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Characterizing archaeological bronze corrosion products intersecting electrochemical impedance measurements with voltammetry of immobilized particles

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ABSTRACT

Application of electrochemical impedance measurements to microparticulate deposits of copper corrosion products attached to graphite electrodes in contact with 0.10 M aqueous $HClO_4$ electrolyte is described. The impedance measurements were sensitive to the applied potential and the amount of solid sample and were modeled taking into account the contribution of the uncovered base electrode. Several pairs of circuit elements provide monotonic variations which are able to characterize different corrosion compounds regardless the amount of microparticulate solid on the electrode. Application to a set of archaeological samples from the archaeological Roman site of Gadara (Jordan, 4th century AD) permitted to establish a grouping of such samples suggesting different provenances/manufacturing techniques.

1. Introduction

Tracing the provenance and technique of fabrication of archaeological objects are obvious targets for archaeologists, conservators and restorers. In the case of metal artifacts, this information can be derived from the chemical composition of the alloy, isotope ratios, and the microstructure of the alloy and patina from metallographic cross sections [1–4]. In general, however, sampling the metal core is not allowed or seriously restricted for archaeological objects, so that the characterization of the metallic material, manufacturing technique, etc. have to be obtained from the physico-chemical properties of the metal patina [5–8]. For this purpose a wide variety of microscopy, spectroscopy, diffraction and electrochemistry derived techniques have been used [9–15].

In this context, the voltammetry of immobilized particles (VIMP), a solid-state electrochemical methodology developed by Scholz et al. [16,17], was applied to obtain analytical information on archaeological materials [18–20]. This technique, which provides information on sparingly soluble solids attached to inert electrodes, has been applied for identifying [21–25] and quantifying [26] metals and alloys. Sampling strategies based on 'graphite pencil' electrodes [27–29], have been exploited for mapping [30] and layer-by-layer [31] analysis and implemented for characterizing corrosion products [32], authentication [33,34] and dating [35,36].

In turn, electrochemical impedance spectroscopy (EIS), is an electrochemical technique extensively used in the study of metal corrosion [37,38], which has also been applied to characterize archaeological copper/bronze [12,39–43], and dating purposes [44,45]. All these approaches involve the study of the archaeological object or a representative fragment and its placement in contact with a suitable electrolyte, and require the existence of metal core available for establishing electrical contact. In most cases of archaeological interest, however, there is no possibility of accessing to the metallic core and only the more or less

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