Study of Various Interventions in the Façades of a Historical Building—Methodology Proposal, Chromatic and Material Analysis

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Abstract: Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), and energy dispersive X-ray spectroscopy (EDS) in addition to scanning electron microscopy (SEM) have been used for determining the color and chemical composition of the architectural elements of the façades of a historical building, which today is the seat of the Diputación Provincial *of Cadiz. It dates from 1770 and was built as Custom Headquarters. It is near the port and is almost encircled by the walls of the city. The determination of the color and chemical composition of the materials that provoke this color and the determination of the layers found in the extracted samples from significant zones allow to define the various interventions over the façade and to localize the time in which they were made. This is possible by comparing with graphical registries and historical documentation. The objective is a study of the color of the different façades that the building has had in order to know the history of the building and to choose materials and colors that should be used in a restoration intervention of this historical building.* © 2005 Wiley Periodicals, Inc. Col Res Appl, 30, 382–390, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/col.20142

Key words: pigments; chromatic measurements (CIE64); scanning electron microscopy (SEM); energy dispersive X-ray spectroscopy (EDS); FTIR spectroscopy

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INTRODUCTION

Façade color is one of the most important aspects of city life and a major element affecting the general appearance of cities.[1] For that reason, the study of the color and materials of the different architectural elements that form the façades of a building is tackled from the perspective of a material scientific study, using spectroscopic techniques. In addition, in the case of façades of historical buildings, we put special emphasis on the superimposition of materials in order to associate them with dates of modifications of the building. The sequence of these layers and the kind of the materials contribute to the historical documentation of the building.

Now, the need of a new intervention on the building, to tidy up the façades and protect the oyster stone, which has deteriorated has been considered. The building is now the seat of the *Diputación Provincial* of Cadiz (Fig. 1) and was originally the Custom Headquarters of this city. Therefore, the President of the *Diputación Provincial* has requested a scientific report about the color and materials used in previous interventions for having a reference document and for taking the decisions in this new intervention. The methodology used for determining the color and materials used throughout its history, is shown in this article.

EXPERIMENTAL METHOD

The methodology developed for studying this building can be outlined in the following stages:

FIG. 1. Photography of the building of the *Diputación Provincial* of Cadiz.

Taking of Data

One of the most important aspect of the study has been the taking of samples, because it is the basis of all the subsequent analysis. The further processes are as follows:

1. Localization and preliminary study of the building in a meticulous and detailed way for checking the surface of the different architectural elements and for observing the presence of interesting zones, cracks, possible underlying polychromes, etc.
2. Execution of an illustrated feature that helps to determine exactly the zones to study, avoiding the indiscriminate forays by the geography of the building and choosing only the strictly necessary ones.
3. Taking of samples in strategically important places using a 35 mm crowning drill in such a way that the layers of material that define each architectural element, in various interventions, can be obtained.

To extract samples in zones that have been greatly modified was not possible because the original materials have not been found. Neither do we have data from some zones that were impossible to access. In case that the sample cannot be removed, but it is accessible, the color has been in situ determined using a Dr. Lange Colorpen portable spectrophotometer, by Neurtek S.A. Therefore, this has been performed in similar experimental conditions than those used in the laboratory for the other samples.

Chromatic Characterization

The extracted samples are prepared in laboratory for determining the color in sections selected as representative zones, using direct observation or with light microscopy.

Normally, the chromatic characterization of the pictorial layer is made by means of subjective methods, based on the visual comparison between the sample and a table of pre-established colors such as, for example, the Munsell notations.[2,3] This method can lead to serious errors, since it is very much influenced by external factors such as the illumination used during the comparison, the subjective observational abilities of the researcher, or the chromatic stability of the patterns used for the comparison.

In this work, an objectively reproducible chromaticity characterization has been carried out using electronic spectroscopy. The method consists of the determination of the optical reflectance within the visible frequency range by means of an Otsuka MCPD 1100 visible ultraviolet spectrophotometer. The system is equipped with optical fiber-light-conducting elements, which enables the direct study of the pictorial surface of the material to be made without perturbing it.

CIE $L^*a^*b^*$ system[2–4] has been used as the parameter for the color of the samples. The variables that define the tonality and color saturation have been represented in the color space diagram. An incandescent tungsten lamp with a filtered emission was used as illumination system, and the CIE illuminant was the standard source D65. As white pattern, a polymeric tablet supplied for Top Sensor Systems (model WS-2) was used. The sample chamber has a normalized geometry of 0°/45° for the illumination/observation process, in order to minimize the specular/diffuse reflectance ratio of the captured radiation and to obtain a realistic chromaticity value.

It is necessary to notice that different layers of color and materials have been observed in some samples. All of them have been directly analyzed and measured, either with the spectrophotometer illuminating spot, or if the zone is smaller than the spot size, using (for localizing) a microscope with light and reflection through an optical fiber connected between the spectrophotometer and microscope.

Chemical Analysis of Pigments, Mortars, and Supports

The chemical identification of the pictorial and substrate substances was performed using scanning electron microscope (SEM), energy dispersive X-ray spectroscopy, (EDS) and Fourier transform infrared spectroscopy (FTIR) techniques.[5–7]

SEM, in secondary electrons and backscattering mode, has been used for observing interesting microstructures like microorganisms, tempers, vitrifications, crystallizations, or particles of heavy elements that cannot be detected in general analysis. In addition, EDS has been used in elementary chemical analysis on the zone that is visualizing in the monitor. A LINK AN10000 energy dispersive X-ray detector system, in addition to a JEOL JSM820 SEM, was used. To prevent surface charging, the samples have been gold-coated; then a constant gold signal appears in all the EDS. Some fragments or chips of about 1 mm^2 have been obtained for observing the pictorial layer.

Molecular information has been achieved by FTIR, using a Nicolet Impact 410 spectrophotometer with OMNIC software. The FTIR spectral analysis was made using the search

TABLE I. Values of CIE$L^*a^*b^*$ chromatic coordinates of each layer of the different architectural elements of the building of *Diputación de Cadiz,* arranged according to approximated times.

	Approximated times														
	1778–1862			1862–1940			1940–1950			1950–1964			1964–now		
Element	L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*
Vertical Faces (Ground Floor)	100	0	0	72.8	13.8	19.7	72.8	13.8	19.7	100	0	0	Oyster stone		
Vertical Faces (First and Second Floor)	100	0	0	66.8	14.6	11.8	66.8	14.6	11.8	81.2	6.3	13.9	100	0	0
Pilasters (Ground Floor)	81.6	7.1	16.5	100	0	0	72.8	13.8	19.7	100	0	0	Oyster stone		
Pilasters (First and Second Floor)	81.6	7.1	16.5	100	0	0	77.5	10.2	13.6	100	0	0	Oyster stone		
Window surrounds (Ground Floor)	81.6	7.1	16.5	79.2	6.6	8	80.1	6.6	8.0	100	0	0	71.0	0.4	1.4
Window surrounds (First and Second Floor)	100	0	0	79.2	6.6	8	80.1	6.6	8.0	100	0	0	71.0	0.4	1.4
Decorations and Pediments	100	0	0	79.2	6.6	8	80.1	6.6	8.0	100	0	0	71.0	0.4	1.4
Decorations of windows (Second Floor)	100	0	0	79.2	6.6	8	80.1	6.6	8.0	100	0	0	71.0	0.4	1.4
Decorations (Internal Zone)	100	0	0	66.8	14.6	11.8	66.8	14.6	11.8	81.2	6.3	13.0	100	0	0
Parapet (Face)	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0
Parapet (Edge)	81.6	7.1	16.5	Oyster stone			54.8	29.9	6.3	Oyster stone			Oyster stone		
Cornices	81.6	7.1	16.5	Oyster stone			77.5	10.2	13.6	100	0	0	Oyster stone		
Grilles	60.5	20.6	7.2	44.7	29.8	10.4	60.7	−7.5	−3.6	15.7	−9.4	8.5	14.9	9.0	7.9

function of the software, searching in several commercial libraries with an amount of 40,000 spectra, including U.S. Geological Survey Minerals, Commercial Material Painter Minerals, Sigma Dyes, Stain and Natural Pigments, Aldrich Condensed Phase, and Coating Technology. To analyze using this technique, the samples were prepared (for the transmittance study) by grinding little pieces of the pictorial layer with spectroscopic quality potassic bromide that works like a support.

Data Processing

All the data obtained and images processed for this study, are organized in a computerized database. In case that the samples have not been extracted and, based on historical documentation, the same colorimetric data have been assigned as the zones that have the same color as that of the sample and symmetrical architectural elements. On the other hand, the values of the theoretical white ($L^* = 100$, $a^* = 0$, $b^* = 0$) have been assigned whenever the sample is white. This is because the spectrophotometer always shows any impurity or dirt, getting gray tonalities, that can confuse to the observer when they are reproduced. In the same way, the value of the theoretical black ($L^* = 0$, $a^* = 0$, $b^* = 0$) has been assigned when the sample is black.

We understand that this is an approximation; however, we think that by knowing the chemical composition of the white or black color, it is possible to reproduce, faithfully, the original color of the corresponding architectural elements of the building.

Proposal of Color

According to the objective data of color and materials, documented historical data, old graphical records, and comparing with other buildings and constructive customs, computerized colored vertical sections have been made following time intervals and the interventions in the building. For example, in the samples obtained from the paint of the grilles, the use of copper arsenate green has allowed to localize the time of its application, because it is a pigment whose industrial production was limited in time.

RESULTS AND DISCUSSION

As we already said, the experimental results of the material and color study are shown depending on notable historical period for the building, combining historical graphic and material data. Therefore, in the first place, the found historical data for the building are exposed. Later, after knowing the materials and colors depending on the localized layers (Table I), five possible situations of the façades are shown, which are classified within a reasonable margin of error in the several periods and interventions on the building.

The reflectance spectra from each pictorial layers, measured maintaining the previous layers underneath it, have been registered, for all the samples, in the visible range on several zones (about 3 mm in diameter illumination spot size) in order to obtain a statistically representative value.

Historical Data

This building was the consequence of an intervention project in the Cadiz port zone. The original idea was to organize an important defensive system along this front and to accompany the necessary buildings for the administrative development of the commerce, especially with the Indies. Between these buildings, the construction of Custom Headquarters began in 1765 under the guidance of Juan Caballero, a military engineer, and was probably inaugurated in 1773. However, some authors[8] think that the work lasted until 1784. Four important interventions in the façade of the building have been documented from this date.[8–13] The first important modification dates from 1862. Because of a trip

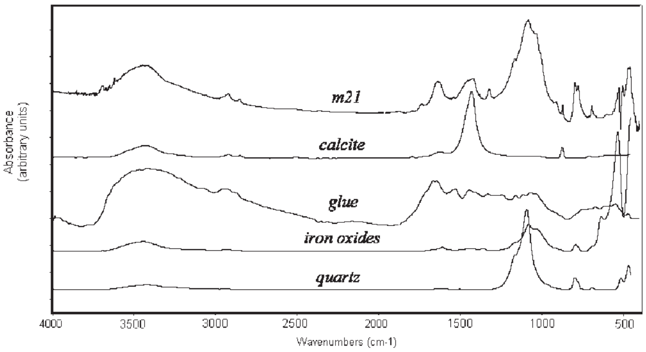

FIG. 2. FTIR spectrum of a vertical face sample, where calcite, quartz and glue, iron oxides as pigment of the pictorial surface can be detected.

that Queen Isabel II took around Andalusia a series of substantial improvements in the building was done, thereby making it more suitable for accommodating the royal guests during their short stay. Juan de la Vega was the person responsible for the improvements and preparations. He was the province holder architect and member of the local Beaux-arts Academy, and he counted on a great team of artists. In 20th century, between 1940 and 1950, this building was the seat of the Official Organisms of the Spanish State, like Customs, Civilian Government, and Local Treasury Office. According to the historical documentation, a second modification in the color of the façade occurred. From 1950, the final property of the Palace by the *Diputación Provincial* and the fact that the rest of the Official Organisms of the State have their respective seats allow that the Council embarks on an important succession of restoration, adaptation, and improvement works. From 1964, in the last intervention, the stonework of oyster stone became known in live stone, and the faces were plastered in white as is still observed today. Since then, other minor painting and repairing works have taken place for maintaining the building.

Data About Color and Kind of Materials from Sampling

Vertical Faces

Ground Floor is made up of oyster stone ashlars. "Oyster stone" is a pliocenic or plioquaternary conglomerate of calcarenites that includes seashells remains. There are some quarries in Puerto Real and other littoral zones of Cadiz.

Remains of covering material have been found in some holes, corners, and fissures of this stone. The same 4-layer sequence has been found in all the samples. The most internal or the first layer is a lime and sand mortar that appears filling the stone. On this, a white layer of lime appears. A third layer is made up of a pinkish color mortar. The FTIR spectrum of a sample of this third layer is shown in Fig. 2, and the presence of calcite, iron oxides, and glue has been detected. Finally, a white lime layer appears. Now, this face is naked oyster stone.

First and Second Floor. One sample was extracted from the first floor using a drill and two pieces had come off. The piece that corresponds to the exterior part is formed by a white paint over a cement layer of 1 cm thickness. In the piece of the interior part, some layers and a lime and sand mortar base about 2 cm thick are observed.

The first internal layer is made up of a white lime mortar and a sand colored mortar. On these mortars, a white layer of lime is observed. The next layer in a deep ochre color is a colored lime mortar. The EDS spectrum of this layer is shown in Fig. 3, and the chemical elements that correspond with calcium carbonate and red earths are observed. Red earths are natural clays containing iron oxides.

The next layer is white. An analysis using EDS indicates that this layer shows the constituent elements of barium sulfate, calcium carbonate, and lead carbonate (Fig. 4a and 4b).

The last layer that appears in the internal fragment is an ochre color layer and is made up of barium sulfate, calcium carbonate, and red earths. EDS spectrum is shown in Fig. 5, where the constituent elements of the aforementioned compounds are shown.

The external fragment is made up of an internal layer of cement and an external white layer that is constituted of titanium oxide and calcium and aluminum silicates. According to Laver,[14] titanium oxide is a pigment used from the 20th century. In Fig. 6, EDS spectrum of this layer is shown.

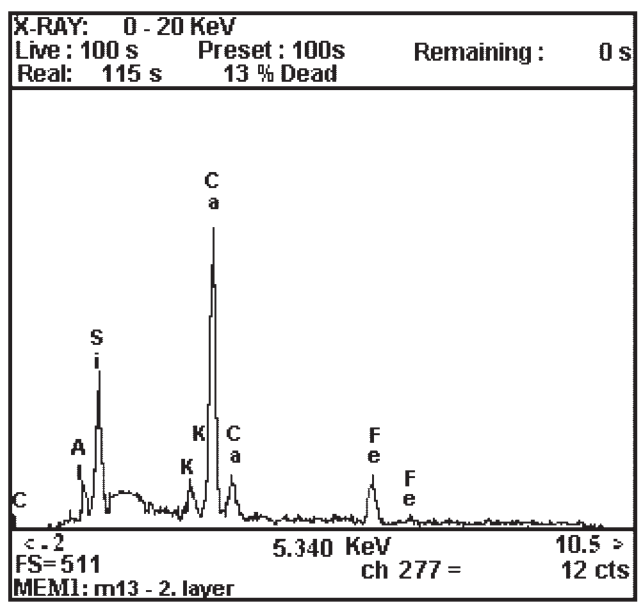

FIG. 3. EDS spectrum of deep ochre color layer observed in a sample of the vertical face of the first floor, where the chemical elements that correspond with calcium carbonate and red earths are observed.

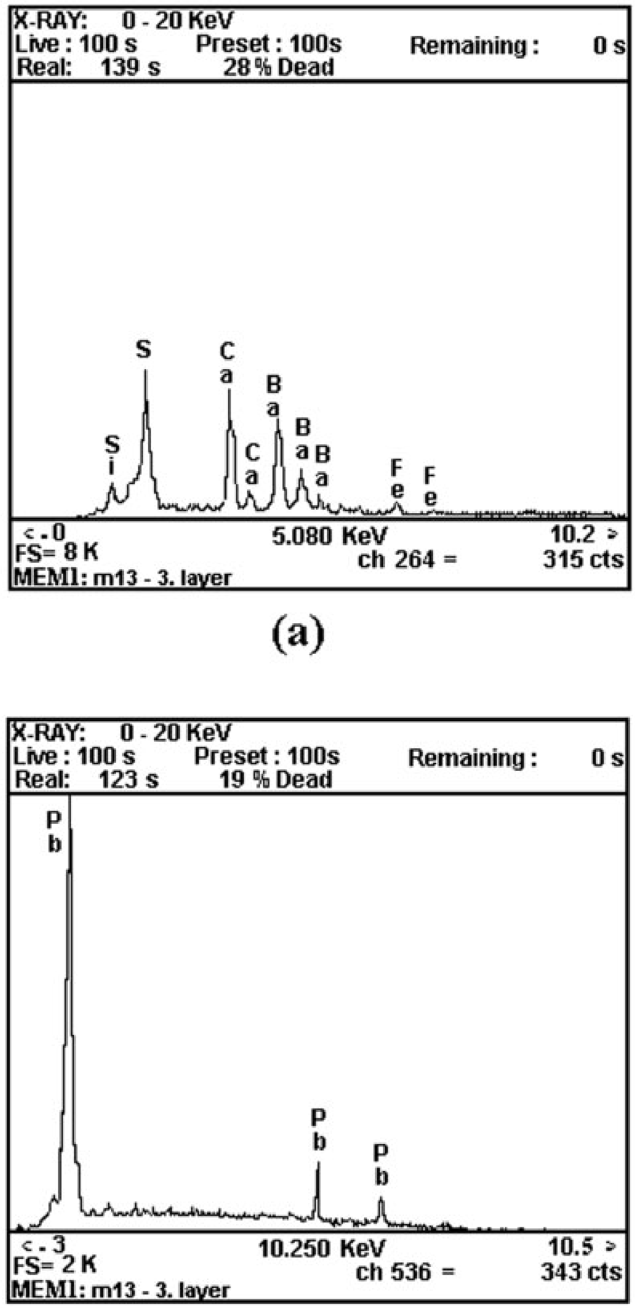

FIG. 4. Precise EDS spectra of the white color layer observed in a sample of the vertical face of the first floor. (a) Constituent elements of barium sulfate and calcium carbonate are observed. (b) Constituent elements of lead carbonate are observed.

Pilasters

The pilasters are formed by oyster stone ashlars. Remains of covering materials have been found in some holes, corners, and fissures.

The pilasters of the ground floor appear to have had different coverings depending on different times, as well as the faces and the upper pilasters. The samples found show

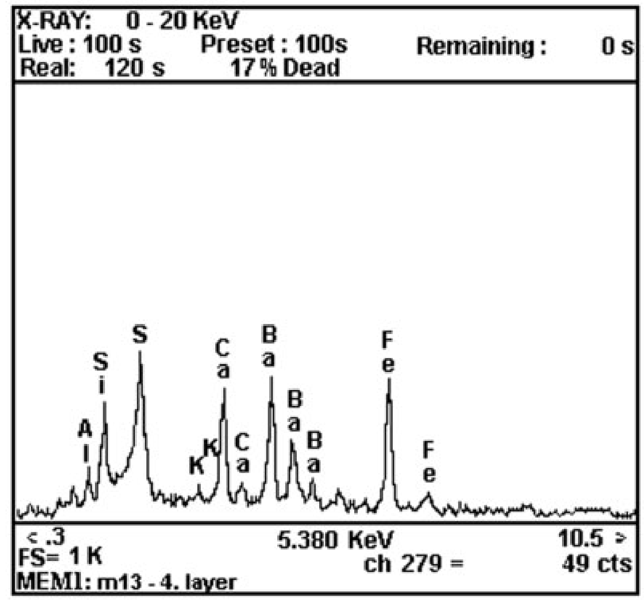

FIG. 5. EDS spectrum of ochre color layer observed in a sample of a vertical face in first floor, where the constituent elements of barium sulfate, calcium carbonate, and red earths are observed.

a layer sequence similar to that found in the faces, but the ochre colors are slightly different. The layer sequence found in the ground floor pilasters is described next. The internal layer is made up of the stone, with sand mortar in the joints and holes. On this, a lime white layer rests. Later, it was covered with a layer of pinkish orange color. Finally, a white lime layer appears. The pilasters are now shown with naked stone.

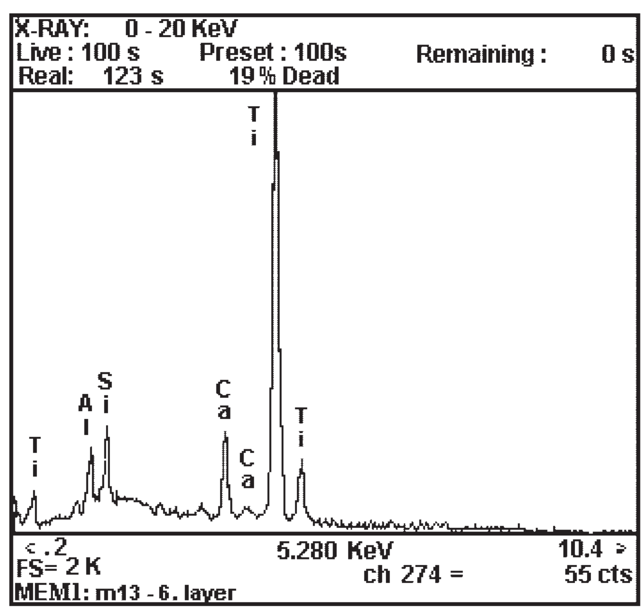

FIG. 6. EDS spectrum of the external layer observed in a sample of vertical face of the first floor, where the constituent elements of titanium oxide and calcium and aluminum silicates are observed.

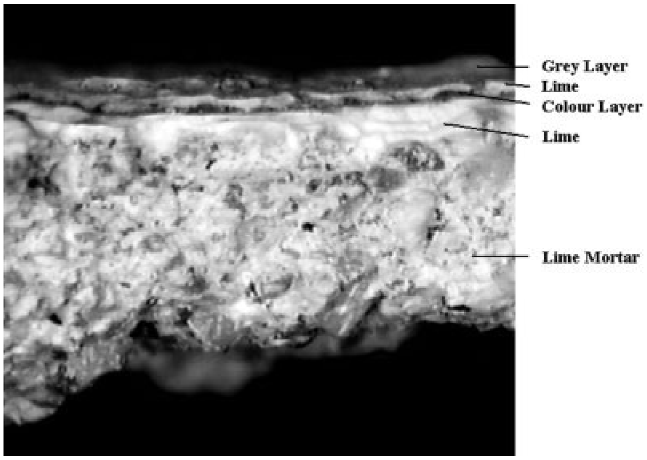

FIG. 7. Layer sequence observed in the first floor surrounds.

The layer sequence in the pilasters of the first and second floors is similar to the ground floor sequence; however, after the pinkish orange layer, the forth lime layer has not been found. As in the pilasters of the ground floor, now they are with naked stone.

Joints

Any way, special characteristic has not been determined, which indicates a different execution than the normal one. Remains of white and pinkish covering material and very sandy lime-mortar-like base have been found.

Window Surrounds

Several interventions in the window surrounds of the entire floor are observed, and they are now in gray color. Therefore, in one window of the ground floor and under the present cement, an oyster stone frame covered with a pinkish lime mortar has been observed, and on this there is a white layer. On the cement, a white layer appears and finally a gray layer. The window surrounds of the first and ground floor do not seem to have had the same interventions. The layer sequence in the window surrounds of the first floor seems to be more simple: lime mortar, lime, color layer, lime, and gray layer (Fig. 7) being observed that the cement has not been coated in all the window surrounds.

Decoration of Windows

In the windows of the second floor, the central part of the decoration follows the same scheme as that in the window surrounds, whereas the internal zone follows the same sequence as that in the faces. The colors measured on the samples match up with the colors of these elements. According to the graphical historic documentation, it has been assumed that the pediments of the balconies of the first floor follow the same sequence as that in the window surrounds.

Parapet

In the face of the parapet, cement with white paint has only been found and underneath lime and sand mortar. Regarding the edge of the parapet, oyster stone and a deep pink color covering in the internal zone of the brick have been found. Remains of this covering are observed in all the contour of the building. EDS spectrum and infrared spectrum of this pinkish layer are shown in Figs. 8 and 9. The study of these spectra indicates that it is a lime mortar with iron oxide.

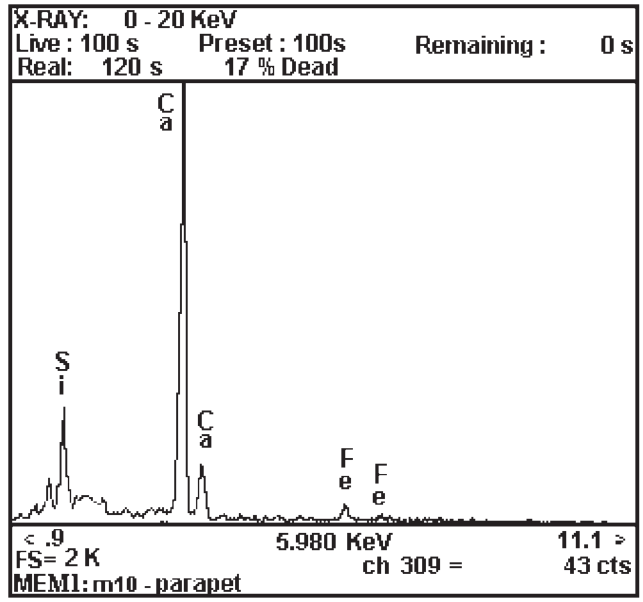

FIG. 8. EDS spectrum of the pinkish color layer observed in the edge of the parapet, where the elements of a lime mortar with iron oxide are observed.

Cornices

Nowadays, they appear naked in oyster stone form. It was not possible to gain access to the cornices between floors, but the next layer sequence has been found in the upper cornices of the terrace roof: stone protected with sand mortar, lime mortar, pinkish lime mortar, and the stone at the end.

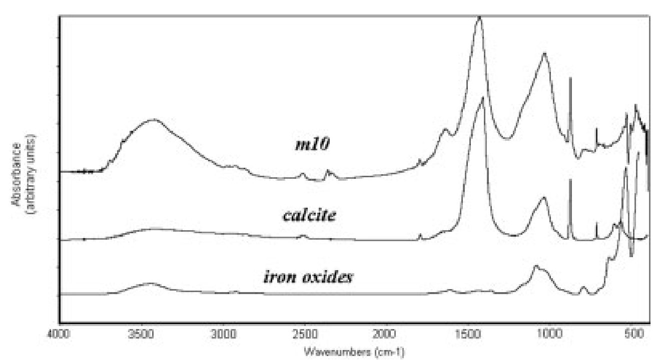

FIG. 9. FTIR spectrum of the pinkish color layer observed in the edge of the parapet. The calcite and iron oxide spectra are taken from spectral libraries.

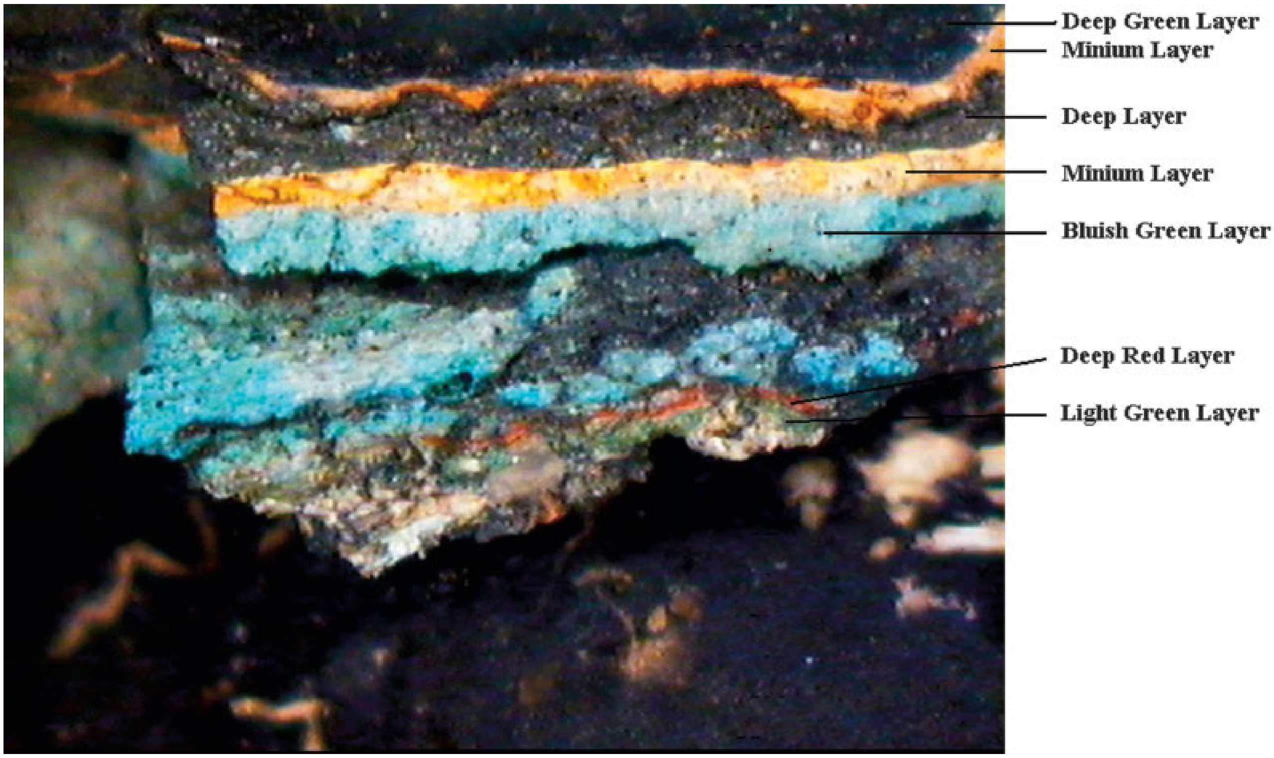

FIG. 10. Layer sequence observed in the grilles of the windows.

Grilles

Under the present deep green color and the minium paint, several layers of green, red, and light green color (Fig. 10) have been found in the ground floor windows. From the older to the more modern, the layer sequence may be:

First Layer of Light Green Color. EDS spectrum of this layer is shown in Fig. 11, and these elements are detected: arsenic, copper, sulphur, and barium, corresponding to copper arsenate and barium sulfate. A photograph of the typical crystals of copper arsenate is shown in Fig. 12.

This pigment began to be used in 1814 and was forbidden in 1880 because of its toxicity, although it was still used until beginning 20th century for painting ships.[15] This is the oldest layer that has been found but does not correspond with the original situation. If we consider the kind of pigment criterion, a logical deduction would be that in the first time the grilles were not painted, and later at the beginning of the 20th century they were painted in light green color, a copper arsenate-based. This pigment was also found in several façades in "El Pópulo" and "Santa María," two quarters on which studies were carried out by our research team.

Second Layer of Deep Red Color. EDS spectrum of this layer (Fig. 13) corresponds with the constituent elements of barium sulfate and iron oxides. One might think that the red layer is due to a painting between 1862 and 1940. In addition, we have considered that this could be a corrosion zone expanded from a contiguous layer. This has been ruled out for two reasons: (a) Elements of other pigmentary substances that contribute to the color are not found and (b) there is no variation of concentration of the iron oxides, as the diffusion would generate.

Third layer of bluish green color. EDS spectrum is shown in Fig. 14, and the constituent elements of chromic oxide with barium sulfate load are observed. The manufacturing of this pigment began in 1860.[15]

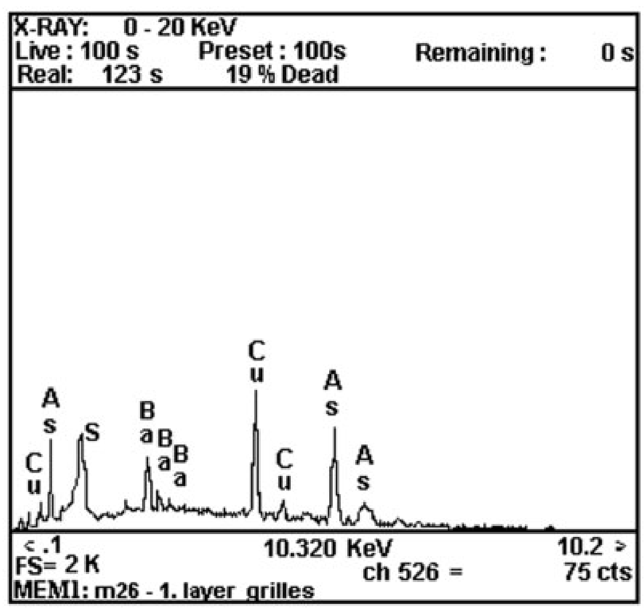

FIG. 11. EDS spectrum of the first light green color layer of the grilles. The constituent elements of copper arsenate and barium sulfate are observed.

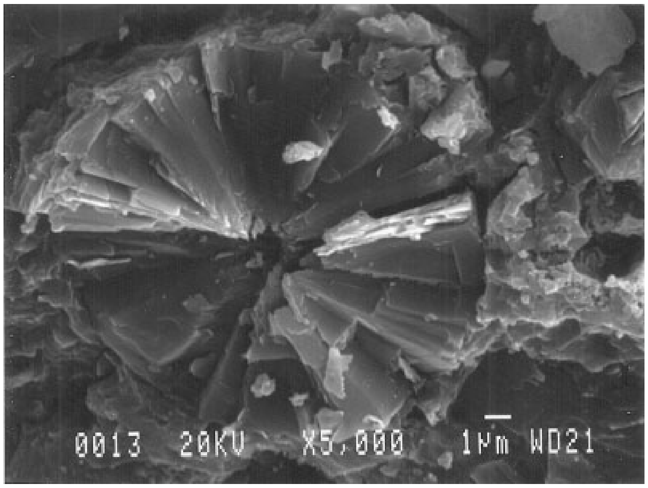

FIG. 12. Enlargement of SEM image of copper arsenate crystals observed in the first layer of light green color of the grilles.

On this a forth layer appears and is made up of minium, say lead oxide, recently used as protective. The following layers are a deep one of iron and copper oxide with barium sulfate load, a minium layer, and at the end the present layer appears.

Both the balustrades and the wood of the frame of the windows are not included in this study. Although the samples have been taken, they have not provided information about their materials or color at previous times to the present day.

Hypothesis and Proposal of Color from the Observed, Graphic Registers, and Historical Documents

The proposal of color according to significant times have been carried out using the relation of data over the pigment

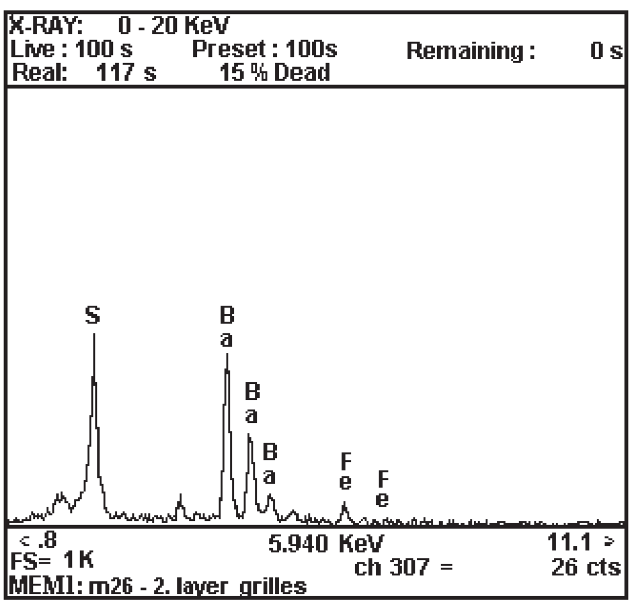

FIG. 13. EDS spectrum of the second layer of deep red color of the grilles. The constituent elements of iron oxide and barium sulfate are observed.

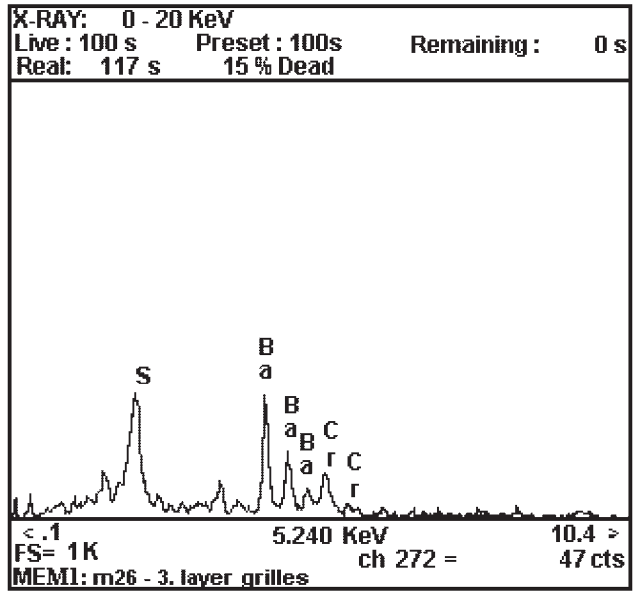

FIG. 14. EDS spectrum of the third layer of bluish green color of the grilles. The constituent elements of chromic oxide and barium sulfate are observed.

layers found, the kind of materials, etc., with historical data, as the visit to de city of Queen Isabel II, or with documents, as the works made in 1964, or with photographs of the different façades of the building.

These proposals are shown in Fig. 15 and from them the first two can be the most certain ones and of course, the last one. The intermediate situations may be less sure, but they may be possible because we have had to combine the layer sequence in the samples of the different architectural elements with all the rest of the data.

The computer colored vertical section from the objective data of color are referred to the building, as it has the structure and decorations at present time. We must warn that the printing of the color depends on the condition of the paper and the printer; therefore, the colors that are observed are always approximated.

CONCLUSIONS

The determination of the color and chemical composition of the substances that provoke it, of the different layers that appear in the samples extracted in significant zones, allow to define the different modifications to the façade and to localize the time in which they were carried out, after contrasting data with graphic registers and historical documentation.

The information that is provided is an objective contribution about the color of the different façades that the building has had, in order to record the history of the building and to choose the materials and colors that could be used in a restoration of this historical building.

The spectroscopic techniques and the methodology used

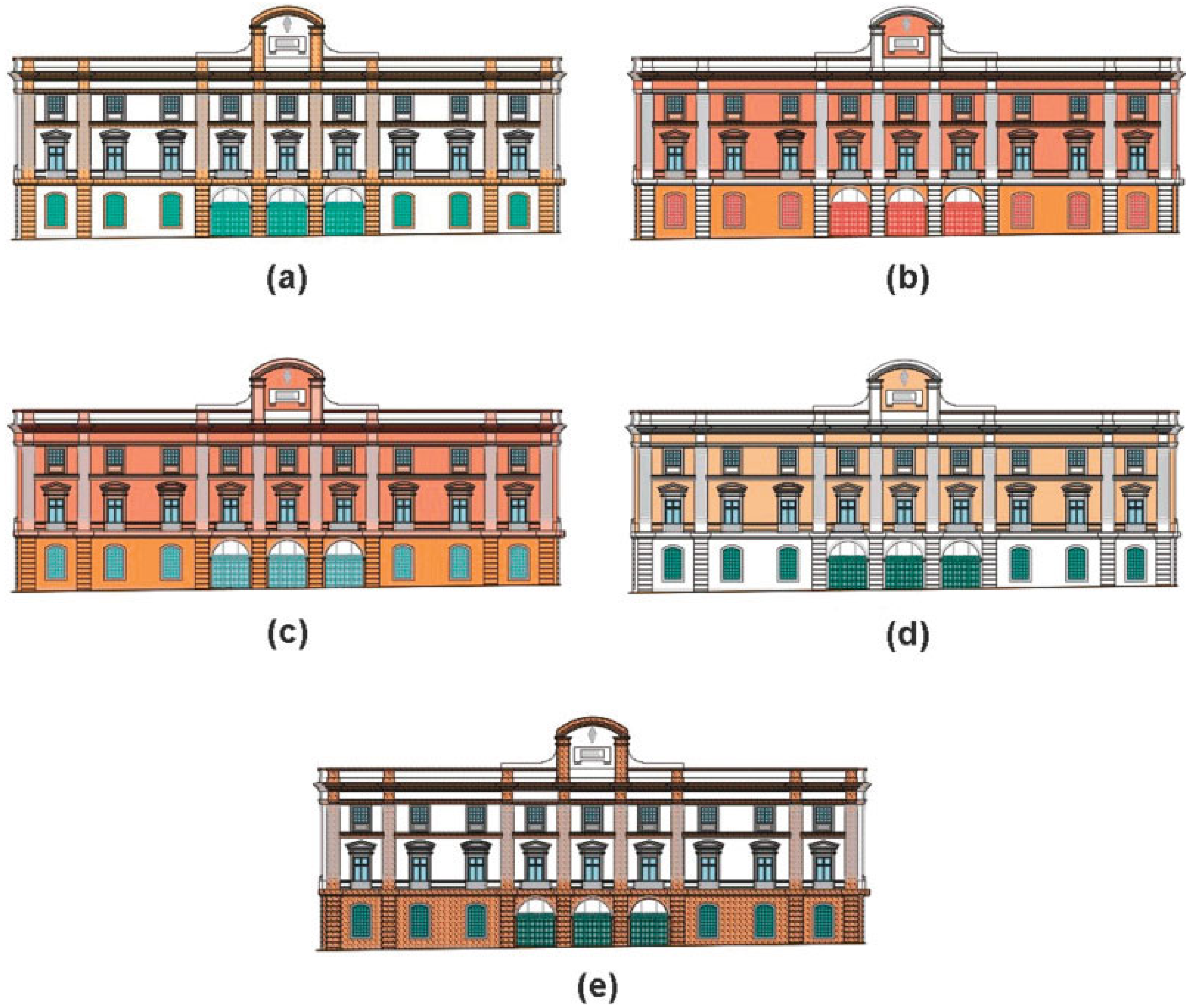

FIG. 15. Proposal of color that shows the *Diputación* of Cadiz façade between: (a) 1778–1862, (b) 1862–1940, (c) 1940–1950, (d) 1950–1964, and (e) 1964–now.

have shown the usefulness in the determinations of the different layers and its corresponding color. This interdisciplinary exposition has been highly efficient for knowing a piece of the Cultural Heritage of Cadiz.

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