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Photoacoustic Analysis of Pigments from Archeological Ceramics[1]

J. L. Jiménez-Pérez,[2,3] J. Jiménez-Pérez,[4] A. Brancamontes Cruz,[4] A. Cruz-Orea,[5] and J. G. Mendoza-Alvarez[5]

Photoacoustic spectroscopy (PAS) is widely used for diverse applications in different areas. These include studies in material, environmental, and life sciences. In the present work the study of pigments from pottery surfaces and volumes of Mexican (Aztec) and Poblana cultures that were developed in central Mexico from 1325 to 1521 and 1521 to 1800, respectively, is reported. The optical absorption spectra from each archeological sample was obtained using PAS. The superficial spectra were also compared with standard color pigments and archeological registers. Complementary energy dispersive spectroscopy (EDS) analysis of these archeological potteries gave us their elemental composition which agreed with other studies about their composition and technology of the pottery manufacturing.

KEY WORDS: ceramics; energy dispersive spectroscopy (EDS); nanostructures; pottery; photoacoustic spectroscopy (PAS).

1. INTRODUCTION

The application of materials science techniques to prehispanic potteries has produced very interesting results in the study of origin and manufacturing of these materials. In particular, the use of photoacoustic spectroscopy (PAS) has become an important tool, because it is a nondestructive analytical technique used "*in situ*." Furthermore, its use to measure absorption

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[2] Cicata-IPN, Calz. Legaría 694, Col. Irrigación, 11500 México D.F., México.

[3] To whom correspondence should be addressed. E-mail: jimenezp@fis.cinvestav.mx

[4] INAH, Periférico Sur y Zapote, Col. Isidro Fabela, 14030 México D.F., México.

[5] Depto. de Física, Cinvestav-IPN, A.P. 14-740, 07000 México D.F., México.

optical spectra has advantages over the usual transmission measurements in which the sample needs to be prepared to have good quality surfaces. Using PA measurements we can avoid the optical interference effects and obtain well resolved transitions. The combination with x-ray energy dispersive spectroscopy (EDS) as previously defined, can be helpful to understand the chemical properties of these materials.

The archeological pieces were discovered in the excavations from the "Templo Mayor" (main Temple), archeological site of downtown Mexico City. Several potteries were found in different stratigraphic natural layers of prehispanic and colonial pottery [1–8]. In the present work we report the study of Mexican ancient pottery from the Aztec culture (1325 to 1521) and Maiolica or Poblana ceramic (1780 to 1800). The first potteries analyzed were the Aztec potteries that by their style and decorations were attributed to Aztec III (1450 to 1525) and Aztec IV (1525 to 1550) periods [1, 2]. The second pottery analyzed was the Poblana or Maiolica (1780 to 1800), which was introduced by the Spaniards in Colonial Mexico [2, 3].

With regard to the decoration and finishing of these ceramics, the ancient Aztecs used organic colors and minerals oxides, as well as varnish partially vitrificated for the finishing with gumming of iron, Al, and Si which have similar color to grey [1]. In the colonial ceramic a varnish or glaze was used, which is a vitrificated, transparent and colorless coating

Fig. 1. Pottery from "Templo Mayor" archeological sites of Mexico City.

based in a mixture of Pb, Co, sand, and salt (called Plumbed) that is applied to the ceramic pieces in order to give brilliance and impermeability after a second firing. In this case if a metallic oxide is added, this pottery will be colored. This kind of enamel ceramic was named Maiolica Spanic or Puebla Talabera [3, 5]. Pigments of different colors (blue, red, yellow, black, and white) were found in the “Templo Mayor” site, and these colors were employed over different ceramics. It is important to consider the preservation materials used in the ceramics and murals and the environmental factors that affect their properties, such as humidity, pressure, pollution, etc. These factors may cause structural modifications in pigments and consequent changes in their chemical and physical properties. In Fig. 1 we show a picture of an Aztec III ceramic with its respective decoration. In this work we used PAS and EDS to characterize archeological potteries from Aztec and Poblana cultures.

2. EXPERIMENTAL

The optical absorption spectra were obtained in the range of 300 to 950 nm by using a homemade PA spectrometer as shown in Fig. 2. The experimental setup consisted of a 1000 W xenon lamp (Oriel), a variable frequency mechanical chopper set at 17 Hz, a monochromator, and an

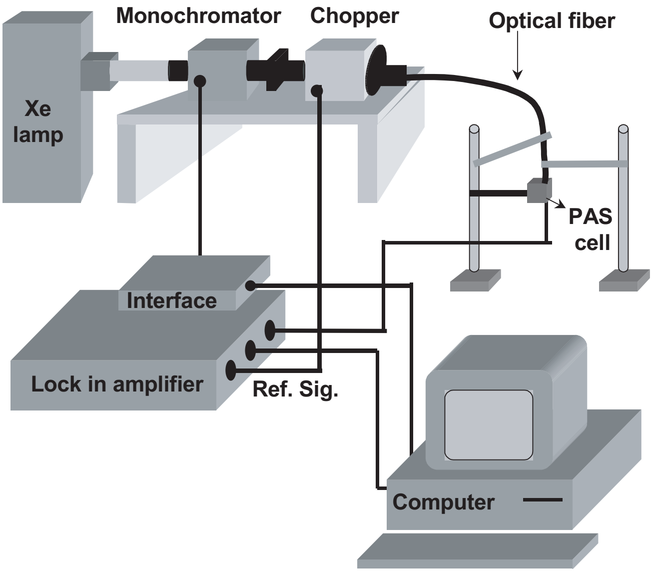

Fig. 2. Experimental setup used in photoacoustic spectroscopy.

air-filled brass cell with a condenser microphone. The PA signal from the microphone provided the input to the signal channel lock-in amplifier (SR-850) which is interfaced to a personal computer, displaying the wavelength-dependent signal amplitude and phase simultaneously. In order to take into account the Xe lamp emission spectrum, the PA signal was normalized to the signal obtained from charcoal powder [9]. In the case of x-ray energy dispersive spectroscopy (EDS) analysis, we used EDS 2100/2110 System Noran instruments.

3. RESULTS

The photoacoustic (PA) technique was employed to obtain the optical absorption spectra of the samples. Figure 3 shows the bulk PA spectra for different ceramics; the solid, dashed, and dotted line spectra correspond to bulk Aztec III, Aztec IV, and Poblana potteries, respectively. We can observe two main absorption centers that contribute to the photoacoustic signal. The first one is located around 460 nm and the second at 760 nm. The first absorption center is located in the blue region and the second one in the red of the visible spectrum. For all the samples the first absorption

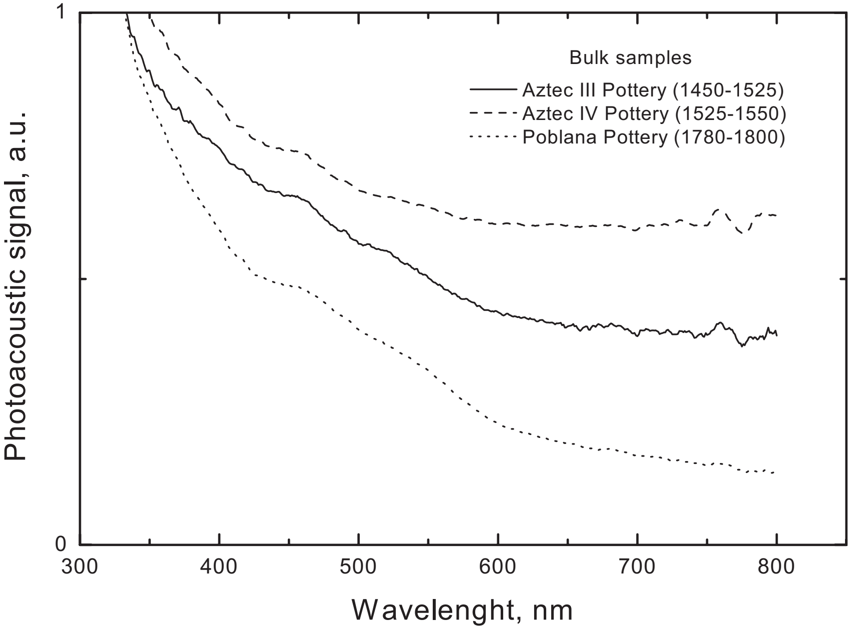

Fig. 3. Photoacoustic absorption spectra of bulk Aztec III, Aztec IV, and Poblana potteries.

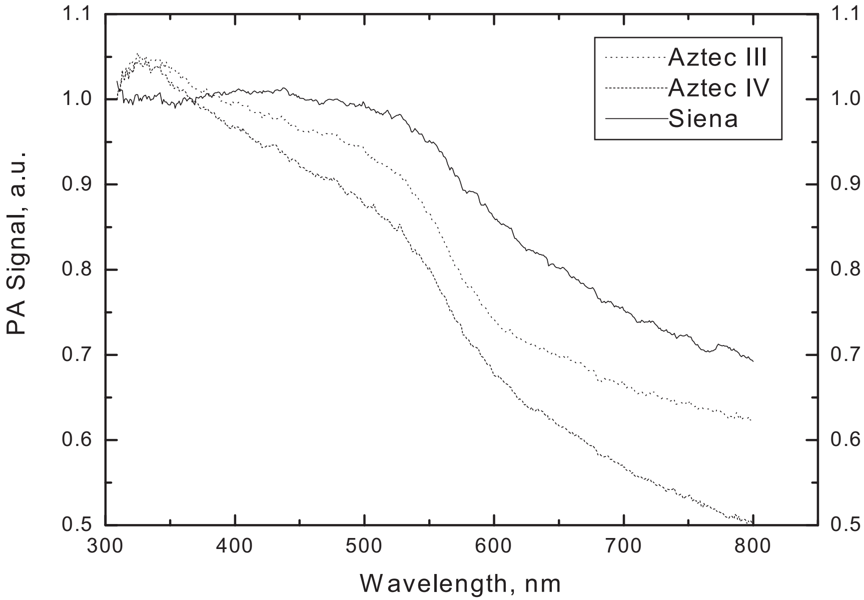

Fig. 4. Photoacoustic absorption spectra of superficial Aztec III and Aztec IV potteries and earth sienna standard. Pigments of Aztec III, IV, and sienna have an important decrease around 530 nm.

center, around 460 nm, corresponds to an absorption band of Fe^{3+} ion [10], the other peak, around 750 nm, corresponds to the absorption of some Fe oxides [10]. We also obtain the superficial PA optical absorption spectra of these ceramics, which are shown in Fig. 4. For all ceramics we observe a peak absorption around 530 nm which is characteristic of the Fe^{3+} ion absorption band. Edwards et al. [10] observed these bands as well.

The 760 nm peak, in the red region of the visible spectrum, could be explained by using EDS analysis in which we obtain the composition of the ceramic color pigments. The red pigment of bulk Aztec IV is composed of oxygen (54.9%), iron (3%), and a significant quantity of Al (5.5%) and Si (6.6%). These composition values are similar with those obtained for us from EDS on greyish red standard pigments, whose composition values were oxygen (53.2%), iron (6%), Al (5.65%), and Si (6.92%). The optical absorption spectrum of bulk Aztec IV showed a strong absorption in the red region (around 760 nm). On the other hand in Fig. 4, it is possible to observe that superficial Aztec III and IV spectra have an important decrease at 530 nm, which corresponds to ionic Fe as we discussed above. In the EDS analysis of Aztec III and Aztec IV surfaces, we obtain the

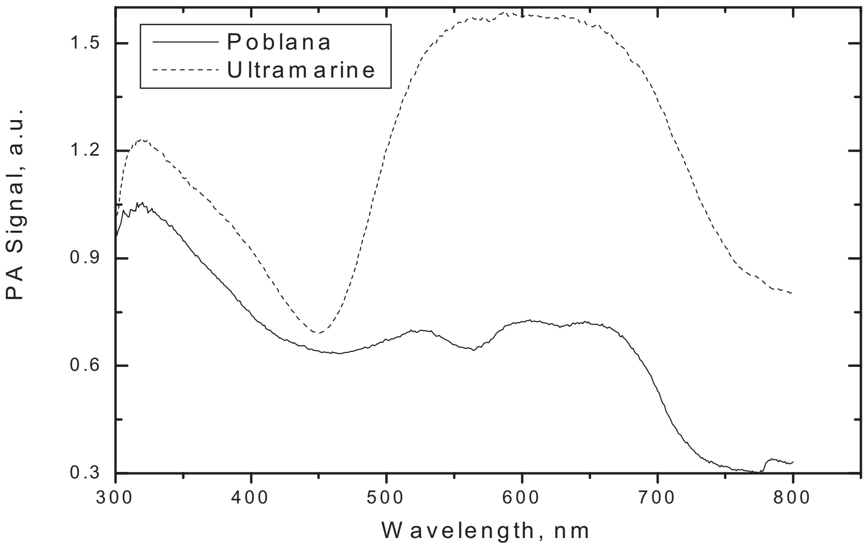

Fig. 5. Photoacoustic optical absorption spectra of Poblana ceramic and french ultranavy blue standard pigments. Both spectra have a transmission peak around 460 nm, and Poblana ceramic also shows a peak around 530 nm.

following composition values: O (61.98%), iron (2%), Al (1.9%), and Si (5.66%). The corresponding composition for earth sienna was as follows: O (62.57%), iron (2.9%), Al (1.99%), and Si (5.62%). As we can see, we have approximately the same composition for Aztec III and Aztec IV surfaces and earth sienna. Also in Fig. 4 are shown the photoacoustic spectra of sienna standard pigments.

On the other hand in Fig. 5, we can observe a 462 nm optical transmission peak from the PAS spectrum of superficial Poblana ceramic that is characteristic of blue standard pigments. The comparison of the optical absorption spectra of Poblana ceramic and ultramarine blue standard pigments shows the similarity of both spectra in which a transmission peak is observed around 460 nm. Also, in this figure an absorption peak is observed around 530 nm that corresponds to an important decrease observed in the absorption spectra for superficial Aztec III and Aztec IV analysis. The EDS analysis obtained from superficial Poblana ceramic gave mainly Fe (0.4%), Si (12.99%), Al (4.29%), and Mg (2.98%) proportions. In the case of French ultra navy blue color, the EDS analysis showed the following composition: Fe (0.21%), Si (13.33%), Al (4.61%), and Mg (3%). Once again we observed the similarity in the elemental composition between these samples.

4. DISCUSSION

The bulk spectra of Aztec III and IV ceramics are similar, but Aztec IV presents more optical absorption in the red region (around 760 nm). This could be due to a higher iron concentration or oxygen reduction during the firing of this ceramic as is suggested by EDS analysis mentioned above. EDS analysis confirms the existence of iron in all ceramics. Also photoacoustic optical absorption spectra, obtained from the superficial ceramic, show the presence of iron due to the absorption around 530 nm (characteristic of earth sienna) and for the superficial Poblana ceramic spectrum a transmission peak around 460 nm (characteristic of blue). Different iron percentages in the pigments correspond mainly to different colors (red, sienna, blue, black, white, etc.) used for the decoration and finishing of ancient ceramics [5, 11].

5. CONCLUSIONS

Photoacoustic spectroscopy and EDS has yielded new information about the pigments used in archeological ceramics. The PAS technique is easy to implement, does not require extensive sample preparation or chemical processes in order to analyze the samples, and can be done "*in situ*." The obtained results are in agreement with archeological studies about the manufacturing of ancient Mexican pottery. The treasures under study include pigments on pottery and ceramic. As the value of this conservation approach is realized, we think that the PA technique will soon help in the study and restoration of archeological treasures.

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