Analysis of Catalonian silver coins from the Spanish War of Independence period (1808–1814) by Energy Dispersive X-ray Fluorescence

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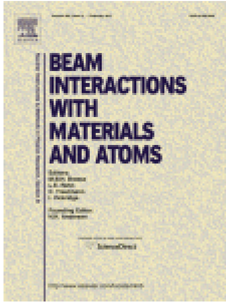

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Abstract

Between the years 1808 and 1814, the Spanish War of Independence took place. This period, locally known as “Guerra del Francès”, generated the need for money and consequently five mints were opened around the Catalan territory. To mark the 200th anniversary of the beginning of the war, an extensive campaign of Energy Dispersive X-ray Fluorescence measurements of some of these “emergency coins” was carried out. Apart from the silver (major constituent of all the studied coins) it has been possible to recognize copper as main metal alloying element. Likewise, the presence of zinc, tin, lead, gold, platinum, antimony, nickel and iron has been also identified. The obtained results have been useful not only for the characterization of the alloys, but also to determine the differences and analogies between the emissions and for historical explanations.

Introduction

Energy Dispersive X-ray Fluorescence (EDXRF) has become a very relevant tool to study the chemical composition of Cultural Heritage materials since it is a non-destructive, fast and multielemental technique which analyses the surface layer of samples and determines qualitatively and semi-quantitatively the major, minor and trace elements [1–4]. In recent years, numerous authors have pointed out the suitability of this technique in providing information from objects of all sizes and forms [5–7]. In the particular field of numismatics, EDXRF has been extensively applied [8–11] since the relationship between the chemical composition of the alloys, the economic features of the mintage period and the differences between mint factories are subjects of interest for archaeologists and historians. The possibility of distinguishing between original and counterfeit coins is another application of this technique [11–14]. It is certain that these kind of metallic objects are usually covered by corrosion layers, but when the corrosion layer is thin enough [15,16] or there is no alteration on the surface, EDXRF can be used without any sample surface pre-treatment (such as polishing, scrapping off, etc.). The obtained data allows us to identify the type of alloy employed in the manufacturing process used for the silver production and its main distinctive features.

In this work a total of 130 coins belonging to the Spanish War of Independence collection of the Catalonian Numismatic Department (GNC) at the National Museum of Fine Arts of Catalonia (MNAC) have been examined.

1.1. Historical context

The type of coins we studied in this investigation was minted during the War of Spanish Independence. The city of Barcelona was occupied by the French from February 1808 till the end of the war in May 1814. During the French occupation, due to the lack of coinage, the Barcelona mint was reopened. In line with these events, on June 18th 1808 the Superior Committee of the Principality was created (a body that coordinated the defence of Catalonia against Napoleon’s armies). This committee allowed some cities in the Principality, the ones not occupied by the French, to mint emergency coinage in the years 1808 and 1809. Thus, Girona, Lleida, Tarragona and Tortosa minted the so-called “duros” (silver coins equivalent to five pesetas, being peseta the coin unit for Spain territory), just to satisfy the financial necessity generated by the war. The simplicity of the manufacture reflects the precarious nature of the available means to manufacture [17].

During that period, plundering dynamics were promoted in order to obtain the raw metal to mint coinage, thus causing huge loss, plunder, thefts and destruction of the cultural and artistic heritage [18,19]. In this way, the silver was obtained from different silvery sources, not only from civil productions (such as tableware, chalices or candelabrum) but also from religious works (such as silver sculptures or liturgical objects). They all were brought to the mint and then melted.

Taking into consideration the historical context, the general objectives of this paper were the characterization of the type of alloy used for the manufacture of the coins and the determination of differences and analogies between the different emissions using EDXRF.

2. Materials and methods

2.1. Sampling

The major requirement for this analytical campaign was the ability to perform *in situ* non-destructive measurements, due to the value of the coins and the rules preventing their transport to the X-ray laboratory. The analysis, then, have been carried out after bringing the EDXRF equipment to the National Museum of Fine Arts of Catalonia (MNAC). The coins for analysis came from the five different mints existing in Catalonia during this period and can be easily identified by the illustration and images of the coin surface.

An extensive campaign of EDXRF measurements took place, with a very large number of medieval silver coins that circulated during the Spanish War of Independence period investigated. A total of 130 coins, see Table 1, have been examined. The coins were analyzed directly in a non-destructive way and without applying any cleaning treatment. In order to avoid possible surface heterogeneities, two EDXRF measurements, one for each side of the coin, were performed on the flat bright regions of all the coins. This method of measurements has been previously reported in other works [20–22].

Table 1. Main features of the analyzed coins.

Mint	Typology	Reference	Number of samples
Barcelona	5 pesetas	0021–013787	68
Girona	Duro	1242–032393	19
Lleida	5 pesetas	1256–013779	9
Tarragona	5 pesetas	1270–040723	20
Catalonia	8 rals	1298–037670	14

2.2. Experimental

Energy Dispersive X-ray Fluorescence spectroscopy was used to analyse the elemental composition of coins. The instrument consisted of a FISCHERSCOPE® X-RAY XAN spectrometer (Helmut Fischer GmbH, Germany), equipped with a micro focus tungsten X-ray tube (operating at 10, 30 or 50 kV and at maximum intensity of 1 mA), a Si-Pin detector with 180 eV of resolution at Mn Kα energy, several filters to improve peak/background ratio and four X-ray beam collimators (0.2, 0.6, 1 and 2 mm in diameter). According to a previous work [23] and taking into account the particular features of our samples, the analyses were carried out using a nickel primary filter to avoid tungsten signal from tube and 100 s of acquisition time, allowing a relative standard deviation lower than five percent for the main part of elements of interest. Moreover, we used a collimator of 2 mm in diameter to adjust the X-ray focal spot in order to better irradiate the surface of the coins.

The spectral data treatment (processing and quantification) is described elsewhere [23]. The quantification limits, Table 2, were calculated using the data obtained from the analysis of fourteen certified pure metals (from silicon to lead) used as reference materials. The results have been interpreted through typical multivariate statistic methods such as principal component analysis (PCA).

Table 2. Quantification limits.

Ag	Cu	Zn	Sn	Pb	Au	Ni	Fe
0.10%	0.03%	0.03%	0.20%	0.13%	0.14%	0.03%	0.04%

3. Results and discussion

The analyzed coins were found to have a very high fineness. The average concentrations of silver (main constituent of the alloy) and copper in each group of coins are very close to each other and, respectively, are around 93% for silver and around 6% for copper. The Cu can be considered as base alloying metal. Additionally, the presence of minor constituents (0.1–1%) and trace elements (less than 0.1%) such as zinc, tin, lead, gold, platinum, antimony, nickel and iron has been identified. Minor and trace elements impurities can be due to: (a) the raw metal used in coin production, (b) the manufacturing process and, (c) in some coins could be from surface contamination [21].

If we focus our attention in the compositional analysis of each mint, Table 3, we can clearly see that an approximate average silver content of 95% and about 4.5% for copper is recorded in Barcelona mint. The average silver concentration found for the coins minted in the Catalonia workshop is 95% and a 4% of copper. Regarding the other mints, Lleida, Girona and Tarragona, although in general they present a high Ag content, coins from Girona mint have a lower Ag content (the average content is about 91.7%), which implies an increase of the copper proportion (average content about 7.6%). Likewise, the Cu content of this mint has the lowest coefficient of variation of all the groups, thus revealing that the level of copper is not by chance but probably an addition to the melting batch.

Table 3. Elemental concentration of the examined coins from different mints (%wt) .

Barcelona	Ag	Cu	Zn	Sn	Pb	Au	Pt	Sb	Ni	Fe
n	68	68	68	18	68	68	68	52	68	68
min.	91.40	2.02	0.05	0.02	0.07	0.08	0.02	0.01	0.01	0.00

Barcelona	**Ag**	**Cu**	**Zn**	**Sn**	**Pb**	**Au**	**Pt**	**Sb**	**Ni**	**Fe**
max.	97.30	8.40	0.30	0.42	0.32	0.43	0.10	0.40	0.13	0.27
mean	94.95	4.45	0.12	0.12	0.18	0.19	0.05	0.17	0.06	0.08
stdesv.	1.33	1.42	0.05	0.12	0.05	0.06	0.02	0.11	0.03	0.05
C.O.V.	1.4	31.9	39.0	95.4	30.8	32.4	35.2	65.7	44.6	62.4
Catalonia										
n	13	13	13	5	13	13	13	13	13	13
min.	93.50	2.63	0.02	0.05	0.09	0.02	0.04	0.01	0.01	0.02
max.	96.40	5.75	0.44	0.18	0.30	0.40	0.09	0.41	0.08	0.19
mean	94.94	4.23	0.16	0.09	0.20	0.21	0.06	0.22	0.05	0.07
stdesv.	0.91	0.91	0.11	0.05	0.06	0.11	0.01	0.13	0.02	0.05
C.O.V.	1.0	21.5	72.4	57.7	27.4	51.4	19.4	58.0	40.4	76.1
Lleida										
n	9	9	9	2	9	9	9	8	9	8
min.	91.50	3.07	0.07	0.04	0.12	0.09	0.01	0.08	0.02	0.03
max.	96.20	7.11	0.24	0.19	0.47	0.66	0.10	0.33	0.12	0.47
mean	94.14	5.06	0.15	0.11	0.25	0.22	0.07	0.14	0.07	0.09
stdesv.	1.65	1.49	0.05	0.11	0.10	0.17	0.03	0.08	0.03	0.15
C.O.V.	1.8	29.4	31.7	94.1	38.2	78.9	41.4	58.0	48.8	162.3
Girona										
n	18	18	18	4	18	18	18	13	18	18
min.	89.30	5.34	0.09	0.02	0.19	0.14	0.02	0.02	0.04	0.02
max.	93.90	9.62	0.26	0.13	0.53	0.41	0.09	0.45	0.14	0.89

Barcelona	Ag	Cu	Zn	Sn	Pb	Au	Pt	Sb	Ni	Fe
mean	91.68	7.55	0.17	0.07	0.30	0.20	0.06	0.13	0.09	0.10
stdesv.	1.11	1.22	0.05	0.05	0.08	0.06	0.02	0.12	0.03	0.20
C.O.V.	1.2	16.2	26.9	68.3	27.0	29.6	32.6	89.8	28.3	188.7
Tarragona										
n	17	17	17	3	17	17	17	15	17	17
min	90.00	3.45	0.15	0.02	0.12	0.01	0.02	0.00	0.05	0.01
max	95.30	9.26	0.31	0.21	0.43	0.32	0.09	0.21	0.13	0.12
mean	92.10	7.25	0.20	0.10	0.26	0.12	0.06	0.10	0.08	0.06
stdesv	1.49	1.49	0.05	0.10	0.09	0.07	0.02	0.06	0.02	0.03
C.O.V.	1.6	20.5	23.1	99.8	32.8	59.4	32.1	61.3	27.8	47.2

In order to identify clustering concerning the five mint factories, a statistical analysis by means of multivariate statistical methods (principal components analysis) has been performed with the software package SPSS Statistics 17.0. In this particular case, the PCA analysis has been restricted to minor and trace elements because, according to the data present in Table 3, they have a high C.O.V. The Catalan coins of the five different mints show similar trends in their composition, which clearly evidence the regularity of the manufacturing process, so that by using PCA statistical routine no significant clustering has been obtained concerning the minor and trace constituents of the alloy. As shown in Fig. 1 (a scatter plot of the coins of mints of Barcelona, Catalonia, Lleida, Tarragona and Girona) once the factor analysis is applied, an overlap of the samples is observed, which does not allow us to distinguish the five mints between them. Once more it is demonstrated the sophisticated and controlled technology used by all the different mint in Catalonia region.

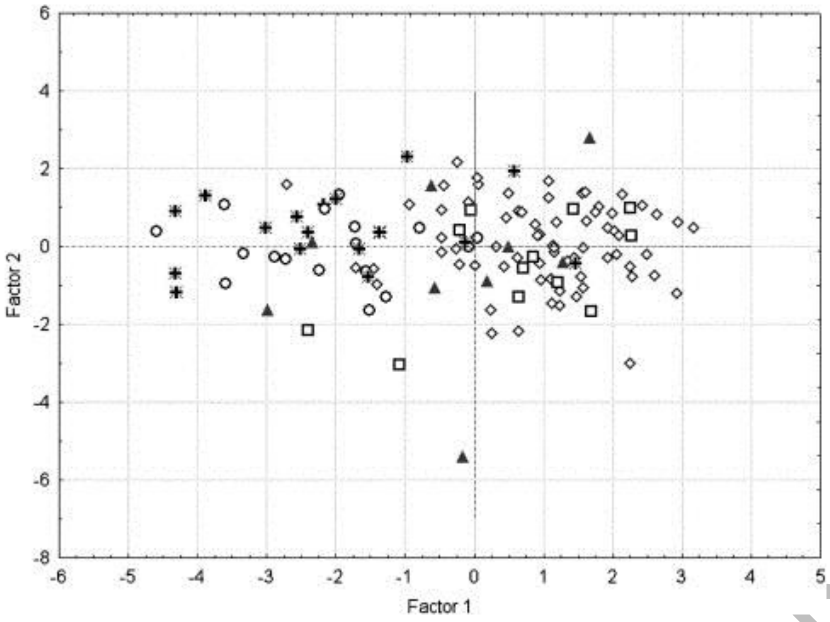

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Fig. 1. Scatterplot of factor 1 vs. factor 2 of some of the coins from different mints. 5 pessetes from the mint of Barcelona are represented by rhombus; 8 rals from the mint of Catalonia are shown by squares; duros from the mint of Girona are represented by circles; 5 pessetes minted in Lleida are shown by triangles and 5 pessetes from the mint of Tarragona are represented by stars.

During this period (1809–1814) the craftsmen were able to produce alloys of great precision. According to Estrada-Rius [24], the determination of the assay value was a constant concern during all the process and was carried out at the same time and twice by the two assayers in the mint. Equally, the metal weight was controlled after every transformation process. This could be an explanation for the lack of significant compositional variations between the alloys in the different mints.

Nevertheless, some little differences are observed regarding the Ag/Cu and Ag/Pb ratios, especially between the Catalonia and Girona mints. Concerning the silver and copper contents of the coins, the results in Fig. 2 show that all the groups of coins which belong to different mints are made of a similar Ag–Cu alloy. The logical strong negative correlation between Ag and Cu indicates the binary composition of silver-based coins and the deliberate controlled addition of this last metal in the batch used for the manufacturing of the coins. Copper has been added to debase the silver coins and save the more expensive silver or to increase the strength, hardness and wear-resistance of silver [20–21,25]. On the other side, if we focus our attention in the silver and lead contents of the coins, Fig. 3, we can clearly see that there is a low degree of correlation between Ag and Pb. The presence of Pb, then, is totally random and it could be explained not only for the metallurgic process of the obtaining of silver but also for manufacturing process of the coins.

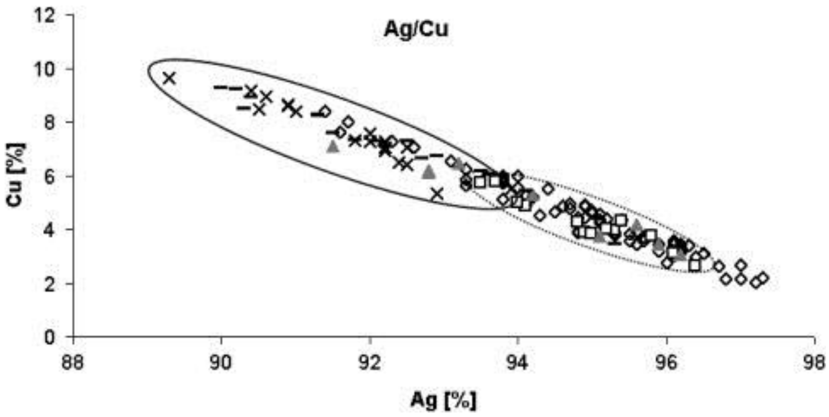

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Fig. 2. Silver and copper contents of the coins from different groups. 5 pessetes from the mint of Barcelona are represented by rhombus; 8 rals from the mint of Catalonia are shown by squares; duros from the mint of Girona are represented by crosses; 5 pesetas minted in Lleida are shown by triangles and 5 pesetas from the mint of Tarragona are represented by hyphens.

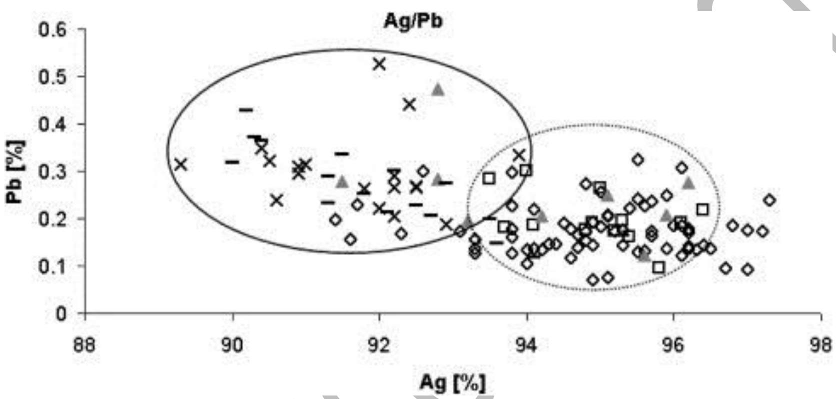

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Fig. 3. Silver and lead contents of the coins from different groups. 5 pesetas from the mint of Barcelona are represented by rhombus; 8 rals from the mint of Catalonia are shown by squares; duros from the mint of Girona are represented by crosses; 5 pesetas minted in Lleida are shown by triangles and 5 pesetas from the mint of Tarragona are represented by hyphens.

4. Conclusions

From the above results, the subsequent conclusions may be drawn. First, the results of EDXRF analyses of this Catalan coins collection exhibit a great uniformity of the elemental chemistry of its alloys from different workshops. The high *silver* content indicates the high quality control of the manufacturing process of these Catalan coins. Zinc, tin, lead, gold, platinum, antimony, nickel and iron were the minor or trace constituents of the alloy. Second, despite the fact that the mints were under the control of different authorities (The Barcelona mint operated under the commandment of Joseph Bonaparte and Catalonia, Lleida, Girona and Tarragona mints worked under the direction of the Superior Committee of the Principality), and that on the numismatic point of view there are strong differences not only for its weight but also for its style, according to the EDXRF results we can affirm that there are no compositional differences between the alloys of the five mints. However, the average silver content of Girona mint is slightly lower than the other mints, especially than the Catalonia mint. This tendency allows us to differentiate, on the compositional point of view, the coins from both mints. Finally, the non-destructive direct analyses of ancient coins by means of EDXRF could be a very useful tool for the investigation of alloys. Always keeping in mind the limitations of the technique, coins can be examined in a non-destructive way for a general screening, contributing to significant data useful for historical explanations.

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References

- [1] M.F. Guerra **Analysis of archaeological metals. The place of XRF and PIXE in the determination of technology and provenance** X-ray Spectrom., 27 (1998), pp. 73-80
  CrossRefView Record in Scopus
- [2] K. Janssens, G. Vittiglio, I. Deraedt, A. Aerts, B. Vekemans, L. Vincze, F. Wei, I. Deryck, O. Schalm, F. Adams, A. Rindby, A. Knöchel, A. Simionovici, A. Snigirev **Use of microscopic XRF for non-destructive analysis in art and archaeometry**. X-ray Spectrom., 29 (2000), pp. 73-91
  CrossRefView Record in Scopus
- [3] K. Janssens, R. Van Grieken **Preface**
  K. Janssens, R. Van Grieken (Eds.), Non-destructive microanalysis of cultural heritage materials, Wilson and Wilson's, comprehensive analytical chemistry, vol. XLII, Elsevier (2004), pp. 1-10
- View Record in Scopus
- [4] A. Gianoncelli, G. Kourousias**Limitations of portable XRF instruments in evaluating depth information: an archaeometric perspective**. Appl. Phys. A, 89 (2007), pp. 857-863
  CrossRefView Record in Scopus
- [5] M. Manso, M. Costa, M.L. Carvalho**X-ray fluorescence spectrometry on paper characterization: a case study on XVIII and XIX century documents**, Spectrochim. Acta Part B, 63 (2008), pp. 1320-1323
  ArticleDownload PDFView Record in Scopus
- [6] L. de Viguerie, V. Armando Sole, Philippe Walter **Multilayers quantitative X-ray fluorescence analysis applied to easel paintings**. Anal. Bioanal. Chem., 395 (2009), pp. 2015-2020
  CrossRefView Record in Scopus
- [7] A. Guilherme, S. Pessanha, M.L. Carvalho, J.M.F. dos Santos, J. Coroado **Micro energy dispersive X-ray fluorescence analysis of polychrome lead-glazed Portuguese faiances**. Spectrochim. Acta Part B, 268 (10) (2010), pp. 328-333
  ArticleDownload PDFView Record in Scopus
- [8] Zs. Sándor, S. Tölgyesi, I. Gresits, Zs. Kasztovszky **Determination of the alloying elements in ancient silver coins by X-ray fluorescence**. J. Radioanal. Nucl. Chem., 254 (2) (2002), pp. 283-288

CrossRefView Record in Scopus

- [9] R. Linke, M. Schreiner, G. Demortier**The application of photon, electron and proton induced X-ray analysis for the identification and characterization of medieval silver coins**. Nucl. Instrum. Methods B, 226 (1-2) (2004), pp. 172-178
ArticleDownload PDFView Record in Scopus
- [10] V. Vijayan, T.R. Rautray, D.K. Basa**EDXRF study of Indian punch-marked silver coins**. Nucl. Instrum. Methods Phys. Res. B, 225 (2004), pp. 353-356
ArticleDownload PDFView Record in Scopus
- [11] B. Constantinescu, R. Bugoi, E. Oberländer-Târnoveanu, K. Pârvan **Some considerations on X-ray fluorescence use in museum measurements – The case of medieval silver coins**. Rom. Rep. Phys., 57 (4) (2005), pp. 1021-1031
View Record in Scopus
- [12] B. Constantinescu, V. Cojocaru, R. Bugoi, Towards a more objective approach in numismatics research using compositional analyses based on nuclear methods, publication of the muzeul national de istorie a romanei. periodice. Cercetari numismatice. Numismatica medievala, 09-2005.
- [13] I. Queralt, A. Morer, A. Estrada-Rius, Analysis of Catalonian Medieval silver coins by means of XRF techniques, TECHNART 2007: Non-destructive and Micro analytical Techniques in Art and Cultural Heritage Research, Lisbon, 25–28 April 2007, book of abstracts, p. 40.
- [14] B. Constantinescu, R. Bugoi, E. Oberländer-Târnoveanu, K. Pârvan **Medieval silver coins analyses by PIXE and ED-XRF techniques**. Rom. J. Phys., 54 (5–6) (2009), pp. 481-490
View Record in Scopus
- [15] A.G. Karydas, D. Kotzamani, R. Bernard, J.N. Barrandon **Ch. Zarkadas, A compositional study of a museum jewellery collection (7th–1st BC) by means of a portable XRF spectrometer**. Nucl. Instrum. Methods Phys. Res. B, 226 (2004), pp. 15-28
ArticleDownload PDFView Record in Scopus
- [16] A. Denker, W. Bohne, J. Opitz-Coutureau, J. Rauschenberg, J. Röhrich, E. Strub**Influence of corrosion layers on quantitative analysis**. Nucl. Instrum. Methods Phys. Res. B, 239 (2005), p. 65
ArticleDownload PDFView Record in Scopus
- [17] M. Campo, A. Estrada-Rius, M. Clua**The French Occupation in Numismatics guide.** Museu Nacional d'Art de Catalunya, Barcelona (2006) pp. 166–173
- [18] J. Bracons, Per una història del vandalisme a Catalunya (segles XV-XX), Unicum. Revista de l'Escola Superior de Conservació i Restauració de Béns Culturals de Catalunya, 2 (2003) 44–51.
- [19] J. Bracons, L'aprovisionament de les seques i la pèrdua de patrimoni a Catalunya, in: A. Estrada-Rius et al. (Eds.), Monedes en lluita: Catalunya a l'Europa napoleònica, 85–93. Edited by Museu Nacional d'Art de Catalunya, Barcelona (2008).
- [20] N. Civici, Sh. Gjongecaj, F. Stamati, T. Dilo, E.P. Avlidou, K. Polychroniadis, Z. Smit**Compositional study of III century BC silver coins from Kreshpan hoard (Albania) using EDXRF spectrometry**. Nucl. Instrum. Methods B, 258 (2007), pp. 414-420
ArticleDownload PDFView Record in Scopus
- [21] B. Constantinescu, A. Sasianu, R. Bugoi**Adulterations in first century BC: the case of Greek silver drachmae analyzed by X-ray methods**. Spectrochim. Acta Part B, 58 (2003), pp. 759-765
ArticleDownload PDFView Record in Scopus
- [22] M.M. Al-Kofahi, K.F. Al-Tarawneh**Analysis of Ayyubid and Mamluk dirhams using X-ray fluorescence spectrometry**. X-ray Spectrom., 29 (1) (2000), p. 39
CrossRefView Record in Scopus

- [23] A. Pitarch, I. Queralt**Energy dispersive X-ray fluorescente análisis of ancient coins: the case of Greek silver drachmae from the Emporion site in Spain** Nucl. Instrum. Methods B, 268 (10) (2010), pp. 1682-1685 ArticleDownload PDFView Record in Scopus
- [24] A. Estrada-Rius, Fabricar moneda en temps de guerra: organització i processos de producció a la seques catalanes (1808–1814), in: Estrada-Rius et al. (Eds.), Monedes en lluita: Catalunya a l'Europa napoleònica, 95–105. Edited by Museu Nacional d'Art de Catalunya, Barcelona (2008).
- [25] Z. Al-Saad M. Bani Hani, Corrosion behaviour and preservation of Islamic Silver Coins, in: V. Argyropoulos, A. Hein, M. Abdel-Harith (Eds.), Strategies for Saving Our Cultural Heritage: Papers presented at the International Conference on Strategies for Saving Indoor Metallic Collections with a special section on Legal Issues in the Conservation of Cultural Heritage, Cairo 26–28 February 2007, pp. 177–183.