heritage

MDPI

Article

Preliminary X-ray Fluorescence Analysis of Metallic Samples from the Chovdar Necropolis in Azerbaijan

Bakhtiyar Jalilov [1], Safar Ashurov [1], Muzaffar Huseynov [1], Lola Huseynova [1], Nicola Laneri [2,3], Stefano Valentini [2], Bruno Cocciaro [4], Stefano Legnaioli [4], Giulia Lorenzetti [4], Beatrice Campanella [4], Simona Raneri [4], Francesco Poggialini [4] and Vincenzo Palleschi [4,*]

1 Institute of Archeology, Ethnography and Anthropology, Azerbaijan National Academy of Sciences, AZ1001 Baku, Azerbaijan
2 Center for Ancient Mediterranean and Near Eastern Studies, 50123 Florence, Italy
3 Department of Archaeology, University of Catania, 95131 Catania, Italy
4 Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, National Research Council, 56124 Pisa, Italy
* Correspondence: vincenzo.palleschi@cnr.it

Abstract: Several samples coming from the recently discovered (February 2019) Late Bronze Age/Early Iron Age Chovdar necropolis in Azerbaijan were analysed using the X-ray fluorescence (XRF) technique. The analysis allowed a preliminary classification of the samples in eight groups based on their composition, obtained from the XRF spectra using the fundamental parameter method. A more detailed classification was then obtained using the graph clustering method.

Keywords: bronze age; archaeometry; X-ray fluorescence; graph clustering; Chovdar necropolis; Late Bronze Age; Early Iron Age

Citation: Jalilov, B.; Ashurov, S.; Huseynov, M.; Huseynova, L.; Laneri, N.; Valentini, S.; Cocciaro, B.; Legnaioli, S.; Lorenzetti, G.; Campanella, B.; et al. Preliminary X-ray Fluorescence Analysis of Metallic Samples from the Chovdar Necropolis in Azerbaijan. *Heritage* **2023**, *6*, 199–211. https://doi.org/10.3390/heritage6010010

Academic Editors: Corinna Ludovica Koch Dandolo and Jean-Paul Guillet

Received: 27 November 2022
Revised: 16 December 2022
Accepted: 21 December 2022
Published: 25 December 2022

1. Introduction

A classification of archaeological findings according to their composition is often necessary in the study of ancient necropolises, which in some cases may demonstrate century-long human frequentation. The study of the materials recovered in these contexts can give precious information about the technological knowledge of the population which inhabited the region as well as the possible commercial exchanges with neighbouring cultures [1]. The archaeometric study of metallic objects, when present, is particularly important and can be performed using a number of analytical techniques, ranging from the traditional atomic absorption spectroscopy (AAS) [2], inductively coupled plasma optical emission spectroscopy (ICP-OES) and scanning electron microscopy with energy dispersion spectrometry (SEM-EDS) [3] to more modern methods such as laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) [4], laser-induced breakdown spectroscopy (LIBS) [5] and energy dispersive X-ray fluorescence (ED-XRF) [6].

This latter technique is particularly interesting in archaeological contexts, because of the peculiar features of ED-XRF (ease of use, portability, robustness) which allow in situ as well laboratory qualitative and quantitative analysis. The XRF technique is very sensitive to the elements that might be encountered in archaeological research (iron, copper, zinc, tin, lead, gold, silver, arsenic, antimony, bismuth, cobalt, mercury, etc.) and environmental elements (sulfur, calcium, potassium, manganese, titanium, barium as well as bromine, strontium, etc.).

Although in most cases the XRF spectra are strongly influenced by the possible presence of surface corrosion layers, in the past it has been demonstrated that a meaningful classification of corroded metallic samples can be obtained with this technique, even when an accurate quantitative determination of the alloy composition cannot be achieved [7].

In the present work, we report the results of the analysis of 18 bronze samples coming from the Late Bronze Age/Early Iron Age Chovdar necropolis (Azerbaijan).

The necropolis was discovered in February 2019, in the Dashkesan region (western Azerbaijan) on a high mountain plateau at the geographical coordinates 40°35′39.9″ N 46°04′46.0″ E, at an altitude of 1550 m above sea level, during construction works carried out by AzerGold CJSC in a mining area rich in gold, silver, copper and iron ore deposits.

One hundred and fifty-six stone box graves were investigated during the archaeological excavations in 2019, and another 58 in 2021. The tomb chambers studied were built of raft rocks of various sizes and directions. The typology of these graves is commonly found in the western and southern regions of Azerbaijan, in Karabakh, in the territory of the Nakhchivan Autonomous Republic. According to comparative analysis, the graves discovered in the Chovdar area belong to the Late Bronze–Early Iron Age (late 2nd millennium BCE—early 1st millennium BCE). Archaeological materials found in the necropolis belong to the Khojaly-Gadabay culture, which was widespread in the South Caucasus during the Late Bronze–Early Iron Age. Similar necropolises and graves (Khachbulag, Zeylik, Zagali and Galakend in Gadabay districts, Garamurad, Jannat fortress, Goydaya territories) were extensively studied near the Chovdar necropolis [8].

A large number of pottery samples, decorations, weapons, work tools, household and farm items were found in the grave cells. Blue beads from Egypt and Central Asia and *kauris*[1], typical of the Indian Ocean, were found in the archaeological site, demonstrating the cultural and economic ties of the communities which inhabited this area during the study period.

Metal samples have a special weight among them in terms of quantity and quality inside the archaeological finds. Along with the richness of metal objects, it also attracts attention to the variety of uses. Weapons, jewellery, clothing accessories, household items and tools were found in the graves. The metal objects consist of daggers, knives, spearheads, walking sticks, arrowheads, belts, pins, buttons, bracelets, rings, earrings, bird figures, beads, hanging ornaments of different shapes, needles, etc. Similar metal objects are widespread in the South Caucasus [9,10].

The large majority of the metal samples found in the necropolis come from the local area, which is rich in sources of raw metal materials. Their diversity according to the purpose of use and the refined realization demonstrates the extensive experience in metallurgy and metal production of the ancient communities inhabiting the area.

2. Materials and Methods

The travel restrictions imposed due to the COVID-19 emergency have denied the possibility of performing an in situ study of the metallic findings of the Chovdar necropolis. However, 18 samples from metallic objects were available for spectral analysis, each of them found in a different grave during the 2019 excavation campaign (see Table 1 for a description of the objects).

Table 1. List of the metallic objects analysed by XRF.

Q-2	Knife	
Q-4	Dagger	

Table 1. *Cont.*

Q-19-4	Horseshoe-shaped object	
Q-26	Rod head	
Q-29-5	Bird figure	
Q-35-1	Ring	

Table 1. *Cont.*

Q-38-1	Bracelet	
Q-52-2	Spiral Decoration	
Q-53-6	Button	

Table 1. *Cont.*

Q-63-1	Bracelet	
Q-68-5	Bracelet	
Q-77-2	Bracelet	

Table 1. *Cont.*

Q-80	Spearhead	
Q-90-5	Pin	
Q-111-1	Tabarzin[2]-shaped hanging	
Q-122-5	Bell-shaped decor.	

Table 1. *Cont.*

Q-136-11	Bird Figure	
Q-138	Dagger	

The samples were taken from the objects in the form of small metal chips (see Figure 1).

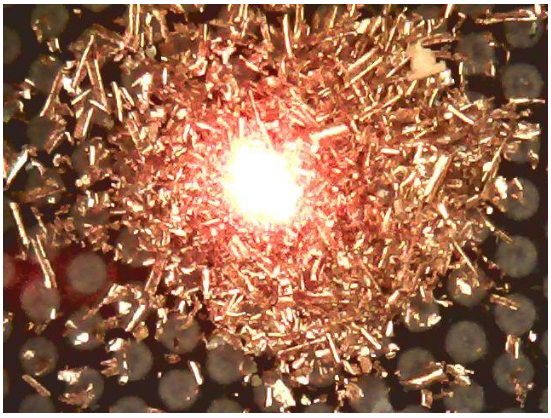

Figure 1. The metal chips taken from one of the samples. The red spot is the laser pointer of the XRF instrument. The plastic support does not contribute to the XRF spectrum.

For the XRF analysis, the chips were loosely compacted on a plastic substrate and fully recovered at the end of the measurement. The spectrum of the plastic substrate was acquired before the analysis, to be sure of not introducing any contribution of the substrate in the spectrum of the samples.

The instrument used for the analysis was the Elio XRF spectrometer from Bruker. The measurement was performed in 60 s, with the X-ray tube voltage set at 40 kV and a current of 80 µA (320 mW). The anode is made of rhodium; the characteristic fluorescence lines of the anode do not interfere with the emission of the samples (Cu-based alloys).

3. Results

The main elements detected in the alloys, in different proportions, are Cu, Zn, Pb, As, Sn, Sb, Fe. Environmental elements such as calcium, strontium and potassium were detected but not considered for classification and analysis (see Figure 2)

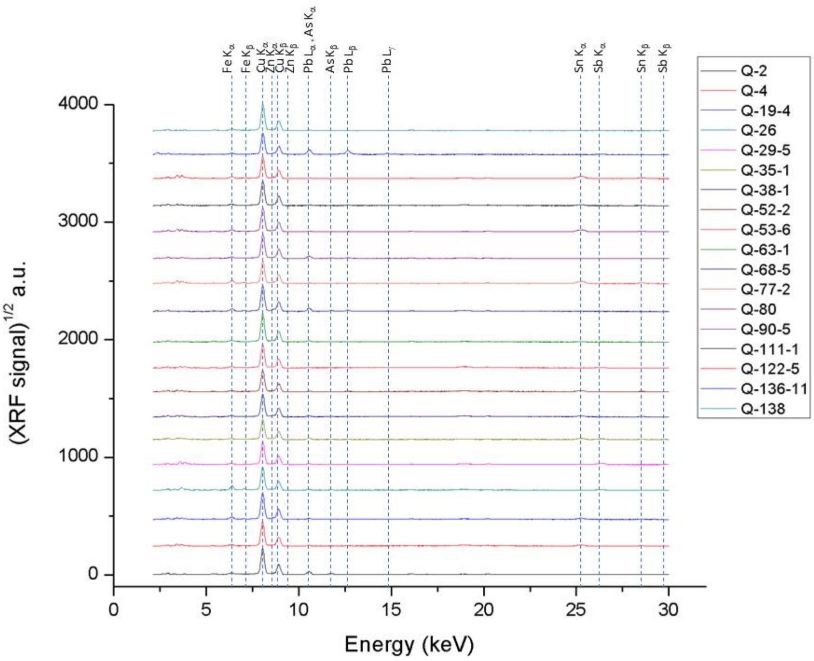

Figure 2. The XRF spectra of the 18 samples. The spectra are shifted vertically for a better legibility. The square root of the spectra is plotted to demonstrate the weak lines of the minor elements. The vertical lines mark the XRF emission of the main elements of the samples.

The quantitative analysis of the alloys' composition was performed using the fundamental parameters method [11] with the open-source software pyMCA [12]. The results obtained have a relatively large uncertainty, since the method would require the use of at least one standard of similar matrix, which in our case was not available. However, by imposing the conditions that the sum of all element concentrations should be equal to 100%, a reliable estimation of the samples' composition can be obtained, with relative errors in the order of 10% for the elements with concentrations higher than 1 wt%. Larger relative errors (of the order of 50%) are expected for trace elements at lower concentrations. The accuracy of the results is in any case sufficient for a classification of the samples, because the composition of the samples is also qualitatively different. The discriminating elements for classification are zinc (Zn), lead (Pb), arsenic (As), tin (Sn) and antimony (Sb).

In Table 2, we report the estimated compositions of the samples.

Table 2. Estimated elemental composition of the samples.

Sample	Fe (w%)	Cu (w%) (Rest)	Zn (w%)	As (w%)	Sn (w%)	Sb (w%)	Pb (w%)
Q-2	0.4	95.4	0.4	3.5	0.0	0.1	0.1
Q-4	0.7	95.6	0.4	0.4	2.1	0.2	0.4
Q-19-4	1.6	93.9	0.8	0.6	2.6	0.1	0.4
Q-26	5.0	92.7	0.4	0.7	0.1	1.0	0.2
Q-29-5	0.5	93.3	0.3	0.8	0.2	4.8	0.2
Q-35-1	0.4	91.7	0.3	1.3	3.6	2.3	0.4
Q-38-1	0.6	95.8	0.6	0.5	2.0	0.1	0.4
Q-52-2	0.5	95.3	0.5	0.1	2.9	0.3	0.5
Q-53-6	0.8	96.2	0.5	0.3	0.3	1.6	0.2

Table 2. *Cont.*

Sample	**Fe (w%)**	**Cu (w%) (Rest)**	**Zn (w%)**	**As (w%)**	**Sn (w%)**	**Sb (w%)**	**Pb (w%)**
Q-63-1	0.9	96.3	0.5	1.0	0.5	0.2	0.7
Q-68-5	2.0	90.1	1.3	4.1	0.1	0.1	2.3
Q-77-2	2.6	88.4	0.6	0.2	8.0	0.0	0.2
Q-80	0.6	95.1	0.3	2.2	0.3	0.2	1.3
Q-90-5	1.0	92.1	0.5	0.1	6.0	0.0	0.3
Q-111-1	0.7	94.7	0.5	0.2	2.6	0.2	1.1
Q-122-5	1.3	87.3	0.6	0.2	10.4	0.1	0.3
Q-136-11	0.6	74.1	0.7	0.8	0.2	0.9	22.7
Q-138	1.0	97.0	0.6	0.4	0.2	0.6	0.2

We found at least eight different types of alloy, described qualitatively in Table 3.

Table 3. Preliminary classification according to the characteristic elements in the alloy.

Types of Alloy	**Samples**	**Main Elements**
1	Q-2	Cu and As
2	Q-4, Q-19-4, Q-38-1, Q-52-2, Q-63-1, Q77-2, Q-90-5, Q-111-1, Q-122-5	Cu, Pb and Sn
3	Q-26, Q-29-5, Q-138	Cu, Pb, As and Sb
4	Q-35-1	Cu, Pb, As, Sn and Sb
5	Q-53-6	Cu and Sb (Pb/As in traces)
6	Q-68-5	Cu, As, Pb and Zn
7	Q-80	Cu, As and Pb
8	Q-136-11	Cu, Pb and Sb

It can be observed that half of the samples (9 over 18) are made by a Cu-Sn-Pb alloy. To verify if these samples can be really considered as a single group, we applied the graph clustering (GC) method, firstly introduced by the Pisa Laboratory for the unsupervised classification of materials by laser-induced breakdown spectroscopy (LIBS) [13] and later also used for the classification of archaeological objects based on their XRF spectra [14]. The classification is performed based on the distance d_{12} between the spectra, which is considered as inversely proportional to their correlation

$$d_{12} = \left(\frac{\langle S_1 S_2 \rangle}{\sqrt{\langle S_1^2 \rangle \langle S_2^2 \rangle}} \right)^{-1} \tag{1}$$

The graph built using this metric is undirected ($d_{12} = d_{21}$); the distance defined by Equation (1) is always positive ($d_{12} \geq 1$). The GC method classifies the samples based on the similarity of their spectra. In our case, all the spectra are very similar, dominated by the strong K lines of Cu at 8.05 and 8.91 keV (see Figure 2). However, the GC method is very sensitive to the minimal differences between the spectra, as can be seen in the graph shown in Figure 3.

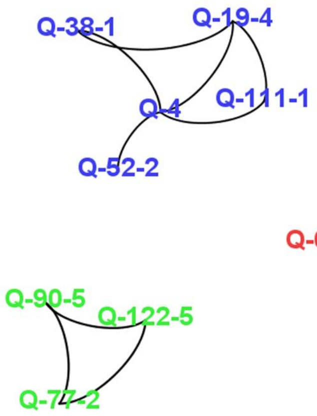

Figure 3. Output of the graph clustering algorithm for the Cu-Sn-Pb samples (group 2 in Table 3. Blue: Cluster 2A; Green: Cluster 2B; Red: Cluster 2C, see Table 4).

Table 4. Final classification according to the graph clustering method.

Cluster	Samples	Main Elements
1	Q-2	Cu and As
2A	Q-4, Q-19-4, Q-38-1, Q-52-2, Q-111-1	
2B	Q77-2, Q-90-5, Q-122-5	Cu, Pb and Sn
2C	Q-63-1	
3	Q-26, Q-29-5, Q-138	Cu, Pb, As and Sb
4	Q-35-1	Cu, Pb, As, Sn and Sb
5	Q-53-6	Cu and Sb (Pb/As in traces)
6	Q-68-5	Cu, As, Pb and Zn
7	Q-80	Cu, As and Pb
8	Q-136-11	Cu, Pb and Sb

The GC algorithm clearly distinguishes three clusters, corresponding to the samples Q-4, Q-19-4, Q-38-1, Q-52-2, Q-111-1 (Cluster 1), Q77-2, Q-90-5, Q-122-5 (Cluster 2) and Q-63-1 (Cluster 3). The reliability of the output of the GC algorithm can be visually checked comparing the XRF spectra of the samples in the three clusters (see Figure 4)

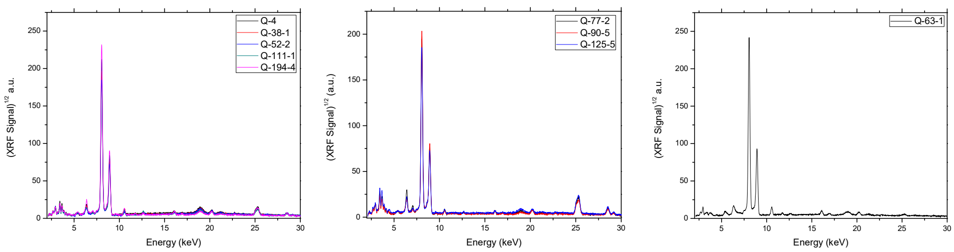

Figure 4. Comparison of the XRF spectra corresponding to the samples in the three clusters.

4. Discussion

In this study, we analysed 18 metallic objects coming from the same number of stone graves in the recently discovered (February 2019) Late Bronze–Early Iron Age necropolis of Chovdar in Azerbaijan. Despite the very limited number of samples (in the excavation campaign which followed the discovery of the necropolis, 156 graves were discovered, containing more than 6000 artifacts), the XRF analysis evidenced an exceptional variability in the composition of the metallic alloys. Eight main compositional groups were individuated from the quantitative analysis of the XRF spectra, which were further split into a total of 10 groups after the application of graph clustering (see Table 4).

The only clusters with more than one member are groups 2A, 2B and 3. In group 2A, the five elements in the group (a dagger, the horse-shoe shaped objects, a bracelet and a spiral decoration) are characterized by the same, or very similar, Cu, Pb and Sn alloy. A different Cu, Pb and Sn alloy seems to have been used for the three members of cluster 2B (a bracelet, a pin and the bell-shaped decor). A Cu, Pb, As and Sb alloy was used for the three objects belonging to group 3 (a rod head, a bird figure and a dagger), instead.

It is also interesting to note that the three bracelets Q-38-1, Q-63-1 and Q-68-5, although visually similar, belong to different clusters for concerning their composition. Similarly, the two bird-shaped objects (Q-29-5 and Q-136-11) and the two daggers (Q-2 and Q-138) are also classified into different clusters, with the composition of one of the bird-shaped objects (Q-29-5) being at least qualitatively similar to the one of the dagger Q-138.

It is of great interest that the analysis results of a small part of Chovdar's metal collection show that at least 10 different types of alloys were used in the production of the studied samples. So far, according to the results of spectral analysis of metal objects found in the archaeological excavations in the monuments of the Late Bronze Age and Early Iron Age in Azerbaijan, eight types of alloys of the objects produced in this period, consisting of copper and other polymetallic mixtures, were identified [9]. The spectral analysis of the chemical composition of the bronze objects found in the area of Chovdar shows that the level of professional knowledge of metalworking craftsmen of the mentioned period was high. The results of this research suggest that ancient artisans used more complex and quantitatively richer alloy types in metal production, calling for a reconsideration of such issues. The mentioned period is characterized by the use of advanced technical achievements in metalworking. The research technique for making metal objects shows that technical methods such as forging, casting, chiselling, flattening, twirling, rolling, embossing, stamping, minting, brazing, tracery/decorative patterning, engraving were used in the metal handicraft of the Late Bronze and Early Iron Ages.

The results of the analysis of 18 samples taken from the metal objects found in the monument show that the amount of lead, tin and other metals added to copper did not reach 15% (sample Q-136-11 is an exception). Historical analytical studies have shown that the amount of arsenic, tin and other metals in the copper alloy was lesser than 20% in the Late Bronze and Early Iron Age [9]. As we know, these additional impurities in the composition of bronze significantly reduce the melting temperature of copper. In fact, when adding any artificial additive to the copper smelting process, its melting process is accelerated by taking place at a relatively low temperature. On the other hand, the presence of such additives may increase the fragility of bronze. Additionally, a bronze object with 2% to 5% artificial additives can be effectively beaten and is easier to form into any shape [14].

The historical and spectral analysis of the bronze objects found in the area of Chovdar shows that the Late Bronze Age and Early Iron Age metalwork handicraft of the region used advanced techniques which allowed the production of various items of peculiar shapes, with a complex mixture of alloys, for different areas of use.

Looking at the chemical composition of the metal samples of Chovdar, it is clear that the ancient metalsmiths were well acquainted with the chemical properties of bronze, with different percentages of metals added to the copper base. Experts believe that the cold forging method can be used in the production of bronze objects only when the volume of polymetals in the alloy is around 4–6%. The presence of large amounts of polymetallic compounds in bronze requires the use of hot forging techniques [15]. Among the samples studied, the amount of tin, lead and other mixtures in the weapons, bracelets, pendants and buttons is less than 4 percent. Ornamental items, on the other hand, are mainly made from an alloy containing 6–10% tin, which gives the bronze a golden colour and makes it brittle and suitable for carving [16,17]. In the territory of Azerbaijan, metal objects with a similar purpose and similar alloy composition are widely found in Zayamchay [18], Hajivelilar [19], Kizilburun [20], Karabachlar [21], Mingachevir [22], Khachbulaq [23] and other Late Bronze–Early Iron Age sites [9].

Despite the similarities with the bronze items found from the archaeological monuments of the mentioned period, there are local variations and specific features in certain areas and individual sites. The analysis results of Chovdar samples show that 6 out of

18 studied samples contain an antimony mixture, and in three samples, antimony is the main element in the mixture with copper. The alloys used in the manufacture of bronze objects sometimes depended on their intended use, and sometimes on the raw materials available to the craftsman [9]. Sometimes, the ancient metallurgists used antimony in the absence of tin and lead. The use of antimony together with tin and lead, however, demonstrates that these metals were widely available in the Late Bronze–Early Iron Age in the South Caucasus.

In conclusion, it should be remarked as the unique climatic conditions of Azerbaijan's territory and the presence of abundant raw materials brought the ancient metalwork handicraft to the highest level of development of the times in the region. The information recovered on the objects under study, although limited by the small number of the samples that could be analysed, opens up interesting discussions among scholars studying ancient metallurgy in the South Caucasus. It may also trigger, whenever possible, a more articulated and representative study on the numerous metallic samples recovered in the 2019 and 2021 excavation campaigns.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage6010010/s1.zip, Spectra S1: XRF spectra in .spt format.

Author Contributions: Conceptualization, B.J., N.L., S.V. and V.P.; methodology, V.P.; validation, B.J., S.A., L.H., M.H., N.L., S.V. and V.P.; formal analysis, V.P.; software, V.P.; investigation, V.P. and S.L.; resources, V.P.; data curation, V.P.; writing—original draft preparation, V.P.; writing—review and editing, B.J., S.A., L.H., M.H., N.L., B.C. (Bruno Cocciaro), S.L., G.L., B.C. (Beatrice Campanella), S.R., F.P., S.V. and V.P.; visualization, V.P.; supervision, B.J., N.L., S.V., V.P.; project administration, B.J., N.L., S.V., V.P.; funding acquisition, B.J. and V.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the Italian Ministry of Education, University and Research, Research Projects of National Relevance PRIN 2020, Project UNDERLANDSCAPE, grant n. 2020428LS8. Archaeological research was carried out with the support of the Heydar Aliyev Foundation and "AzerGold" CJSC.

Data Availability Statement: The XRF spectra are available as Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Notes

[1] Seashells
[2] Type of axe

References

1. Jones, A. Archaeometry and materiality: Materials-based analysis in theory and practice. *Archaeometry* **2004**, *46*, 327–338. [CrossRef]
2. Hughes, M.J.; Cowell, M.R.; Craddock, P.T. Atomic absorption techniques in archaeology. *Archaeometry* **1976**, *18*, 19–37. [CrossRef]
3. Renzi, M.; Montero-Ruiz, I.; Bode, M. Non-ferrous metallurgy from the Phoenician site of La Fonteta (Alicante, Spain): A study of provenance. *J. Archaeol. Sci.* **2009**, *36*, 2584–2596. [CrossRef]
4. Giussani, B.; Monticelli, D.; Rampazzi, L. Role of laser ablation–inductively coupled plasma–mass spectrometry in cultural heritage research: A review. *Anal. Chim. Acta* **2009**, *635*, 6–21. [CrossRef] [PubMed]
5. Palleschi, V. Laser-induced breakdown spectroscopy: Principles of the technique and future trends. *ChemTexts* **2020**, *6*, 1–16. [CrossRef]
6. Pauna, C.; Constantinescu, B.; Constantin, F.; Bugoi, R.; Stan, D.; Vasilescu, A.; Caballero, J.A.; Alonso, C.E.; Andrés, M.V.; García Ramos, J.E.; et al. Archaeometrical studies using X-ray fluorescence methods. *AIP Conf. Proc.* **2010**, *1231*, 187–188. [CrossRef]
7. Ferretti, M.; Cristoforetti, G.; Legnaioli, S.; Palleschi, V.; Salvetti, A.; Tognoni, E.; Console, E.; Palaia, P. In situ study of the Porticello Bronzes by portable X-ray fluorescence and laser-induced breakdown spectroscopy. *Spectrochim. Acta Part B At. Spectrosc.* **2007**, *62*, 1512–1518. [CrossRef]

8. Nagel, W.; Strommeger, E. *Kalakent: Früheiszeitliche Grabfunde Aus Dem Transkaukasischen Gebiet von Kirovabad, Jelisavetopol*; Berlin Wissenschaftsverlag Volker Spiess: Berlin, Germany, 1985.
9. Jalilov, B.M. *Ancient Metallurgy and Metalworking in Azerbaijan*; Science and Education: Baku, Azerbaijan, 2019.
10. Courcier, A.; Jalilov, B.M.; Aliyev, I.; Guliyev, F.; Jansen, M.; Lyonnet, B.; Mukhtarov, N.; Museibli, N. The Ancient Metallurgy in Azerbaijan from the End of the Neolithic to the Early Bronze Age (6th–3rd Millennium BCE): An Overview in the Light of New Discoveries and Recent Archaeometallurgical Research. In *From Bright Ores to Shiny Metals*; Festschrift for A. Hauptmann; Körlin, G., Prange, M., Stöllner, T., Yalçin, U., Eds.; Deutsches Bergbau-Museum: Bochum, Germany, 2016.
11. He, F.; Van Espen, P.J. General approach for quantitative energy dispersive X-ray fluorescence analysis based on fundamental parameters. *Anal. Chem.* **1991**, *63*, 2237–2244. [CrossRef]
12. Solé, V.A.; Papillon, E.; Cotte, M.; Walter, P.; Susini, J. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. *Spectrochim. Acta Part B At. Spectrosc.* **2006**, *62*, 63–68. [CrossRef]
13. Palleschi, V. (Ed.) *Chemometrics and Numerical Methods in LIBS*; John Wiley & Sons: Hoboken, NJ, USA, 2022; ISBN 978-1-119-75957-7.
14. Odelli, E.; Palleschi, V.; Legnaioli, S.; Cantini, F.; Raneri, S. Graph clustering and portable X-Ray Fluorescence: An application for in situ, fast and preliminary classification of transport amphoras. *Spectrochim. Acta Part B At. Spectrosc.* **2020**, *172*, 105966. [CrossRef]
15. Kashkay, M.A.; Selimkhanov, I.R. Investigation of copper-arsenic objects from the excavations of the Kultepe hill in the Nakhichevan Autonomous Soviet Socialist Republic. *Rep. Acad. Sci. Azerbaijan SSR* **1957**, *4*, 449–454.
16. Kashkay, M.A.; Selimkhanov, I.R. *From the History of Ancient Metallurgy in the Caucasus*; Elm: Baku, Azerbaijan, 1973.
17. Selimkhanov, I.R. *Unraveled Secrets of Ancient Bronze*; Nauka: Moscow, Russia, 1970.
18. Jalilov, B.M. *Metal Products Found from Archaeological Excavations at New Construction Sites, AMEA AEİ, Materials of the Scientific Session Devoted to the Results of the Archaeological Excavations Carried Out in 2003–2004*; Nafta Press: Baku, Azerbaijan, 2005; pp. 53–54.
19. Jalilov, B.M. *Metal Items from the Hajivellersky Necropolis, International Scientific Conference "Archaeology, Ethnology, Folklore of the Caucasus"*; Nurlar: Baku, Azerbaijan, 2005; pp. 96–99.
20. Spitsyn, A.S. Some Transcaucasian Burial Grounds. *News Imp. Archaeol. Comm.* **1909**, *29*, 3–15.
21. Bakhshaliev, V.B. *Ancient Metallurgy and Metalworking in the Territory of Nakhichevan*; Elm: Baku, Azerbaijan, 2005.
22. Aslanov, G.M.; Vaidov, R.M.; Ione, G.I. *Ancient Mingachevir*; Publishing House of the Academy of Sciences of the Azerbaijan SSR: Baku, Azerbaijan, 1959.
23. Kesamanly, G.P. *Archaeological Monuments of the Bronze and Early Iron Age of the Dashkesan Region*; Agridag: Baku, Azerbaijan, 1999.