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Neutron Activation Analysis of the Metals from Ancient Coins Dating Back to Roman Age

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Concentration levels of various elements have been estimated in ancient coins dating back to Roman age, which have been found in a sewage system of the ancient Ainos (Enez, Turkey). The coins are distributed into two groups on the basis of elemental composition: Pb and Cu based or Fe and Mn based coins indicating that two different ore deposits were used for issuing these coins. Other minor elements present in varying proportions are Ca, As and Sn. Besides to these major and minor elements, the coins were found to contain Na, K, Sc, Cr, Co, Ni, Zn, Br, Ag, Sb, Ba, Au as impurities.

Key Words: Neutron activation analysis, Ancient coins, Archaeometry.

INTRODUCTION

Enez (Ancient Ainos), in the Northern Coast of the Aegean Sea, has been described as one of the most important archaeological sites in Turkey. The first residents of Enez have not been known yet but the found remains show that first residents were dated back to 7300 years from now and life in here has continued till today.

During the archaeological excavations, a group of coins have been found in a sewage system dating back to Roman age. The sewage system constructed under a street dating back to the Roman age (4th century AD) is located parallel to Bekir Kara street at the center of city of Enez. Inscriptions and motifs on the coins are not identifiable. Probably defects have

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occurred during the minting process of these coins and because of that they were thrown away to the sewage system of the ancient Ainos.

Determination of the constituents of ancient coins is important[1-4], since it gives valuable information about the commercial exchanges between various states and one may deduce information about the quality control practices adhered to various mints issuing the coins.

In this study, the element constitutions of the 4 selected coins have been determined by instrumental neutron activation analysis (INAA). Additional information has been obtained by energy dispersive X-ray fluorescence analysis, which was performed for determination of the concentration levels of Ca, Fe, Cu, Zn, As, Sn, Pb and Mn on total 9 coins.

EXPERIMENTAL

The analyses were done by instrumental neutron activation analysis (INAA) method and for some elements by using EDXRF technique. In Fig 1, a set of coins are shown after their excavation. The coins were cleaned with water and soap using a steel brush and then dried with a clean piece of cloth. Soft cotton and acetone were then used to clean the coins from any residues that may have been left on their surfaces. INAA analysis was performed on 4 selected coins (Fig 2). EDXRF analysis was done for Ca, Fe, Cu, Zn, As, Sn, Pb and Mn elements on total 9 coins including the four coins analyzed by INAA.

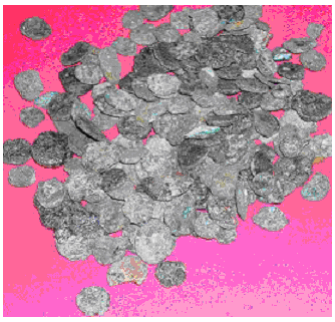

Fig. 1. Metal coins after their excavation in Ancient ainos, Turkey

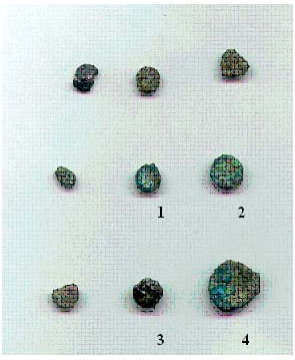

Fig. 2. Selected 9 coins that EDXRF analysis was performed. The INAA analysis was carried on the coins numbed 1-4

In case of INAA, for the measurement and the treatment of the sample spectrum, HPGe coaxial γ-ray detector (the resolution 1.8 keV at 1332.5 keV, relative efficiency 15%) with charge sensitive preamplifier and multichannel analyzer DSA-1000 with software Genie-2000 (Camberra Industries) were used. The samples of 0.1-0.15 g mass were irradiated

simultaneously with reference materials at nuclear reactor of Institute of Nuclear Physics, Tashkent, Uzbekistan. The contents of Th and U were calculated from using γ-line intensities of radionuclides ^{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), resulted from the following reactions, respectively:

$$^{232}Th\ (n,\gamma)\ ^{233}Th \xrightarrow[22.12\ min]{\beta^-,\gamma} {}^{233}Pa \xrightarrow[27.1\ d]{\beta^-,\gamma} {}^{233}U\ (\alpha\text{-decay},\ T_{1/2}=1.6\ .\ 10^5\ yr)$$

$$^{238}U\ (n,\gamma)\ ^{239}U \xrightarrow[23.54\ min]{\beta^-,\gamma} {}^{239}Np \xrightarrow[2.35\ d]{\beta^-,\gamma} {}^{239}Pu\ (\alpha\text{-decay},\ T_{1/2}=24360\ yr)$$

The detection limit for Th and U was 0.01 mg/kg and 0.03 mg/kg, respectively. The Th and U error (S_r = relative standard deviation) of determining[5] was 0.1. The characteristics for the determination of the impurities in the coins were given in Table-1.

TABLE-1
CHARACTERISTICS FOR THE DETERMINATION OF THE IMPURITIES IN COINS

Elements	Density of neutron flux and its spectra ($cm^{-2}\ s^{-1}$)	Time of irradiation (h)	Time of cooling (d)	Time of measuring (min)
Na, K, Cu, As	6.5×10^{10} (thermal)	65	1	3-5
Others	5.7×10^{13} (fission spectra)	10	5-10	3-5

In EDXRF analysis, ^{241}Am source (activity of 3.8×10^9) was used to excite X-ray lines from samples. Si(Li)-detector (the resolution 150 eV at 5.9 keV) with X-ray spectrometer (Camberra Industries) was applied for measuring of X-ray lines. In Fig. 3, the EDXRF spectra of the 4 coins are shown. Old coins contain a considerable amount of light elements such as carbon, oxygen, nitrogen and others, whose X-ray lines are not revealed in the spectra. As seen in the Fig. 3, in the X-ray spectra L-lines of Pb and K-lines of Mn are well visible. The details of the analysis are given elsewhere[5].

RESULTS AND DISCUSSION

Since the coins have been buried in the sewage system for centuries, corrosion phenomena must be observed on their surfaces. The typical green patina on the surface of the coins is a consequence of leaching process of copper (Fig. 1). Table-2 gives the INAA and XRF results of the selected coins. The major elements of the three coins numbered 1, 2 and 4 are Pb and Cu. Coin numbered 3 different in concentration to the others, and Fe & Mn are the highest major elements. Probably two different ore deposits

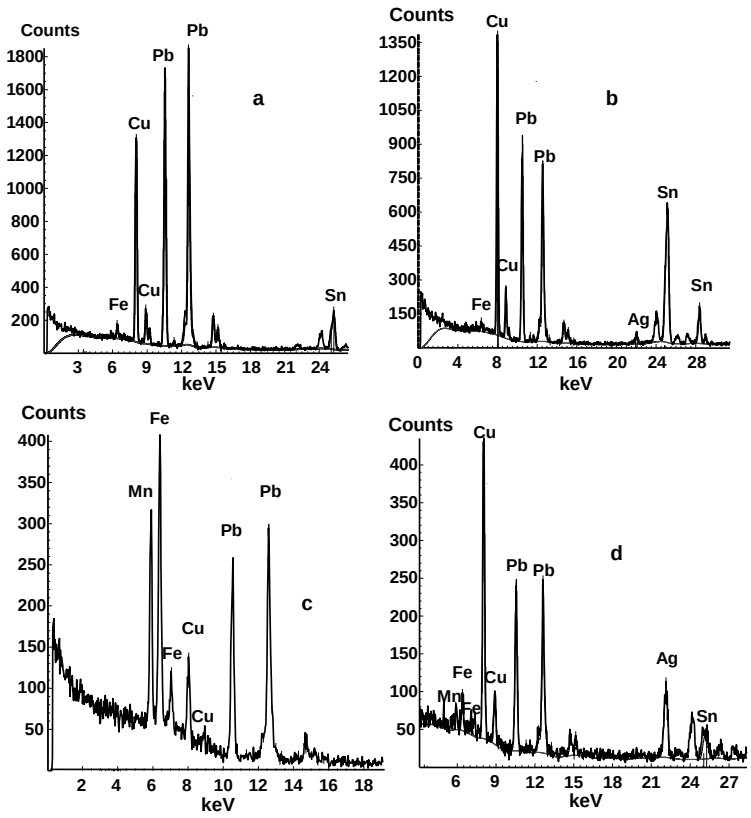

Fig. 3. EDXRF spectra of the coins numbered 1 (a), 2 (b), 3 (c) and 4 (d)

were used. XRF analysis results on total 9 coins were also supported this result and revealed the presence of two district groups. Around the Enez archaeological site there are a lot of small ore deposits and ore veins[6,7] which contain different amounts of Pb, Cu, Zn, Mn and Fe. Canakkale-Yenice area is quite close to Enez, and the geology of the area features a Palaeozolic metamorphic basement, Triassic sedimentary rocks including the carbonate blocks, early tertiary granitoids and neogene volcanics[7]. The metallurgical composition of the coins studied is found to be in accord with the ore deposits and ore veins of the Canakkale-Yenice area[6,7] indicating that local ore deposits had been used for issuing these coins.

The investigated coins were found to have composition ranging from about 6 to 30 % Cu, 3 to 17 % Pb, 0.4 to 25 % Fe, < 0.01 to 4 % Ca, 0.13 to 1.00 % As, 0.05 to 2.2 % Sn and 0 to 22 % Mn. Besides to these major elements, the coins were found to contain following elements with different concentrations: Na, K, Sc, Cr, Co, Ni, Zn, Br, Ag, Sb, Ba and Au. The maximum Ag concentration is found to be 2400 mg/kg for coin number 4. The classification of the elements is not strict, because element concentrations are not homogeneous.

TABLE-2
CHEMICAL ANALYSES RESULTS (mg/Kg) OF THE COINS
FROM ANCIENT AINOS

Elements	INAA results of 4 coins				XRF results of 9 coins	
	1st group			2nd group	1st group	2nd group
	1	2	4	3		
Na	190 ± 10	630 ± 10	2100 ± 100	5600 ± 100		
K	< 100	< 100	3500 ± 100	< 100		
Ca %	4.00 ± 0.07	< 0.01	< 0.01	< 0.01	0.02-1.7	0.02-0.1
Sc	0.14 ± 0.01	0.23 ± 0.01	0.89 ± 0.07	2.8 ± 0.1		
Cr	< 1	< 1	10 ± 1	10 ± 1		
Fe %	0.39 ± 0.02	0.54 ± 0.01	1.9 ± 0.1	25.0 ± 0.1	0.4-1.9	22.4-25.2
Co	16 ± 1	5.5 ± 0.3	9.4 ± 0.4	13 ± 1		
Ni	83 ± 5	< 1	< 1	180 ± 10		
Cu %	12.7 ± 0.5	29.8 ± 1.5	26.5 ± 1.3	6.0 ± 0.4	12.6-30.0	5.9-8.0
Zn	380 ± 10	150 ± 5	140 ± 5	930 ± 30	140-395	880-931
As %	0.13 ± 0.01	1.00 ± 0.02	1.00 ± 0.02	0.20 ± 0.01	0.13-1.00	0.20-0.15
Br	17 ± 1	16 ± 1	20 ± 1	10 ± 1		
Ag	340 ± 10	660 ± 10	2400 ± 50	140 ± 10		
Sn %	0.70 ± 0.02	2.2 ± 0.1	0.70 ± 0.02	<0.06	0.66-2.2	0.05-0.10
Sb	660 ± 30	1000 ± 100	830 ± 50	36 ± 3		
Ba	n.d.	300 ± 50	160 ± 20	480 ± 50		
Au	7.7 ± 0.1	31.0 ± 0.1	35.0 ± 0.1	0.60 ± 0.02		
Pb (XRF) %	16.2 ± 0.4	16.8 ± 0.4	9.2 ± 0.3	3.0 ± 0.3	8.7-17.0	3.0-4.5
Th	< 1.0	< 1.0	1.0 ± 0.1	1.9 ± 0.1		
U	< 0.3	< 0.3	< 0.3	< 0.3		
Mn (XRF) %	n.d.	n.d.	2.0±0.2	22.0±2	n.d.- 2.1	15.0- 22.0

n.d.= not detected.

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