Characterization of Costa Rican Archaeological Ceramics From the Formative Period: Preliminary Electrochemical Studies

Gerardine Conejo-Barboza1*, Jean Sanabria-Chinchilla1, Francisco Corrales Ulloa2, and Mavis Montero Villalobos3

1Escuela de Química - Centro de Electroquímica y Energía Química, Universidad de Costa Rica, San José, Costa Rica.
2Departamento de Antropología e Historia, Museo Nacional de Costa Rica, San José, Costa Rica.
3Escuela de Química - Centro de Electroquímica y Energía Química - Centro de Investigación en Ciencias e Ingeniería de los Materiales, Universidad de Costa Rica, San José, Costa Rica.

Abstract The study of archaeological samples through electrochemical methods may render valuable information about the manufacturing technology of ancient societies in the Costa Rican territory. The combination of immobilized micro-particles of archeological samples into a glass-conducting (ITO) substrate as an electrode with a Naion® binder, and the use of square wave voltammetry as analytical tool proved to be an advantageous method for the analysis of ceramic pieces in order to determine the ratio Fe3+/Fe2+ in the analyzed samples.

Statement of significance
Acquire information regarding the manufacturing and technological development from the oldest archaeological ceramic pieces found in Costa Rica, to understand the dynamic of the groups forming the ceramic complex of Tronadora and most important to improve a modified electrode in which is possible to analyze micro-particles from archaeological samples by using electrochemical methods which gives a precedent for novel studies.

Keywords ceramic; Formative Period; electrochemistry; micro-particles; modified electrode; Costa Rica; square wave voltammetry

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Introduction
Studies of archaeological materials may render valuable information regarding culture, technological processes and history of the past native societies offering valuable information for conservation and/or restoration of these materials (Gebhard 2003). Usually the analysis of archaeological artifacts is complex concerning the fact that there is not enough information related to their composition and provenance, nevertheless there are a lot of different techniques nowadays that can be very useful in order to obtain that type of information. One of those analytical techniques is electrochemistry. This technique is very versatile because it can be used for different approaches such as determining the chemical composition of cultural materials, also as a conservation or restoration procedure to improve the state of an artifact (Doménech-Carbó, Doménech-Carbó, and Costa 2009; Doménech-Carbó 2010).

*Corresponding author. email: cbgeraldine@gmail.com

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There are different electrochemical methods, the most common are: cyclic voltammetry (CV), linear sweep voltammetry (LSV) and square wave voltammetry (SWV) (Bard and Faulkner 2001). The advantage of using a pulsed technique such as SWV resides in obtaining a current signal with minimal capacitive (non-faradaic) contributions allowing an improvement in the sensitivity. These three electrochemical techniques have been used to study the composition of pigments in paints and glasses, iron components in ceramic pieces (Doménech-Carbó 2010; Doménech-Carbó, Doménech-Carbó, and Vázquez De Agredos-Pascual 2011; Pérez-Arantegui and Cebría 2014) and composition of metal objects (Costa et al. 2010; Degrigny 2010; Elia, Dowsett, and Adriaens 2015). The biggest challenge in this type of studies is the use and assembly of modified electrodes to immobilize the solid particles from the samples. It is difficult to control the amount of solid that is transferred to the electrode and to avoid losing solid particles during the measurements. There are several types of electrodes that can be used for the immobilization of particles such as carbon paste electrodes, polymeric film electrodes with embedded particles, paraffin impregnated with graphite electrodes. The majority of these systems keep the solid particles on the electrode; however, one disadvantage is that the amount of particles of the sample cannot be quantified when the impregnation is by mechanical means because there is not a relationship between the area under de curve for each signal (which is proportional to the amount of substance present in the sample) and a specific amount of sample initially placed on the electrode. It is important to improve this step in the electrode assembly in order to achieve an accurate determination (Doménech-Carbó, Labuda, and Scholz 2013; Scholz et al. 2014).

This work is based on the study of ceramic materials that belongs to the Formative Period in Costa Rica (2000 to 300 B.C). Ceramic pieces from this period correspond to the oldest artifacts found until now in the Costa Rican territory; however, most of pieces were fragments or shreds, just a few ones were in a complete state. Main forms were: ollas tecomates, globular vessels, plates and tecomates (globular vessels with comma-shaped restricted rims), while among the decorative modes it is possible to observe incising, shell and nail stamping, punctuation and the use of red pigments (Corrales Ulloa 2001; Snarski 1984; Reyes Paniagua 2009a).

Historically this period is related to the beginning of agriculture; a change that promoted a new way of living, from semi-nomads –sedentary and still egalitarian societies (Corrales Ulloa 2001; Reyes Paniagua 2009b). Along with this change, new requirements emerged, like the need of utensils to cook, eat and store food, and as consequence, the production of ceramic began or was adopted from neighbor societies.

To understand the Pre-Columbian period, the Costa Rican territory was divided according to spatial and temporary criteria in order to comprehend the distribution and particular characteristics of ancient societies in the country; the division

Figure 1 Location of ceramic complexes from the Formative Period in Costa Rica. Elaborated by María Lopez Rojas (Corrales Ulloa, Montero Villalobos, and Conejo Barboza 2015).
proposes three archaeological regions: Greater Nicoya, that goes from northeast Costa Rica to Pacific Nicaragua; the Central Region, from the Pacific coast to the Caribbean coast of Costa Rican territory; and Greater Chiriquí that goes from the southeast of Costa Rica to western of Panama (Corrales Ulloa 2001). Within these regions, eleven ceramic complexes have been associated to the Formative Period. This study will focus in the Tronadora complex (see Figure 1).

Tronadora was described by archaeologist John Hoopes in 1984. The complex is located in the Greater Nicoya archaeological region and it was found, mainly, in the Tronadora Vieja (G-163) site near the Arenal lagoon in the Guanacaste Range (Hoopes 1985; Snarskis 1978). This ceramic complex has five ceramic types that describe the complex: Tonjibe beige, Tronadora incised, Tigra Grooved-Punctate, Zetillal Shell-Stamped and Atlantic Red-Filled Black. The difference among the types of ceramic resides in the decoration of the pieces. The main representative of this complex is the tecomate vessel.

The analysis of archaeological ceramic of Costa Rica constitutes a mean to obtain valuable information about the manufacturing process of this type of artifacts, especially with samples from the Formative Period. The ceramic of this period is one of the least studied cases, and the importance of their study is focused in understanding the dynamic and technological development of the society of this period.

These ceramic materials are mainly composed by feldspar such as anorthite (Ca,Na(Si,Al)O₃), albite (Na (AlSi₃O₈), and silicon oxides like quartz (α-SiO₂) and cristobalite (SiO₂), also iron oxides such as hematite (α-Fe₂O₃), and augite (Mg,Fe,Ti,Al(Ca,Fe,Na,Mn) (SiAl)₂O₅ which are the main source of iron ions, and magnetite (Fe₃O₄) in a very low proportion for some studied cases, and the importance of their study is focused in understanding the dynamic and technological development of the society of this period.

Table 1 shows the six samples from the Tronadora complex used for the analysis by electrochemical methods. Samples were provided by the National Museum of Costa Rica. The selection of the samples was made using X-ray diffraction measurements of the ceramic pieces to check if there was presence of iron minerals. Also there is at least one sample per ceramic type, so in this way there is a representation of all the ceramic types that the complex posses.

Description of Archaeological samples

Modified electrodes preparation

To prepare the modified electrodes first it was necessary to grind a part of the ceramic pieces in an agate mortar. A sample of 2.5 mg of the powder was mixed with 1.99 mL of Milli-Q water, 500 µL of isopropanol and 10 µL Nafton® to form a suspension. The suspension was sonicated during 10 minutes and 200 µL of the suspension was applied over the conducting glass (ITO) and allowed to dry overnight.

Electrochemistry measurements

All measurements were carried out in an Autolab PGSTAT128N potentiostat/galvanostat using cyclic voltammetry (CV) and square wave voltammetry (SWV) as method of analysis. Experiments were performed at room temperature in acetate buffer as supporting electrolyte (pH= 4.72, 1.0 mol/L) under nitrogen atmosphere. All the potentials were referenced versus an Ag/AgCl, KCl (3.0 mol/L) reference electrode; a Pt-wire was used as auxiliary electrode. CV experiments were performed at a scan rate of 20 mV/s. SW experiments were performed under the following experimental conditions: amplitude (25 mV), step potential (4 mV), and frequency (10 Hz). Blanks were carried out using the conducting glass without the presence of the ceramic particles, at the same experimental conditions.

Results and Discussion

For the analysis of archaeological samples it is important to take into account the nonconductor nature of the samples, therefore the use of an electrode that provides both a good pathway for electron transfer and a consistent amount of electroactive material on the electrode surface are crucial steps in order to detect
and quantify the signals related to ions in the sample. Due to the unique nature of the material (archeological ceramic samples) all the preliminary tests were performed with magnetite (Fe₃O₄) as a reference material. This material was used due to the absence of certified reference material in our laboratory; additionally, it is easy to prepare and do not require an expensive characterization procedure. Additionally, magnetite contains Fe³⁺ and Fe²⁺ in the same matrix.

The first attempt to immobilize the magnetite micro-particles into an electrode was performed by pressing the material against a graphite bar. Graphite has good conductivity and is soft enough to mechanically embed the particles into the electrode. This approach was not entirely successful because it was observed that some of the particles detached from the electrode during the measurements. An extra problem with this system was the impossibility of knowing exactly the mass of the particles transferred to the electrode by pressing the material against it.

A paraffin impregnated graphite electrode (PIGE) was then used. Finely pulverized graphite was mixed with the magnetite micro-particles and paraffin (ratio 30:30:40, respectively) to obtain a paste consistence in the mixture. This mixture was not quite stable and the material was still falling down during the measurements. One advantage of this type of electrode is that an accurate amount of sample can be added; however, not all the sample mixed with the graphite would be electrochemically active since most of the material will be away from the interface with the solution. Furthermore, contributions in the total current coming from the paraffin and graphite would complicate the features in the voltammograms.

The electrochemical performance of these two types of electrodes was followed by cyclic voltammetry. As an example, Figure 2a shows the current-potential curve of magnetite on a graphite bar. The cathodic feature observed at -0.34 V is related with the reductive dissolution of the solid material; whereas, the broad anodic signal at +0.15 V corresponds to the combination of the oxidative dissolution of the solid material and the oxidation of solution-Fe²⁺ species to Fe³⁺ (Doménech-Carbó et al. 2002). The difference in intensity of these two signals can be correlated with the fact that from the electrochemical point of view, magnetite is described as (Fe³⁺)₂(Fe²⁺)(O²⁻)₄ where the Fe³⁺/Fe²⁺ molar ratio corresponds to 0.67 (Encinas et al. 1994).

In combination with magnetite, an archaeological sample (DA-12) was used to compare the observed voltammetric features; this sample was chosen because preliminary analysis of this sample by XRD shows the presence of magnetite in its structure. Figure 2b shows the CV of the archeological sample DA-12 showing a cathodic wave at -0.74 V and an anodic signal at +0.22 V. The signal at -0.74 V can be attributed to the reduction of previously dissolved Fe²⁺ species to Fe⁰ (Doménech-Carbó et al. 2002; Doménech-Carbó, Doménech-Carbó, and Osete-Cortina 2008). A closer look to these voltammograms indicates the presence of other very weak signals; however, CV is not sensitive enough to obtained defined signals.

The third option to immobilize the sample in an electrode was using a conductor glass (ITO) as support and the use of a binder such as a Nafion®. ITO was chosen in part because it was necessary to have an electrode with a constant surface area where the electroactive material (sample) would be applied in a thin layer to increase the exposure of the sample to the interface with the solution, additionally it has really good electrical conductive properties. Nafion® has been successfully used in modified electrodes with very good results in the preparation of electrocatalysts for fuel cell studies because allows a better contact of catalyst particles with the conductive substrate and improve the conductivity of the system as well. Furthermore, ITO can be reutilized because the composite layer is physically adsorbed on the substrate surface and by just washing the electrode with soap and water, the sample can be eliminated from the surface of the conductive glass, so the cost of the material laboratory can be lowered. Due to the small intensity of the signals observed in the CV with
the other type of electrodes, square wave voltammetry (SWV) was used. This technique allows analysis in samples where the signal/noise ratio is too low by CV (Bard and Faulkner 2001; Moretto et al. 2013).

The first measurements were performed with magnetite as a reference material in order to optimize the experimental conditions of the analysis. Figure 3 shows SW voltammetric anodic and cathodic scans for the magnetite electrode. Figure 3a shows five consecutive anodic scans and by comparison with figure 2a, it indicates the presence of two new features: The signal at −0.78 V corresponds to the oxidation of Fe⁰ (previously formed when the potential was set at −1.00 V) to Fe²⁺ and the signal at −0.34 V corresponding to the oxidative dissolution of Fe²⁺ from the magnetite micro-particles to Fe³⁺. Similarly, figure 3b shows five consecutive cathodic scans and by comparison with figure 2b, extra features at +0.03 V were observed. Signals around 0.00 V (vs. Ag/AgCl) have been associated with the reduction of solution-Fe²⁺ ions to Fe⁰ (Doménech-Carbó et al. 2002). It is important to notice that intensity of the signals in figure 3 decreases with the number of runs (from R1 to R5) indicating the dissolution of the material, also it has been demonstrated that the intensity and position of the peaks depends on the particle size, type of iron oxide, type of working electrode and electrolyte solution (Encinas et al. 1994; Doménech-Carbó 2010; Mouhandess, Chassagneux, and Vittori 1982).

Doménech-Carbó et al. developed three different quantification methods to estimate the ratio of iron species (as Fe³⁺/Fe²⁺) in archeological samples (Doménech-Carbó et al. 2002). From the three methods, the one based in the ratio of anodic signals seems to be more suitable because minimizes the contribution of solution species in the electrochemical response of solid-state iron species. Shortly, the chosen method consists in calculating the areas underneath the anodic peaks; then, the area of the peak at +0.20 V is divided by the sum of the areas of all the anodic peaks. This ratio corresponds to the molar ratio of Fe³⁺ in the sample. The obtained value for the magnetite sample analyzing the voltammetric curves in figure 3 corresponds to 0.63 in good agreement with the theoretical molar ratio of 0.67.

In the case of the archaeological samples the use of cyclic voltammetry with the ITO electrode did not show signals in the cathodic direction in most of the measured samples. For the anodic direction, it was possible to observe signals, but with low intensity, as in the case of the reference material; therefore, square wave voltammetry was selected as the method to study archeological materials. Six different archeological samples (TR01 to TR06) where analyzed by means of SW voltammetry. Figure 4 shows the SW voltammograms corresponding to sample TR06. As in the case of the magnetite, five consecutive anodic and cathodic runs were recorded. Anodic features are shown at −0.78 V and +0.19 V (figure 4a); whereas, cathodic signals are present at −0.25 V in the first scan and at +0.15 V in the following consecutive scans. Similar behavior was observed with the magnetite sample (figure 3b). Some of the analyzed samples (TR02, TR03) did not show signals during the cathodic SW voltammograms, not necessarily because there was not iron present in the sample. This behavior can be attributed to very low quantities of iron available in the sample, or dissolution processes of the electroactive species in the aqueous media during the electrochemical experiment. In this regard, obtaining the Fe³⁺ molar ratio of these samples is only possible utilizing the method previously described and used to determine the Fe³⁺ molar ratio in the magnetite sample. Results are summarized in table 2.

As it can be seen in table 2, all the ratios resulted with a value less than 1, this means samples contain mixtures of Fe³⁺ and Fe²⁺ oxides. Considering Doménech-Carbó’s work with certified clays (Doménech-Carbó et al. 2002), samples with values closer to 1 contain higher percentages of Fe₂O₃ vs. FeO. This do not means that these two type of oxides are the only iron species present in the sample; for example, presence of magnetite will change the molar ratio as well due to the combination of Fe³⁺ and Fe²⁺ in its structure.
Regarding the manufacture of ceramic pieces by native inhabitants in Costa Rica, the method of cooking ceramic pieces used in the Formative Period was the pit firing, which began by making a hole in the ground, then a combustible source like wood or charcoal was added, and above the fuel the ceramic pieces were placed; the hole was covered with plantain leaves or earth to conserve the heat of the fire. With this method, the maximum cooking temperature only was maintained for short period of time, not like more complex methods like the kiln firing. The atmosphere during the cooking process was mainly reductive, which means that is expected to have a mayor part of the iron minerals in the form of Fe$^{2+}$. Regarding the data obtained in Table 2, the molar fraction of Fe$^{3+}$ is low, which in the case of the samples analyzed is possible to said that the iron mineral present in the samples are mainly in the Fe$^{2+}$ form. This could be related to the mineral composition of the samples which is mainly hematite, magnetite and augite, where there is a complex mixture of sources of Fe$^{2+}$ and Fe$^{3+}$.

Additionally, it was possible to confirm that the cooking temperature for Tronadora samples was between 573-650 °C due to the presence of α-quartz in the X-ray diffraction pattern of the analyzed samples (Heaney and Veblen 1991; Leoni and Nesper 2000; Maritan et al. 2006; Sowa and Koch 2002), with an angle between 26 - 27 °, also the presence of this mineral was confirmed by the data base PDF-2 2007 of the International Centre for Diffraction Data (ICDD) (see Figure 5).

The final content of Fe$^{3+}$ and Fe$^{2+}$ species in the ceramic materials will depend of several factors such as chemical composition of starting materials, cooking temperature, length of the firing process of the pieces and oxidative or reductive conditions during the firing process.

### Table 2  Fe$^{3+}$ molar ratio for the archaeological samples and magnetite as a reference material, calculated by integration of anodic peaks (A) and determining the ratio A1/(A1 + A2).

| Sample (Tronadora Site) | A1       | A2       | Fe$^{3+}$ molar ratio (± 0.03) |
|-------------------------|----------|----------|-----------------------------|
| TR01                    | 3.30E-07 | 9.63E-07 | 0.26                        |
| TR02                    | 1.67E-07 | 2.73E-07 | 0.38                        |
| TR03                    | 1.27E-07 | 3.65E-07 | 0.26                        |
| TR04                    | 1.95E-07 | 4.31E-07 | 0.31                        |
| TR05                    | 2.73E-07 | 7.59E-07 | 0.26                        |
| TR06                    | 3.87E-07 | 9.52E-07 | 0.29                        |
| Magnetite               | 2.77E-06 | 1.60E-06 | 0.63                        |

Figure 4  Square wave voltammetry of sample TR06 in a) anodic and b) cathodic direction. Step potential: 4 mV, frequency: 10 Hz, amplitude: 25 mV.

Figure 5  X-Ray diffraction pattern of sample TR02.
cooking method. Due to the complexity of the process it is impossible to correlate the Fe$^{3+}$ molar ratio values obtained in this study with the conditions in which the ceramic pieces where prepared, but the data obtained provide a closer look of the technology used in the firing cooking for the ceramic samples. Further studies are necessary to establish the changes in chemical composition of the material with respect to the mentioned experimental conditions utilized during the manufacture of the ceramic pieces.

**Conclusions**

The use of a conducting glass substrate (ITO) in combination with Nano® as a binder improved some of the main disadvantages of the most common used electrodes for the analysis of archeological samples by electrochemical methods. The use of square wave voltammetry in contrast with cyclic voltammetry demonstrated to have a very good sensibility to the detection of iron ions from archaeological samples, which allows a quantification of the Fe$^{3+}$ molar ratio in the ceramic materials. This ratio gave information regarding the manufacturing technology used for cooking ceramic pieces in the Formative Period for the Tronadora complex. This information represents an important step in the journey to understand the technological development of the pre-Columbian groups in the Costa Rican territory.

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