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Enhancement and recovery of the tiles affected by atmospheric pollutants in the Galleries of Punta Begoña, Getxo (Bizkaia)

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ABSTRACT

Punta Begoña Galleries, built in 1918 and located in the municipality of Getxo (Bizkaia, Spain) have a remarkable glazed ceramic decoration, whose current state of conservation presents an advanced level of deterioration. The study of the historical cultural property is framed within a multidisciplinary project, which aims to restore, recover and improve its historical and artistic value. In this sense, the recovery of the ceramic tiles is one of the crucial points, since it involves one of the visually most notorious elements. On the surface of the tiles, different degradations were observed, being the yellowish patina, one of the most significant.

In order to carry out a cleaning treatment, the nature of the patina was evaluated, whose coating is a consequence of atmospheric contamination, as the chemical analyzes showed. Furthermore, a comparison was performed among four reactants both applied in reproduced pieces and *in situ*. To evaluate the effectiveness of the products, a quantitative evaluation was applied by colorimetry.

In addition, this work shows an interdisciplinary methodology based on the scientific method as the best guide to achieve durable, safe and effective restoration methods.

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Puesta en valor y recuperación de los azulejos afectados por contaminantes atmosféricos en las Galerías Punta Begoña de Getxo (Bizkaia)

Palabras clave:
Patrimonio cultural
Revestimientos
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RESUMEN

Las Galerías Punta Begoña, construidas en 1918 y ubicadas en el municipio de Getxo (Bizkaia, España) poseen una destacable decoración de cerámica vidriada, cuyo actual estado de conservación presenta un avanzado nivel de deterioro. El estudio del inmueble histórico cultural está enmarcado dentro de un proyecto multidisciplinario, que tiene como fin restaurar, recuperar y mejorar su valor histórico y artístico. En este sentido, la recuperación de la cerámica es uno de los puntos más cruciales, ya que supone uno de los elementos visualmente más notorios. En la superficie de los azulejos, se observaron diferentes degradaciones, siendo la pátina amarillenta, una de las más significativas.

Con el fin de llevar a cabo una limpieza de la misma, se evaluó la naturaleza de la pátina, cuya veladura es consecuencia de la contaminación atmosférica, como mostraron los análisis químicos. A continuación se llevo a cabo una comparación entre cuatro disolventes orgánicos, aplicados tanto en probeta como *in situ*. Para evaluar la efectividad de los reactivos, se realizó una valoración cuantitativa mediante colorimetría.

Además, el presente trabajo muestra una metodología interdisciplinaria basada en el método científico como la mejor guía a seguir para lograr métodos de restauración duraderos, seguros y efectivos.

Introduction: Punta Begoña Galleries

Punta Begoña Galleries are located on the left bank of the Nervión River, in the city of Getxo (Bizkaia). Horacio Echevarrieta – a prominent Spanish industrial businessman of the twentieth century – founder of Portland Cement Iberia Company or Iberia Airlines amongst others [1], commissioned the construction of this monumental complex in 1918. The commission was placed on the architect of Bilbao Ricardo Bastida, who, studied architecture in Barcelona, where he was imbued with the modernist esthetic. He expressed in these galleries, a harmonious and classic style at the same time. He was one of the best architects of the time. Amongst his main works can be highlighted the Municipal Alhóndiga and the Doña Casilda Iturriza park, both in Bilbao.

The galleries present ceramic coatings characteristic of the southern area of Spain. Notable among them is the tile with pomegranates iconographies as a reference theme on it, being the most abundant (Fig. 1). The pomegranate has been used throughout history as a symbol of creation and fecundity because it is a multi-seed container. Reference of its great symbolism are widespread in all cultures. Used in Christianity as a precursor symbol of passion and resurrection [2].

During the interventions in the galleries, it was found in the reverse of a tile the seal of manufacture of the tiles that cover all the galleries. In negative relief, in the mortar of the wall, the imprint of *José Mensaque Sevilla* can be seen. Indeed, the iconography of the tile decorations, has been identified in the Mensaque Rodríguez y Cía catalog, in the Lamina n°3.

Mensaque Company was run by a family of potters with a long lasting history in the city of Seville, more specifically in the neighborhood of Triana. The factory is linked to the world of ceramics since the 18th century. According to historical records, it is known that, after the death of José's brother in 1905, the factory would be under the responsibility of *José Mensaque y Vera*. After his death in 1916, the company changed the name again to *José Mensaque's Widow and Children*. Therefore, we can date the manufacture of these tiles in the period of 1905–1915. Although, it cannot be ruled out that for a few years afterwards they continued to use the *José Mensaque* brand until the stock was finished [3]. Currently, the company runs under the name *Mensaque Rodríguez y Cía* and still offers the same ceramic models used in Punta Begoña Galleries, although the glazes include some modification color [4] and, of course, composition.

In any case, the monumental complex has been abandoned for more than forty years leading to deplorable conditions. That is why in 2014 an intervention project was designed for its recovery and enhancement, between the City Council of Getxo and the University of the Basque Country (UPV/EHU), with the collaboration of the Basque Government and the Provincial Council of Bizkaia. The multidisciplinary project involves different research groups that are: Environmental Analytical Chemistry (IBeA), Hydrogeology, Geotechnics and Environment (HGI), Built Heritage Research (GPAC), UNESCO Cultural Lanscape and Heritage (UPV/EHU) Chair and Cultural Property Conservation Group of Fine Arts. All of them are developing their research, in unison, with the work execution projects carried out by the municipality of Getxo [5,6].

Within this project, the recovery of ceramics takes on special relevance due to its historical and cultural value. However, as the rest of the set presents important degradations (Fig. 2) that should be subjected to evaluation, identification and removal following a conservation criterion that guarantees the effectiveness, harmlessness and durability of them.

Fig. 1 – Representative tile of Punta Begoña Galleries and imprint on the mortar with the seal of manufacture.

Fig. 2 – Deterioration agents present in Punta Begoña Galleries.

In this sense, one of the most striking deteriorations presented by the tiles is a yellowish patina that, although did not hide them completely, it confers them an aged aspect. It is absolutely necessary to implement an intervention protocol specific to each case, always starting from the chemical analysis of the materials involved in each degradation agent [7–9], and in this way intervene in the elimination with greater precautions.

Taking all of these premises into account, the aim of this study was to identify, evaluate and restore the ceramics affected by the yellowish-brownish patina to recover their original appearance. For this purpose, an intervention methodology was proposed based on objective criteria. Thus, firstly an evaluation of the decaying was carried out, in order to understand it, and secondly, the associated degradation pathways were explored to propose the bests cleaning products. Moreover, a cleaning test with different chemical products was developed to recover the ceramics and define a proposed cleaning methodology. Moreover, the demonstration of the usefulness of the restoration works to minimize the protocols based on "trial and error" was proposed.

Methodology

To carry out this project first of all, the characterization of the unaffected glazes has been carried out. In addition, the diagnosis has been performed, in order to evaluate, the specific problem and finally, a comparison among four reactants has been carried out to determine the appropriate treatments. The analytical techniques employed have been the following ones:

SEM-EDS

A first evaluation of the ceramic tiles was performed by scanning electron microscopy coupled (SEM-EDS). The elemental composition of glazes was determined by EDS, using an X-Max (Oxford Instruments) equipment. Data were collected at two different voltages of 20 and 30 keV and a current of 50 μA for the acquisition of images and 200 μA for the acquisition of spectra. The working distance ranged between 9 and 11 mm. The EDS spectra were acquired and treated using the INCA software (Oxford Instruments). A selection of 8 tiles including all colors were selected for the elemental analysis.

Colorimetry

These measurements were made using a tristimulus colorimeter PCE-CSM 5 with D65 illuminant, and CIE 10° standard observer. The measurement geometry is *diffused* illumination with 8° viewing angle, specular component included, silicon photoelectric diode sensor, with 0.4 s of measurement and with an accuracy less than 0.5 ΔE^*ab. The measurements were made using the opening diameter of 4 mm that allows measuring smaller color surfaces so that it is possible to discriminate colors with greater precision.

Tests pieces manufacturing

SIO-2 ARGILA (Ceramic Collet, Spain) was selected for the clay. The tiles were made manually using a Forns ceramic laminating machine (Forns, Spain) because it was a small amount of test pieces (5 test pieces, one for each color). They were dried by turning the tiles so that, the drying was uniform and no cracks occurred. For the colored glazes, a percentage of 60% frit and 40% water was added to the mixture. To this solution, to incorporate color, oxides were added, in the desired proportion. For the glaze, frit 12215 transparent Pb single firing enamel (J.L. Vicentiz S.L supplies Ceramics, Spain) was used and mixed with the selected oxides. For each color, 250 g of frit mixture was prepared and mixed with a percentage of oxides (J.L. Vicentiz S.L Supplies Ceramics, Spain) according to the color to be obtained. In the case of cobalt blue 1 wt% cobalt oxide was added, 3 wt% of iron oxide was added for the honey color, 2 wt% copper oxide for the green, 3 wt% cobalt oxide and 3% manganese dioxide for black and finally, 8 wt% tin oxide for white.

After the application of the colored glaze, the pieces were subjected to a firing process with a temperature ramp of 100 °C/h up to 950 °C (9.5 h), temperature was kept for 0.5 h and 9 h of cooling.

Reactants

The chosen reactants, with which the patina could presumably be eliminated, were two commercial products besides, two industrial chemicals:

1. KH7: Commercial degreaser KH7 (KH Lloreda SA, Spain) diluted 2% in water.
2. Amon-Proquimia: Ammonia detergent Amon-Proquimia, (Proquimia, SA Spain) at 2%.
3. Oxalic acid in aqueous solution: Oxalic acid ($H_2C_2O_4$) (PanReacQuimica SAU, Cartelles del Valles Barcelona, Spain) at 3% in water.
4. Cellulose paper and ammonia

ARBOCEL® BC 200 cellulose paper (CTS, Europe, Srl, Italy) saturated with 5 drops of ammonia (NH_3, PanReacQuimica SAU, Cartel del Valles Barcelona, Spain) diluted in 250 ml of lukewarm water.

Fig. 3 – Ceramic tiles covered by atmospheric pollutants.

These percentages were established according to previous trials performed on the laboratory. However, in case of needing to readjust the percentages according to the effectiveness of the cleanings, either in this test or in the in situ test, it would be essential to re-perform the resistance test in order to guarantee the innocuousness of new solvents.

Results and discussion

Characterization of the patina

The degradation of the ceramic glazes appears as a yellowish patina that masks the ceramic coatings as seen in Fig. 3. At first glance, it could seem a structural affection of the decaying. However, after the cleaning of other substances accumulated on the pieces, it was verified that this patina could be removed. For this reason, as a parallel work in the mentioned global project, chemical analyses were conducted to determine the origin and composition of this yellowish layer.

The chemical analysis of the building presents a strong impact due to atmospheric contamination [10,11]. It is necessary to mention that, due to the location of the galleries, the ceramics are exposed directly to the marine aerosol and pollution from the industrial port of Bilbao, road and maritime traffic and various industries (Fig. 4). Taking this into account, the patina could be formed by a film of combustion products and other atmospheric pollutants as has been detected for nearby buildings [12]. This type of degradation is very dangerous, both for the ceramic pieces and for the mortars that support them, generating coating in glazes that are very difficult to remove [13]. This film could be formed by dicarboxylic acids generated in the atmosphere as the photochemical oxidation of higher molecular weight organic compounds generated by both biological activity and human activity. This oxidation takes place due to the reaction of hydrocarbons and fatty acids with the ozone present in the atmosphere, which, in turn, is related to solar radiation and creates dicarboxylic acids [14].

Generally speaking, rough surfaces are more prone to host this types of pollutants rather than a smooth and shiny surfaces like those of the glazed tiles. However, this fact might be originated by the phenomenon called thermophoresis, which involves the deposition of the aerosols, caused by the

Fig. 4 – Location of Punta Begoña Galleries in a semi industrial environment.

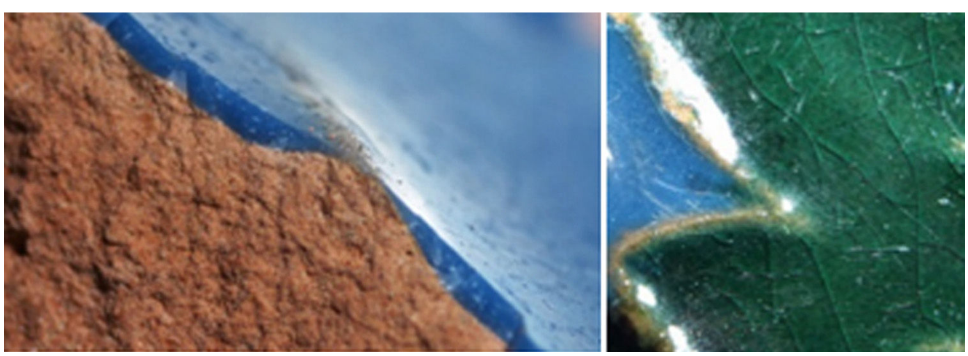


Fig. 5 – Glass layer and ceramic paste (left). Crackle glass layer (right).

difference of temperatures between the tiles and the room environment [15]. The tiles could also generate electrostatic forces that, in the presence of moisture, produce the adhesion of particles in the surface. Moreover, air currents are another very common cause of the adhesion of unburnt carbon particles, or similar, which could be trapped by the vitreous layer (Fig. 5).

The chemical analysis showed that the depositions in the galleries were directly related with atmospheric gases (CO_2, SO_2 and NOx), solid micro-materials in form of particles mixed with soot and marine aerosol. Salts such as NaCl (marine aerosol) as well as sulphates and nitrates were identified in high concentrations. Moreover, ions such as Ca^{2+}, K^+, Mg^{2+}, Fe^{3+}, Al^{3+}, Sr^{2+}, NH_4^+, HCO_3^- and Br^-; heavy metals such as Pb, Cd, Cr, Mn, Cu, Mo, Rh, Ni, As, Ti, V and Hg, and organic pollutants such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) or volatile organic compounds (VOCs) were identified [16,17].

For all this, and based on the chemical analysis carried out within the project and the findings observed in the inspection of the ceramics, a cleaning test was proposed with the most suitable solvents for the elimination of organic compounds related to air pollution.

Characterization of the tiles

The tiles of the Punta Begoña Galleries were manufactured using the technique called *Cuenca o Arista*. This technique, already used since the end of 15th century consists of stamping a motif mechanically on the fresh clay by pressing a mold.

Fig. 6 – Mechanical elimination of atmospheric pollutants.

The dividing partitions that remain after the stamping prevent the mixing of the colors once the liquid suspension of the glaze has been applied, separating them in the resulting cavities. The clay bodies include homogeneous calcareous pastes of fine grain that are well decanted.

The glazes are 400–600 μm thick and the different colorations are obtained by traditional recipes as SEM-EDS results showed (Table 1). Thus, the compositions revealed common mixtures of Si (19.0–21.2 wt%) and Pb (25.9–38.1 wt%). The opaque glazes have been obtained by cassiterite (SnO_2). The honey colored ones, are translucent and their final appearance is the combination of the translucent glaze, that includes iron oxides and the underlying buffer colored paste. The translucent glaze shows the highest Pb concentration (38.1 ± 5.3 wt%) Moreover, the colors where obtained by different metallic oxides. In this way, CoO was used for blue and black, MnO for black and CuO for green [18].

Mechanical removal

As an initial step, it was decided to carry out a mechanical cleaning. An inconspicuous area of approximately 5 × 5 cm was chosen. The mechanical cleaning was performed at the tip of a wooden scalpel without the use of any other physical or chemical agent. The observed result could be accepted as partially acceptable with respect to the quality of the cleaning but it could be improved very much because, as can be seen in Fig. 6, there are still rests of the patina covering the ceramic.

In addition, in terms of effectiveness and considering the time required to perform this cleaning operation, the result of the trial was very negative, with more than 10 min needed to clean the chosen area. Anyway, this cleaning test served to confirm that the observed deterioration was a removable patina and not a crust or permanent reaction with the glaze as it could be initially thought. Therefore, it was required to develop a method to proceed with the elimination that combines effectiveness and speed. In this sense, the use of chemical solvents seemed to be the next logical step, and for this, it was necessary to carry out the corresponding resistance tests, prior to the intervention.

Table 1 – Semi-quantitative concentrations (wt%) of the different colors present in the tiles. Average obtained from 8 different tiles.

	O	Na	Al	Si	K	Ca	Mn	Fe	Cu	Sn	Pb	Co
White	37.4 ± 2.3	2.3 ± 0.6	1.5 ± 0.7	20.6 ± 2.3	1.9 ± 0.8	1.3 ± 0.7	ND	0.2 ± 0	ND	5.5 ± 0.3	25.9 ± 4.9	ND
Blue	41.4 ± 3.9	2.9 ± 1.2	1.7 ± 0.9	21.2 ± 2.2	1.9 ± 0.9	1 ± 0.3	ND	0.2 ± 0	ND	2.9 ± 0.6	26 ± 6.2	0.2 ± 0.1
Green	36.0 ± 3.0	1.6 ± 0.5	2.8 ± 1.7	20.4 ± 3.5	1.2 ± 0.3	1.5 ± 0.5	ND	0.4 ± 0.1	1.3 ± 0.4	1.7 ± 1.5	29.5 ± 8.1	ND
Honey	32.9 ± 4.5	1.4 ± 0.5	1.5 ± 0.5	17.8 ± 2.3	1 ± 0.1	1.3 ± 0.3	ND	3.2 ± 0.5	0.4 ± 0	ND	38.1 ± 5.3	ND
Black	32.2 ± 2.3	1.5 ± 0.4	1.8 ± 0.6	19.0 ± 2.7	1.1 ± 0.2	1.5 ± 0.5	0.8 ± 0.1	0.6 ± 0.1	0.6 ± 0.1	3.9 ± 0	34.9 ± 5.1	0.2 ± 0

Fig. 7 – Test piece-manufacturing process.

Resistance test on probes

Glazing resistance tests were carried out on reproduction of the tiles performed in the laboratory. In order to match as much as possible the original compositional matrix, the characterization of the ceramic glazes was used as a guide (Section 'Characterization of the tiles').

In contrast, the impossibility of reproducing the patina formation, which is the resuts of decades of abandonment and atmospheric pollution, the cleaning treatments could not be performed in the laboratory, before intervening *in situ* on the original ceramic pieces.

Taking all this into account, the test pieces were divided into four parts, to test the four selected products in each color (Fig. 7). The application was made with a cotton cloth impregnated with the corresponding product in each case, except for the cellulose paper, which was applied in the selected area during an application time of three minutes.

In all cases, once the application was complete, any remaining solvent was removed from the ceramic layer and neutralized with limewater (3 wt% CaOH in water, CTS, Europe, S.r.l, Italy) in the case of acids.

Finally, it was observed how none of the selected products generated problems in the glaze, neither in the physical surface nor in the coloration. Therefore, the four solvents in the mentioned concentrations were validated to carry out the *in situ* cleaning.

In situ cleaning test

Once the innocuousness of the products chosen on the specimens was confirmed, the *in situ* cleaning test was carried out in areas of 10 × 15 cm, always in areas more or less inconspicuous to avoid visual impact in case of error and following the same methodology applied in the probes. Regarding the mode of application, it was performed in a similar way, but with a time control. Thus, a cotton cloth impregnated with the prepared solution was used, gently massaging the surface in four consecutive batches of 10 s each one, to be able to influence in the holes of the tiles.

To minimize subjective conclusions, two criteria were established in order to evaluate the effectiveness of the cleaning of the glaze covering the ceramic base: (1) the quality of the cleaning based on the colorimetric measurement before and after and (2) the speed of cleaning.

Regarding the first criterion, colorimetric measurements were made in areas of white glaze affected by the atmospheric pollution patina before and after cleaning. This color was selected after different colorimetric tests in all the colors showing being the most affected one, and therefore, the most appropriate to check the efficiency of the cleaning. In addition, the value collected is the average of, at least, three measurements of the white points in the same test area. However, it is necessary to clarify that the effectiveness evaluation in this step was carried out by the comparison of the data before and after cleaning. It was because the selected areas were quite small to be comparable with a bigger area, thus, the purpose in this step was to evaluate the patina removed to select the best product which will be demonstrated in the next step in a larger area.

On the other hand, and as a control, different measurements were made on diverse white areas without patina but affected by atmospheric pollution: a white located in an inner area of a column without solar exposition and an exterior white exposed to sunlight. These data is collected in Table 2 where it is possible to observe that the lightness (value of L) decreases with the formation of the patina and is aggravated by the effect of the sunlight by the increase of the yellowing (higher value of b), being all these observations maximum when the glaze appears. These results seemed to confirm that sun exposure is an important factor when fixing pollutants, as mentioned in the introduction.

Table 2 – White comparison.

	L	a	b
White Punta Begoña Interior Column without degradation	73.23	0.42	12.18
White exposed to sun light without degradation	71.19	−1.22	20.78
White with patina	68.99	4.92	20.48

Table 3 – Colorimetry results of the *in situ* trials before and after the cleaning operations.

	Before cleaning			After cleaning			Effectiveness of the cleaning		
	L	*a*	*b*	*L*	*a*	*b*	*L*	*a*	*b*
Trial 1	71.14	5.15	21.48	76.60	0.45	5.04	8%	91%	77%
Trial 2	68.49	8.43	25.66	68.93	5.44	19.57	1%	35%	24%
Trial 3	69.09	6.14	22.68	73.57	2.95	8.68	6%	52%	62%
Trial 4	64.75	5.87	20.21	65.77	2.98	17.26	2%	49%	15%

Trial 1 – commercial degreasing agent (KH7)

In the first test, a specific commercial product has been applied for the elimination of greasy compounds. During the application, the cloth began to be dyed yellow indicating the effectiveness of it. The product eliminated the patina showing the original color of the tiles, above all, more perceptible in the white color. Quantitatively, as shown in Table 3, it can be seen how the cleaning efficiency was very good, as well as the values were very close to the reference values of the control brick.

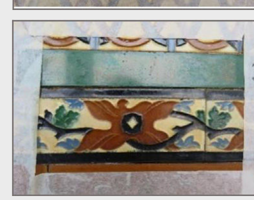
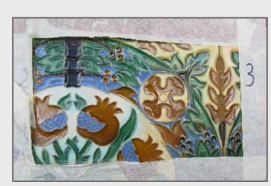
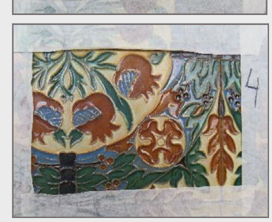
Trial 2 – commercial ammonia based cleaning agent (Amon-Proquimia)

This second test was performed with a diluted ammonia detergent. The initial result was very poor, without the removal of pollutants and the cloth remained white. Therefore, it was repeated the same sequence in the application of the solution, to influence again the deterioration agent, with the same response. Even so, in terms of the analysis of effectiveness, although in lightness there was hardly any difference, the yellowing improved slightly, although very far from the control values (Table 3).

Trial 3 – oxalic acid in aqueous solution

Metal particles were found among the components introduced by the atmospheric pollution. Then oxalic acid was selected as a specific product in cleaning of oxides and metals. In this case, as in trial 1, a good reaction was quickly obtained, since the cloth was dyed and it became clear that the cleaning was being effective. The 3 wt% solution in water was sufficient to obtain a good result, without damaging the ceramic material. In a quantitative way, the brightness was recovered in a remarkable way, as well as the yellowing decreased by more than 50 wt%.

Table 4 – Atmospheric pollutants removal results.

Product	Name	Results	
KH7	Commercial degreasing agent	Positive. Effective	
Amon-Proquimia	Ammonia based detergent	Negative. Limited effectiveness	
Oxalic acid	Oxalic acid dissolution in H_2O	Positive. Effective	
Ammonia (NH_3) + H_2O	Cellulose paper with ammonia 5 drops of ammonia in 250 ml of H_2O	Negative. Limited effectiveness	

Trial 4 – cellulose paper with ammonia
Finally, the solution of ammonia was applied in cellulose paper saturated in the solution mentioned for a prolonged time without obtaining a visible response. Regarding the values of the colorimetry, as can be seen in Table 3, no significant changes were obtained with respect to lightness, with only a slight better response for yellowing.

Therefore, the first trial (commercial degreaser) and third (oxalic acid) provided interesting results since in both cases the hidden white color – typical of the tiles – emerged obtaining values near the reference in the colorimetric measurements. Table 4 summarizes the experiments carried out with the four cleaning solvents chosen for this purpose. The data were significant since they showed that the best product was the commercial degreaser with little difference with respect to the dissolution of oxalic acid. In addition, in view of the speed of elimination, both were satisfactory obtaining an immediate response after the application. In any case, the need for the use of a solvent for cleaning was evident, as the lack of effectiveness of mechanical cleaning.

Application of the proposed cleaning methodology

For the cleaning of the glaze that masks the ceramic material, the commercial degreaser and the oxalic acid proved to be suitable products, fulfilling the two criteria studied: the efficiency and recovery of the white tone and the speed of response. For the choice of one or another, the surface of the ceramics (approximately 230 m^2) and the required quantity of product were considered. The commercial product, despite having obtained a slightly higher efficacy than oxalic acid, has a complex and not totally available composition, so that, the damage to the tiles at long-term presented more uncertainty. In addition, for long-term use, a commercial product has the drawback that might be discontinued and might require a new trial work. Therefore, taking into account that oxalic acid showed good effectiveness in a short time of application, it was decided to use the oxalic acid solution.

In addition, during the measurement of the white area after the application of the oxalic acid it was observed that the white glaze had a small contamination of the adjacent color, typical in the manufacture. Therefore, the efficiency calculated with the colorimeter could have been conditioned by this contamination, showing less efficiency that the real one. Thus, the efficiency of the oxalic acid would surely be greater in the case of having a glaze without color contamination.

It is for all this that the proposed cleaning methodology was 3 wt% oxalic acid in water. After deciding the final methodology, a larger test (60 × 60 cm) was carried out to demonstrate the validity of the methodology as shown in Fig. 8.

To perform the quantitative demonstration of the method and considering the problem with the color contamination measured in the oxalic test, the colorimetric measurements of the targets were carried out again in this case. However, in this demonstration step, as a reference, the same tiles located inside of a contemporary construction were used. The Iruña Café (Bilbao), which opened its doors in 1903 and it was characterized by an unusual decoration in Bilbao at the time with its walls covered with tiles manufactured in Seville (Fig. 9) such as those found in Punta Begoña Galleries. In this way, the measurements of these whites were considered as the maximum reference values to obtain in the cleaning tests, as external agents did not affect them. Table 5 shows the results obtained, this time, as an average of different measurements in the whole area of the testing and in the same area of reference, allowing multiple analysis of different whites, which generates a result more representative of the efficiency of the global cleaning. In this sense, the obtained white tone is slightly more yellowish than the control white of the Iruña Café, but practically with the same lightness and values of b, being the best results obtained compared with the *in situ* tests. Therefore, the

Fig. 8 – Test pieces and methodology applied to clean the atmospheric pollutants.

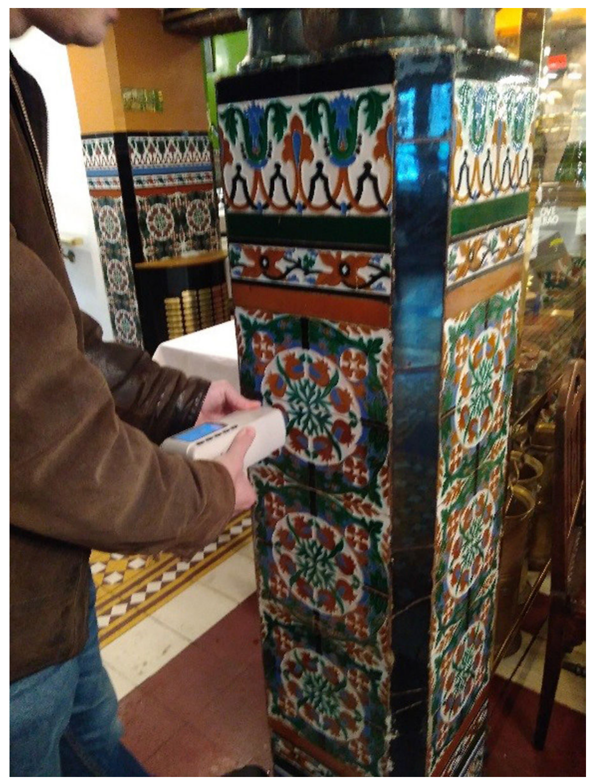


Fig. 9 – Café Iruña interiors in Bilbao.

Table 5 – Color recovery of the cleaning with 3% oxalic acid taking into account the reference ceramics (Café Iruña).

	L	*a*	*b*
Café Iruña Interiors	78.61	−0.11	4.14
Trial 5. Punta Begoña Galleries	76.46	1.92	4.60
Initial	70.96	6.63	21.09
Recovery of the reference color	8%	71%	78%

hypothesis that the contamination of the adjacent color could be masking cleaning efficiency was clearly demonstrated, proving without any doubt that oxalic acid (3 wt% in water) was the best product for the cleaning of the tiles under study.

Conclusions

This study pointed out the relevance of the interdisciplinary work to recovering and valuing the ceramic material of Punta Begoña Galleries. The chemical analyses conducted in parallel to this work provided the necessary data to begin the intervention on the tiles. It was essential to choose the appropriate solvents in an intervention with criteria and rigor, avoiding the use of unnecessary products (only 4 products were tested).

Considering that the studied building is an outdoor monumental complex, and it is impossible to avoid future contamination, it was crucial to establish a cleaning methodology. In this sense, it was demonstrated that the use of a solution of 3 wt% oxalic acid in water, on the area affected by contaminants, guarantees an effective and respectful response with the glaze of the tiles under study. This action was completed with a neutralization of the acid, after its assignment, with a base (3 wt% calcium hydroxide in water).

In addition to all this, the present work shows an interdisciplinary methodology based on the scientific method as the best guideline to follow to achieve durable, secure and effective restoration methods. This is a very important in an area in which the "trial and error" with multiple products is still a tool too widespread.

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