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PIXE analysis of medieval silver coins

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ABSTRACT

We applied the proton-induced X-ray emission (PIXE) analytical technique to twenty-eight medieval silver coins, selected from the Tunisian treasury. The purpose is to study the fineness evolution from the beginning of the 7th to the 15th centuries AD. Each silver coin was cleaned with a diluted acid solution and then exposed to a 3 MeV proton beam from a 1.7 MV tandem accelerator. To allow the simultaneous detection of light and heavy elements, a funny aluminum filter was positioned in front of the Si(Li) detector entrance which is placed at 135° to the beam direction. The elements Cu, Pb, and Au were observed in the studied coins along with the major component silver. The concentration of Ag, presumably the main constituent of the coins, varies from 55% to 99%. This significant variation in the concentration of the major constituent reveals the economical difficulties encountered by each dynasty. It could be also attributed to differences in the composition of the silver mines used to strike the coins in different locations. That fineness evolution also reflects the poor quality of the control practices during this medieval period. In order to verify the ability of PIXE analytical method to distinguish between apparently similar coins, we applied hierarchical cluster analysis to our results to classify them into different subgroups of similar elemental composition.

1. Introduction

Since 1953, several atomic and nuclear techniques have been developed and applied to the non-destructive elemental analysis of archaeological artifacts [1–3]. During the 1960s and 70s, the development of solid-state detectors [4], proton activation analysis (PAA) method [5] and ion beam analysis (IBA) techniques (mainly particle-induced X-ray emission (PIXE), particle-induced γ-ray emission (PIGE), and Rutherford backscattering (RBS)) allowed growth of manufacturing and origin technologies for archaeological materials [6–10]. Nowadays, expansion of new research areas in archeometry is noted [11–14] and new methods are established to improve artifacts analysis. Jamieson et al. [15] proposed combinative method of PIXE, nuclear elastic backscattering spectrometry (BS), channeling contrast microscopy (CCM), and secondary electron microscopy to image the structural and elemental composition of materials and to get, from the images, reliable quantitative information about materials.

Ancient coins are often struck with a well-controlled alloy by a known mint with a date of issue and so, for most of them, references can be found in ancient documents dealing about their typology, metrology and chronology. Nevertheless, cases exist where the lack of written documentation brings obscurity to numismatists. For the investigation of such “obscure” ancient coins PIXE is very attractive: it combines interesting analytical capabilities together with a non-destructive character. The PIXE method makes possible to analyze simulta-

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neously a great number of elements (from sodium to uranium) in a wide concentration range. Ehrhardt et al. [16] used PIXE to determine the elemental compositions of artifacts and stated that PIXE application contributes strongly to identify related manufacturing techniques and technical processes employed. However, when applied to corroded coins without sample preparation, the accuracy of PIXE results can be affected [17–19]. It is because PIXE method has the disadvantage of low penetration depths (the penetration range of 2.5–3.0 MeV protons is about 30 μm) [20]. If ancient silver coins are adequately cleaned and possible enriched layer is removed, the study of their chemical composition with PIXE technique will bring a real success to determine their fineness and to provide valuable information about the economy of the time of their minting [21]. It was demonstrated that, if six cited experimental conditions [20] are carefully controlled, PIXE appears a very promising method and the suitable one for determining ancient silver coins fineness.

In this work, we applied the PIXE technique to study twenty-eight Tunisian silver coins, called "Islamic dirhams" (a unit of currency in several Arab nations) [22], belonging to six successive dynasties from the beginning of the 8th century (Umayyad dynasty 702–748 AD) until the 16th century (Hafsid dynasty 1230–1574 AD). According to Islamic law, the Islamic dirham has a specific weight of pure silver equivalent to 3.0 g, nevertheless, there were many silver coins produced before 1468 AD which were issued in different weights [23]. The coins were supplied from the treasury collection of the numismatic museum of Tunisia, and were chosen to cover a large medieval minting period. We indicated in Table 1 the name and the period of the dynasty from which each group of coins is issued. The PIXE spectra of all the analyzed coins were proceeded with the well known GUPIX [24] software (Fig. 1).

Table 1 – Characteristics of the twenty-eight analyzed silver coins.

Coin ref.	Dynasty	Period (A.D)	Mass (g)	Shape	Dimension (mm)
U1	Umayyad	702–748	2.87	Disc	13<r<14
U2			2.69		
A1	Abbasid	775–833	2.96	Disc	13<r<14
A2			2.83		
F1	Fatimid	909–975	2.25	Disc	7<r<10
F2			1.68		
F3			1.39		
F4			1.16		
F5			1.67		
F6			1.37		
Z1	Zirid	975–1159	1.45	Disc	8<r<9
Z2			1.41		
Z3			1.39		
Z4			1.14		
Z5			1.33		
Z6			1.30		
M1	Mowahid	1159–1230	1.50	Square	14<l<15
M2			1.53		
M3			1.52		
M4			1.53		
M5			1.54		
M6			1.52		
H1	Hafsid	1230–1574	1.45	Square	14<l<15
H2			1.29		
H3			1.52		
H4			1.52		
H5			1.52		
H6			1.34		

In this paper, we present the obtained results and we determine the fineness evolution during the medieval period, ranging from 702 to 1574 AD, and deduce the difficult economical situation of the country encountered during successive dynasties. Also we introduce here our hierarchical cluster analysis, using Stat-Graphics [25] program, to classify our studied coins into groups of similar elemental composition.

2. Experimental Setup

For fear of silver surface enrichment of silver–copper alloys caused by suspect cleaning procedures, different kinds of harmless cleaning protocols were adopted. Hence, our coins were first immerged in a highly diluted acid solution for about 5 h and then washed in distilled water. Dirt layers on the surface were thereby removed. The coins were then subjected to PIXE analysis.

According to Beck et al. [26], this cleaning procedure may induce silver surface enrichment causing a limitation for the

Fig. 1 – Six groups of medieval silver coins supplied from the treasury collection of the numismatic museum of Tunisia.