# Use of Discriminant Analysis of Data from the Fluorescence Spectometry Analysis of Archaeological Metal Artefacts

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## Abstract

This paper aims to present application of methods of mathematical statistics of performed on archaeological metal artefacts, in particular bronze ferrules dated to the period of Avar Khaganate (8<sup>th</sup>–9<sup>th</sup> century), which were found at burial site in the municipality of Obid, Slovakia. Based on the results of X-ray fluorescence spectrometry, which was applied for determination of the proportional content of chemical elements in archaeological metal findings, three types of bronze alloys were recognized that the ferrules were made of. In order to identify the ability of variables (chemical elements) to discriminate the bronze ferrule types and also in order to categorise the non-classified bronze ferrules in the three groups the method of canonical discriminant analysis was employed.

Keywords	JEL code
Bronze ferrules, discriminant analysis, X-ray fluorescence spectrometry, Avar bronze ferrules	C38, B19, Z13

# INTRODUCTION

X-ray fluorescence spectrometry of archaeological metal artefacts has been known for several decades. The objective of these analyses is to determine the composition of alloys and, thus, contribute to, *inter alia*, the understanding of the production technology of the historical artefacts. This issue has been addressed by many researchers, such as J. Condamin and S. Boucher (1973), J. Riederer and E. Briesse (1974), P. T. Craddock (1978), L. Költő (1982), J. Bayley (1985, 1989), F. Beck et al. (1988), J. Frána and A. Maštalka (1992), B. Tobias (2007), E. Horváth et al. (2009), P. Craddock et al, (2010) and N. Profantová (2010). Liritzis, I. and Zacharias, N. (2011) wrote about portable X-ray devices (PXRF) as instruments that

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are aligned along this leading research trend. Issues of performance and reliability of portable X-ray fluorescence (pXRF) instrumentation in archaeological investigations have been studied also by Goodale, N. et al. (2012) and Speakman, R. J. and Shackley, M. S. (2013).

Many of these researchers named the historical bronze or brass artefacts by their principal component, such as tin bronze, leaded bronze, tin lead bronze, leaded brass. In order to determine the chemical composition of historical artefacts the methods of non-destructive X-ray fluorescence analysis were applied.

In this paper we focused on the issue of employment of spectral analysis, more specifically the X-ray fluorescence, in investigation of bronze archaeological artefacts found at the burial site in Obid. In the analysis of the objects, classical names of alloys, namely bronze (copper alloy with tin) and brass (zinc copper alloy), were added along with the addition of other elements such as, for example, bronze containing lead, silver and zinc, respectively brass containing lead, tin, gallium. For the statistical evaluation of the bronze artefacts the method of discriminant analysis was applied.

#### **1 METHODOLOGY OF RESEARCH**

In 1963 supervised by Z. Liptáková and later on in 1981 till 1984 supervised by J. Zábojník an in-town archaeological investigations were conducted in the municipality of Obid, locality Fenyes árok. Their results are known solely from papers in the yearbook AVANS (Zábojník, 1982; 1983; 1984; 1985). Altogether 195 graves were excavated.

At the burial site dated to the period of Avar Khaganate various 8<sup>th</sup>-9<sup>th</sup> century artefacts were found, such as women's jewellery, parts of belts and decorative parts of horse harnesses. The composition of alloys that the artefacts had been made of was studied by means of fluorescence method. Since most of the findings were parts of bronze ferrules of belts (54 pieces), our analyses were focused on belt bronze ferrules. Analyses of the artefacts were performed in 2016 with the use of manual X-ray fluorescence spectrometer DELTA CLASSIC+ produced by Olympus, USA. DELTA CLASSIC + is an energy-dispersive X-ray fluorescence spectrometer used for the analysis of small objects or heterogeneous materials (detailed technical information: 4 watt RTG lamp with current up to 200 uA; detector: Si-PIN; integrated full VGA camera; the possibility of narrowing the X-ray beam from 9 to 3 mm).

One of the drawbacks is that the spectrometer DELTA CLASSIC + measures only the surface of the examined material and therefore the choice of the location of the measurements on the studied subject is very important. In the actual measurements it should be noted that if the material is gold-plated or otherwise surface-treated, the chemical composition may not correspond to the weight percentages of the whole artefact volume but only to the weight percentages of the measured surface layer at the measuring site. In addition, as far as the location of a measurement is concerned, the reliability and the calibration of the measuring instrument is also essential. This issue was studied in detail by Hunt, A. M. W. and Speakman, R. J. (2015). In our case, for measuring the content of chemical elements in the bronze ferrules, we used a hand-held X-ray fluorescence spectrometer DELTA CLASSIC +, which is calibrated annually by certified company Olympus Industrial Systems Europe, the Czech Republic.

The spectrometer was employed for determination of the proportional content of seven chemical elements (Cu, Sn, Pb, Zn, Ag, As and Ga) in each of the bronze ferrules. Based on the determined content of the elements the bronze ferrules were divided into three groups, i.e. we have created the following three types of bronze alloys which were recognized in the ferrules – tin bronze group (bronze alloy containing less than 5% of Pb), tin lead bronze ferrules (bronze alloy containing from 5 to 10% of Pb) and leaded bronze group (bronze alloy containing more than 10% of Pb). The first group of bronze ferrules is a bronze alloy containing lead and other elements that were probably a natural part of the copper ore or tin ore used for the alloy production. The other two groups consist of a bronze alloy with an intentional addition of lead in the manufacture of the casts of bronze Avar artefacts for their better formability.

Table 1         Mean proportional content of chemical elements (%)							
	Cu	Sn	Pb	Zn	Ag	As	Ga
Tin bronze	87.55	8.28	1.55	1.71	0.64	0.11	0.00
Tin lead bronze	72.06	18.16	7.07	1.90	0.73	0.00	0.00
Leaded bronze	69.17	14.73	13.26	1.09	0.73	0.11	0.69

For each group, the arithmetic mean of the proportional contents of each of the chemical elements was calculated (Table 1).

Source: Own construction

The mean proportional content of chemical elements in the three bronze alloy groups are also displayed in Figure 1.

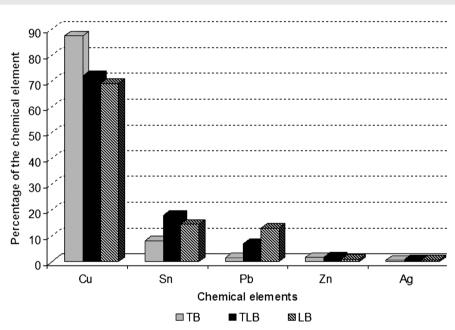


Figure 1 Mean proportional content of chemical elements in the three types of bronze alloys

Source: Own construction

As shown in Table 1 and Figure 1, each type of bronze alloy (tin bronze, tin lead bronze, and leaded bronze) contains different mean values of the chemical elements, which indicates that the proportional content of the elements varies in the three groups.

Our aim was to find a classification criterion for sorting bronze ferrules into the proposed three groups according to the chemical composition of these ferrules.

In order to verify the rightness of the categorization of the bronze ferrules in the three groups created by us the statistical method of discriminant analysis (DA) was used (Hebák, P., Hustopecký, J. et al., 2007). By means of DA the discriminative ability of the observed variables can be identified, and thus, the existing groups and the groups of statistical units of the population known in advance can

be discriminated. In addition, based on these variables it can be predicted which group a previously not categorized unit belongs to.

In DA, the process of classification follows various rules depending on the observed variables. An often used method is the canonical DA. By means of canonical DA it can be traced which variables (Cu, Sn, Pb, Zn or Ag) in the best way predict/determine the categorization of the bronze ferrules in the groups. The main idea and the procedure of the canonical DA application are described below.

Suppose that there are  $n_i$  statistical units (bronze ferrules) which are divided into K groups (K > 1), and for every unit the values of p quantitative variables  $X_{j}$ , j = 1, 2, ..., p were detected (in this case p = 5, the percentage of the chemical element (Cu, Sn, Pb, Zn and Ag) in the bronze artefact. Then, the  $i^{\text{th}}$  unit of the  $k^{\text{th}}$  group is characterized by the vector of values:

$$\mathbf{x}_{ki}^{T} = (x_{ki1}, x_{ki2}, ..., x_{kip}), \quad k = 1, ..., K.$$
(1)

In canonical DA in order to discriminate the groups we look for so-called canonical discriminant functions, which present linear combinations of the studied variables  $X_j$ , j = 1, 2, ..., p. First, we calculate the matrix expressing the within-group variability:

$$\mathbf{E} = \sum_{k=1}^{K} \sum_{i=1}^{n_k} \left( \mathbf{x}_{ki} - \overline{\mathbf{x}}_k \right) \left( \mathbf{x}_{ki} - \overline{\mathbf{x}}_k \right)^T$$
(2)

and the matrix expressing the between-group variability:

$$\mathbf{B} = \sum_{k=1}^{K} \sum_{i=1}^{n_k} \left( \overline{\mathbf{x}}_k - \overline{\mathbf{x}} \right) \left( \overline{\mathbf{x}}_k - \overline{\mathbf{x}} \right)^T,$$
(3)

where  $\overline{\mathbf{x}}_k$  is the vector of means in the  $k^{\text{th}}$  group and  $\overline{\mathbf{x}}$  is the vector of means of variables in the whole sample. The discriminant functions can be expressed as follows:

$$Y = v_1 x_1 + v_2 x_2 + \dots + v_p x_p.$$
(4)

The objective of the analysis is to find such a vector  $\mathbf{v}^T = (v_1, v_2, ..., v_p)$  that the ratio of the between-group and the within-group variability of the variable *Y* were the greatest possible, in other words, the discriminant function would discriminate the groups of statistical units in the best possible way. This ratio, denoted by *F*, is referred to as Fisher discriminant criterion and is expressed as follows:

$$F = \frac{\mathbf{v}^T \mathbf{B} \mathbf{v}}{\mathbf{v}^T \mathbf{E} \mathbf{v}}.$$
(5)

The solution (5) that maximizes values *F* are the eigenvalues of the matrix  $\mathbf{E}^{-1}\mathbf{B}$  and their corresponding eigenvectors  $\mathbf{v}_1, \mathbf{v}_2, ..., \mathbf{v}_r$ . The matrix  $\mathbf{E}^{-1}\mathbf{B}$  has *r* eigenvalues (nonzero), where  $r = \min(p, K - 1)$ . Suppose that eigenvalues arranged in descending order are  $\lambda_1, \lambda_2, ..., \lambda_r$ . Their corresponding eigenvectors  $\mathbf{v}_1, \mathbf{v}_2, ..., \mathbf{v}_R$  are not unique, since e.g. if  $\mathbf{v}_1$  is an eigenvector of the matrix  $\mathbf{E}^{-1}\mathbf{B}$ , then also  $a\mathbf{v}_1$  is an eigenvector of the matrix  $\mathbf{E}^{-1}\mathbf{B}$  for any real number *a*. If the eigenvector  $\mathbf{v}_1 = (\mathbf{v}_{11}, \mathbf{v}_{21}, ..., \mathbf{v}_p)$  is such that  $\mathbf{v}^T \mathbf{E} \mathbf{v} = 1$ , i.e. the within-group variability of the variable  $Y_1 = v_{11}x_1 + v_{21}x_2 + ... + v_{pr}x_p$  equals 1, then it holds that  $\lambda_1 = \mathbf{v}^T \mathbf{B} \mathbf{v}$ , i.e. the between-group variability of the variable  $Y_1$  equals the first eigenvalue. Consequently, if  $\mathbf{v}_1$  is such that the within-group variability of the variable  $Y_1$  equals 1, i.e.

$$\frac{1}{n-K}\mathbf{v}^T\mathbf{B}\mathbf{v} = 1,\tag{6}$$

then it holds that:

$$\lambda_1 = \frac{1}{n - K} \mathbf{v}^T \mathbf{B} \mathbf{v},\tag{7}$$

i.e. the within-group variability of the variable  $Y_1$  represented by the variance equals the first eigenvalue. Then, the total variance of the variable  $Y_1$  equals  $1 + \lambda_1$ . The function  $Y_1$  is referred to as the first discriminant or the first canonical variable. Analogously we calculate all the discriminant functions  $Y_1$ ,  $Y_2$ ,...,  $Y_R$ .

For every statistical unit (bronze ferrule) a so-called discriminant score can be computed when the values of variables found for this unit are taken for corresponding variables in the discriminant function which is further modified by such a constant that the mean discriminant score in the set of all units equals zero. Thus, the score of  $R^{th}$  discriminant variable for the  $i^{th}$  unit of the  $k^{th}$  group is computed by the following formula:

$$y_{kir} = -(v_{1r}\overline{x}_1 + v_{2r}\overline{x}_2 + \dots + v_{pr}\overline{x}_{p}) + v_{1r}x_{ki1} + v_2x_{ki2} + \dots + v_px_{kip},$$
(8)

where  $\overline{x}_j$  is the arithmetic mean of values of the  $j^{\text{th}}$  variable (j = 1, 2, ..., p) detected in all statistical units. For every group k (k = 1, 2, ..., K) the mean values  $\overline{x}_{k1}, \overline{x}_{k2}, ..., \overline{x}_{kp}$  for all p variables are calculated first, and these are then put into the canonical variables. This way we obtain the vector of mean values of discriminants for the group k, i.e. the vector of group centroids  $\overline{\mathbf{y}}_k^T = (\overline{y}_{k1}, \overline{y}_{k2}, ..., \overline{y}_{kR})$ . By comparison of the group centroids it can be found which groups are separated by the first discriminant function, which groups are discriminant etc.

The coefficient  $v_{jr}$  describes the individual effect of the  $j^{th}$  variable  $X_j$  on the  $r^{th}$  canonical variable  $Y_r$  (in case the rest of them are constant). It is preferable to have the variables  $X_1, X_2, ..., X_n$  standardized. In case the variables have not been previously standardized, the discriminants are standardized by the following formula:

$$\mathbf{v}_r^* = \frac{1}{\sqrt{n-K}} \mathbf{F} \mathbf{v}_r,\tag{9}$$

where **F** is a diagonal matrix, the non-zero elements in the diagonal being the square roots of the entries of the matrix **E**. In order to see which variable is characteristic for the  $r^{\text{th}}$  discriminant, the canonical correlation coefficient can be computed. The vector of the correlation coefficients of the canonical variable and variables  $X_1, X_2, ..., X_n$  is obtained by the formula:

$$\mathbf{r}_r = \frac{1}{\sqrt{n-K}} \mathbf{F}^{-1} \mathbf{E} \mathbf{v}_r \,. \tag{10}$$

Up to this point the DA was applied just to describe the between-group differences. Next, we focus on the question to what extent the particular variables affect the categorization, and whether it is necessary to use all of the variables for the discrimination purposes. Whether the chosen statistical method is suitable and which variables (Cu or Sn, Pb, Zn, Ag) are useful for discrimination of the groups, it is necessary to test the null hypothesis  $H_0$ : All eigenvalues equal zero, i.e. none of the discriminants is useful for discrimination of belt bronze ferrules groups.

The above mentioned hypothesis is equivalent to the hypothesis that the vectors of mean values corresponding to the discriminant functions are mutually equal in all *K* groups. To test the null hypothesis we can use Bartlett's statistic *V* which has  $\chi^2$  (*p*(*K*-1)) distribution and is obtained by the formula:

$$V = \left(\sum_{i=1}^{K} n_i - 1 - \frac{p+K}{2}\right)(-\ln\Lambda),$$
(11)

where  $\Lambda$  is Wilks statistic expressed as:

$$\Lambda = \prod_{i=1}^{r} \frac{1}{1+\lambda_i}.$$
(12)

Hypothesis is rejected at significance level  $\alpha$ , if V exceeds the critical value  $\chi_{1-\alpha}^2$ . If the hypothesis  $H_0: \lambda_1 = \lambda_2 = \ldots = \lambda_r = 0$ , is rejected, it means that there is at least one non-zero eigenvalue. In fact, it is the first to eigenvalue  $\lambda_1$ , since the eigenvalues are arranged in descending order, so the first of them is the greatest. Next, we proceed to test the other eigenvalues, testing, actually, the hypothesis  $H_0: \lambda_2 = \lambda_3 = \ldots = \lambda_r = 0$ , applying the testing statistics:

$$V = \left(n_{i} - 1 - \frac{p + K}{2}\right) \sum_{i=2}^{r} \ln(1 + \lambda_{i}),$$
(13)

which has  $\chi^2((p-1)(K-2))$  distribution. The test procedure runs until the hypothesis is rejected, i.e. until no non-zero eigenvalue remains. The hypothesis  $H_0: \lambda_1 = \lambda_2 = ... = \lambda_r = 0$  can be also tested by Rao's statistic *F* whose formula we do not present here. The test is used to determine the number of discriminatory functions that significantly separate the groups.

For a statistical unit the vector of discriminant scores is computed as well as Mahalanobis distance (Euclidean distance, as the canonical functions are not correlated) of this vector from the group centroid of each group by the formula:

$$d_{ik}^{2} = \sum_{r=1}^{P} (y_{ir} - \overline{y}_{kr})^{2}, \ k = 1, 2, ..., K ,$$
(14)

where  $y_{ir}$  is the  $r^{\text{th}}$  discriminant score of the  $i^{\text{th}}$  observation and  $\overline{y}_{kr}$  is the vector of the mean scores for the centroid. The statistical unit is then categorized in the group for which this distance is the smallest.

## 2 RESULTS AND DISCUSSION

Before using the discriminant analysis method, it is useful to verify the assumptions that the analyzed data must meet so that this method can be used. The assumptions of using discriminant analysis are:

- multivariate normality (it is assumed that data represent a sample from multivariate normal distribution),
- homogeneity of variances/covariances. (it is assumed that the variance/covariance matrices of variables are homogeneous across groups),
- multicollinearity (there must be no correlation between independent variables).

The assumptions of the multivariate normality were verified by the test of Henze-Zirklerovym IRR (Henze, B. and Zirkler, N., 1990) and the test of Royston (Royston, J. P., 1983) in the program R through the package IRR (Korkmaz, et al., 2014; R Core Team, 2017).

Based on the test of Henze-Zirkler's IRR the assumption of multivariate normality only in the group of the tin bronze was rejected and for the other two groups it was not rejected (tin bronze: HZ = 0.450 p = 0.420; leaded bronze: HZ = 0.680, p = 0.110; tin bronze: HZ = 1.730, p < 0.001).

Based on Royston's test the assumption of multidimensional normality in the tin bronze group was also rejected but in the other two groups, it was not be rejected (tin lead bronze: H = 1.570, p = 0.181; leaded bronze: H = 4.640, p = 0.062; tin bronze: H = 9.040, p = 0.005).

When checking one-dimensional normality, only one variable was problematic (Pb) and only in one group. Based on this fact, we consider the assumption of the multivariate normality as fulfilled.

Based on the result of Box's *M* test (M = 39.080, F = 5.770, p < 0.001), we reject the hypothesis about the equality of the variance-covariance matrix among the groups. The test is very sensitive for multivariate normal distribution. However, the logarithms of the determinants of covariance matrices for each group do not show a significant difference (tin lead bronze: log |D| = 4.670; tin bronze: log |D| = 3.790; leaded bronze: log |D| = 6.490), which indicates the non-breach of the variance-covariance matrices equality assumption.

Based on the values in the pooled within-groups matrix, we noted that in the data (if we consider all 5 original variables), there is multicollinearity caused by a pair of Cu and Sn variables (r = -0.910). The remaining correlations of the pairs of the variables are in the absolute value less than 0.400. However, if we consider that the stepwise procedure was the Cu variable eliminated in the DA and the DA was already realized with only a pair of variables Pb and Sn, which are uncorrelated (r = 0.030), we can conclude that the multicollinearity in the data is not present.

In our case we applied canonical discriminant analysis to analyze 54 pieces of bronze ferrules, observing 5 variables in each ferrule, i.e. the detected content of the percentage part of five chemical elements – copper (Cu), tin (Sn), lead (Pb), zinc (Zn), and silver (Ag), contained in the ferrules. Canonical discriminant analysis was carried out in the software STATISTICA. A stepwise method was used. Having set the input data, we received the following results (Table 2).

Table 2         Results of stepwise MANOVA				
Element	Wilks' Lambda	Partial Lambda	F test	<i>p</i> -value
Cu	0.149	0.999	0.002	0.998
Zn	0.147	0.982	0.457	0.636
Ag	0.146	0.973	0.681	0.511
Pb	0.712	0.210	94.070	0.000
Sn	0.175	0.857	4.204	0.020

Source: Own construction

In Table 2, the results are of the stepwise MANOVA in Table 2. The aim MANOVA was to find out which variables are unnecessary in the presence of other variables when separating groups. Based on the results shown in Table 2, we can see that the Cu, Zn and Ag variables do not contribute to the separation of the groups and therefore need to be excluded in the next analysis.

In further analysis of the bronze ferrules only those variables (Sn and Pb) were calculated by the discriminant analysis whose eigenvalues most contribute to the minimal value of the discriminative criterion, i.e. those variables which according to the results of the previous analysis discriminate the alloys in a significant way.

Table 3 Chi-square test of gradual roots						
	Eigenvalue	Canonical correlation R	Wilk's Lambda	Chi-square	df	<i>p</i> -value
0	4.928	0.912	0.150	95.948	4	0.000
1	0.128	0.337	0.887	6.074	1	0.014

Source: Own construction

The eigenvalues (Table 3) are computed as the ratio of between-group and within-group sums of squares. A high eigenvalue (4.928) corresponds to a strong discriminant function. Since the value of the canonical correlation coefficient is high (r = 0.912), the first discriminant function discriminates the groups well. Wilks lambda is the ratio of the within-group squares and the total sum of squares. Wilks lambda equals 1 if the group means for the first canonical variable whose the equivalence verify by this test. These group means are mutually equal; lambda is small if the group means are different.

The significance of the difference is expressed by the *p*-value. Since in this case p = 0.000, the group means are significantly different.

Next, the standardized coefficients of canonical discriminant functions for variables Pb and Sn were computed (Table 4).

Table 4         Coefficient of canonical discriminant function			
Variable	Root 1	Root 2	
Sn	-0.207	-0.979	
Pb	-0.972	0.240	
Eigenvalue	4.928	0.128	
Constant	2.346	1.271	
Sn	0.175	0.020	

Source: Own construction

Therefore, the obtained canonical discriminant functions are as follows:

for  $\lambda = 4.928$ 

 $Y_1 = -0.207 \text{ Sn} - 0.971 \text{ Pb} + 2.346,$ 

for  $\lambda = 0.127$ 

 $Y_2 = -0.979 \text{ Sn} - 0.240 \text{ Pb} + 1.271.$ 

On the bases canonical discriminant functions above we can see, that the Pb variable most contributes to the separation of groups in the direction of the first canonical discriminant function, whereas in the case of the second canonical discriminant function, it is the variable Sn. By these functions we can compute scores for every statistical unit, i.e. for every bronze ferrule.

Finally, applying the model of canonical DA we obtained the means of the discriminant scores of the objects in groups for the first and second canonical discriminant functions (Table 5). These numbers express the coordinates of the centroids in two-dimensional space of the canonical discriminant functions. Canonical functions represent the transformation of two-dimensional vectors determining particular variables into plane.

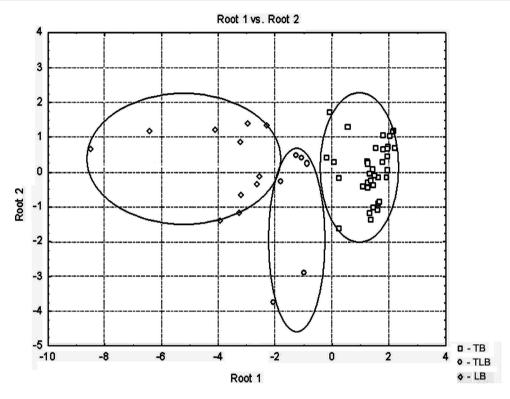
Table 5 Functions at Group Centroids

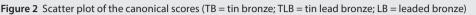
Groups	Root 1	Root 2
Tin bronze	1.386	0.075
Tin lead bronze	-1.354	-0.958
Leaded bronze	-3.923	0.270

Source: Own construction

The situation is displayed in the following scatterplot (Figure 2). Based on the scatterplot it can be decided if both discriminant functions contribute to the group discrimination, or whether one

of the functions is sufficient. As shown in the scatterplot, it suffices to apply one of the discriminant functions to discriminate the groups, and it discriminates in a very good way the groups, i.e. the alloys which the bronze ferrules were made of.





Source: Own construction

One of the well-known Czech archaeologists who were concerned with the statistical methods in archaeological research which are used to acquire, discover and explore various archeological structures, was professor Neustupný, E. (1993). Professor Neustupný in his study (Neustupný, E., 2005) describing the properties of archaeological artifacts, stated as one of the properties the localization of these artifacts in the space, and then he compared the results of the analysis with the reality. Our main goal was to find a classification criterion for classifying bronze ferrules into three groups only based on their chemical composition, not the spatial localization of the bronze ferrule findings. For illustration, we have plotted the occurrence of all the analyzed bronze ferrules in the map of the burial site Obid, Slovakia (Figure 3).

If we simultaneously consider the real occurrence of bronze ferrules (Figure 3) and the results obtained by the discriminant analysis (Figure 2), it can be observed that the spatial localization of the bronze ferrules is not closely related to the chemical composition of the ferrules. It can be explained by the fact that the bronze ferrules were found only in 11 graves out of the total 199 graves uncovered by the archaeological excavation. Furthermore, the bronze ferrules were placed unevenly in the site, in other words in some of the graves many more bronze ferrules were found than in other graves. The occurrence of a larger number of bronze ferrules

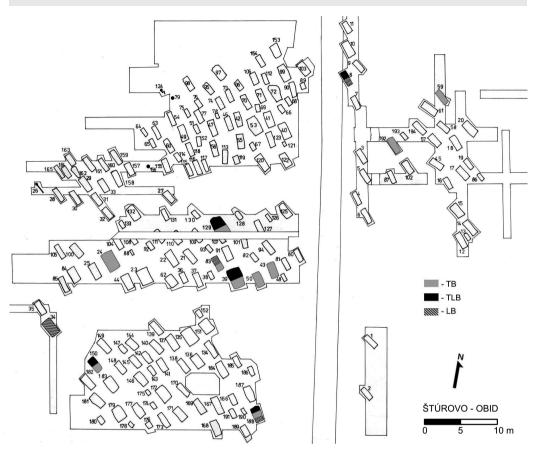


Figure 3 The occurrence of bronze ferrules in the map of the burial site Štúrovo-Obid (TB = tin bronze; TLB = tin lead bronze; LB = leaded bronze)

Source: Own construction

in the graves was usually related to the level of social layer the buried individual had belonged to. Nevertheless, certain group localization of the occurrence of individual types of bronze ferrules can be recognized.

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# CONCLUSION

Having employed the canonical discriminant analysis in processing the results of X-ray fluorescence spectrometry performed on bronze archaeological artefacts found at the burial site in Obid, Slovakia out

of seven observed chemical elements two elements, namely tin (Sn) and lead (Pb), with high discriminative ability were identified, i.e. these two alloy components in a significant way discriminate three types of bronze ferrules. The analysis confirmed that the proportional content of the two elements in bronze ferrules was characteristic for a particular type of bronze alloy. The discriminant functions obtained by means of the discriminant analysis enable us to calculate the score for every bronze ferrule, including ferrules which have not been previously categorized, and, thus, also to categorize them into groups according to the bronze alloy types. Based on the presented results we argue that in order to categorize bronze archaeological artefacts into one of the three groups according to the bronze alloy type it is sufficient to determine the proportional content of as few as two chemical elements, tin and lead.

The results of the presented archaeometric study confirmed, inter alia, the important role of the non-destructive analytical methods in archaeological interpretation of artefacts, their composition, origin of the raw material, and the production technology. In addition, the findings support the fact that the excavated burial site shows signs of social stratification via the contents of the graves. The objects found in the graves had been made of precious as well as common alloys, which indicate the economic level as well as the sophistication of the production technologies in the period society.

#### References

- BAYLEY, J. Analysis and examination of roman brooches from Tiddington, Warwks. Ancient Monuments Laboratory Report 85/89, London: Historic Buildings and Monuments Commission for England, 1989, 11 p. 01-973-3320.
- BECK, F., MENU, M., BERTHOUD, T., HURTEL, L-P. Me'tallurgiedes bronzes. In: HOIRS, J. eds. Recherches Gallo-Romaines I. Paris: Laboratoire de Recherches de Muse'es de France, 1985, pp. 70–139.
- CONDAMIN, J. AND BOUCHER, S. Recherches techniques sur des bronzes de Gaule Romaine. Gallia, 1973, 31, pp. 157-183.
- CRADDOCK, P. T. The composition of the copper alloys used by the Greek, Etruscan and Roman Civilizations 3. The origins and early use of brass. *Journal of Archaeological Science*, 1978, 5, pp. 1–16.
- CRADDOCK, P., COWELL, M., HOOK, D., HUGHES, M., LA NIECE, S., MEEKS, N. Change and stasis: the technology of Dark Age metalwork from the Carpathian Basin. British Museum Technical research bulletin, London, 2010, Vol. 4, pp. 55–65.
- FRÁNA, J. AND MAŠTALKA, A. Röntgenfluoreszenzanalyse von frühmittelalterlichen Bronzen aus Böhmen und Mähren. In: DAIM, F. Awarenforschungen II, Wien, 1992, pp. 779–801.
- GOODALE, N., BAILEY, D. G., JONES, G. T., PRESCOTT, C., SCHOLZ, E., STAGLIANO, N., LEWI, CH. pXRF: a study of inter-instrument performance. *Journal of Archaeological Science*, 2012, 39, pp. 875–883.
- HEBÁK, P., HUSTOPECKÝ, J., et al. *Vicerozměrné statistické metody* (Multivariate Statistical Methods). 2<sup>nd</sup> Ed. Prague: INFORMATORIUM, 2007, 236 p. ISBN 978-80-7333-056-9.
- HENZE, N. AND ZIRKLER, B. A class of invariant consistent tests for multivariate normality. Communications in Statistics. *Theory and Methods*, 1990, 19(10), pp. 3595–3617.
- HUNT, A. M. W. AND SPEAKMAN, R. J. Portable XRF analysis of archaeological sediments and ceramics. *Journal of Archaeological Science*, 2015, 53, pp. 626–638.
- KORKMAZ, S., GOKSULUK, D., ZARARSIZ, G. MVN: An R Package for Assessing Multivariate Normality. The R Journal, 2014, 6(2), pp. 151–162.
- KÖLTŐ, L. Avar kori bronztárgyak röntgenemissziós analízise (X-ray emission analysis of bronze objects from the Avar Age). SMK, 5/1, 1982, pp. 5–68.
- LIRITZIS, I. AND ZACHARIAS. N. Portable XRF of archaeological artifacts: current research, potentials and limitations. X-ray fluorescence spectrometry (XRF) in geoarchaeology. New York: Springer, 2011, pp. 109–142.
- NEUSTUPNY, E. Archaeological method. Cambridge University Press, 1993.
- NEUSTUPNÝ, E. Syntéza struktur formalizovanými metodami-vektorová syntéza. Příspěvky k archeologii, 2005, 2, pp. 127-152.
- PROFANTOVÁ, N. Awarische Funde in der Tschechischen Republik. Forschungsstand und neue Erkenntnisse, Acta archaeologica Carpathica, 2010, 45, pp. 203–270.
- R CORE TEAM. R: A language and environment for statistical computing. R Foundation for Statistical Computing. Vienna, Austria, 2017. <a href="https://www.R-project.org">https://www.R-project.org</a>>.
- ROYSTON, J. P. Some techniques for assessing multivariate normality based on the Shapiro-Wilk W. Applied Statistics, 1983, 32(2), pp. 121–133.
- RIEDERER, J. AND BRIESE, E. Metallanalysen römischer Gebrauchsgegenstände. Jahrbuch des Römisch-Germanischen Zentral Museums Mainz, 1974, 19, pp. 83–88.

- SPEAKMAN, R. J. AND STEVEN, M. S. Silo science and portable XRF in archaeology: a response to Frahm. *Journal of Archaeological Science*, 2013, 40, pp. 1435–1443.
- TOBIAS, B. Néhány érdekes tárgy a Zillingtal-Unterer Kapellenberg D 41. Sírból. Csatfibulák és ecsetek. Arch. Ért., Budapest, 2008, 132, pp. 325–341.
- ZÁBOJNÍK, J. Výskum slovansko-avarského pohrebiska v Štúrove-Obide (Research of the Slavonic-Avars burial ground in Štúrovo-Obid). AVANS 1981, publ. 1982, pp. 305–308.
- ZÁBOJNÍK, J. Výskum pohrebiska a sídliska z doby avarskej ríše v Štúrove-Obide (The research of the burial ground and settlement from the period of the Avarian Empire in Štúrovo-Obid). AVANS 1982, publ. 1983, pp. 261–264.
- ZÁBOJNÍK, J. Tretia sezóna výskumu pohrebiska a sídliska z obdobia avarskej ríše v Štúrove-Obide (The third season of burial research and settlement from the period of the Avarian Empire in Štúrovo-Obid). AVANS 1983, publ. 1984, pp. 225–227.
- ZÁBOJNÍK, J. Výskum pohrebiska a sídliska z obdobia avarského kaganátu v Štúrove-Obide (The research of the burial ground and settlement from the period of the Avarian Caganate Štúrovo-Obid). AVANS 1984, publ. 1985, pp. 257–259.