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Electrochemical techniques applied to the study of archaeological pigments. The Voltammetry of Microparticles

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Abstract— The Voltammetry of Microparticles (VMP) is an analytical technique mainly applied to the industrial field. The present work explores its utility in Archaeology, through the identification of the mineral composition of paints and engobes used in the coating of archaeological ceramic pieces. Its application enabled the detection of the use of mineral composites such as magnetite and hematite in the obtention of black and red pigments.

Index Terms— Voltammetry of Microparticles, archaeological ceramics, pigments, minerals

1 Introduction

THE Voltammetry of Microparticles (VMP) is currently one of the most appropriate electrochemical techniques for the characterization of low-electrical and weakly-magnetic conductivity in solids. It is applied to the identification of iron oxides and oxyhydroxides in synthetic and natural samples.

Contrasting with magnetic methods, which depend heavily on the presence of magnetite, VMP is sensitive to the identification of other weak-magnetism minerals, such as goethite and hematite [1], [2], [3]. In addition, it only requires a few micrograms of sample, regardless of their degree of crystallinity (also amorphous phases can be detected), yielding precise and fast measurements.

So far, this technique was effectively applied fundamentally in the industrial sphere, although its potential for other fields such as environmental and palaeoenvironmental studies have already been posited [4], [5], [6]. In this work, we aim to make a preliminary contribution to the exploration of its utility in archaeological pigmentary samples, commonly used in the coating of pieces manufactured in pre-Hispanic times, particularly in the form of total coating (engobe) or partial coating (paints).

In archaeological ceramics, the use of these pigment mixes for decorative purposes is widespread and functional as well. Typically, they are obtained through the mixing of clay, water and minerals, achieving a fluid suspension applied to the surface of the pieces after they are shaped [7].

2 Materials and Methods

The equipment used in the application of VMP is comprised by an electrochemical cell containing three electrodes immerse in a saline solution (0.2M of acetic acid + 0.2M of sodium acetate) acting as an electrolyte and a PAR model 273A potentiostat controlled by the Soft Corr corrosion Software, which conducts the monitoring.

The electrodes used are: a platinum wire electrode acting as an anode (it liberates electrons through oxidation), a Saturated Calomel electrode (used as referential electrode) and a graphite electrode, or cathode, where the reduction of the iron oxides occurs.

The electrochemical reduction of the oxides present in the sample is conducted through linear potential sweeping at a rate of 0.3 V (SCE) and -1.2 V (SCE) with a sweeping speed of $4 mV.s^{-1}$. The sweep time applied to the ceramics pieces was six minutes.

In order to achieve a better definition of the current peaks and minimize the effects of bottom current, three successive sweeps were conducted. The results were obtained on the basis of the difference between the first and the second, and between the second and the third [1], [8], [3].

The studied samples are comprised of fine dust, corresponding to the engobe or paint of three ceramic fragments from two archaeological sites of the Inca Period (1480-1530 AD) from the Tafí Valley, Tucumán, Argentina (Table 1). The fragments were previously studied to determine macroscopic characteristics pertinent to the current study, such as surface color, coating degree and degree of alteration of the pigmented coating. In addition, the microscopic characteristics of the ceramic pastes were studied in order to obtain an overall characterization of the manufacturing technology behind the piece [9].

The studies were conducted at the Multidisciplinary Training Laboratory for Technological Research (LEMIT-CIC) and at the Research and Development Centre for Paint Technology (CIDEPINT-CONICET) and they were headed by Dr. J.C.Bidegain and Lic. Yamile Rico. The Equipment used in the measurement of the volume magnetic susceptibility, in SIx10-5 units, was a Bartington Susceptibilimeter with a MS2F sensor.

The measurement of the magnetic susceptibility of the ceramic pieces yielded the preliminary information on the mineral magnetic distinction on the basis of color. Black yielded SI susceptibility values significantly higher to red, as indicated by the measurements conducted on sediments [10], indicating

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a higher proportion of titanomagnetite minerals in the first and more oxidized phases, hematites, in the second. On the basis of these data and the granulometry of the ceramics, the Voltammetry of Microparticles technique was applied to determine the minerals causing the differences.

TABLE 1
DETAIL OF THE STUDIED SAMPLE

Identification	Archaeological Site	Type decora-	Pigment analized
LC(1)21	LC(1)	Belén	Red engobe
LC(1)109	LC(1)	Santa	Black paint
LC61b28	LCZVIIIS1	Famaba-	Black paint

3 Results

The results obtained through the application of this technique yield the presence of hematite and magnetite iron oxides in the studied pigments. The current peak potentials (Pps), Pp2:-0,44V, Pp3:-0,58V y Pp4:-0,71V, obtained for sample LC(1)109, evidence the presence of different hematite crystalline phases, while peaks Pp1:-0,15V and Pp5:-1,09V correspond to a magnetite (Figure 1).

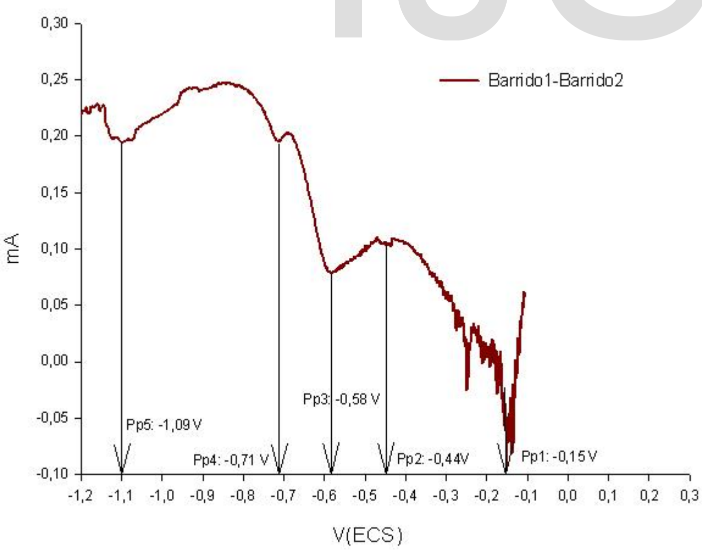

Fig. 1. Voltammogram of sample LC(1)109

For sample LC61b28, it was possible to distinguish two current peaks corresponding to a hematite (Pp2:-0,38V y Pp3: -0,62V), and two others (Pp1:-0,16V y Pp4:-1,15V) indicating the presence of a magnetite [Figure 2]. For LC(1)21, two current peaks were determined, one at -0,18V (Pp1) and the other at -0,65V (Pp2), the latter being the most characteristic among in the hematite phase as indicated in previous works [Figure 3].

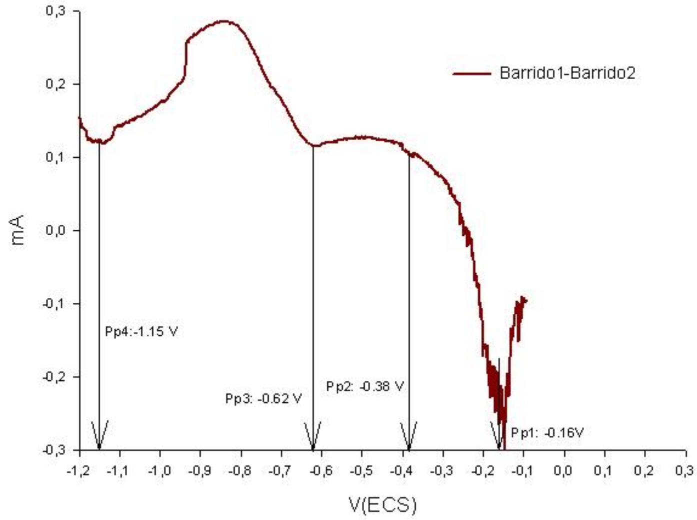

Fig. 2. Voltammogram of sample LC61b28

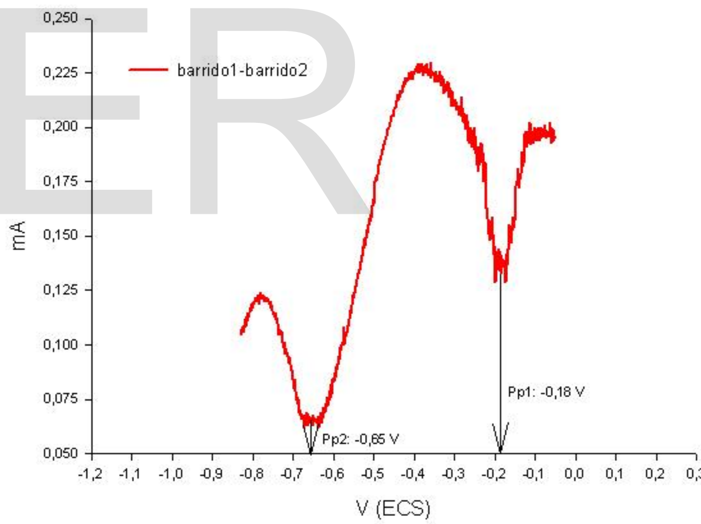

Fig. 3. Voltammogram of sample LC(1)21

The similarity between the voltammograms obtained for samples LC(1)109 and LC61b28, and the difference between them and sample LC(1)21 are noteworthy. This enables the inference of a similar mineral composition for the first two pigments, which, in turn, is different from the latter.

This results are ratified by magnetic susceptibility measurements conducted prior to the application of the VMP, which, in the case of the black pigments [LC(1)109 and LC61b28], doubled the values yielded for the red pigments [LC(1)21].

Thus, the information obtained from the study of the three samples indicates the use of hematite and magnetite in the

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pigment mixes comprising red and black respectively.

4 Conclusions

The studies performed are a preliminary approximation for the application of VMP to archaeological pigment samples. The technique used does not allow the identification of non-oxide mineral compounds, such as the carbonates which were identified in the whitish pigments.

However, its utility was confirmed for the identification of some compounds used in archaeological coating, which makes VMP a proper complementary technique in pigment analysis.

The adjustment of the methodological aspects in this field encourages the possibility to develop the research on the field of ceramics manufacture of pre and post-Hispanic times.

Acknowledgment

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