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# ELEMENTAL ANALYSIS OF THE ANCIENT BRONZE COINS BY X-RAY FLUORESCENCE TECHNIQUE USING SIMULTANEOUSLY RADIOISOTOPE SOURCE AND X-RAY TUBE

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**Abstract.** *The results on elemental analysis of the vietnamese ancient bronze coins during the time of the Nguyen dynasty (19th century) are presented. The samples were provided by the Vietnam National Historical Museum and the elemental analysis was performed on the home-made model EDS-XT-99-01 X-ray fluorescence spectrometer in the Institute of Materials Science, NCST of Vietnam. The samples exited simultaneously by radioisotope source and X-ray tube. The analytical results show the similarity in the elemental composition of the coins issued by different kings of the Nguyen dynasty, but there is the difference in the concentration of the used elements. Another interesting point is that all the coins have zinc (Zn) in their composition, which shows clearly the influence of the occidental metallurgical technology on the money-making technique in Vietnam during the 19th century.*

## I. INTRODUCTION

X-ray fluorescence (XRF) analysis is a commonly used technique for archaeological samples because of its non-destructive character. Nowadays in this technique one widely used method is the Fundamental Parameters Method (FPM), which is particularly suitable for special case of the alloy samples as ancient bronze coins.

The FPM was proposed in 1968 by J. W. Criss and L. S. Birks [1]. The idea is to carry out a best estimate (normally by regression) of sample composition, consistent with the measured fluorescence intensities from the unknown sample and standard reference materials, by indirect use of a physical-mathematical model for emitted intensities. By this method for calibration are needed the pure elements samples and only one reference sample with the composition and element concentrations in the same range as those of the analysed samples. At present, in our group we have a set of the Cu-alloy reference samples from the former Czechoslovakia (6 samples denoted from Cu-318 to Cu-323) with the composition similar with those of the ancient vietnamese bronze coins, therefore the analysis of the above mentioned coins by the FPM can be performed without difficulties. From the other side, we have written a special FPM software package for XRF analysis of the Cu-alloy samples [2].

## II. BASIS OF METHOD

Theoretical intensities are obtained by calculating primary and secondary fluorescence for flat, homogeneous and thick specimens, when monochromatic excitation:

The primary fluorescence intensity:

$$P_{i,s} = qE_iC_i\frac{\mu_{i,\lambda}U_\lambda}{\mu_{s,\lambda} + A\mu_{s,\lambda}} \tag{1}$$

And secondary fluorescence intensity:

$$S_{i,S} = \frac{1}{2}qE_iC_iE_jC_j\frac{\mu_{j,\lambda_j}}{\mu_{S,\lambda_j}}\mu_{j,\lambda}L\frac{\mu_{i,\lambda}U_\lambda}{\mu_{s,\lambda} + A\mu_{s,\lambda_i}} \tag{2}$$

where $A = \sin\psi_1/\sin\psi_2$ is the geometrical factor; $q = \sin\psi_1/\sin\psi_2 * \Omega/4\pi$ is the collimation factor and the parameter $L$ is:

$$L = \frac{ln(1 + \frac{\mu_{S,\lambda}/sin\psi_1}{\mu_{S,\lambda_j}})}{\mu_{S,\lambda}/sin\psi_1} + \frac{ln(1 + \frac{\mu_{S,\lambda_j}/sin\psi_2}{\mu_{S,\lambda_j}})}{\mu_{S,\lambda_j}/sin\psi_2} \tag{3}$$

The intensity of the pure element is obtained by making $C_i = 1$

$$P_{i,1} = qE_i\frac{\mu_{i,\lambda}U_\lambda}{\mu_{s,\lambda} + A\mu_{s,\lambda}} \tag{4}$$

The total fluorescence intensity $I_{i,s}$ of $i$ element in the sample is:

$$I_{i,s} = P_{i,s} + S_{i,s} \tag{5}$$

It depends on two sets of parameters:

Those relating to the specimen: the concentration $C_i, C_j, C_k$... of elements and three of their properties; $\mu_i$ is mass absorption coefficient; $\lambda_{abs,i}$ is wavelengths of absorption edges of elements, and $E_i$ is excitation factors.

Those relating to the instrumentation: parameters $\psi_1$ is incidence angle of primary radiation; $\psi_2$ is emergence angle of fluorescent radiation; $q$ is collimation factor and $U_\lambda$ is the intensity of the incident radiation, which in turn depend on the exitation condition.

Applying Eqs. (1)-(6), the relative intensities for specimen s are calculated

$$R_{i,s} = \frac{P_{i,s} + S_{i,s}}{P_{i,1}} \tag{6}$$

where

$$S_{i,s} = \sum_j S_{i,j} \tag{7}$$

is the sum of secondary fluorescence contributions from all the lines of the reinforcing elements in the specimen.

## III. EXPERIMENT

All the XRF measurements were done on our home-made model EDS-XT-99-01 XRF spectrometer system [3,4]. For XRF analysis, after cleaning and mechanical polishing, all the Cu-alloy reference samples, pure element samples and the ancient bronze coin samples were excited simultaneously by radioisotope source and X-ray tube as follows:

The point Am-241 radioisotope source (excitation energy 59.54 keV, intensity 140 mCi, incoming angle $\psi_{1a} = 45^o$, outgoing angle $\psi_2 = 90^o$).

The X-ray emission tube operating at 40 kV, 0.3 mA with the Zr secondary target, which results in the mean excitation energy 16.08 keV, incoming angle $\psi_{1b} = 51^o$, outgoing angle $\psi_2 = 90^o$.

The experimental setup is shown in Fig. 1. The total fluorescence intensity $I_{i,s}$ obtained of $i$ element in the sample s simultaneous excitation by radioisotope source and X-ray tube:

$$I_{i,s} = (P_{i,s} + S_{i,s})_{Isotop} + (P_{i,s} + S_{i,s})_{Tube} \tag{8}$$

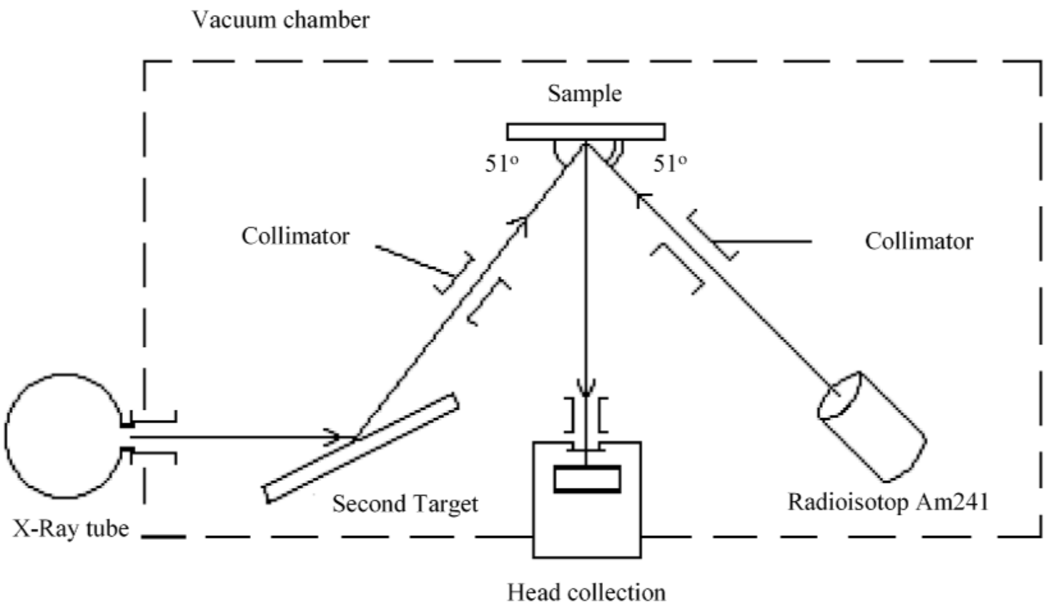


**Fig. 1.** Diagram excitation simultaneous by radioisotope source and X-ray tube.

At first, for checking the developed FPM programme and the equipment, the above mentioned set of the Cu-alloy reference samples (from former Czechoslovakia) has been XRF analysed. In these measurements the Cu-318 sample was used as reference. The progression of an iterative calculation is shown in Table 1 for Cu-319 sample. The calculations show that six iteration are sufficient. The computer program makes sure that the calculations converge, but it is obvious that the accuracy of the results depend on the accuracy of the intensity measurements and the all the parameters involved.

**Table 1.** *Compositions calculated with FPM program as a function of number iteration steps.*

| Iteration Steps | Concentrations(%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | ptMn | ptFe | ptNi | ptCu | ptZn | ptSn | ptSb | ptPb |
| 1 | pt0.07 | pt0.19 | pt0.71 | pt87.50 | pt2.40 | pt6.73 | pt0.22 | pt2.17 |
| 2 | pt0.08 | pt0.20 | pt0.74 | pt86.91 | pt2.51 | pt7.06 | pt0.23 | pt2.28 |
| 3 | pt0.08 | pt0.20 | pt0.73 | pt87.13 | pt2.47 | pt6.94 | pt0.22 | pt2.24 |
| 4 | pt0.08 | pt0.20 | pt0.73 | pt87.05 | pt2.49 | pt6.98 | pt0.22 | pt2.25 |
| 5 | pt0.08 | pt0.20 | pt0.73 | pt87.08 | pt2.48 | pt6.96 | pt0.22 | pt2.25 |
| 6 | pt0.08 | pt0.20 | pt0.73 | pt87.07 | pt2.48 | pt6.97 | pt0.22 | pt2.25 |
| 7 | pt0.08 | pt0.20 | pt0.73 | pt87.08 | pt2.48 | pt6.97 | pt0.22 | pt2.25 |
| 8 | pt0.08 | pt0.20 | pt0.73 | pt87.07 | pt2.48 | pt6.97 | pt0.22 | pt2.25 |

## IV. RESULTS AND DISCUSSION

**Table 2.** *The results of elemental concentration analysis of the Cu-alloy reference samples by the XRF technique.*

| Sample and Measurement | | Fe (%) | Ni (%) | Cu (%) | Zn (%) | Sn (%) | Sb (%) | Pb (%) | Total |
|---|---|---|---|---|---|---|---|---|---|
| Cu-318 (ref) | Given | 0.10 | 0.22 | 87.12 | 3.40 | 4.20 | 0.07 | 4.45 | 99.56 |
| Cu-319 | Given | 0.40 | 0.40 | 87.21 | 2.30 | 6.60 | 0.25 | 2.40 | 99.56 |
| | Meas. | 0.20 | 0.67 | 87.15 | 2.42 | 6.90 | 0.23 | 2.22 | 99.12 |
| | Error | ±0.02 | ±0.12 | ±1.81 | ±0.10 | ±0.16 | ±0.02 | ±0.15 | |
| Cu-320 | Given | 0.01 | 0.85 | 87.68 | 0.05 | 9.70 | 0.005 | 1.25 | 99.55 |
| | Meas. | <0.10 | 1.05 | 87.37 | 0.19 | 10.32 | 0.01 | 1.26 | 100.26 |
| | Error | | ±0.14 | ±1.79 | ±0.05 | ±0.23 | 0.01 | ±0.12 | |
| Cu-321 | Given | 0.005 | 0.01 | 87.25 | 0.01 | 12.60 | 0.005 | 0.02 | 99.90 |
| | Meas. | 0.05 | 0.21 | 86.45 | 0.23 | 12.86 | <0.10 | <0.08 | 99.89 |
| | Error | ±0.02 | ±0.10 | ±1.77 | ±0.05 | ±0.30 | | | |
| Cu-322 | Given | 0.04 | 0.04 | 85.31 | 0.50 | 13.50 | 0.03 | 0.39 | 99.81 |
| | Meas. | 0.08 | 0.17 | 83.82 | 0.63 | 14.59 | <0.02 | 0.56 | 99.87 |
| | Error | ±0.02 | ±0.09 | ±1.74 | ±0.06 | ±0.32 | | ±0.09 | |
| Cu-323 | Given | 0.005 | 0.005 | 84.87 | 0.08 | 14.75 | 0.04 | 0.02 | 99.77 |
| | Meas. | 0.06 | 0.21 | 83.98 | 0.29 | 15.03 | 0.02 | 0.31 | 99.77 |
| | Error | ±0.02 | ±0.09 | ±1.72 | ±0.05 | ±0.35 | ±0.01 | ±0.08 | |

The results of this check are presented in Table 2, where the given and the found (measured) concentrations of the chemical elements included in the samples and the errors of XRF analysis are shown. The check showed that the errors of XRF analysis by the FPM are completely acceptable.

As we can see, the highest values of the Zn and Pb concentration in the set of Cu-alloy reference samples are 3.40 % and 4.45%, respectively. But it was founded that in the bronze coins of the Nguyen dynasty period, the Zn and Pb concentrations can be much more higher than such values in many cases. For verifying the results of the XRF analysis of the coins with such a high concentration of Zn and/or Pb, we have used the atomic absorption (AA) as a second analytical method. The double analysis (XRF and AA) was done for 3 samples: one modern bronze coin (DV-1) and two ancient bronze coins (Dt-2 and Dt-4), with the AA analysis performed on the Shimadzu AA6501S equipment ($10^{-2}$% sensitivity) in the Analytical Laboratory of the Vietnam Geological and Mineralogical Agency and the results are shown in the Table 3. By comparing the results of the two mentioned above methods we can see that the divergence between two methods is acceptable.

Accordingly, we come to conclusion that the FPM programme developed by us can be used for analysis of the Cu-alloys with the Zn content up to 34% and the Pb content up to 24% with acceptable accuracy.

**Table 3.** *The results of analysis of the test samples by two methods X-ray Fluorescence (XRF) and Atomic Absorption (AA).*

| Sample and Method | | Fe (%) | Cu (%) | Zn (%) | Sn (%) | Sb (%) | Pb (%) | Total |
|---|---|---|---|---|---|---|---|---|
| DV1 | AA | 0.163 | 63.05 | 34.54 | 0.89 | 0.028 | 1.35 | 100.00 |
| | XRF | 0.210 | 64.75 | 32.98 | 0.61 | 0.030 | 1.34 | 99.83 |
| | | ±0.020 | ±1.36 | ±0.71 | ±0.03 | ±0.010 | ±0.11 | Errors |
| Dt-2 | AA | 0.043 | 68.52 | 0.015 | 6.24 | 0.105 | 23.42 | 98.34 |
| | XRF | 0.060 | 70.61 | 0.16 | 6.95 | 0.095 | 22.40 | 100.28 |
| | | ±0.070 | ±1.62 | ±0.07 | ±0.19 | ±0.070 | ±0.68 | Errors |
| Dt-4 | AA | 0.602 | 61.03 | 32.09 | 1.33 | 0.025 | 3.52 | 98.60 |
| | XRF | 0.530 | 62.45 | 32.36 | 0.79 | 0.030 | 2.56 | 98.72 |
| | | ±0.043 | ±1.59 | ±0.69 | ±0.08 | ±0.010 | ±0.25 | Errors |

When only radioisotopic source Am241 was used for analysis of the elements Sn, Sb, etc, having the K-shell electron binding energy higher than 25 keV. The results of analysis have higher accuracy while for Cu, Zn and Pb the accurancy is lower.

When only the tube was used for analysis of elements Fe, Cu, Zn, Pb, Sn, Sb etc., (for Fe, Cu, Zn $K_\alpha$ - lines and for Pb, Sn, Sb $L_\alpha$ - lines was used) electron binding energy in the range 3-14 keV. The results analysis have high accuracy concentration of Cu, Zn and Pb, results analysis have very low accuracy concentration of Sn and Sb. Lines $L_\alpha$( Sn) = 3.443KeV, $L_\alpha$( Sb) = 3.604KeV, thus the analysis samples wanted chamber vacuum.

With technique using simultaneously radioisotope source and X-ray tube excited sample. We are analysis simultaneously all elements in the bronze alloy samples. Results analysis have been high accuracy, the time analysis faster and the analysis unwanted chamber vacuum.

**Table 4.** *The results of XRF analysis of the vietnamese ancient bronze coins issued during the time different kings of the Nguyen dynasty.*

| Coin Sample | Fe (%) | Cu(%) | Zn (%) | Sn (%) | Sb (%) | Pb(%) | Total |
|---|---|---|---|---|---|---|---|
| Gia-Long | 0.68 | 71.41 | 22.17 | 1.45 | 0.38 | 3.96 | 100.05 |
| | ±0.02 | ±1.42 | ±0.64 | ±0.01 | ±0.02 | ±0.13 | Errors |
| Minh-Mang | 0.77 | 68.65 | 24.78 | 0.57 | 0.67 | 4.66 | 100.10 |
| | ±0.03 | ±1.50 | ±0.64 | ±0.02 | ±0.05 | ±0.22 | Errors |
| Thieu-Tri | 0.16 | 72.26 | 20.77 | 1.23 | 0.09 | 5.33 | 99.84 |
| | ±0.02 | ±1.65 | ±0.47 | ±0.05 | ±0.01 | ±0.23 | Errors |
| Tu-Duc | 0.73 | 70.25 | 25.32 | 0.67 | 0.09 | 2.98 | 100.04 |
| | ±0.02 | ±1.52 | ±0.64 | ±0.03 | ±0.01 | ±0.19 | Errors |
| Thanh-Thai | 1.34 | 81.58 | 15.95 | 0.10 | 0.04 | 1.30 | 100.31 |
| | ±0.05 | ±1.75 | ±0.42 | ±0.02 | ±0.01 | ±0.15 | Errors |
| Duy-Tan | 0.26 | 78.91 | 7.57 | 0.77 | 0.25 | 12.07 | 99.83 |
| | ±0.03 | ±1.74 | ±0.23 | ±0.05 | ±0.02 | ±0.44 | Errors |
| Khai-Dinh | 0.19 | 71.73 | 27.62 | 0.02 | 0.02 | 0.29 | 99.87 |
| | ±0.02 | ±1.57 | ±0.63 | ±0.03 | ±0.01 | ±0.09 | Errors |

The results of XRF analysis of the vietnamese ancient bronze coins issued by different kings of the Nguyen dynasty are shown in Table 4. Examples of the mentioned above coin XRF spectra are represented in Fig. 2.

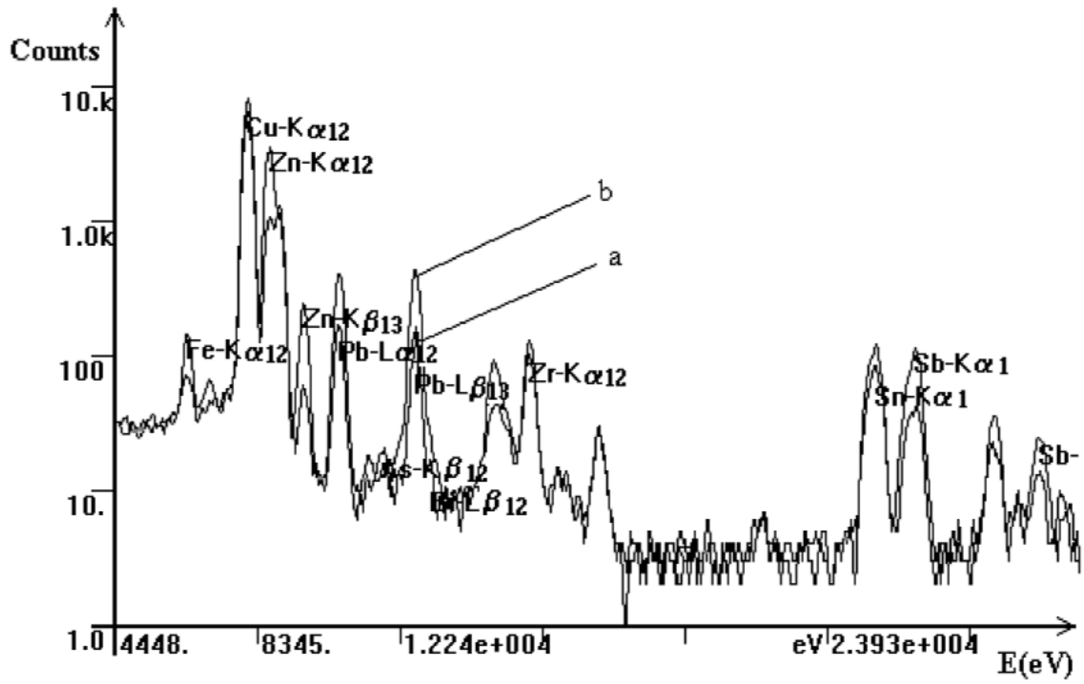


**Fig. 2.** X-ray fluorescence spectra of two coin samples issued during the time of kings Minh-Mang (a) and Duy-Tan(b) in the comparison mode.

From the results obtained we could say that there exists the difference in the concentrations of the used elements. There is a similarity in the elemental compositions of the coins is issued by different Kings of the Nguyen Dynasty.

Another interesting point is that all the coins contain zinc (Zn) with rather high concentrations in their compositions, This shows clearly the influence of the occidental metallurgical technology on the money-making technique in Vietnam during the 19th century.

We could also said that the home-made model EDS-XT-99-01 XRF spectrometer system connected with the FPM program is a effective tool for elemental analysis of Cu-alloys as well as archaeological bronze objects.

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