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Analysis of antique bronze coins by Laser Induced Breakdown Spectroscopy and multivariate analysis

M. Orlić Bachler^a, M. Bišćan^b, Z. Kregar^{b,1}, I. Jelovica Badovinac^{c,d}, J. Dobrinić^e, S. Milošević^b

^a Zagreb University of Applied Sciences, Avenija Većeslava Holjevca 15, HR-10000 Zagreb, Croatia
^b Institute of Physics, Bijenička 46, HR-10000 Zagreb, Croatia
^c University of Rijeka, Department of Physics, Radmile Matejčić 2, HR-51000 Rijeka, Croatia
^d Centre for Micro and Nano Sciences and Technologies, Radmile Matejčić 2, HR-51000 Rijeka, Croatia
^e University of Rijeka, Faculty of Engineering, Vukovarska 58, Rijeka, Croatia

Abstract

This work presents a feasibility study of applying the Principal Component Analysis (PCA) to data obtained by Laser-Induced Breakdown Spectroscopy (LIBS) with the aim of determining correlation between different samples. The samples were antique bronze coins coated in silver (follis) dated in the Roman Empire period and were made during different rulers in different mints. While raw LIBS data revealed that in the period from the year 286 to 383 A.D. content of silver was constantly decreasing, the PCA showed that the samples can be somewhat grouped together based on their place of origin, which could be a useful hint when analysing unknown samples. It was also found that PCA can help in discriminating spectra corresponding to ablation from the surface and from the bulk. Furthermore, Partial Least Squares method (PLS) was used to obtain, based on a set of samples with known composition, an estimation of relative copper concentration in studied ancient coins. This analysis showed that copper concentration in surface layers ranged from 83% to 90%.

Keywords: LIBS, Laser ablation, Principal Component Analysis, Partial Least Squares, Bronze coins

1. Introduction

Studying the element content of ancient coins is important, among other things, since the concentration of silver or gold provides an insight in economy of the historical period, while exploration of copper alloy coins is important for numismatics and broader aspects of history of economy, such as exploitation of resources and transfer of technology. Determining element content of samples may provide answers to several other questions, such as whether the present element content of coins is equal to the original content at the time of production. Sample surface content may be modified due to influence of corrosion, storage environmental conditions or impact of modern conservation methods. It is not likely that after hundreds of years of exposure to aggressive environment the surface element content will correspond to the bulk element content, the more so, it may be completely different. Therefore, in order to learn about the ancient world, its economy, technology and society, it is necessary to define composition of alloys used at the time of their production. This is only possible by using

^{*}Corresponding author: Tel., +385 14698851

Email address: mbiscan@ifs.hr (M. Bišćan)

¹Present address: DG Environment Unit C3, European Commission, Brussels, Belgium

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