Photoacoustic Analysis of pigments from archeological ceramics

J.L. Jiménez - Pérez,

CICATA-IPN, Calz. Legaría 694, Col. Irrigación, 11500 México D. F., México.

A. Cruz - Orea, J.G. Mendoza –Alvarez

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

Abstract

Photoacoustic spectroscopy (PAS) is widely used nowadays for diverse applications in different areas. These include studies in material, environmental and life sciences. In the present work we report the study of pigments from potteries surface and volume of Mexican (Aztec) and Poblana cultures which were developed in central Mexico from 1325-1521 AD and 1521-1800 respectively. It was obtained the optical absorption spectra from each archeological sample by using PAS. The superficial spectra were also compared with standard color pigments and archeological registers. Complementary energy dispersive spectroscopy (EDS) analysis, on these archeological potteries give us their elemental composition which agree with other studies of these archeological ceramics about their composition and technology in the pottery manufacturing.

Keywords: ceramics, potteries, Photoacoustic spectroscopy, nanostructures, EDS

Introduction

The application of material 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 an nondestructive analytical technique used "in situ", also to measure absorption optical spectra has advantages over the usual transmission measurements in which the sample needs to be prepared to have good quality surfaces, and also because with PA measurements we can avoid the optical interference effects and obtain well resolved transitions. The combination of X-ray Energy Dispersive Spectroscopy (XEDS), 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 Mexico City downtown. 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 Aztec culture (1325-1521) and Maiolica or Poblana ceramic (1780-1800). The first potteries analyzed, were the Aztec potteries that by their style and decorations were attributed to Aztec III (1450-1525) and Aztec IV (1525-1550 AD)[1], [2] periods. The second pottery analyzed was the Poblana or Maiolica (1780-1800) which was introduced by the Spaniards in the 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 varnish partially vitrificated for the finishing with gumming of iron, Al, and Si which have similar color to grey [1]. In the colonial ceramic it was used the varnish or glazed, which is a vitrificated, transparent and colorless coating 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 fired. 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 "Templo Mayor" site these colors were employed over different ceramics. It is important to consider the used preservation materials in the ceramics and murals and the environmental factors that affect their properties, as humidity, pressure, pollution, etc. These factors may cause structural modifications in pigments and consequent changes in their chemical and physical properties. In the Fig. 1 we show a picture of an Aztec III ceramic with its respective decoration. In this work we used PAS and XEDS to characterize archeological potteries from Aztec and Poblana cultures.

Experimental

The optical absorption spectra were obtained in the range of 300-950 nm by using a homemade PA spectrometer as showed 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 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].

For X-ray energy dispersive spectroscopy (XEDS) analysis [10], was used a XEDS 2100/2110 EDS System Noran Instruments.

Introduce Figure 1 and Figure 2

Results

The photoacoustic (PA) technique was employed to obtain the optical absorption spectra of the samples. Fig. 3 shows the bulk PA spectra for different ceramics, the solid, dashed and dotted lines spectra correspond to bulk Aztec III, Aztec IV and Poblana potteries respectively. We can observe two mainly absorption centers that contribute to 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 center, around 460 nm correspond to an absorption band of Fe^{3+} ion [12], the other peak, around 750 nm, corresponds to the absorption of some Fe oxides [12]. 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., 1972 [12], observed these bands. (The Poblana absorption spectrum will be showed in Figure 5).

Introduce Figure 3

The 760 nm peak, in the red region of the visible spectrum, could be explain by using EDS analysis in which we obtain the composition of the ceramic color pigments. The red pigment is composed by oxygen (50.4 %), iron (2 %) and a significant quantity of Al (3.26 %) and Si (22.51%) [11]. 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 530nm, which corresponds to an ionic Fe as we saw above. In the EDS analysis, of Aztec III and Aztec IV surfaces, we obtain approximately the same composition of sienna standard color [11] but with a bigger proportion of Si (20.3 %), Al(6.83 %) and O(58.45 %) but less proportion of Fe(2 %) . Also in Fig 4 it is showed the photoacoustic spectra of sienna standard pigments. By other hand in Fig. 5 it is observed 462 nm optical transmission peak from PAS spectrum of superficial Poblana ceramic which, is characteristic of blue standard pigments. Also in Fig. 5 it is compared the optical absorption spectra of Poblana ceramic and ultramarine blue standard pigments. From this figure we can see the similarity of both spectra in which a transmission peak is observed around 460 nm.

Introduce Figure 4 and Figure 5

Also in this figure it is observed an absorption peak around 530 nm which corresponds to an important decreased observed in the absorption spectra for superficial Aztec III and Aztec IV analysis. The EDS analysis obtained from superficial Poblana ceramic gives mainly Fe (0.8 %), Si (8.4 %) and Al (3 %) proportion. It is really significant the contribution of Mg (1.1 %) in the case of Blue color in which its percentage is smaller than Al (3%) [11].

Discussions

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 fired of this ceramic as it is suggested by EDS analysis mentioned above. Other articles in the literature [1,4,7] about fired of ancient ceramic or EDS studies on red archeological pigment [11], show that the elemental composition of this archeological color is similar to obtained in our samples. EDS analysis confirm 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 sienna) and for the superficial Poblana ceramic spectrum it is observed 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].

Conclusions

Photoacoustic spectroscopy and EDS has yielded new information about the pigments used in archeological ceramics. PAS technique is easy to be implement and don't require extensive sample preparation or chemical processes in order to analyze the samples and can be done " in situ" analysis. 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 could help in the study and restoration of archeological treasures.

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Figure Captions

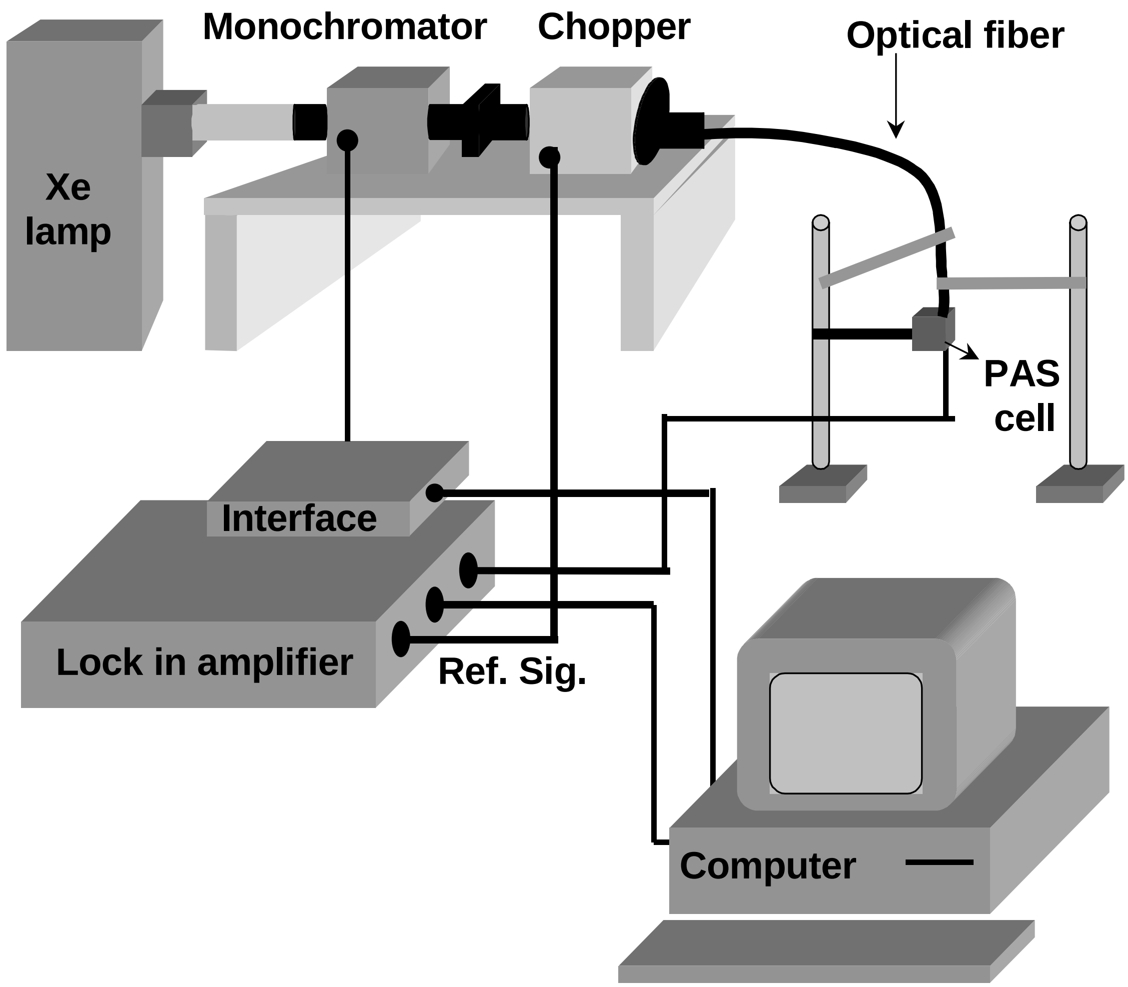
Fig. 1. In this picture we see a pottery obtained from “Templo Mayor” archeological sites of Mexico City.

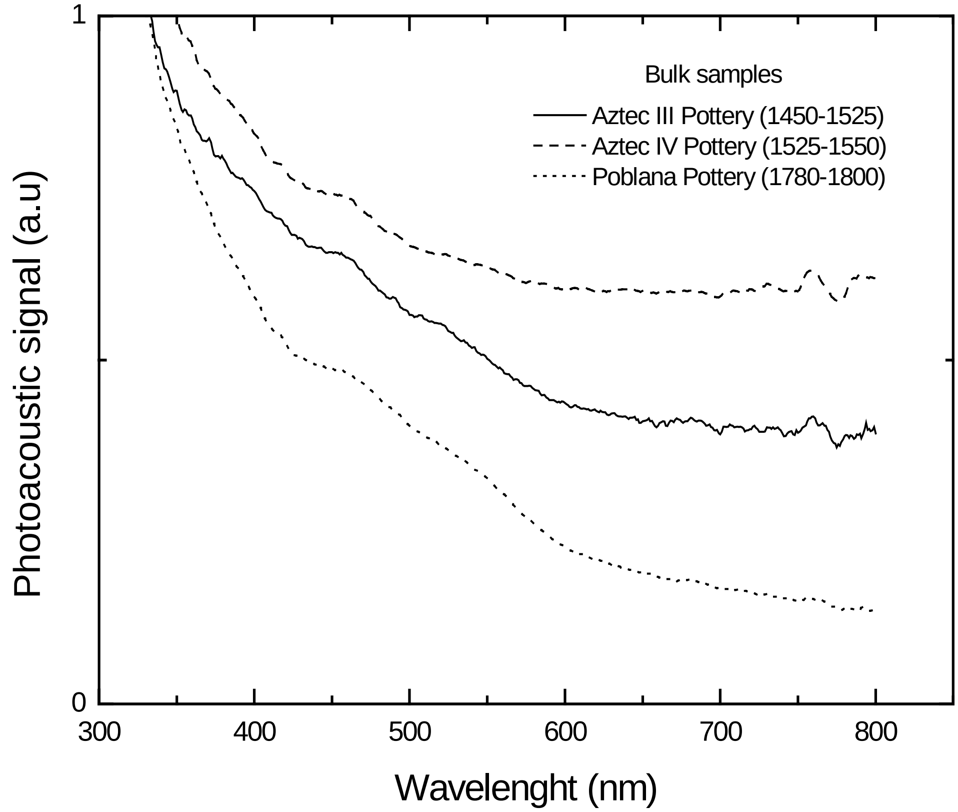
Fig. 2. Experimental set-up used in Photoacoustic spectroscopy.

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

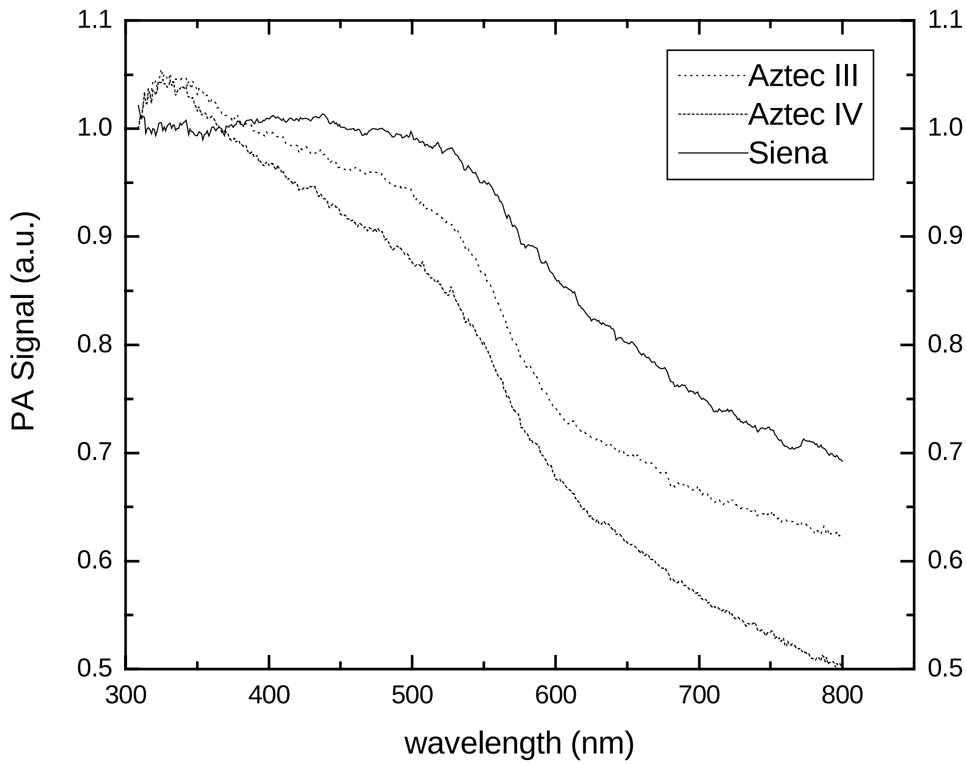
Fig. 4. Photoacoustic absorption spectra of superficial Aztec III, Aztec IV potteries and sienna standard. Pigment we can observe that Aztec III, IV and sienna have an important decreases around 530 nm.

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

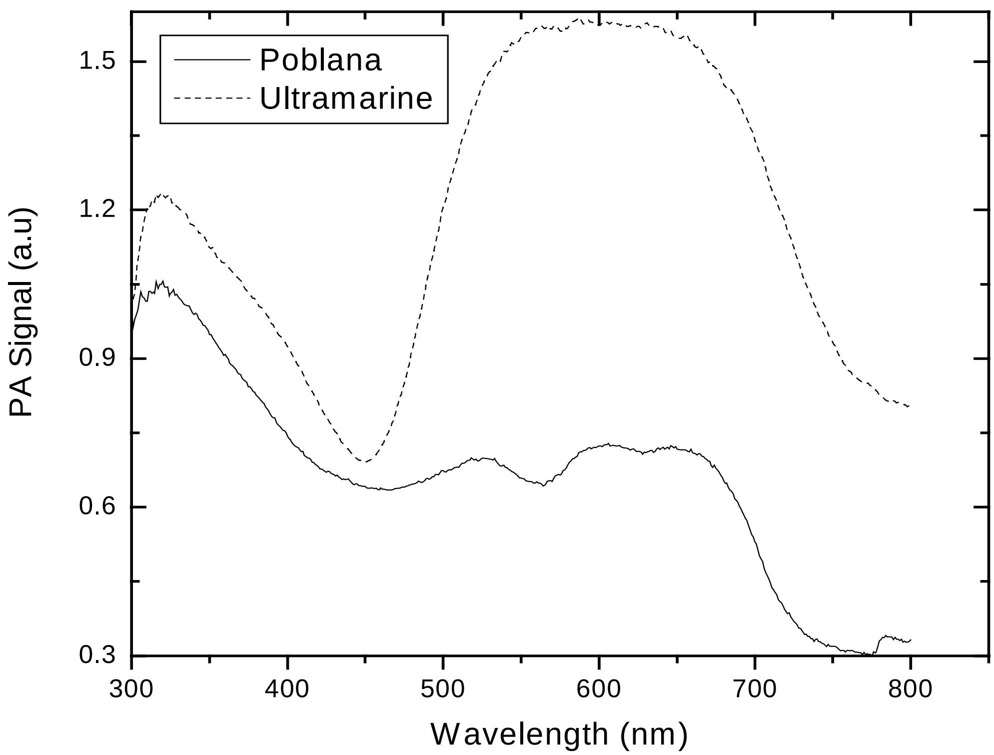

Monochromator
Chopper
Optical fiber
Xe
lamp
PAS
cell
Interface
Lock in amplifier
Ref. Sig.
Computer



Bulk samples
Aztec III Pottery (1450-1525)
Aztec IV Pottery (1525-1550)
Poblana Pottery (1780-1800)
Photoacoustic signal (a.u)
Wavelenght (nm)
1
0
300
400
500
600
700
800



Aztec III
Aztec IV
Siena
PA Signal (a.u.)
wavelength (nm)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
300
400
500
600
700
800


Poblana
Ultramarine
PA Signal (a.u)
Wavelength (nm)
1.5
1.2
0.9
0.6
0.3
300
400
500
600
700
800