MICRO-RAMAN SPECTROSCOPY OF DECORATED POTTERY OF THE DIAGUITA CULTURE FROM IV REGION, CHILE (9TH–15TH CENTURY AD)

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ABSTRACT

Raman spectroscopy pigments on decorated antique Chilean pottery belonging to the Diaguita's culture deposited in Museum of Limarí, have been studied by using Raman spectroscopy. Four ceramic fragments from the unknown contexts were examined. Four colors were found with certainty: red, black, brown and white. Quartz and manganese (kempite) salts, as well as different types of oxide pigments: hematite, tenorite and possibly goethite, were identified.

Keywords: Raman spectroscopy; pigment analysis; archaeometry; Diaguita ceramics

INTRODUCTION

The knowledge of the materials involved in artistic and cultural heritage, allows a better understanding of our civilization, and an improvement of the restoration and conservation methods. But, until recently, the study of works of art remained mainly the concern of research by art historians because the scientific techniques required a quantity of materials unacceptable for the integrity of the works. In fact, spectroscopic analyses are the most frequently used methods in the field of cultural heritage^{1,2}. Among them, Raman spectrometry is one of the most powerful due to its characteristics. The unique properties of this technique involve non-destructive nature, no sample preparation, reliability, specificity and sensitivity³⁻⁵. Thus, Raman spectrometers have become the instrument of choice when analyzing archaeological artifacts and pigments on art works⁶.

It is also amenable to *in situ* analysis, based in the development of fiber optics technology⁷⁻⁹. During the 1990s, the development of CCD as spectroscopy detectors and lasers led to cheaper and easy-to-use Raman spectrometers. Due to these special features, the literature shows that Raman spectroscopy has been studied extensively and applied widely.

The main applications in heritage studies concern the identification of pigments on various kinds of support materialities. Pigments, together with binders and fillers, give important information about artists, artistic schools or technological evolution; mainly inorganic compounds, pigments are good candidates for Raman identification. In order to enhance its efficiency, Raman spectrometers are typically coupled with a microscope in order to observe the sample and can take a Raman spectrum from a small area down to one micrometer^{10,11}. The use of Raman microscopy gives information on the microstructure of analyzed samples and also improves the spatial resolution. Nevertheless, its meaningful disadvantage still lies in the formation of undesirable fluorescence, which is an accompanying phenomenon of measurements of diverse materials and which is very difficult to forecast.

This paper reports on the micro-Raman spectroscopic investigation of pigments in decorated pottery from the Museum of Limarí, in Chile. These objects are belonging of the Diaguita culture, one of the distinct original people mainly settled during the pre-Columbian period in the III and IV region of the actual Chilean territory. Far as we know, this is the first time that this noteworthy kind of ceramics from the Valle del Elqui has been investigated by means of micro-Raman spectroscopy.

The Diaguita's people

The Diaguita's culture was mainly developed in different stages between the 9th and 15th century AD; this culture is recognized in the pre-Columbian American territory because of the plastic richness of its pottery¹². Geographically, the Diaguita culture spreads in the north of Chile over the transversal valleys of the Copiapó, Huasco, Elqui, Limarí and Choapa rivers, 18° to 31° south latitude. Three development phases in the Diaguita's culture have been recognized on the basis of the complexity in the manufacturing of pottery's artifacts. The last phase corresponding to Inca rule period¹³.

EXPERIMENTAL

Objects and sampling

It has been worked on 4 samples of ceramics fragments belonging to the Museum of Limarí; samples are arbitrarily classified as L01, L02, Q01 and R01. See Fig. 1. The analysis of these samples was focused on presenting the colors, the main ones being black (bl), white (wh), red (re) and brown (br). The tonality of these colors is visually classified as intense (int) or tenuous (ten). The rating given to identify the area of the samples analyzed is: L01wh.int, L01wh.ten, L02bl.int, L02bl.ten, Q01bl.ten, Q01br.ten, Q01wh.int, R01br.int, R01br.ten and R01wh.int.

Figure 1. Diaguita decorated potteries from the archaeological site of Valle del Elqui, Las Animas. The samples are arbitrarily classified as L01, L02, Q01 and R01. The colored areas are displayed by squares and correspond to black (bl), white (wh), red (re) and brown (br) colors.

Pieces labeled L01 and L02 are fragments of triangular shaped ceramic having two main shades of color, black and white, see Fig. 1. In both pieces is found very deep black lines, almost entirely in perfect maintenance. Regarding, to the white color two cases are presented, very intense white light in some areas and a rather faint tonality in other zones. The Q01 pottery fragment, displays 3 colors, white, black and red-brown, see Fig.1, this fragment have three sectors appear: intense white, deep black and a faint brown. The R01 pottery fragment is the best preserved in terms of visual coloring, see Fig. 1. This part shows three quite deep hues. Micro-Raman spectra of all sectors, the bright white, deep red and brown were scanned.

Raman spectroscopy

The Raman measurements were performed using a Renishaw micro-Raman RM 1000 spectrometer, equipped with laser lines 514, 633 and 785 nm. The apparatus is coupled to a Leica microscope and a CCD camera cooled electrically. The Raman signal was calibrated to the 520 cm⁻¹ line of silicon and lens of 50x objective. The laser power on the sample is about 2 mW. Acquisition time was set between 10 and 20 s per accumulation; the average of accumulations was 10 with spectral resolution of 4 cm⁻¹. The spectra were recorded between 100 and 1800 cm⁻¹. Spectral recording conditions and the

choice of the laser line to be used is selected in order not to cause degradation of the sample; in this sense, the 633 and 785 nm lines were used.

Raman spectra of samples which were impossible to be accommodated in the area of logging instrumentation, were obtained by using a spectrophotometer Raman portable model MiniRamanTM series III Thumbnail TE, equipped with a laser line of 785 nm and one meter of optical fiber.

RESULTS AND DISCUSSION

White zones. In the L01wh.int, L01wh.ten, Q01wh.int and R01wh.int zones, the micro-Raman spectrum presents intense fluorescence, see Fig. 2A. However, it was possible to identify the characteristic sharp band of quartz at 464 cm^{-1} . This normal mode attributed to the Si-O stretching vibration, showing some degree of shifting wavenumbers due to variations in the crystallinity of the sample, has been reported by several authors¹⁴⁻¹⁷.

Figure 2. Raman spectra collected from the Diaguia decorate potteries. A) White color was attributed to quartz. B) Black color presenting characteristics bands of kempite. C) Intense black color presenting characteristics bands of tenorite. D) Red color was assigned to hematite. E) Brown color was attributed to hematite and tenorite or goethite mineral.

Black zones. Fig. 2B and 2C illustrates micro-Raman spectra of the black coloration part of the L02.bl.int, L02.bl.ten y Q01.bl.ten zones, as representative spectra of the investigated samples. The micro-Raman spectra of these samples indicated that the regions with similar colors were not homogeneous and did not necessarily give similar spectrum, pointing out different composition. It was initially believed that the black pigment used to paint these ceramics was only a manganese salt ($\text{Mn}_2\text{Cl}(\text{OH})_3$) or kempite¹⁴, which was found in L02bl.ten and Q01bl.ten, because of the band detected at 293 cm^{-1} ¹⁴. In samples where deep black dashes were observed (L02bl.ten), the Raman spectrum also present bands at 343, 632 and 1224 cm^{-1} belonging to copper oxide (II) or tenorite¹⁴, as is observed in Fig. 2C. Further, less fluorescence is presented in L02bl.int. The copper presence it has been reported in the black pigments of Pre-Columbian Chilean potteries¹⁸.

Red zone. Concerning the red color, Raman spectroscopic studies of the composition of archaeological objects (ceramics and other clay pottery) revealed that hematite, $\alpha\text{Fe}_2\text{O}_3$, or derivatives such as Fe_3O_4 , FeO and $\text{FeO}(\text{OH})$, were commonly used as pigments¹⁵⁻²⁰. In accordance to this fact, the micro-Raman spectrum of sectors that present red coloration, Fig. 3D, in R01re.int, shows characteristics bands of hematite at 223, 289, 411 and 613 cm^{-1} , therefore suggesting this compound as the red pigment present in the ceramic sample. Hematite has also been found in different red tonalities from orange to brown in the decoration of Viluco and Chilean Diaguia type ceramics²¹. Additional bands reported in the literature for this compound^{22,26,27} at 247 and 498 cm^{-1} , were not observed in the present work.

Brown zones. The micro-Raman spectrum (Fig. 2E) of the Q01br.ten and R01br.int zones presents several bands which are in the same or very close to those wavenumbers registered for hematite ($221, 289, 410, 613\text{ cm}^{-1}$) as well as bands at 1228 and 1307 cm^{-1} , which can proceed from tenorite. Also it is possible to consider this spectrum as coming from a variety of hematite like $\text{FeO}(\text{OH})$ (goethite)¹⁴, which color is described, among others, as a red-brownish or ochre^{28,29}.

CONCLUSIONS

The determination of chemical components in pottery archaeological objects of Diaguia origin confirmed the effectiveness of micro-Raman spectroscopy in the analysis of these objects. Some chemical components identified were crystalline silicates, namely, quartz, and pigments such as kempite, tenorite, hematite and potentially goethite. Additionally, in the case of the brown color is possible to interpret this tint either as a mix of different pigments or due to only one genuine pigment (goethite). Hematites recognized in the present work, are also detected in the red type color of the Diaguia and Viluco culture and in Norwest Argentinian ceramics *Aguada de Portezuelo*³⁰. The copper content of the black colour appears to be a particularity of Diaguitas, because in other cultures of South America the black pigment content iron, manganese and carbon³⁰⁻³³ in their composition. Finally, it is intended that these results will help in revealing the potential of Raman spectroscopy as a tool in analyzing pottery shards and their methods of production in other ancestral cultural groups in Chile.

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