





Specialized Analysis of Timurid Coins Using X-ray Fluorescence Spectroscopy: A Step Toward Greater Precision in Historical Studies

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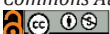
Abstract: Timurid coins serve as a mirror reflecting the significant economic and political events of the era, and their study can provide deeper insights into the economic and social dynamics of the Timurid period. This research examines the Timurid coins housed in the Museum of Bu-Ali Sina Mausoleum using X-ray fluorescence spectroscopy. A specialized review of the initial results obtained from XRF spectroscopy, particularly in numismatic studies, holds significant importance and can be a fundamental step toward reducing errors and enhancing precision in interdisciplinary analyses. XRF technology, as a non-destructive method, enables precise examination of the chemical composition and identification of elements present in coins. However, without meticulous monitoring and comprehensive reevaluation of the obtained results, misinterpretations and uncertainty in historical analyses may arise. The research questions focus on the value of reinterpreting and analyzing XRF spectroscopy data and their role in identifying counterfeit coins and understanding economic and cultural characteristics in numismatic studies. The central hypothesis of the study posits that raw XRF spectroscopy data do not provide accurate results, and in-depth analysis by experts is required for a precise examination of coins. This research also highlights the importance of detailed spectrum analysis, technical challenges in data interpretation, and the use of interdisciplinary approaches to enhance the accuracy of results. The findings reveal that a more profound reinterpretation of XRF spectroscopy data significantly contributes to better understanding the chemical composition of coins and preserving cultural heritage treasures. It also provides deeper insights into the economic policies and activities of the Timurid period.

Keywords: X-ray fluorescence spectroscopy, Timurid coins, interdisciplinary studies, numismatics, elemental composition of coins.

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1. Introduction

The Timurid coins (1370–1507AD) represent significant economic and political transformations of their era. The study of these coins can provide valuable insights into the economic and social conditions of the Timurid dynasty. The analysis of inscriptions, styles, and patterns used in coin designs, created by skilled calligraphers and prominent artists of the time, reflects the unique artistic and ideological trends of this period (Mirakhourlou & Sharafi, 2022: 160; Bragin & Petrov, 2017: 161). In recent years, specialized studies have increasingly leaned towards interdisciplinary knowledge. One practical approach in this field is analyzing the chemical elements of ancient coins through the method of "X-ray fluorescence spectroscopy." X-ray fluorescence spectroscopy, as a non-destructive analytical method, has gained considerable attention in numismatics studies, particularly in museums and among numismatic collectors. This method enables rapid and accurate multi-elemental analysis, both quantitatively and qualitatively, without altering or manipulating the sample's surface, making it highly suitable for preserving valuable artifacts (Mantouvalou et al., 2014: 9774). The non-invasive and non-destructive nature of X-ray fluorescence spectroscopy ensures the integrity of the coins is preserved without causing any damage, a critical factor in safeguarding cultural heritage. During the process of X-ray fluorescence spectroscopy, X-rays from an external source are directed onto the sample. These high-energy X-rays interact with the atoms in the sample, exciting the electrons in the inner shells of the atoms and ejecting them from their orbits (Streli et al., 1999). To return to a stable state, the atoms transfer electrons from higher-energy shells to the inner shells. This process results in the emission of fluorescent X-rays with characteristic energy levels specific to each element. These fluorescent X-rays are measurable and can help identify the elements present in the sample (Karathanasis & Hajek, 1996: 167). All this information is presented in tables as outputs by the device (Weltje & Tjallingii, 2008: 6). At this stage, these data are considered raw information. Along with these tables, spectra labeled as spectrometer outputs are provided, which, based on the horizontal and vertical axes, indicate various parameters related to X-ray fluorescence (XRF) spectroscopy. The horizontal axis displays the energy scale of X-rays in kiloelectronvolts (keV). Each element in the sample emits X-ray fluorescence at specific wavelengths or energies due to its unique atomic properties (Shackley, 2011). Therefore, by identifying the energy of different peaks, it is possible to determine the various elements present in the sample. The vertical axis represents the number of photons detected at each specific energy (intensity), referred to as the "count rate." The height of the peaks in this chart correlates with the concentration of that specific element in the sample. The peaks visible in the spectrum correspond to different elements. Typically, each element has characteristic peaks in the energy spectrum. For instance, the tall peaks in Figure 1 indicate the primary elements present in the sample (Ag), while smaller peaks may represent trace elements. This chart enables researchers to identify the type and concentration of elements in the sample by observing the energy peaks. To correctly interpret these spectra, understanding the characteristics of the studied materials and utilizing advanced analytical methods is essential. The raw data from X-ray fluorescence spectroscopy only reveal the chemical composition of the coins. However, for a precise and comprehensive understanding of these data, human interpretation and analysis are crucial. This research investigates how human interpretation of X-ray fluorescence spectroscopy data can lead to accurate and meaningful results in understanding the chemical composition and authenticity of coins. This study holds importance for several reasons. First, by analyzing the elemental composition and inscriptions of Timurid coins, it contributes to a deeper understanding of the economic, political, and cultural aspects of this period. Second, the research emphasizes the significance of combining scientific X-ray fluorescence spectroscopy data with expert inter-

pretation to achieve more precise and meaningful results in numismatic studies.

Additionally, the importance of non-destructive methods like X-ray fluorescence spectroscopy in preserving cultural heritage and historical coins becomes evident through this study. For the coin analysis, a portable X-ray fluorescence (XRF) spectrometer, Bruker S1 TITAN, was utilized. The S1 TITAN is equipped with a 50 kV X-ray tube and a high-precision silicon drift detector (SDD), enabling the detection of elements ranging from magnesium (Mg) to uranium (U). This device is integrated with advanced software for qualitative and quantitative analysis. For qualitative analysis, spectrum acquisition, and data processing, the built-in S1 TITAN software was employed. This software facilitates spectrum acquisition and qualitative identification of elements. During qualitative analysis, spectra were acquired using the device's default settings, operating at 50 kV voltage and 50 μ A current. The S1 TITAN's capability allows for the excitation and detection of X-ray fluorescence from elements in the sample at concentrations as low as approximately 1 ppm and above. The same conditions, with 50 kV voltage and 50 μ A current, were maintained throughout the analysis to ensure consistency and reliability of all results. Research Objectives are : To highlight the limitations of raw data obtained from X-ray fluorescence (XRF) spectroscopy and the necessity of human interpretation and analysis in numismatic studies. To examine the impact of interdisciplinary analyses in accurately identifying and analyzing Timurid coins and gaining a deeper understanding of the economic and political contexts of that era. To emphasize the importance of precise interpretation of XRF spectra for identifying the composition and production methods of coins, preventing misinterpretations. Research Questions are How can human studies contribute to a more accurate identification and analysis of Timurid coins? What is the impact of interpreting and analyzing XRF spectroscopy data on research outcomes? Hypotheses are : 1-Raw X-ray fluorescence spectroscopy data alone is insufficient to provide a comprehensive understanding of the chemical composition of Timurid coins. Human interpretation and data processing are essential for accurate authentication and identification. 2: Analysis of X-ray fluorescence spectroscopy data can contribute to the authentication of coins, facilitate the identification of counterfeits, and enhance our understanding of regional trade networks during the Timurid period. This research is constrained by limited access to Timurid coin samples and a scarcity of detailed historical information regarding minting processes. These limitations can pose challenges in data interpretation and statistical analysis.

Literature Review

Acquafredda (2019) introduced energy-dispersive X-ray fluorescence (EDXRF) as a non-destructive, rapid, multi-elemental, and precise analytical method for elemental analysis. The author emphasized the broad applications of EDXRF in quality control, environmental monitoring, and cultural heritage analysis. Oyedotun (2018) provided a comprehensive review of XRF applications in geo-materials analysis, highlighting its speed and accuracy while cautioning against calibration errors. Hajivaliei et al. (2008, 2012) employed PIXE to study Sasanian and Parthian coins, respectively. Salehi et al. (2015) and Hajivaliei and Sodaee (2016) utilized PIXE and WDXRF, respectively, to investigate Sasanian coinage. Kakooei et al. (2022) offered an overview of the potential of archaeometry in Iran. Hajivaliei et al. (1401) and Mirsafdari and Hajivaliei (2022) employed XRF to examine the silver coins of Khosrow Parviz and Ilkhanid coins, respectively.

Descriptions

The two fundamental principles of quality in XRF analysis are accuracy and sensitivity. These principles are essential for unbiased analyses. Accuracy refers to how closely a measurement aligns with the true value, while sensitivity indicates the ability to detect low concentrations

of elements. Expert review of the initial results from X-ray fluorescence spectroscopy is crucial to ensure the accuracy and analytical capability of elements in scientific studies. This process aids in identifying potential errors and mistakes in data interpretation, which can significantly impact research outcomes. The following sections elaborate on the importance of expert review in XRF analysis. One of the errors that necessitates a re-examination of results is calibration error. Although a high-precision technique can provide unbiased results, these results may still be incorrect, especially if impurities were introduced during sample preparation or due to calibration errors. To achieve high-quality and acceptable XRF results, attention must be paid to both accuracy and precision. To address deviations (inaccuracy, whether short-term or long-term), several variables must be considered. These variables include the stability of the XRF device, accuracy in sample preparation, calibration of the device with the most suitable and acceptable reference standards, monitoring and managing room temperature, monitoring voltage fluctuations due to power variations, and considering other external factors (Oyedotun 2018: 148). In X-ray fluorescence spectroscopy, identifying and distinguishing between different elements in samples can become complex and challenging when they have similar energy characteristics. This issue is particularly prevalent for elements that are close to each other in the periodic table or have similar electronic properties. For example, elements like cobalt (Co) and nickel (Ni) emit fluorescent rays that have closely related energies: the $K\beta$ peak of cobalt (Co) is approximately at an energy of 7.650 keV, while the $K\alpha$ peak of nickel (Ni) is around 7.480 keV. Although this difference in fluorescent energies is measurable, its amount is very small, and therefore, we need a high level of precision and experience to analyze and identify these elements. Otherwise, similar energies may overlap, which can lead to misidentification and ultimately inaccurate results. In the analysis of samples using X-ray fluorescence spectroscopy, detecting surface contaminants or thin layers of other materials is very important. This method becomes particularly significant due to its capabilities in identifying chemical elements at the surface of the sample, especially in cases where the samples may have been moved under unusual conditions, such as those seized from traffickers. When contaminants or external layers are present on the surface of the sample, the results obtained from X-ray fluorescence spectroscopy can be affected, as this method fundamentally relies on the energies emitted from within the materials. For this reason, the presence of surface compounds may lead to erroneous or invalid results. At this point, the role of specialized individuals in interpreting the results of X-ray fluorescence spectroscopy becomes evident. Skilled analysts, with their experience, can determine which data may be invalid due to surface contaminants and what actions should be taken to correct them. Trace elements refer to those elements that are present in very small amounts in samples, typically constituting less than 1 percent by weight of the total sample. In analytical methods such as X-ray fluorescence spectroscopy, detecting these elements is challenging because their intensity is weaker than that of the major or abundant elements in the sample. In other words, since the concentration of these elements in the sample is low, the X-ray energy produced from these elements is also lower, making their identification more prone to error. Regarding X-ray fluorescence spectroscopy analysis, scientific sources generally do not provide a precise definition of the detection limits for these trace elements and often do not mention specific examples. However, one source specifically noted that in a study, the detection limit of the X-ray fluorescence spectroscopy device was approximately 0.1 percent by weight. This means that elements or compounds with amounts below this threshold may be identified with low accuracy or may even be undetectable in some cases. Detecting trace elements in X-ray fluorescence spectroscopy analysis is considered a challenge due to their weak intensity and competition with the intensity of dominant elements, and improving the accuracy of the analysis requires precise

adjustments and specialized interpretation. In the analysis of heavy elements such as gold using X-ray spectroscopy, spectral overlap occurs between the X-ray lines of heavy and light elements, such as K X-ray and L X-ray. For example, the energy of K X-ray from iron (Fe) and L X-ray from the element dysprosium (Dy) are similarly located in the energy range of 6.40 keV. This overlap can significantly impact the accuracy and precision of measuring the concentration of heavy elements in samples. Therefore, a thorough analysis of the results from X-ray fluorescence spectroscopy and the correct interpretation of the obtained data are essential to ensure the validity and accuracy of the results and the proper interpretation of the chemical compositions of the samples. Now, let's take a look at the table of X-ray fluorescence results for the Timurid coins at the Avicenna Mausoleum for review and further examination:

Table 1: Specifications of the studied coins (prepared by the authors)

Coin No.	1	2	3	4	5	6	7	8	9	10
Diameter (mm)	27	16	17	23	25	17	22	24	23	25
Mass (g)	5	2	1.9	5	3.7	2.8	3	2.3	2.4	2.8

In the analysis of coins using this method, the aim is qualitative analysis; therefore, depending on the coin numbers, the elements titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), arsenic (As), gold (Au), silver (Ag), and lead (Pb) were detected.

Analysis of Tracing Elements in Ancient Coins

Titanium

The presence of titanium in base metals may be due to their extraction from areas with mineral deposits containing this element. In the past, the technology for extracting and refining metals was not as precise as it is today, and ores often included impurities such as titanium.

Iron

The presence of iron in coins can be attributed to several factors: Burial conditions: Contact with iron-bearing minerals or chemical reactions in the soil can lead to the accumulation of iron on the surface of the coin. Surface contamination: Sometimes, iron is reported as surface contamination (Geimer-Breitenstein et al., 2013: 957). One reason for the presence of iron in the analysis is human sweat.

Corrosion: Iron present at less than 1% is likely a result of melting and refining processes and is not due to corrosion. If the percentage of iron exceeds 1%, the possibility of corrosion is raised.

Copper and Lead

Copper and lead are often attributed to ancient processes of cupellation:

Cupellation of lead: a technique in which lead and silver ore are melted, then lead is oxidized to obtain pure silver (Casas & Sordo, 2006). One of the applications of lead in coinage is to lower the melting point. In these coins, the edges have a broken appearance.

Low concentration of lead: In cases such as coins number 1, 3, 6, 9, and 10, where the concen-





















Table No.2: Introduction of the studied coins (the coins have been edited and made readable using Photoshop) prepared by the authors.			
Coin No.	King's Name	Reverse	Obverse
1	Babur		
2	?		
3	Amir Timur		
4	Shahrokh Bahadur		
5	?		
6	Shah Rukh, the Great Sultan of Samarkand		
7	Suspected of Mahmud Khan or Timur		
8	Mughal Emperor of India		
9	Shahrokh Timuri		
10	Amir Timur		

Table No.3: The initial results announced by the XRF device (prepared by the authors)										
Coin No.	Pb	Ag	Au	As	Zn	Cu	Fe	Mn	Cr	Ti
1	0.07	99.0	0.8			0.44	0.32	0.01	0.07	
2	0.65	97.7	0.2			0.98	0.70	< LOD	0.01	
3	0.08	98.7	0.3			0.52	0.62	0.01	0.01	
4	0.81	97.4	0.3			0.68	1.09	0.01	0.01	0.02
5	0.78	< LOD	0.1	0.5	0.06	98.70	< LOD	< LOD	0.02	
6	0.41	98.4	0.3			0.75	0.44	0.01	0.02	
7	0.69	96.2	0.3			2.15	0.89	0.01	0.09	
8	0.95	97.7	0.1			0.75	0.54	0.01	0.08	
9	0.44	98.7	0.2			0.40	0.44	0.01	0.09	
10	2.12	95.3	0.1			0.56	1.91	0.01	0.01	

tration of lead is below 0.5%, this amount indicates an effective melting and refining process (Civici et al., 2007).

Gold

The presence of gold has sometimes been reported as a components of silver ore (Gale et al., 1980). This reference is incorrect.

Trace Elements and Impurities (some elements at very low percentages)

Trace elements and impurities are usually a result of the production process, but they may also be observed due to surface contamination (Constantinescu et al., 2003). Some elements, such as rhodium (Rh), may be recorded in spectral data due to the lamp radiation conditions of the device and argon (Ar) used as a filler gas in the space between the device and the sample, as well as the presence of air in the environment. This phenomenon is related to external influences and the lack of purity in the analysis environment.

Arsenic in Counterfeit Coins

The presence of arsenic in the alloy of counterfeit coin number 5 is likely indicative of its fabrication and the use of minting methods (Hajivaliei et al., 2023). The spectrum of coin number 8 is given in Fig.1 in which the K X-rays of silver are indicated. After a thorough review and re-assessment, and based on the errors and information presented in the article, the final results deemed significant in numismatic studies are reported below in Table 4.

Conclusion

Compared to other analytical methods, X-ray fluorescence spectroscopy can quickly identify the chemical compositions of valuable historical samples without causing damage. However, as Mantouvalou and colleagues (2014) have pointed out, more precise analysis is essential for the correct interpretation of the data. According to the findings, spectral overlap among certain elements and challenges arising from surface contamination of the samples may reduce the accuracy of the results. Trace elements present at very low concentrations may also remain undetected or not be accurately identified due to weaker intensity. This issue clearly highlights the importance of fine-tuning the equipment and the need for specialized interpretation of the data by experts. Interdisciplinary research that combines archaeology and technical expertise can provide better solutions for analyzing and understanding the historical and cultural contexts of numismatics. The overlap of various elements, challenges arising from surface contaminants, and the presence of trace elements are among the factors that affect the accuracy of results. Therefore, integrating archaeological knowledge with technical expertise can aid in more precise identification of chemical compositions and a deeper understanding of Timurid coins and their historical contexts. Additionally, this research emphasizes the importance of expert analysis and the processing of raw data from X-ray fluorescence spectroscopy to obtain reliable and meaningful information from historical artifacts. It is worth mentioning that coin number 5 has been mistakenly listed among the silver coins of the museum, and this coin is made of copper.

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Table 4: Percentage of Elements Present in Analyzed Coins (Compiled by the Authors)						
Coin No.	% Ag	% Au	% Cu	% Pb	% Fe	% As
1	99.0	0.80	0.50	0.10	-	-
2	97.6	0.20	1.00	0.70	0.70	-
3	98.7	0.30	0.50	0.08	0.60	-
4	97.4	0.30	0.70	0.80	0.10	-
5	-	0.10	98.70	0.80	-	0.5
6	98.3	0.30	0.80	0.40	0.40	-
7	96.2	0.30	2.20	0.70	0.90	-
8	97.7	0.10	0.70	1.00	0.50	-
9	98.7	0.20	0.40	0.40	0.40	-
10	95.2	0.10	0.60	2.10	1.90	-

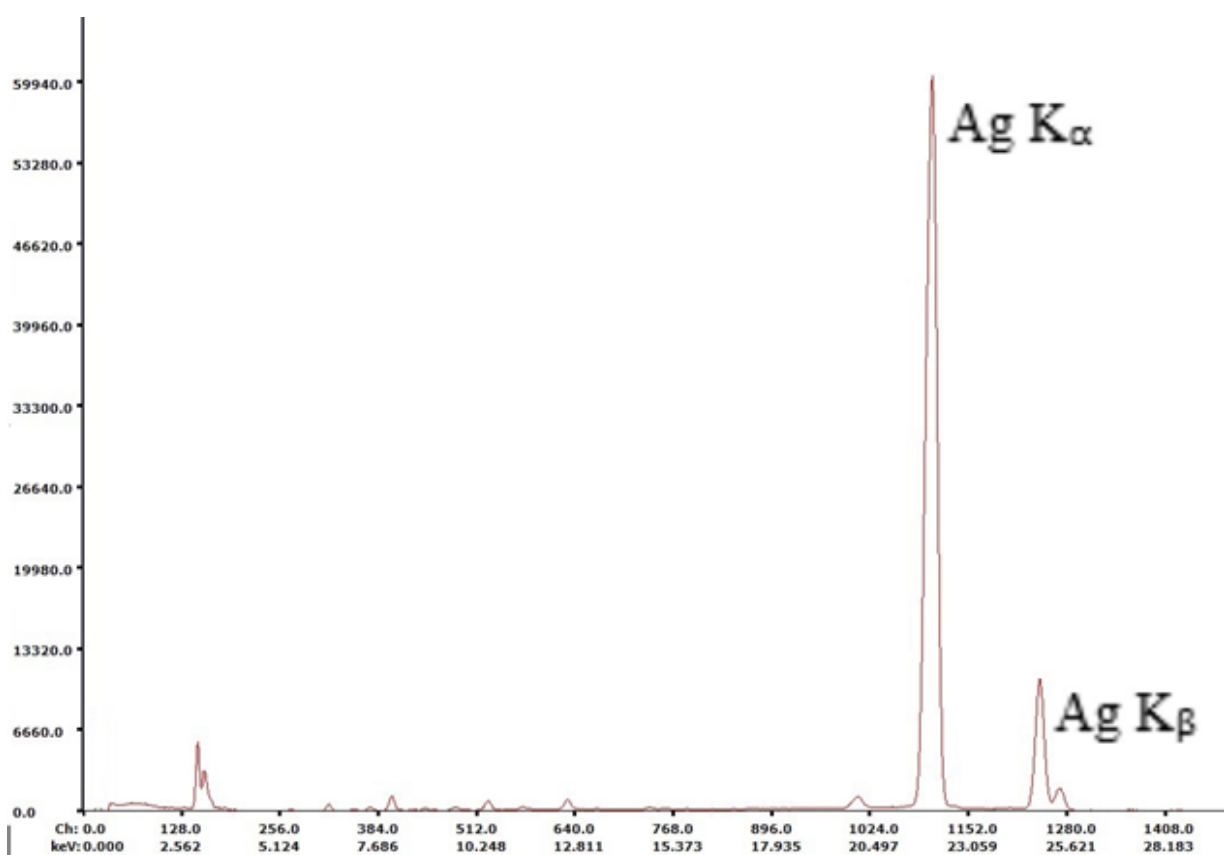


Figure 1: XRF spectrum of coin No.8

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