Investigation of the Element Composition of Barmas Medallion (the 12th – First Half of the 13th Centuries) by Method of Neutron Resonance Capture Analysis

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Abstract

The analysis of element composition of the medallion was carried at IREN Facility in Frank Laboratory of Neutron Physics by Neutron resonance capture analysis (NRCA).The method is based on the registration of neutron resonances and the measurement of the yield of reaction products in the resonances. The resonance energies are known practically for all stable nuclei and the set of energies does not coincide completely for any pair of isotopes. It allows determining the isotope-element composition.

The Barmas medallion dates back to the 12th – first half of the 13th centuries (the ancient Russian time). It was found in historical part of Tver city near the Tver Kremlin. Analogues of this medallion are in the expositions of the Moscow Kremlin which consist mostly of silver or gold; but until today nobody studied the elemental composition of the metal of such objects. The result of investigation of element composition of medallion will be presented in report.

1. INTRODUCTION

In this paper the application of Neutron Resonance Capture Analysis (NRCA) will be discussed. It is a relatively new method for investigation elemental composition of objects. NRCA is based on the detection of the prompt γ-radiation following neutron capture as a function of neutron energy, the latter being determined with the time-of-flight technique [1]. This method is currently being developed in the Frank Laboratory of Neutron Physics [2].

The analysis was applied to a medallion (Fig.1). The medallion is historical artifact, which was discovered during the archeological excavations of Tver scientific and restoration center. The medallion dates back to the 12th – first half of the 13th centuries. It was found in historical part of Tver city near the Tver Kremlin. This is a unique artifact that characterizes the daily life of the ancient Russian city. On the face of medallion on niello layer was engraved a traditional image of six-pointed prosperous cross on triangular base. Most of such medallions were found in the cultural layer dated from the second half of XII c. till 1240, but some medallions were from the cultural layer dated by later period – XIII–XIV c. in the territory of Tver.

Fig. 1. The real view of medallion.

Analogues of such medallion are in the expositions of the Moscow Kremlin Museum which consist mostly of silver or gold. One of the aims of this research is a determination of the main type of metal (silver or copper) on the surface and into the bulk of medallion, and reconstruction the possibility type of manufacturing procedure (silvering etc.).

2. EXPERIMENT

The sample was irradiated with neutrons by pulsed neutron source (IREN) and the time-of-flight spectrum of reactions (n,γ) was registered [3]. The main part of the IREN facility is a linear electron accelerator. The facility parameters: the average energy of electrons was ~ 40 MeV, the peak current was ~ 1.5 A, the width of electron pulse was ~ 100 ns, and the repetition rate was 25 Hz. The total neutron yield was about $3 \cdot 10^{11}$ s^{-1}. The measurements were carried out at the 58.6 meters flight path of the 3rd channel of the IREN. The big liquid scintillator detector was used for the registration of γ-quanta [4]. The sample was placed inside the detector. The neutron flux was permanently monitored by the SNM-17 neutron counter. The signals from the detector and the monitor counter were simultaneously fed to the two independent inputs of time-to-digital converter.

The measurements with the sample lasted about 41 hours. The resonance energies were determined according to the formula:

$$E = \frac{5227L^2}{t^2}, \tag{1}$$

where t – time of flight in microseconds, L – flight path in meters, E – kinetic energy of a particle in eV.

The resonances of silver, gold and copper were identified on the time-of-flight spectrum (Fig. 2) [5, 6]. The measurements with standard samples of silver, gold and copper were made in addition to the measurement with the investigated sample.

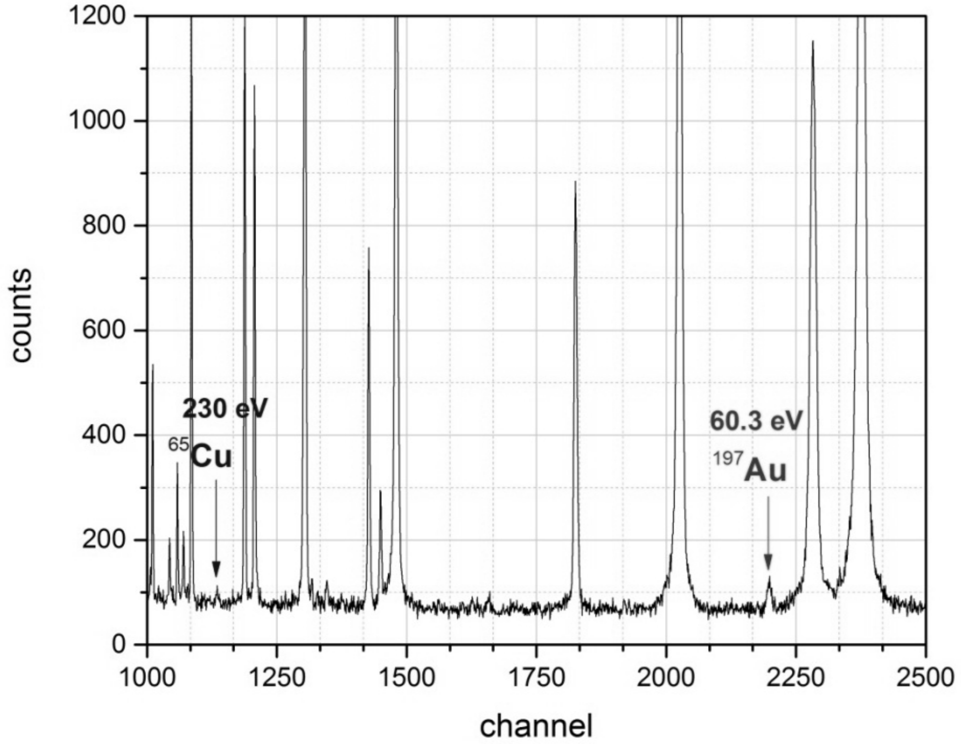

Fig. 2. The time-of-flight spectrum of reactions (n,γ) on the medallion material. The unmarked resonances are resonances of silver. The width of the time channel is 0.25 μs.

3. DATA ANALYSIS AND RESULTS

Five resonances of silver, one resonance of copper and one resonance of gold were selected during the analysis of the experimental data. The sum of the detector counts in resonance is expressed by the formula:

$$\sum N = f(E_0) \cdot S \cdot t \cdot \varepsilon_\gamma \cdot \frac{\Gamma_\gamma}{\Gamma} A. \tag{2}$$

Here $f(E_0)$ is the neutron flux density at the resonance energy E_0, S – the sample area, t – measuring time, ε_γ – the detection efficiency of the detector radiative capture, Γ_γ, Γ – the radiative and total resonance widths.

$$A = \int_{-\infty}^{+\infty} [1 - T(E)]\, \mathrm{d}E \tag{3}$$

is resonance area on the transmission curve, where

$$T(E) = e^{-n\sigma(E)} \tag{4}$$

is the energy dependence of the neutron transmission by the sample; σ(E) – the total cross section at the energy E with Doppler broadening, n – the number of isotope nuclei per unit area. The value A was determined from experimental data for investigated sample by the formula:

$$A_x = \frac{\sum N_x \cdot M_s \cdot S_s}{\sum N_s \cdot M_x \cdot S_x} \cdot A_s. \quad (5)$$

Here $\sum N_x$, $\sum N_s$ are counts under the resonance peak of the investigated and standard samples, S_x, S_s – the areas of the investigated and standard samples, M_x, M_s – the numbers of monitor counts during the measurement of the investigated and standard samples.

The value A_s was calculated by means of well-known parameters of resonances for the standard sample, the value n_x was determined from the value of A_x for the investigated sample. The σ(E) and A values were numerically determined by using the algorithm which was described in [7]. The analysis results are presented in the Table 1.

Table 1. The results of measurements with the medallion by NRCA (the bulk)

№	Element	Mass, g	Weight, %
1	Ag	23.32±0.36	75.5±1.2
2	Cu	1.78±0.83	5.8±2.7
3	Au	0.12±0.02	0.390±0.065

Additional measurements were carried out by X-ray fluorescence (XRF) by Neutron-activation-analysis group in FLNP (Table 2).

Table 2. The results of measurements with the medallion by XRF (the surface)

№	Element	Weight, %
1	Ag	89.78±0.65
2	Cu	1.872±0.077
3	Au	0.653±0.039
4	Pb	2.30±0.14
5	Sn	1.36±0.41

4. CONCLUSION

Analogues of the medallion are in the expositions of the Moscow Kremlin which consist mostly of silver or gold. But knowledge of archaeologists about chemical composition of these metals, especially of their microimpurities, is very scanty. Our study of the elemental composition could clarify this issue.

The application of the XRF analysis allowed us to determining the elemental composition on the medallion surface. To determine the real component of impurities in the metal of archaeological object, an investigation of elemental composition is needed to be carried out in the “bulk-form” without destruction. Thanks to analytical tool of NRCA there was found out that the medallion mostly consists of silver and we know that content of silver in the bulk is less than on the surface. This data is very important fact to further understanding the process of “aging” of silver that we can remark for the archaeological metal. In fact, using this analytical tool of NRCA we can certify the process of silver transition to the surface of objects (segregation).

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REFERENCES

1. H. Postma, M. Blaauw, P. Schillebeeckx, G. Lobo, R.B. Halbertsma, and A.J. Nijboer, *Non-destructive elemental analysis of copper-alloy artefacts with epithermal neutron-resonance capture*, Czech Republic: N. p., 2003. Web.doi:10.1007/s10582-003-0030-y.
2. N.V. Bazhazhina, Yu.D. Mareev, L.B. Pikelner, P.V. Sedyshev, V.N. Shvetsov, *Analysis of element and isotope composition of samples by neutron spectroscopy at the IREN facility*, Physics of Particles and Nuclei Letters, **12** (2015) 578–583.
3. O.V. Belikov, A.V. Belozerov, Yu. Becher, Yu. Bulycheva, A.A. Fateev, A.A. Galt, A.S. Kayukov, A.R. Krylov, V.V. Kobetz, P.V. Logachev, A.S. Medvedko, I.N. Meshkov, V.F. Minashkin, V.M. Pavlov, V.A. Petrov, V.G. Pyataev, A.D. Rogov, P.V. Sedyshev, V.G. Shabratov, V.A. Shvec, V.N. Shvetsov, A.V. Skrypnik, A.P. Sumbaev, A.V. Ufimtsev, V.N. Zamrij, *Physical start-up of the first stage of IREN facility,* Journal of Physics: Conf. Ser. 205 (2010) 012053.
4. H. Maletsky, L.B. Pikelner, K.G. Rodionov, I.M. Salamatin, E.I. Sharapov, *Detector of neutrons and gamma rays for work in the field of neutron spectroscopy,* Communication of JINR 13-6609, Dubna, JINR, (1972) 1–15 (in Russian).
5. S.F. Mughabghab. *Neutron Gross Sections, Neutron Resonance Parameters and Thermal Gross Sections*. Academic Press, New York, 1984.
6. S.I. Sukhoruchkin, Z.N. Soroko, V.V. Deriglazov, *Low Energy Neutron Physics*. Landolt-BornsteinV. I.,16 B, Berlin: Springer Verlag, 1998.
7. V.N. Efimov, I.I. Shelontsev, *Calculation for graphs of determining the parameters of neutron resonances by the transmission method*. Communications of the JINR P-641, Dubna, (1961) 1–19 (in Russian).