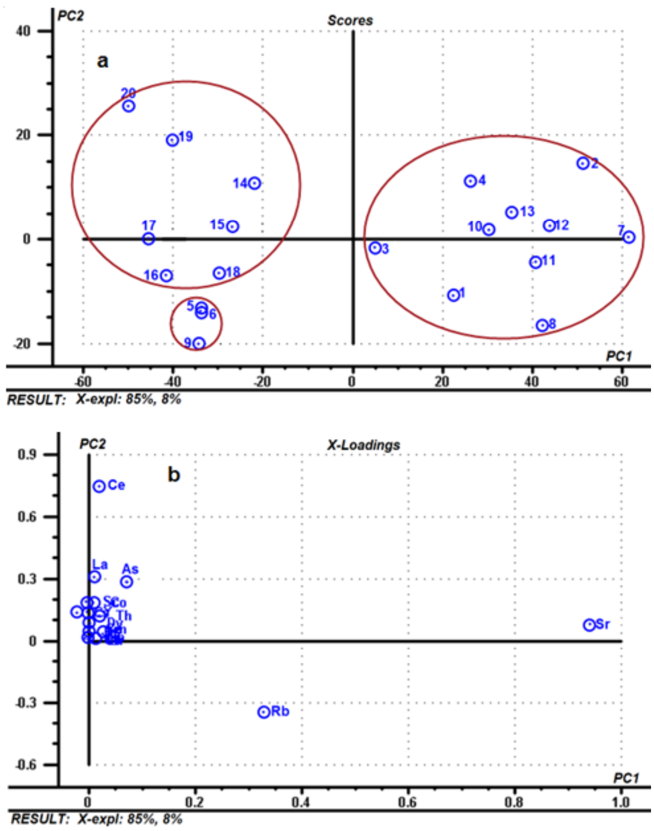


Fig. 3. Scores (a) and loadings (b) of principle components PC1 and PC2 of all sediment samples studied for minor constituents

Ce. In Fig. 3b, Rb contribution to PC1 and La and As contribution to PC2 are also recognizable. As seen in Fig. 3a, scores plot showing the separation of the sediment samples into three major clusters; the first one contains creek sediments except Umurbey (5), Lapseki (6) and Cumali (9), the second one contains all the marine sediments. The creek sediments Umurbey (5), Lapseki (6) and Cumali (9) are separated from the other creek sediments due to their strontium content.

## ACKNOWLEDGEMENTS

In this study concentrations of 23 elements in the sediment samples collected from 7 sampling sides of the Dardanelles and 13 sampling sited of creeks in the area of surrounding the Dardanelles were analyzed quantitatively by instrumental neutron activation analysis. The U and Th concentrations of the sediment samples investigated are found to be in agreement to those of other marine sediments. Results indicated that Lantanites have natural origin. Principle component analysis analysis of the investigated minor parameters indicated that Sr, Ce and Rb concentrations are leading factors that influences sediment characteristics of the Dardanelles area.

## REFERENCES


1. J.F. Dewey and A.M.C. Sengor, *Geol. Soc. Am. Bull.*, **90**, 84 (1979).
2. C. Yaltirak, B. Alpar, M. Sakinc and H. Yuce, *Mar. Geol.*, **164**, 139 (2000).
3. O. Tuysuz, A.A. Barka and E. Yigitbas, *Tectonophysics*, **293**, 105 (1998).
4. M. Varavipour, T. Asadi and Z. Arzjani, *Asian J. Chem.*, **22**, 5201 (2010).
5. S. Burak, S. Unlu and C. Gazioglu, *Asian J. Chem.*, **21**, 3166 (2009).
6. M. Karatas, *Asian J. Chem.*, **20**, 5741 (2008).
7. T. Akyuz and S. Akyuz, *Asian J. Chem.*, **20**, 3657 (2008).
8. O.I. Davutluoglu, T. Yilmaz, G. Seckin, C.B. Ersu and A. Yuceer, *Asian J. Chem.*, **20**, 1567 (2008).
9. T. Akyuz, S. Akyuz, N.M. Mukhamedshina and A.A. Mirsagatova, *Fresen. Environ. Bull.*, **12**, 1505 (2003).
10. R. Ilgar and E. Sari, *J. Appl. Sci.*, **8**, 2919 (2008).
11. L.D. Tochilina, L.K. Kaganov and N.M. Mukhamedshina, *J. Radioanal. Nucl. Chem.*, **201**, 177 (1995).
12. A. Varinlioglu, A. Kose, U. Cevik, A.I. Kopya, M. Altunbas and H. Karal, *J. Radioanal. Nucl. Chem.*, **201**, 31 (1995).
13. S. Akyuz, T. Akyuz, A.O. Algan, N.M. Mukhamedshina and A.A. Mirsagatova, *J. Radioanal. Nucl. Chem.*, **254**, 569 (2002).
14. T. Akyuz, S. Akyuz and A. Bassari, *J. Radioanal. Nucl. Chem.*, **250**, 129 (2001).
15. T. Akyuz, N. Mukhamedshina, S. Akyuz, E. Sari and A.A. Mirsagatova, *J. Radioanal. Nucl. Chem.*, **273**, 747 (2007).
16. E. Romano, A. Ausili, N. Zharova, M.C. Magno, B. Pavoni and M. Gabellini, *Mar. Pollut. Bull.*, **49**, 487 (2004).
17. S.Z. Zulkifli, A. Ismail, F. Mohamat-Yusuff, T. Arai and N. Miyazaki, *Bull. Environ. Contam. Toxicol.*, **84**, 568 (2010).
18. Multivare Data Analysis-In practice, K.H. Esbensen, CAMO Process AS, Norway, ISBN 82-993330-3-2, pp. 19-72 (2004).