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Electrochemistry reveals archaeological materials

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Abstract

The characterization of materials constituting cultural artefacts is a challenging step in their conservation, due to the object's uniqueness and the reduced number of conservation institutes able to supply non-destructive analysis. We propose an alternative analytical tool, which combines accessibility (low cost and portable) and high sensitivity, based on electrochemical linear sweep voltammetry (LSV) with paraffin impregnated graphite electrode (PIGE). To investigate the composition of "white alloys" that certainly have been used as decoration on copper-based Roman fibulae, sampling was done very locally by gently rubbing the selected areas with the PIGE. LSV results evidence the presence of silver, lead, and tin, supporting the argument provided by typological analysis that these metals were used for decoration.

Cultural artefacts are testimony of the past, and their constituting materials carry precious information about techniques used by our ancestors, making adequate characterization an essential step in their right understanding and proper treatment for conservation [1]. Such a characterization is challenging, because of the lack of information about provenance and use of many ancient objects, and also, due to their own chemical and structural heterogeneity. Furthermore, each artefact is unique, and analysis should be carried out without threatening its integrity. To accomplish this task, an emerging multidisciplinary field—conservation science—has been applying "non-destructive" analytical techniques, like x-ray fluorescence, particle-induced x-ray emission, and Raman spectroscopy [2]. Despite the potential of such methods, an obvious drawback exists when balancing their cost and scarce availability to conservators. In this report, we demonstrate that besides the traditional use of electrochemical techniques in the treatment of metallic artefacts [3], linear sweep voltammetry (LSV) on paraffin impregnated graphite electrode (PIGE) is an accessible and effective analytical tool for the identification of their constituent materials [4].

The investigation of component materials of two Roman fibulae exemplifies a common archaeological query. One of them (Fig. 1a) is an Almgren-type, coming from a cemetery in the neighbourhood of Namur (Belgium). The other one (Fig. 1b) comes from a recent excavation in Paris (France). Both artefacts are probably made of bronze or brass, as suggested by the extensive greenish areas, certainly arising from copper corrosion. It is worth noticing the greyish regions (differently arranged on each object), probably originating from a differently coloured alloy applied as decoration. In the case of fibula A, the grey area is sufficiently extensive to confirm that a white metal, either silver or tin alloy, has been applied. Concerning fibula B, the greyish region is powdery and occurs exclusively inside the longitudinal grooves, not clearly evidencing the use of another alloy. Critical examination and assignment of such details is not only essential when defining a conservation treatment but also can help specialists to identify workshops and trade routes [5].

To answer the above query, we performed LSV using a PIGE, which combines stability with simplicity of mechanical renewal of the sampling surface [6]. It was gently rubbed on selected areas of the object in order to transfer extremely small amount of material on its top, which was then immersed in a three-electrode electrochemical cell containing a 0.1-M oxalic acid solution (Fig. 1c). Using a Palmsens potentiostat, a negative potential was first applied in order to reduce the product attached to the PIGE surface. Measurements were then performed by sweeping the potential towards positive values at a rate of 10 mV/s. In this path, any available metal at the top of the PIGE would be oxidised at a characteristic potential, producing a current peak that allows its identification, as demonstrated with the test probes (Fig. 1d, bottom) [7].

In the case of the Almgren-type fibula (analysed area indicated by arrow), LSV reproducibly shows two current peaks (Fig. 1d, upper curve). The one starting at −0.1 V vs mercury sulphate electrode (MSE) corresponds to the oxidation of silver, clearly confirming that this metal, and not tin, was used for decoration. The presence of copper (peak at −0.4 V vs MSE) is probably resulting from an alloy or from corrosion contamination from the body. In the case of the Gallo-Roman fibula, due to the tiny and localised amount of the grey product (arrow 2), we had to use a stainless steel needle under a binocular to collect microsamples, which were then transferred onto the PIGE. Corresponding LSV (Fig. 1d, middle, curve 2) exhibits two peaks: a double one (ca. −0.95 V vs MSE), which is attributed to the oxidation of tin and lead and another one more positive (−0.4 V vs MSE), assigned to copper oxidation. Repeating the same procedure for the green areas outside the grooves (arrow 3) reveals only the presence of copper (Fig. 1d, middle, curve 3), demonstrating, therefore, that tin and lead had been applied exclusively locally.

Our study shows that PIGE/LSV combine into an extremely sensitive method for investigation, locally and non-invasively, of the presence of alloys constituting metallic objects. In addition, its accessibility makes it an excellent tool for preliminary characterization, avoiding inadvertent removal or transformation of pertinent original material during conservation treatments, as well as to complete technical information, which is of great significance in the study of cultural heritage.

References

1. Berducou M (2000) Introduction to archaeological conservation. In: Stanley-Price N, Talley MK Jr, Vaccaro AM (eds) Historical and philosophical issues in the conservation of cultural heritage. Getty Conservation Institute, Los Angeles, p 248
2. Adriaens A, Denker A, Griesser M (2002) Non-destructive analysis and testing of museum objects: the new European Action COST G8, archaeometry in Europe in the

thirdmillennium.Accademia Nazionale dei Lincei, Rome p 169. http://www.srs.dl.ac.uk/arch/cost-g8/. Accessed 29 March 2009
3. Costa V (2005) Electrochemical techniques applied to metals conservation. In: Vandiver P, Mass J, Murray A, Merkel J (eds) Materials issues in art and archaeology VII, vol. 852. Materials Research Society, Warrendale, p 89
4. Domenech-Carbo A (2008) Identification of species by electrochemical methods. In: Domenech-Carbo A, Domenech-Carbo MT, Costa V (eds) Electrochemical methods in archaeometry, conservation and restoration. Springer-Verlag, Berlin Heidelberg, p 33
5. Bailey J, Butcher S (2004) Roman brooches in Britain: a technological and typological study based on the Richborough collection. Society of Antiquaries of London, London
6. Scholz F, Schröder U, Gulaboski R (2005) Electrochemistry of immobilized particles and droplets. Springer, Heidelberg
7. Madec S (2006) Caractérisation électrochimique des matériaux constitutifs des objets archéologiques en métal. Ecole Nationale Supérieure de Chimie de Paris, Paris

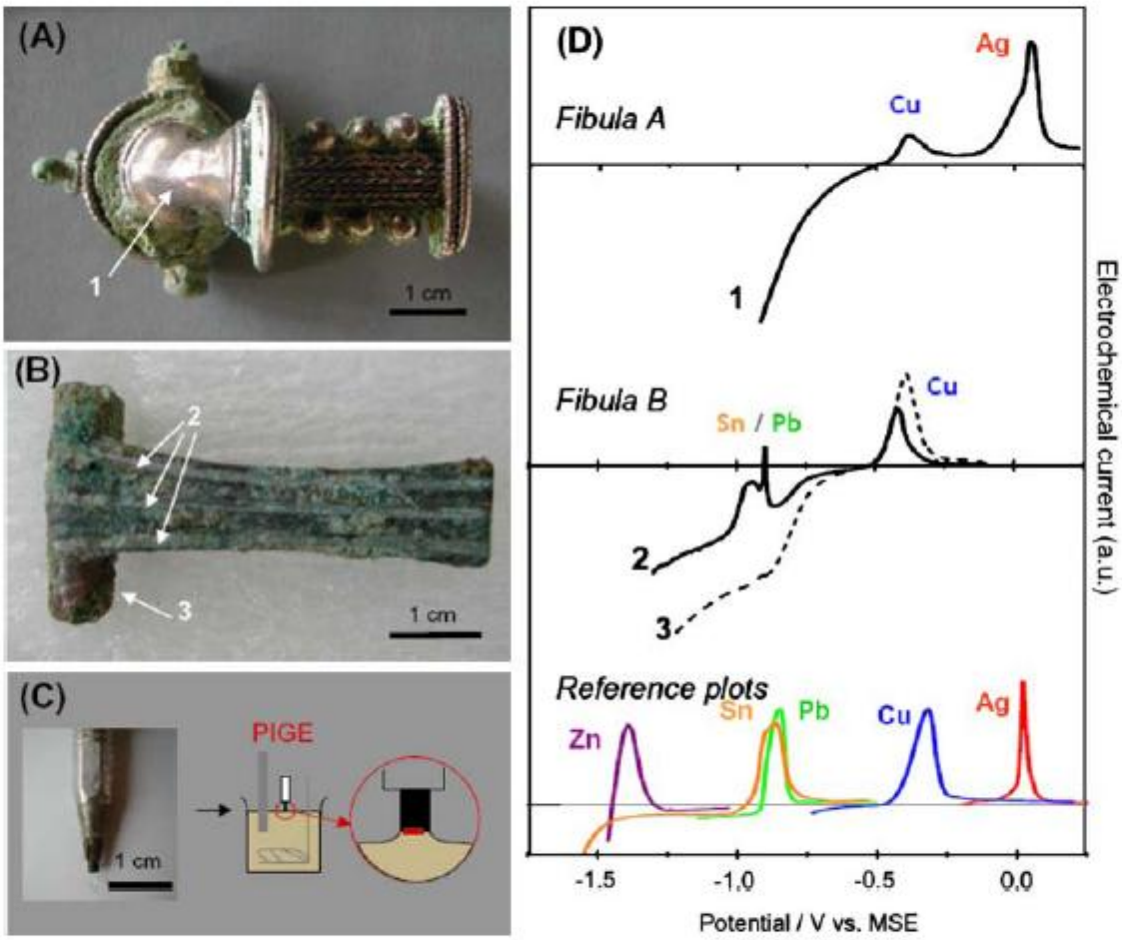

Figure 1. Electrochemical analysis of materials constituting the fibulae. a Almgren. b Gallo-Roman. c Electrochemical set up: PIGE in the three-electrode cell. d LSV (0.1 M oxalic acid)

corresponding to oxidation of a small amount of material transferred on the PIGE: top, from Almgren fibula (area 1), indicating the presence of Cu and Ag; middle, from Gallo-Roman fibula: the greyish region (area 2) contains Sn, Pb, and Cu; the greenish region (area 3) contains only Cu; bottom, the series of reference curves, obtained with particles of pure metals.