NDT Methodology for Copper-Based Artifacts

Subjects: Archaeology
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The great archaeological and artistic value of historic copper-based artifacts from various archaeological sites of Greece results in the restriction or even the prohibition of sampling, settling the need for the employment of non-destructive testing (NDT) techniques. X-ray fluorescence (XRF), fiber optics diffuse reflectance spectroscopy (FORS) and scanning electron microscopy coupled with an energy dispersive X-ray detector (ESEM-EDX).

Keywords: XRF spectroscopy ; FORS ; ESEM-EDX ; arsenical copper ; tin bronze ; corrosion ; alloy composition ; Late Bronze Age ; Early Bronze Age

1. Overview

A multi-analytical non-destructive testing (NDT) methodology was applied to copper-based artifacts originated from various archaeological sites of Greece. X-ray fluorescence (XRF), fiber optics diffuse reflectance spectroscopy (FORS) and scanning electron microscopy coupled with an energy dispersive X-ray detector (ESEM-EDX) were used for the characterization of the alloys and the corrosion products. The key elements of the artifacts belonging to the Early Bronze Age (2700–2300 BC) were copper and arsenic, while tin bronze was used for the fabrication of the Late Bronze Age (1600–1100 BC) artifacts. The effectiveness of XRF for the determination of the bulk composition was confirmed by comparative study with the previously applied atomic absorption spectroscopy (AAS) and inductively coupled plasma–atomic emission spectrometry (ICP-AES) destructive techniques. Significant differences between the artifacts were revealed through the spectral measurement of their surface corrosion products color by FORS. ESEM-EDX provided information on the microstructure, the elemental composition of the corrosion layers and bulk, as well as the distribution of the corrosion products on the surface. Conclusively, the combined NDT methodology could be regarded as a valuable and appropriate tool for the elemental composition of the bulk alloy, thus leading to the classification of their historical period and the corrosion products, contributing significantly to their conservation–restoration.

2. NDT Methodology

Copper was the first metal used and dates back at least ten thousand years B.C. The first evidence for the exploitation of copper ore comes from the region of Anatolia and Iran, where copper objects date from the 9th to the 7th millennium B.C. During the 4th millennium B.C., the practice of alloying became widely known and used during the Early Bronze Age (EBA), unlike the earlier Copper Age (or Chalcolithic period), when copper (Cu) predominated in metalworking [1][2][3].

In Greece, alloying Cu with arsenic (As) begins during the Late Neolithic and the Early Bronze Age (EBA), significantly enhancing the workability. Arsenical copper was used in all parts of ancient Greece and mainly in the Aegean region. Following the arsenical copper, arsenical bronze (as an intermediate step) and then bronze (Cu-Sn alloy) emerged during the Late Bronze Age (LBA), although low (about 1–3 wt%) tin (Sn) alloys can be found in all civilizations and might have been accidentally produced by natural tin bronze deposits. However, bronzes containing Sn in a higher concentration (above 5 wt%) are mostly deliberate alloys by the addition of cassiterite (SnO_2) to molten copper [4].

The investigation of historic copper-based artifacts, of various historical periods and origins, has been the objective of numerous research studies. During the past years, the destructive techniques of atomic absorption spectroscopy (AAS) [4][5][6][7][8][9][10][11][12][13][14] and inductively coupled plasma–atomic emission spectrometry (ICP-AES) [14][15][16][17] predominated for the determination of the bulk chemical composition of historic artifacts. In addition, research is also focused on the characterization of the surface corrosion products and the investigation of their formation mechanism [18][19][20][21][22], via the employment of several different techniques, either alone or combined. Patinas can provide valuable indications for the composition of the bulk, since the nature of the corrosion products that are formed on their surface is differentiated depending on the nature of the alloy used, museum conditions and the burial environment and the species of the environment (moisture, air, pH, ions concentration, soil composition, presence of microorganisms, objects of different composition buried in the same place, etc.). Additional information that can be derived includes their historical period, their place of origin but also their burial environment through the identification of the physicochemical processes that took place during their corrosion [23][24].

However, the great archaeological and artistic value of historic copper-based artifacts results in the restriction or even the prohibition of sampling, settling the need for the employment of non-destructive testing (NDT) techniques.

In the present work, a multi-analytical NDT methodology consisting of *in situ* XRF and FORS was used for the investigation of 32 copper-based artifacts dated at the Early Bronze Age (2700–2300 BC) and the Late Bronze Age (1600–1100 BC). The artifacts originated from various archaeological sites of Greece and belong to the Prehistoric Collection of the National Archaeological Museum of Athens, Greece. A total of 19 copper-based chisels originated from Macedonia, Petralona, and dated at the EBA II (2700–2300 BC) have been examined (Figure 1). The chisels belong to the so-called “Petralona hoard”. The term “hoard” is used to describe a deliberately gathered and hidden group of precious objects during troubled times [13]. .All chisels were cast in an open mold and then finished by hammering. The investigated one-handled bowl, a luxury object of its time (object No. 10816), was found in numerous fragments, being part of the Mycenaean “Andronianoi hoard”, which consists of 9 artifacts (Figure 2), discovered in Andronianoi, Euboea, Greece, and dated at the LBA (1600–1100 BC), specifically to the Late Helladic IIB period (1450–1400 BC). The group from Andronianoi is probably to be assigned to the active scene of metalworking and commercial exchanges of the wider region and the nearby harbor of Kyme, as a hoard for exchange during 1500–1300 BC [25]. Apart from the bowl, 8 copper-based objects of “Andronianoi hoard” such as a saw, double axe, daggers, swords, razor and spearhead were investigated. Among the studied artifacts, two Naue II swords of unknown provenance (Nos. 9885 and 13905), a bowl (No. 11934) and a large basin (No. 11949) from Peloponnese, Argolid, dated back at the LBA (14th–12th Century BC) were also analyzed (Figure 3). The term “Naue II” sword type is believed to be of west European origin and was introduced into the Aegean by way of the Adriatic in the second half of the 13th century BC. During the 12th BC the swords, now of local manufacture, were widely distributed in the Greek Mainland especially in Achaea, Peloponnese and also found in Cyclades, Dodecanese, Crete.

The combined methodology of portable XRF and FORS was applied to multiple spots of the corroded surface of the objects. A small-size fragment of the object No 10816 was analyzed using the ESEM-EDX technique for the microstructure investigation and the analysis of the bulk and the surface corrosion products chemical elemental composition. ESEM-EDX was used in a completely non-destructive manner for the investigation of copper alloy patina and the integrity of the object itself was not affected by the analysis being performed. The quantitative results of XRF analysis were compared with detailed bulk composition analysis obtained by destructive laboratory techniques in order to assess the accuracy and reliability of XRF analysis in corroded surfaces. The bulk composition of the former objects has been determined in the past by means of AAS (performed in the Chemical and Physical Research Department of the National Archaeological Museum of Athens) and ICP-AES (performed in the Chemical Engineering School of National Technical University of Athens) techniques [4][12][15][17].

Figure 1. 19 Chisels originated from Macedonia, Chalkidiki, Petralona, and dated at the Early Bronze Age (2700–2300 BC) —Nos. 17794–17812.

Figure 2. Nine copper-based objects (a saw, a double axe, daggers, swords, a razor, a spearhead and a bowl in fragments) originated from Euboea—the "Andronianoi hoard"—Nos. 10797, 10798, 10810–10816, dated back at the LBA (15th–12th century BC).

Figure 3. Copper-based Naue II swords of unknown provenance (Nos. 9885 and 13905), a bowl (No. 11934) and a large basin (No. 11949) from Peloponnese, Argolid, dated back at the LBA (14th–12th century BC).

3. Discussion

A collection of 32 copper -based artifacts was investigated with the use of a combined NDT methodology for the chemical characterization of the bulk and corrosion products. XRF analysis was applied on the surface of the copper-based artifacts in order to yield qualitative and quantitative information regarding the chemical elemental composition, enabling the characterization of the metal or metal alloy, the identification of the historical period of copper-based artifacts through evidence of key-elements, also having the potential to relate metal compositions to ore deposits through their minor element pattern. The accuracy and resolution of the XRF analysis was confirmed by comparing the acquired XRF data with the former compositional data, obtained by means of and ICP-AES, as mentioned above. XRF analysis enabled the identification of major and minor elements of the Early and Late Bronze Age artifacts and allowed the determination of the key-elements. Apart from the main element Cu, As and Bi were detected in the artifacts from for the Early Bronze Age. Cu and Sn were identified in the objects dated at the Late Bronze Age. The elemental characterization of the alloys (Cu-As and Cu-Sn) became the determinant factors in the classification of the copper-based objects into two different historical periods. The high concentration of As is indicative of a copper-arsenic alloy which provides the alloy with upgraded mechanical properties. An increased concentration of As (>0.5 wt%) enhances cold work hardness and castability and decreases the melting point of copper [26]. Due to the geological co-occurrence of arsenic and copper minerals as well as the smelting of such polymetallic ores for the production of arsenical copper, it has not been established if arsenical copper alloys were deliberately or intentionally created [27]. The presence of Pb can be considered as random and it is probably related to the impurities of particular copper ores used for the fabrication of these alloys or providing a clue for the use of recycled metals [28]. The high Fe content may be attributed to remains from the surrounding environment, deposited on their surface, since the examined Early Bronze Age objects have not been submitted to any cleaning treatment. The chemical characterization of the Late Bronze Age artifacts revealed that they consisted of high purity tin-bronze alloys content and low presence of impurities, independently from their provenance and typology. Due to the mechanical cleaning of their surfaces, lower Fe concentrations were detected, compared to the EBA artifacts.

Although XRF analysis is performed on the corroded surfaces of the artifacts and may alter the determined concentrations of secondary metals, in our case, the accuracy of the XRF analysis was not affected. As a surface technique, XRF analysis is representative for the bulk alloy when the surface is consistent with the underlying metal. Due to its significant advantage over methods that require sampling and a single analysis may or may not represent the entire object, XRF allows the non-destructive examination of multiple spots. Thus, large scale variations can be identified properly and representative results can be obtained [28]. As a result, in situ XRF technique allows the qualitative and quantitative analysis of the determinant elements that classify the copper-based objects into the specific historical period.

VIS-NIR FORS analysis was performed in situ on the green corroded surfaces of the copper-based objects. FORS is a surface analysis and may allow the chemical and mineralogical characterization of surface corrosion products, based on chemical fingerprints, as well as an approach of the identification of the bulk alloy composition through the spectral measurement of their surface corrosion products color. Significant differences were observed in the maximum wavelength of the diffuse reflectance curve and reflectance intensity differences between the EBA and LBA objects reflectance spectra. The presence of malachite was indicated in LBA objects. Malachite is acknowledged as the most usual corrosion product developed by the corrosion of copper alloys buried in the soil. The first product to be formed, adjacent to the metal surface, is cuprite [29][30][31].

According to ESEM-EDX analysis, there are three corrosion layers. The outer corrosion layer presents a green hue and consists of alkaline compounds of copper (II) such as hydrocarbons, hydrochlorides, hydroxides and hydrosilicates together with silica or aluminosilicates due to the burial environment. The intermediate layer contains cuprous oxides as well as chloride ions, while the chemical composition of the internal corrosion layer—in contact with the bulk of the object—is characterized by the presence of Cu with O and locally Si, but also Sn and Cl [19][23][31][32][33][34][35][36][37].

4. Conclusions

Archaeological copper-based artifacts of different historical periods and various origins were studied, via a multi-analytical NDT methodology including portable XRF and FORS. In addition to the former in situ techniques, ESEM-EDX, a laboratory technique, was used in a non-destructive manner, as the integrity of the fragment was not affected. The extensive use of arsenical copper alloys in Early Bronze Age was confirmed due to the determination of copper and arsenic elements by XRF analysis. On the contrary, tin bronze alloys prevailed in Late Bronze Age, as copper and tin were the main elements in the selected copper-based objects. Although XRF technique is performed on the surface, it is well-suited for the identification of the alloys, as the results are in good agreement with the elemental concentration values of previously applied AAS and ICP-AES techniques. Additionally, FORS technique indicates the spectral differences between the Early and the Late Bronze Age objects. ESEM-EDX analysis confirmed the reliability of XRF results and also enabled the differentiation of the surface corrosion products from the elemental composition of the bulk. Conclusively, the combined methodology XRF and FORS could be regarded as a valuable and appropriate non-destructive tool for the identification of the bulk alloy composition of historic copper-based objects, leading to their historical period classification and contributing significantly to their conservation–restoration. The additional application of ESEM-EDX, in case sampling is allowed, can integrate the results concerning the investigation of the corrosion products.

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