The relevance of the use of ionic chromatography for the quantification of soluble salts in the analysis of built heritage: Improving the European norms

Iñaki Vázquez-de la Fuente [a],[*], Nagore Prieto-Taboada [a], Estibaliz Lama [a], David Cristobal [a], Rosa García-Arrona [b], Gorka Arana [a], Juan Manuel Madariaga [a],[c]

[a] *Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), P.O. Box 644, 48080 Bilbao, Basque Country, Spain*
[b] *Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV/EHU), P° Manuel Lardizabal, 3, 20018 Donostia, Basque Country, Spain*
[c] *Unesco Chair of Cultural Landscapes and Heritage, University of the Basque Country UPV/EHU, P.O. Box 450, 01006 Vitoria-Gasteiz, Basque Country, Spain*

A R T I C L E   I N F O

A B S T R A C T

A soluble salt analysis is crucial in the evaluation of the conservation state of the built heritage. In this sense, there are European norms that indicate the way to measure them and the levels that are hazardous. However, in those norms, only a few anions are included, the cations are undervalued, and the required analysis is not simultaneous. All of these could lead to incorrect conclusions because of the lack of representativeness of the real situation. Moreover, there are incongruences observed in the norms, because although the levels of some anions are established the quantitative analysis is only recommended. In this work it is demonstrated how the quantitative analysis of anions and cations is crucial for the correct understanding of the conservation state of a historical building under conservation works. For that, a specific ionic chromatographic system has been designed that provides the analysis of anions, cations and carbonate/bicarbonate in a simultaneous way and it was applied in brick and mortar samples for the study of Punta Begoña Galleries. In this way, it was possible to identify the affection depending on the studied materials, being the atmospheric acid gases the main problems to the mortar and the rainwater and marine aerosol for bricks. Moreover, the damage level of the analysed areas was quantified and the most critical points to be restored were identified. This work demonstrates the need of a change of mind in the soluble salt analysis regarding the ions included in the norms and the way to measure them.

1. Introduction

The soluble salt analysis is crucial in the Cultural Heritage analysis, especially in the built heritage [1,2]. The salts are formed, generally, by the interaction between the original materials and the rainwater, atmospheric pollution (acid gases as CO_2, SO_2 and NO_x) and/or infiltration water rich in ions [3–5].

The formed salts can be accumulated in the porous net of the building materials forming sub-efflorescences, and in the surface of the materials forming efflorescences. The salt formation is not only an esthetical problem, but also produces a considerable decay when salts precipitate beneath the material. In this case, it produces internal tensions that could promote cracks and material losses. Moreover, the soluble salts formation involves, generally, the reaction of the original materials and therefore, the material dissolution.

The most vulnerable materials are the most porous ones, because the water and salts can penetrate easier [6–10]. Thus, the carbonated based materials, as limestone, mortars and so on, are also very susceptible to this deterioration, because the carbonates react easily in slightly acidic conditions.

Hence the analysis of soluble salts is very important, but not only to obtain their total content, but also the concentration of each salt. The European norms have slowly evolved and the NORMAL 13/83, a conductimetric method to determine the total content, was one of the

---

* Corresponding author.
  E-mail address: inaki.vazquez@ehu.eus (I. Vázquez-de la Fuente).

first norms [11]. Nowadays, the European standard method EN 16455/ 2016 for the analysis of soluble salts recommends the measurement of the conductivity but mentions instrumental quantitative analysis as alternative; pointing to ionic chromatography (IC), as the most used one for this purpose. However, it is quite surprising as it only includes this analysis as recommended, when the concentration of the different ion is crucial for the correct evaluation of the damage generated by these salts, as is collected in other norms [4,12–16].

In this sense, there is another problem in the norms, because the EN 16455/2016 norm is focused in the analysis in chloride, nitrite, nitrate, sulphate, sodium, potassium, calcium, magnesium and ammonium [17] but then, there is no indication regarding the levels that are worrying. It is relevant because it is widely known that the knowledge of which ions are present and the concentration of each one is very important because the damage is related to the type of ion and to its content. In this sense, the most common and hazardous soluble salts found in construction materials, as they affect their integrity, are sulphates, nitrates, chlorides and carbonates/bicarbonates [18]. In fact, there are some norms that indicate maximum levels for some of them, and some authors have tried to establish a correlation between the concentration of soluble salts and the decaying that it generates [4,12–16]. However, these norms only limit the concentration of sulphates, nitrates and chlorides, ignoring the effect of cations (whose analysis is only recommended in the EN 16455/ 2016 norm) that are crucial to correlate the results and to try to identify the salts formed and the source of ions. In this sense, especial mention needs the work of E. Pinto involving the different norms to try to establish the total soluble salts (cations and anions) content that affect the buildings and to determine the risk for the materials [12]. However, until now, the norms seem to be quite incoherent recommending quantitative analysis, mentioning cations, but without stablishing levels of damage for them.

Taking all of these into account, this works tries to point out the relevance and utility of the quantification of soluble salt in building materials, going one-step further of the usual analysis in the area and performing simultaneous analyses of cations and anions, including carbonate and bicarbonate. In this sense, a historical building (Punta Begoña Galleries, Getxo, Spain) was selected to demonstrate the utility of these technique. Moreover, the main objective of this work is point out the ionic chromatography technique as the best option to promote the change/modification in the European normative, which currently have some important lacks and incongruences. In this sense, it was designed and validated a modular chromatographic and titrimetric system that provides the analysis of anions, cations and carbonate/bicarbonate in a simultaneous way.

2. Materials and methods

2.1. Punta Begoña galleries

In order to select a building to demonstrate the need of carrying out quantitative analysis of the soluble salts to promote the change in the current European norms, the galleries of Punta Begoña (Getxo, Spain) were selected. This building was built in the beginning of the 20th century (1918) and nowadays is part of an intense project of renovation of the area [19]. The building has a high architectural value because it was the first private building made with reinforced concrete in Biscay. It is composed of several spaces: two outer galleries (lower and upper), outside gardens and a main hall (Fig. 1).

This main hall is decorated with mural paintings but with a limited colour palette and pro-Franco's regime symbols [19]. External stressors such as marine aerosol and atmospheric acid gases from the nearby industrial port, road and marine traffic, together with the bad conservation state of the building enhanced the deterioration processes of the materials [20]. Although their artistic value is limited, the wall paintings are under research because it is possible the presence of an original mural painting behind the observable iconography [21]. For that reason, the integrity of the walls is crucial for the recovery of the original paintings.

The main hall has four different walls, being open to the sea in one side (Fig. 1). The walls are composed by different layers: bricks as structural material, mortar to cover the structure and different preparatory layers of the mural paintings on the top. In the lower part of the
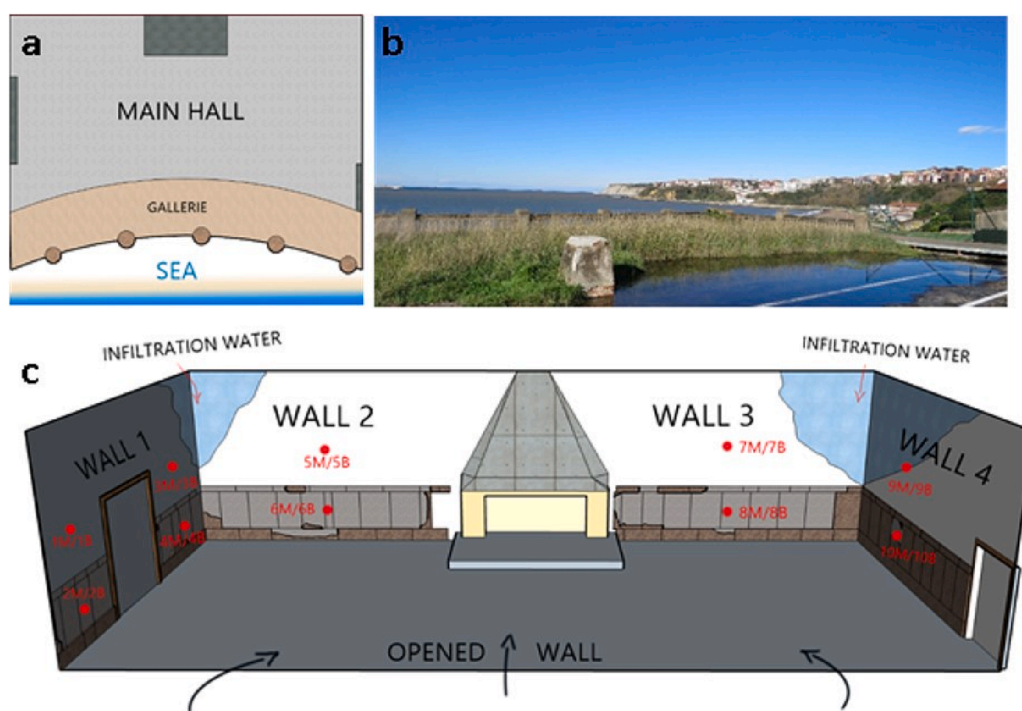

Fig. 1. a) Location of the main hall with respect to the galleries and the sea. b) The garden located on top of the main hall. c) Representation of the main hall in which it is possible to observe the four walls and the open side to the sea, with the sampling and the infiltration water points.

wall, the brick and mortar structure is finished with a cover of marble. Taking this into account, to evaluate the conservation state of the walls, mortar and brick samples were collected using a scalpel and a micro-drill when it was necessary.

The sampling was performed to study all the walls that compose the main hall, to observe differences regarding their orientation. Moreover, the height and the effect of the marble was also studied. For that reason, brick and mortar samples were collected behind the marble (in areas where the marble plate has been detached at around 1 m height) and behind the mural paintings (at around 3.25 m height) in the four walls. And, finally, the different parts of each wall were sampled in case it was not continuous. As can be seen in Fig. 1c, in the case of the wall 1, there was a door in the middle of the wall, thus, both materials were sampled on each side of the door behind the marble and mural painting. Between the walls 2 and 3, there was a fireplace, so the samples were collected from each side, and finally, as the wall 4 was continuous and samples were only taken in the middle of the wall. In this way, 20 samples were collected there, 10 samples of bricks and 10 samples of mortar as can be seen in Table 1.

It is necessary to state that the walls present infiltration waters from the garden located on top of the main hall (Fig. 1b), being the top of both corners affected by this water input (Fig. 1c).

In both types of materials, the samples were almost powder, evidence of the level of disaggregation and extensive alteration of the original materials. For that reason, the size of the samples could not be calculated but, in any case, more than 1 g of powder was collected per sample. The samples were kept in zip bags until the analysis.

2.2. Sample treatment

The solid samples were extracted for the analysis of soluble salt through the protocol optimized by our research group [2] based on the European standard for extraction and determination of soluble salts in natural stone and related materials used in and from cultural heritage (EN 16455:2016), [17] which allows the extraction by ultrasonic energy.

For that purpose, the samples were homogenized and dried before the extraction in an ultrasound bath Ultrasons-H (P-Selecta, Spain), with a working frequency of 40 kHz (1000 W). Then, the solution was filtered with 0.45 μm filters (PVDF, OlimPeak) and measured immediately. It is possible to store them at 4 °C but it is strongly recommended to analyse them after the extraction to guarantee the representativeness avoiding re-precipitations, microbiological activity and so on. Four replicates were carried out for each sample.

2.3. Designed modular analytical setup combining automatic titration and ion chromatography for the simultaneous analysis of soluble salts

Although it is not mandatory in the norms, the most used technique to analyse soluble salts in cultural heritage is IC. However, the analyses of the anions and cations are made separately because it is necessary to

use different columns, or the simultaneous analysis is quite complicated and requires complex set ups for this specific purpose [22,23]. Thus, normally, the analysis is made separately and, in this way, the sample consumption, reactive, and consumables are multiplied and, most importantly, the ions are not obtained in one analysis [24]. This fact is important because the stability of the sample could generate changes in the ion's concentrations giving erroneous results, especially when the cations and anions are correlated. The concentration of ions is quite unstable because of precipitation effects, microbiological activity, oxidation/reduction reactions, and so on [2]. Moreover, the carbonate and bicarbonate analysis by IC is generally avoided because it requires unstable mobile phases such as NaOH instead of carbonated based dissolutions. As an alternative, the carbonate and bicarbonate analysis can be approximated by acid/base balance or measured by a titrimetric methods [25,26]. This last option is the best, but it increases considerably the costs adding a third analysis, expending more time, and increasing the reactive, wastes and sample consumption. However, the most important point is that those results may not be comparable to those of the ionic concentration because it is done in a different moment. In this sense, an equipment to carry out a quantitative simultaneous analysis of all the ions related to soluble salts in built heritage could be useful, improving the quality of the results, time consumption and waste generation, among others.

For all that, a simple modular chromatographic and titrimetric system was designed for the simultaneous quantitative analysis of dissolved cations, anions, carbonate and bicarbonate to obtain representative results and, thus, the real ionic content in built heritage samples but also applicable to any other field.

The designed equipment (Fig. 2) was based in some Metrohm (Switzerland) modular instruments, adapted to achieve a simultaneous analysis of dissolved cations, anions, carbonate and bicarbonate ions. The Metrohm analytical system used is composed by two 930 Compact IC Flex configured as a dual channel ion chromatograph, an 888 Titrando automatic titrator and an 815 Robotic USB Sample Processor for high-throughput automation. The fully automatic system is controlled by MagIC Net, the Metrohm standard software for ion chromatography.

Each 930 Compact IC Flex Metrohm ion chromatograph has an IC Conductivity Detector. In the case of anions, a Metrosep A Supp 7–250/4.0 column was used for the separation and 3.6 mM Na_2CO_3 was used as mobile phase at a flow rate of 0.8 mL/min, with a MSM-Metrohm Suppressor Module for chemical suppression to achieve a base line of 12 μS/cm. Moreover, an MCS Metrohm CO_2 Suppressor was also used to obtain a base line below 2 μS/cm and therefore to improve the limits of detection.

The quantification of cations was conducted by using a Metrosep C 6-150/4.0 column from Metrohm. A HNO_3 1.7 mM/ dipicolinic acid 1.7 mM was used as mobile phase at a flow rate of 1 mL/min. In this case, the chemical and CO_2 suppression was not required.

The system has the inline ultrafiltration technology which filters the samples down to 0.2 μm particle size with generic cellulose filters to protect the modular system before the injection. Once filtered, samples are injected into the two injectors, for anions and cations analysis respectively, each with an injection volume of 20 μL.

For the carbonate/bicarbonate analysis an 888 Titrando Titrator with an 801 magnetic stirrer, 20 mL exchange unit and a combined "Ecotrode Plus" pH glass electrode and AgCl/Ag reference electrode were used. Moreover, an automatic dosing system which makes highly accurate dosing possible (down to 10 μL additions) was used.

Thanks to this system, a unique injection provides the analysis of anions, cations and carbonate/bicarbonate in a simultaneous way. The injection of the sample was controlled by an 815 Robotic USB Sample Procesor XL with a rack for 59 samples. The software used was the MagIC 3.2 and Tiamo 2.5, for the IC and titration systems respectively.

Finally, the modular system allows using each component in a separately way in less than 27 min.

Table 1
List of the collected samples. They are duplicated because in the same point mortar (M) and brick (B) samples were collected.

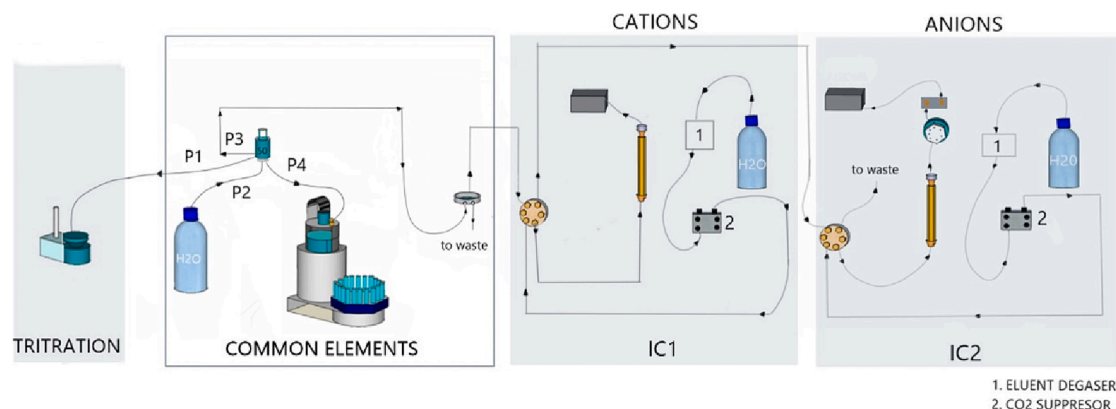| Sample	Wall	Sampling point	
1 M/1B	1	Mural painting	Left (door)
2 M/2B	1	Marble	Left (door)
3 M/3B	1	Mural painting	Right (door)
4 M/4B	1	Marble	Right (door)
5 M/5B	2	Mural painting	Left (fireplace)
6 M/6B	2	Marble	Left (fireplace)
7 M/7B	3	Mural painting	Right (fireplace)
8 M/8B	3	Marble	Right (fireplace)
9 M/9B	4	Top	
10 M/10B	4	Down	

Fig. 2. Scheme of the modular system designed (P: port).

2.4. Reactants

The standard solutions of the anions with 1000 mg/L concentration of fluoride (F^-), bromide (Br^-), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}) and oxalate ($C_2O_4^{2-}$) were from Honeywell Fluka. In the case of cations, the standard solutions of lithium (Li^+), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) were of the same brand and concentration.

The acid for the chemical suppression in the anions analysis was Tracepur H_2SO_4 500 mM (Merck, 96%). The titration was carried out with hydrochloric acid 0.1 M (PanReac, 95%), standardized by tris (hydroxymetyl)aminomethane (Sigma Aldrich, 99,9 %). The system was rinsed using a mix of EtOH:H_2O 1:1 with ethanol (PanReac, 99.5%) and ultrapure water (Milli-Q, Millipore). Moreover, all the water used in the solution preparation was ultrapure water.

2.5. Data treatment

The quantitative data collected was treated by means of individual analyses, correlation analyses and principal component analyses (PCA). The correlation analysis could help to identify the salts formed in the materials. In the last case, the PCA was performed using the software The Unscrambler ® X (CAMO Software, Norway). Moreover, also the orientation, area or material influence were studied, as well as the concentration level regarding the European standards for anions and literature for total content of salt because of the lack of specific normative [12,14].

3. Results and discussion

3.1. Validation of the proposed analytical system

The validation of the proposed analytical system is collected as supplementary material, where the selected ions to be studied, the linearity, sensitivity, selectivity, detection and quantification limits, trueness, and precision obtained with the designed equipment are summarized.

3.2. Quantitative analysis of soluble salts of the Punta Begoña's galleries main hall

The samples were treated with the optimized European standard to the soluble salts extraction and measured by the designed system. The results obtained are summarized in Tables 2 and 3. The results collected show the samples with concentrations above the LOQ and with acceptable RSD considering the concentration levels [27].

A first evaluation was carried out by Principal Component Analysis (PCA) to observe differences between samples. In this sense, a PCA was carried out with brick and mortar samples, obtaining an 87% of explained variance with 3 PC. As can be seen in Fig. 3, the samples were grouped considering two factors: (1) the material and (2) the height. Therefore, it was clear that both materials were not being affected in the same way despite being sampled in the same point. Moreover, as is common in the soluble salt analysis, the height played an important role in their distribution. The differences seemed to be related with the type of the soluble salts and the type of impact. As can be seen in Fig. 3, PC1 seemed to be more related to the ions present in the marine aerosols in

Table 2
Results of the mortar samples expressed in mg/g. Also, the total percentage of salts in weight (in red the values considered very high, and in orange, high), as well as the individual percentage of the ions controlled by European norms (in red the values considered high, and in orange, medium) are shown. The values of fluoride, bromide, phosphate and lithium have been eliminated because more than half of the samples were below the LOD (N.D.) values.

Sample.	pH	$CO_3^=$	HCO_3^-	Cl^-	NO_3^-	$SO_4^=$	$C_2O_4^=$	Na^+	K^+	Ca^{+2}	Mg^{+2}	TOTAL	% Cl^-	% NO_3^-	% $SO_4^=$
1M	9.3	7.6	13.4	1.6	0.3	5.6	0.3	1.0	0.8	9.1	0.3	1.9%	0.16	0.03	0.56
2M	8.5	4.6	22.0	9.5	1.1	21.6	0.3	7.0	3.1	14.1	0.3	5.7%	0.95	0.11	2.16
3M	7.7	N.D.	25.0	2.0	0.3	46.3	1.4	0.8	0.4	25.7	0.4	7.6%	0.20	0.03	4.63
4M	9.2	7.1	14.1	3.4	2.5	37.5	0.1	4.3	3.2	17.1	0.4	6.8%	0.35	0.25	3.75
5M	8.9	6.1	14.4	1.4	0.2	20.8	0.7	0.4	0.3	14.8	0.3	3.8%	0.14	0.02	2.08
6M	8.7	6.7	26.7	2.5	0.3	12.3	0.9	3.0	3.0	13.0	0.3	3.4%	0.25	0.03	1.23
7M	9.1	5.7	16.0	1.5	0.2	23.5	0.8	0.8	0.5	15.6	0.3	4.2%	0.15	0.02	2.35
8M	7.7	N.D.	13.6	0.4	N.D.	38.0	0.3	0.4	0.2	17.7	0.2	5.7%	0.04	–	3.80
9M	8.5	3.2	17.5	2.9	0.5	58.2	1.4	1.3	0.4	28.8	0.3	9.2%	0.29	0.05	5.82
10M	8.4	3.0	17.6	2.4	0.7	41.0	0.5	1.5	0.7	21.1	0.3	6.8%	0.24	0.07	4.10

Table 3

Results of the brick samples expressed in mg/g. Also, the total percentage of salts in weight (in red the values considered very high, in orange, high and in black, medium or less), as well as the individual percentage of the ions controlled by European norms (in red the values considered high, and in orange, medium) are shown. The values of fluoride, bromide and lithium have been eliminated because more than half of the samples were below the LOD (N.D.) values.

Sample.	pH	$CO_3^=$	HCO_3^-	Cl^-	NO_3^-	PO_4^{-3}	$SO_4^=$	$C_2O_4^=$	Na^+	K^+	Ca^{+2}	Mg^{+2}	TOTAL	% Cl^-	% NO_3^-	% $SO_4^=$
1B	8.5	4.1	18.7	0.7	N.D.	N.D.	3.8	0.2	N.D.	0.5	8.6	0.2	1.4%	0.07	-	0.38
2B	6.2	N.D.	5.8	20.2	4.0	0.04	22.0	0.1	13.7	5.3	4.7	0.4	7.0%	2.02	0.40	2.20
3B	8.0	N.D.	27.7	0.5	N.D.	N.D.	1.7	0.2	N.D.	0.3	8.5	0.2	1.1%	0.05	-	0.17
4B	7.0	N.D.	8.5	11.3	6.1	0.03	14.4	0.1	5.9	2.4	6.4	0.5	4.7%	1.13	0.61	1.44
5B	8.9	6.3	18.2	1.2	N.D.	N.D.	7.0	0.5	0.4	0.3	11.2	0.3	2.0%	0.12	-	0.70
6B	9.2	6.5	11.6	1.4	N.D.	0.03	2.3	0.1	1.0	0.9	6.8	0.3	1.3%	0.14	-	0.23
7B	8.9	4.8	14.7	0.6	N.D.	0.04	9.9	0.6	0.2	0.3	10.5	0.2	2.2%	0.06	-	0.99
8B	6.5	N.D.	6.7	10.5	6.6	0.05	15.4	0.04	7.7	2.1	5.0	0.5	4.8%	1.05	0.66	1.54
9B	6.4	N.D.	6.3	N.D.	N.D.	N.D.	3.2	0.1	N.D.	0.1	1.3	0.2	0.5%	-	-	0.32
10B	9.0	4.9	14.8	7.7	2.2	N.D.	5.3	0.1	3.5	0.7	10.0	0.2	3.0%	0.77	0.22	0.53

the negative part and in the positive part with a group of salts affected by atmospheric acid gases as SOx. Thus, PC1 seems to be the components to differentiate the samples through the type of pollution. In this sense, the brick was more affected by marine aerosol despite being in an inner part of the wall and the mortars were more affected by atmospheric acid gases. In the case of the height, the PCA indicated that the height decreases the impact of the affection. This fact must be studied deeply but is a common pattern when the ions are being mobilized by capillarity from the ground. The distribution of salts thought the wall is generally related to the moisture and ionic mobility [4,12]. When the moisture input comes from the low part of the wall, that distribution is observed. In contrast, when infiltration waters appear this distribution can change. In this case, the input probably comes from the low part, due to the accumulation of rainwater in the floor. However, two mortars samples can be seen quite separated from the others in the PCA (with highest PC1 and PC2 values), which could be related to infiltration waters from the garden situated in the top of the galleries. Taking all of that into account, the evaluation of the results according to the materials seemed to be more adequate.

3.3. Mortar samples analysis

The chloride concentration in mortar samples was quite variable, from 0.4 mg/g to 9.5 mg/g. The chloride presence was related to the marine aerosol because the building is just in front of the sea. Despite this, it was possible to observe differences between walls, being the closer areas to the opened wall the most affected. Between them, the wall 1 and, in a less extent, the wall 4 seemed to be the most affected by the marine aerosol. In the case of the wall 1, it could be because it has its both sides exposed, which facilitates the accumulation of chloride. In contrast, the walls 2 and 3 are the inner walls and therefore, they were more protected, being the wall 4 more affected by marine aerosol and wind, but only by one side.

Moreover, it was possible to observe also differences in each wall. In the case of the wall 1 the bottom seemed to be more affected, as can be observed in the PCA, probably by the action of the rainwater accumulated in the floor that promotes the infiltration of water enriched with ions. This fact makes sense, because it was the more exposed area to the rain, water, and wind.

Considering the concentrations and the level of pollution by chlorides, the comparison with the norm [14] indicated that only the wall 1 had a dangerous concentration in the lower part of the wall. The rest of the samples had medium or low concentrations.

In the case of nitrates, only one sample was below the LOD. The concentrations were also variable (0.2 and 2.5 mg/g), but not in such a wide range as in the case of chlorides. In general, the samples had low concentration of nitrates, below 0.7 mg/g, except for two samples of the wall 1, being again the lower part of the wall, the most affected one.

The source of nitrates could be the same of chlorides, because the aerosol around the building has oxidized nitrogen gases, coming from industrial activities and marine ships movements in the industrial port, that evolve to nitric acid droplets. Moreover, it is necessary to remark that samples 5 M, 7 M and 8 M had the lowest concentrations and fitted with the area that was affected by infiltration waters from the garden. That could be the result of a wash effect by those waters.

In the case of sulphate, the concentration levels were in general, very high, up to 58.2 mg/g. In all cases, except two, the contamination was considered very high according to European norms [14–16]. Moreover, the concentration was so elevated that despite the other anions' concentrations were not very elevated, the total soluble salt content of the mortar was considered very high (>3% salts) [12]. The most affected areas were the right side of the wall 1 in the lowest part and the wall 4. The origin of sulphate was generally related to the atmospheric pollution that affects that building area. The industry, road and marine traffic generate sulphur dioxide (SO_2) that reacts with the calcium carbonate ($CaCO_3$) of the wall to promote the formation of calcium sulphate ($CaSO_4$), principally [28]. The environment of the whole main hall was the same, so it was not expected to observe differences. However, there were some phenomena to consider that generated heterogenous impacts. The samples near the infiltration waters of the garden seemed to have higher concentrations. The infiltration water could generate the washing of the materials but also maintain the moisture, increasing the reactivity with the atmospheric gases. Considering that sulphates are less soluble than nitrates, the accumulation of sulphates in these areas was expected rather than their wash. And the results also indicated the accumulation of this anion in areas affected by rainwater.

Finally, the oxalate is not marked in the European norms as dangerous ion, but promotes the solubilization of the materials as well, so to determine its concentration is important and even more, considering that it can act as bioindicator. For that reason, despite the concentrations obtained were low, it was quite significant because it meant a general affection by microorganisms.

Regarding cations, as in the case of oxalate, they do not have established limits or decaying levels associated. Moreover, their concentration is generally neglected in the calculation of the total soluble salt content. However, they were present in high concentrations, especially calcium, and the total concentration of the cation was remarkable.

Sodium and potassium concentration were generally low. Their distribution was similar to that of chloride pattern, which could indicate a common origin, and taking into account the marine aerosol composition (NaCl and, at lower concentrations, KCl), it seemed plausible.

Calcium was related to the original composition of the material. However, this cation is not very soluble if the material is in a good conservation state. Thus, these results indicated the disaggregation of the materials due to the loss of the cement ($CaCO_3$), probably by the action of atmospheric acid gases. The magnesium concentrations
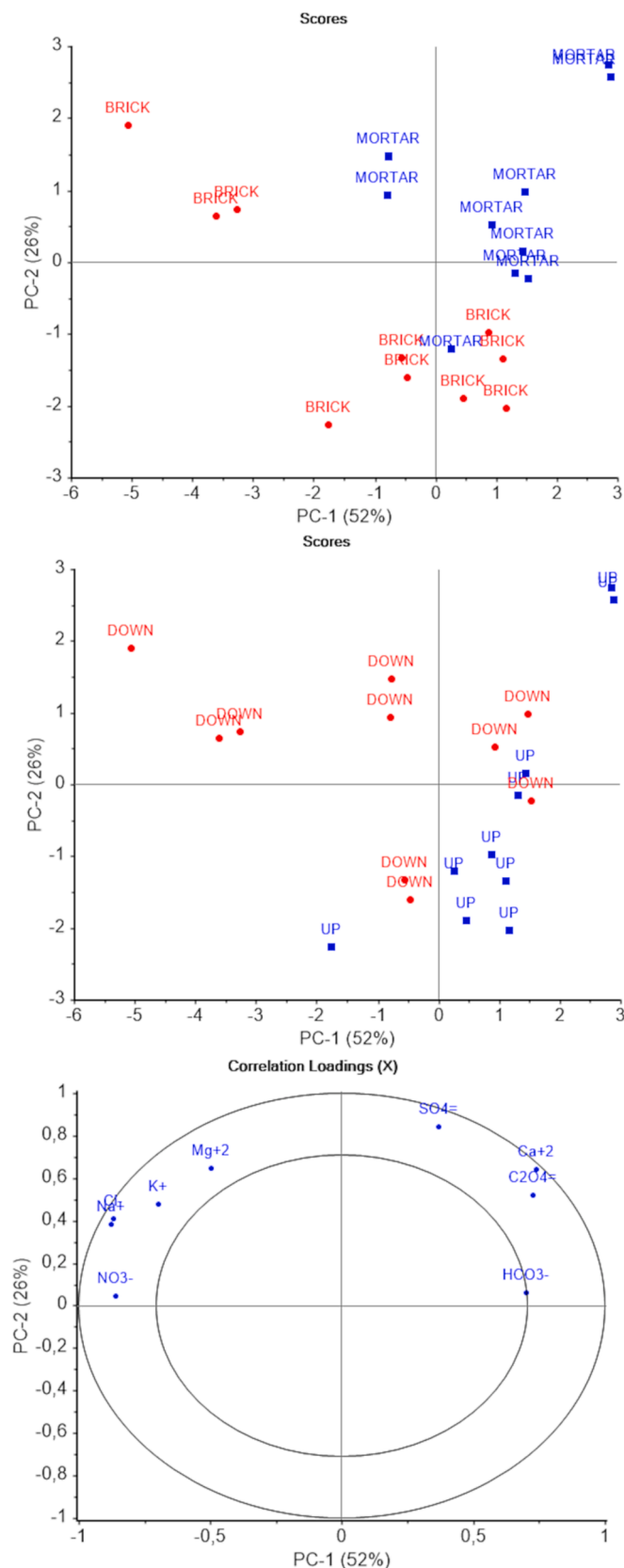
Fig. 3. PCA analysis carried out with the results of brick and mortar samples, where it is possible to observe the grouping by material and height.

interpretation was not easy because the concentration was low and homogeneous, so, its source could be the normal contribution of the original material and it could not be related to a decaying process.

Finally, as has been previously mentioned, the total soluble salt content, was very high for all samples due to the high concentration of sulphate, expect for the sample 1 M, which was considered as, only, high. This level of soluble salt content is related with a poor conservation state that indicates that the mortar was seriously damaged, and it required a corrective action [12].

For the study of the common origin of the ions a correlation analysis was carried out. The results are collected in Table 4 and the marked values are the correlation above the significant level (R critic = 0.549, Pearson, n = 8, 95% confidence level). The higher correlation was between calcium and sulphate, which confirmed the hypothesis of the formation of calcium sulphate pointing out the atmospheric acid gases as one of the most important affection for the mortar. In the same way, the high correlation between sodium and chloride indicates the formation of NaCl and which a smaller correlation, KCl, due to the marine aerosol as had been previously proposed.

Remarkable also are the negative correlations between carbonate, sulphate, and calcium, because the formation of calcium sulphate entails the decrease of the calcium carbonate concentration. This confirmed the decaying pathway for sulphate formation through the atmospheric acid gases attack to the original materials and not the simple accumulation by the adsorption of this anion in the material porous net.

Moreover, the correlation analysis also gave clues of new salt formations that had not been easily observed in the individual analysis. This was the case of potassium nitrate and sodium nitrate. Also, the correlation of oxalate and calcium could indicate the formation of calcium oxalate. The negative correlation between the nitrate and oxalate is remarkable because both could act as indicator of biodecaying, being oxalate more specific because the nitrates could be formed by the atmospheric acid gases, marine aerosol, the decomposition of organic material or the action of microorganisms [4,5,29,30]. Thus, it could indicate that the origin of both was different, pointing out the other sources as more probable that the affection of nitrate by microorganism.

Finally, the PCA of the concentration values in mortar samples was carried out, explaining with 3 PCs more than 85% of the total variance. As can be seen in Fig. 4, it was possible to observe the grouping of calcium and sulphate together with oxalate. In the same way, the ions related to marine aerosol were also grouped, and nitrate seemed to be more related with this source than the other possibilities. However, it was a little bit far from the others, so a mix source could be plausible. Magnesium was related to the neutral values of PC1 without grouping, which supports the hypothesis that its source could be the original materials. Thus, this PCA analysis confirmed the previous observations.

Regarding the diversity of the samples, it was possible to differentiate three big groupings: (2 M, 4 M, 6 M), (5 M, 7 M, 8 M, 10 M) and (3 M, 9 M). The first one could be related more with the marine aerosol, and the third with the formation of calcium sulphate. These last samples were related to infiltration waters points, so, this observation fitted with the hypothesis of the moisture generated by infiltration waters makes easier the attack of atmospheric acid gases being synergic decaying effects. The other walls were also exposed to the water, principally by the rain action, but also to the wind that helps to dry the materials, while the infiltration areas were more protected, and the materials remained wet for longer time.

3.4. Brick samples analysis

The results of the brick samples are collected in Table 3. Following the same analysis than in the mortar samples, in the first step the individual analysis of the results was carried out. In this sense, the chloride concentration was again, very variable from 0.6 to 20.2 mg/g but higher than in the mortar samples and being more accumulated in the low areas (samples 2B, 4B, 8B and 10B). The rainwater accumulation in the floor

Table 4

Correlation analysis of the mortar samples. The correlation coefficients above the R critic for 95% of confidence (0.549) are marked, yellow the positive and orange the negatives.

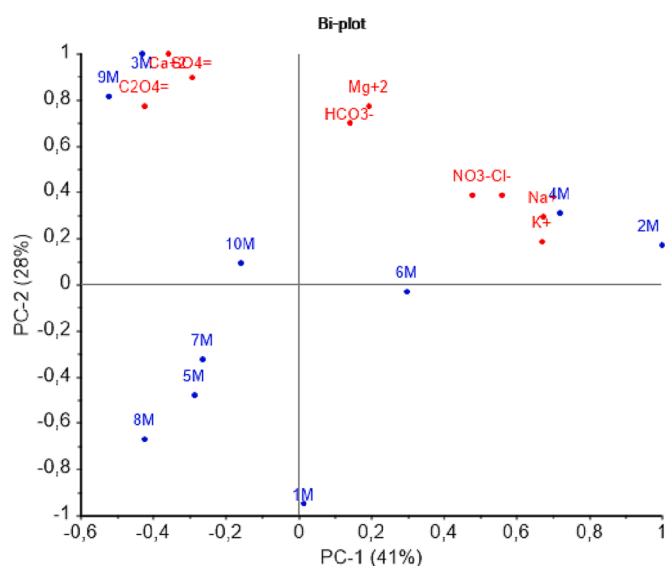|	$CO_3^=$	HCO_3^-	Cl^-	NO_3^-	$SO_4^=$	$C_2O_4^=$	Na^+	K^+	Ca^{+2}	Mg^{+2}
$CO_3^=$	1.00									
HCO_3^-	−0.17	1.00								
Cl^-	−0.24	0.36	1.00							
NO_3^-	0.13	−0.25	0.40	1.00						
$SO_4^=$	−0.73	0.00	−0.08	0.23	1.00					
$C2O_4^=$	−0.44	0.51	−0.20	−0.56	0.46	1.00				
Na^+	0.00	0.33	0.93	0.63	−0.17	−0.38	1.00			
K^+	0.32	0.38	0.67	0.65	−0.32	−0.39	0.89	1.00		
Ca^{+2}	−0.79	0.19	−0.09	0.00	0.96	0.68	−0.24	−0.38	1.00	
Mg^{+2}	0.36	0.50	0.10	0.42	0.10	0.29	0.26	0.44	0.17	1.00

Fig. 4. Bi-plot of the soluble salt analysis of mortars.

seemed to be the reason to observer more concentration in the low parts of the wall, being more mobilized the salts in the brick samples than in the mortars. Moreover, the effect observed in the wall 1 in the mortar analysis was also observed in the brick samples. However, it was clear that bricks were more susceptible of the attack of chloride, despite being more protected in the wall. Considering the concentration and the level of risk associated regarding the reference norm [14], the bricks were above the limits. The wall 1 was the most affected one because it was the most exposed to the marine aerosol, and it had a high concentration level, but also the walls 2 and 3. In contrast, the wall 4 has a medium concentration.

In the case of nitrates, only four samples were above the limit of detection. However, the concentrations were high, between 2.2 and 6.6 mg/g. It is remarkable that these samples were the most affected samples by chlorides, thus, the source of the nitrates could be the same as that of the chloride. However, it was not possible to discard the atmospheric pollution, above all, taking into account the impact of the SOx gases observed in the case of mortars. Regarding the levels of pollution, the samples 2B, 4B and 8B were considered with high concentration and 10B, medium level.

In the case of sulphate, the concentrations were high, with values up to 22.0 mg/g but significantly less than in mortar samples. Only the samples 2B and 8B had a high concentration, while the samples 4B, 5B, 7B, 8B and 10B had medium concentrations taking into account the limits. The samples 5B, 7B and 8B were in the infiltration water area,

thus, again, it seemed to be related with the moisture generated by them, as has been previously mentioned. However, it was clear that the mortars were more vulnerable to the atmospheric acid gases and bricks to marine aerosol. Thus, information is crucial for conservation works because the desalination procedure is not the same for both materials. In this sense, the desalination of bricks seemed to require cleaning the porous net, but in the mortar cases, the sulphate was not accumulated, it was the consequence of the reaction of the SOx with the original materials, losing the carbonaceous cement of the material. Thus, in this case, the consolidation of the materials after the desalination is carried out seems to be crucial.

In the case of oxalate, it was also present in brick samples, but in less concentrations than in mortars. Anyway, its presence indicated the biodecaying of the materials.

Leaving aside anions, regarding cations, sodium and potassium had low concentration expect for the four samples mentioned before. Again, the pattern was like chloride, being related to the marine aerosol. In the case of calcium, the concentrations were high, and in brick samples it was more relevant than in mortars, because the solubilization of the calcium was more difficult. On one hand, and considering that the bricks are baked, their original components are oxides. For that reason, the calcium oxide must be hydrated to form the hydroxide, and then attacked with atmospheric acid gases [31]. Generally, a first carbonation step by the atmospheric CO_2 acid gas is described, followed by the reaction with the other gases to form sulphates and nitrates. Additionally, the step to react with the SOx and NOx gases involves the solubilization of the carbonate, and thus, an acid environment is necessary [28]. This fits with the pattern observed, different from the other ions, and more related with the carbonate concentration, being potassium and sodium more related to sulphate in this material. In this case, the calcium concentrations were higher at the top, and sulphate at the lower level. This could indicate different level of decaying. On one hand, on the top it could be found a first step of carbonation of the materials. On the other hand, at the low part, due to the presence of other salts, appears a secondary reactions to form sulphates. Anyway, although a high concentration of sulphate is not observed, these results indicated the loss of the consolidation of the brick by the dissolution of the original oxides. Thus, the relevance of the cations and carbonate/bicarbonate analysis in the evaluation of the conservation state of built heritage seemed crucial, even though it is not currently regulated in the norms. And, as has been previously mentioned, the consolidation of the brick samples seemed to be not necessary by the observation of only the regulated anions. For that reason, the simultaneous analysis of all the soluble salt related to the cultural heritage decaying is essential for the real evaluation of the conservation state.

As in the mortars, the magnesium concentrations were low and homogenous, so its source could be the original material.

To finish with the individual analyses, the soluble salt total concentration indicated a very high concentration of salts in the four

mentioned samples, in the low part of the wall which required a corrective action due to a worrying damage [12]. Moreover, the rest of the samples, present a high or medium concentration of salts indicating a global damage of the bricks.

The correlation analysis of the brick samples was carried out. In Table 5 it is possible to observe the significant correlations. As with mortars, the higher correlations were related to the marine aerosol (chloride, potassium, and sodium), however, in this case, the sulphates were also related to this group. This could be because of the formation of sulphates of potassium and sodium as has been previously mentioned. Maybe, as bricks were more protected by the mortar and marble, the atmospheric pollution was not so evident in the low part of the wall, and the source of sulphate here could be the rainwater. Moreover, the lack of correlation between calcium and sulphate was relevant because it usually indicates the formation of calcium sulphate. In contrast, calcium was correlated with bicarbonate, so, it was possible that bricks remained in a first step of decaying (carbonation) probably due to the protection of marble. For that reason, at the top of the wall, where there was no marble, the decaying was more evident.

It is remarkable also, the negative correlation between bicarbonate and the other ions, which could indicate different sources, atmospheric pollution for bicarbonate and marine aerosol for the rest. There is a negative correlation also between oxalate and chloride, which probably has the same meaning, different sources, biodecaying for the oxalate, which was correlated with calcium indicating the most common oxalate, the calcium oxalate. As this compound is not soluble in water, its presence in the material probably was higher than that observed.

These mentioned results were confirmed by the PCA analysis that explained more than 95% of variance with 3 PC. In Fig. 5 it is possible to observe the clear group of calcium and oxalate. However, in this case, the rest of the ions were very close to reach other conclusions. It is noteworthy that sulphate was not so grouped, indicating probably a mixed source as had been previously proposed.

Regarding sample's diversity, is possible to observe three groups: (2B,4B, 8B), (7B, 5B) and (1B, 3B, 6B, 10B). The first one, related to marine aerosol and the second with infiltration waters and the biodecaying, so the source of the biodecaying could be the infiltration of the water from the garden located on the top of the building.
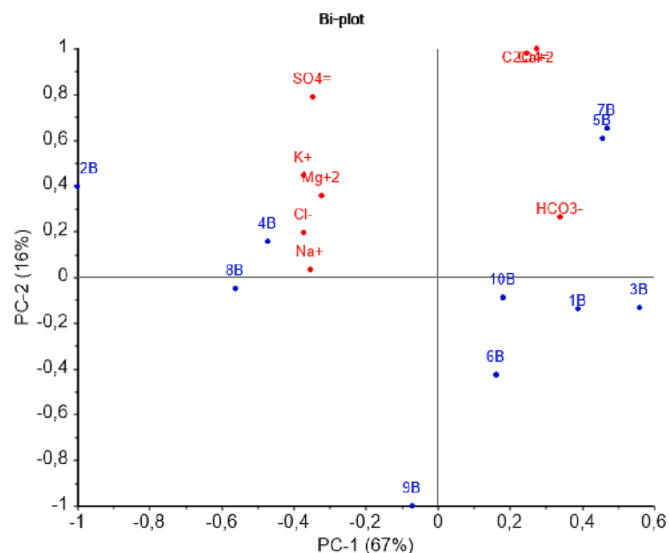

Fig. 5. Bi-plot of the soluble salt analysis of bricks.

4. Conclusions

The validation of the modular systems designed based on ion chromatography and titrimetry for the simultaneous analysis of ions in water dissolution to evaluate the complete affection by soluble salts of built heritage was very satisfactory. In this sense, it was possible to obtain in a simple way the quantitative analysis of the most relevant ions that affect the cultural heritage, included carbonate and bicarbonate.

This has allowed the identification of the most important problems that affect the studied building, giving relevant information to its conservation. Specifically, it was evident the affection of the atmospheric acid gases, that affected, especially, to the mortars. In the case of brick, the principal problem was the rainwater and the marine aerosol. For both materials, the desalination seems to be crucial, but also the consolidation. Moreover, it has been observed the synergic effect of the infiltration water to promote the attack of the dissolved atmospheric acid gases in such waters. Also, this infiltration water seemed to be the responsible of the biodecaying that affect the walls, probably due to the presence of dissolved nitrates and ammonium ions, two excellent

Table 5
Correlation analysis of the mortar samples. The correlation coefficients above the R critic for 95% of confidence (0.549) are marked, yellow the positive and orange the negatives.

	$CO_3^=$	HCO_3^-	Cl^-	NO_3^-	$SO_4^=$	$C_2O_4^=$	Na^+	K^+	Ca^{+2}	Mg^{+2}
$CO_3^=$	1.00									
HCO_3^-	−0.44	1.00								
Cl^-	−0.13	−0.75	1.00							
NO_3^-	−	−0.70	0.04	1.00						
$SO_4^=$	−0.21	−0.61	0.88	0.46	1.00					
$C_2O_4^=$	0.07	0.39	−0.56	0.01	−0.13	1.00				
Na^+	−0.37	−0.85	0.98	0.14	0.88	−0.64	1.00			
K^+	0.37	−0.57	0.95	0.15	0.89	−0.41	0.96	1.00		
Ca^{+2}	−0.18	0.69	−0.72	−0.71	−0.24	0.66	−0.79	−0.38	1.00	
Mg^{+2}	0.74	−0.55	0.73	0.90	0.80	−0.35	0.68	0.76	−0.33	1.00

nutrients for microorganisms. These results indicated that the correct evaluation of the conservation state of a building is important for a global understanding of the processes that are present and to propose adequate corrective actions.

But the most important conclusion achieved, is the demonstration of the real need to quantify the soluble salt to evaluate the level of damage of the material. And not only that, because it is also demonstrated the relevance of not only chloride, sulphate and nitrate, but also all the involved ions in the decaying processes which represent a high percentage of the soluble salt and, generally, are neglected. What is more, in the current form, it is hardly difficult to carry out a quantitative comparison of the soluble salt concentration results between different works, due to the different methodologies used for them, even using the current norms. Cations, carbonates and bicarbonates are not usually analysed or not even by using IC [40–42] so the comparison of the data could lead to errors in the measuring of soluble salts.

Taking all of this into account, this work points out the need of a change of mind in the current European norms with the presented case study because the obtained results could not have been achieved by a simple conductimetric analysis or only by measuring some anions. It is evident the need to quantify all the ion that affect the materials, and for that purpose, the IC must be mandatory in the norms. This work demonstrates with experimental data how the simultaneous analysis is possible in a simple way, without very complicated systems which should facilitate its implementation in the standards. Moreover, the establishment of limits for all the different ions is required, but not only to control their level, but also to help to compare the results in an effective way in the different locations, to help to understand better the results obtained.

Although there have been great advances in recent years regarding these analyses and in the development of European standards, this work demonstrates the need to continue improving for the good of the built heritage.

CRediT authorship contribution statement

Iñaki Vázquez-de la Fuente: Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing, Supervision. **Nagore Prieto-Taboada:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision. **Estibaliz Lama:** Investigation, Formal analysis, Writing – review & editing. **David Cristobal:** Investigation, Formal analysis, Writing – review & editing. **Rosa García-Arrona:** Formal analysis, Writing – review & editing. **Gorka Arana:** Formal analysis, Writing – review & editing, Project administration. **Juan Manuel Madariaga:** Formal analysis, Writing – review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2023.108921.

References

[1] A.E. Charola, Salts in the deterioration of porous materials: an overview, J. Am. Inst. Conservat. 39 (3) (2000) 327–343.
[2] N. Prieto-Taboada, O. Gómez-Laserna, I. Martinez-Arkarazo, M.A. Olazabal, J. M. Madariaga, Optimization of two methods based on ultrasound energy as alternative to European standards for soluble salts extraction from building materials, Ultrason. Sonochem. 19 (6) (2012) 1260–1265.
[3] A. Charola, J. Pühringer, M. Steiger, Gypsum: a review of its role in the deterioration of building materials, Environ. Geol. 52 (2) (2007) 339–352.
[4] E. Doehne, C.A. Price, Stone Conservation: An Overview of Current Research, second edition, Getty Publications, Los Angeles, 2010, p. 157.
[5] N. Prieto-Taboada, S. Fdez-Ortiz de Vallejuelo, M. Veneranda, I. Marcaida, H. Morillas, M. Maguregui, K. Castro, E. De Carolis, M. Osanna, J.M. Madariaga, Study of the soluble salts formation in a recently restored house of Pompeii by in-situ Raman spectroscopy, Sci. Rep. 8 (1613) (2017) 1–8.
[6] E. Doehne, Salt weathering: a selective review, Geol. Soc. 205 (1) (2002) 51–64.
[7] D. Pinna, B. Salvadori, S. Porcinai, Evaluation of the application conditions of artificial protection treatments on salt-laden limestones and marble, Constr. Build. Mater. 25 (5) (2011) 2723–2732.
[8] C. Cardell, F. Delalieux, K. Roumpopoulos, A. Moropoulou, F. Auger, R. Van Grieken, Salt-induced decay in calcareous stone monuments and buildings in a marine environment in SW France, Constr. Build. Mater. 17 (3) (2003) 165–179.
[9] Y. Bai, G.E. Thompson, S. Martinez-Ramirez, S. Brüeggerhoff, Mineralogical study of salt crusts formed on historic building stones, Sci. Total Environ. 302 (1–3) (2003) 247–251.
[10] K. Malaga-Starzec, I. Panas, J.E. Lindqvist, O. Lindqvist, Efflorescence on thin sections of calcareous stones, J. Cult. Herit. 4 (4) (2003) 313–318.
[11] Consiglio Nazionale delle Ricerche and Istituto Centrale del Restauro (CNR-ICR), Dosaggio dei sali solubili (Determination of Total Amount of Soluble Salts) Raccomandazioni Normal 13/83: Dosaggio dei Sali solubili (Normal 13/83 recommendation: Determination of Total Amount of Soluble Salts. *Dosaggio dei sali solubili (Determination of Total Amount of Soluble Salts)* 1983.
[12] E. Pinto Guerra, Rissanamento di murate umide e degradate, second edition, Dario Flaccovio, Italia, **2011**, p. 296.
[13] N. Stefanis, P. Theoulakis, C. Pilinis, Dry deposition effect of marine aerosol to the building stone of the medieval city of Rhodes, Greece, *Build. Environ.* 44 (2) (2009) 260–270.
[14] WTA-Merkblätter, WTA 4-5-99: Evaluation of masonry. **1999**.
[15] Österreichisches Normungsinstitut, Dehumidification of masonry - Structure diagnosis, planning principles, execution and monitoring (Ö NORM B 3355-1). **2006**.
[16] Ministère de la culture et de la communication, Ouvrages en pierre de taille: fascicule technique, **2003**.
[17] European Committee for Standardization (CEN), Conservation of cultural heritage - Extraction and determination of soluble salts in natural stone and related materials used in and from cultural heritage (EN16455:2014). **2014**.
[18] H. Brocken, T.G. Nijland, White efflorescence on brick masonry and concrete masonry blocks, with special emphasis on sulfate efflorescence on concrete blocks, Constr. Build. Mater. 18 (5) (2004) 315–323.
[19] Galerías Punta Begoña, **2019**, https://puntabegonagetxo.eus.
[20] C. García-Florentino, M. Maguregui, H. Morillas, U. Balziskueta, A. Azcarate, G. Arana, J.M. Madariaga, Portable and Raman imaging usefulness to detect decaying on mortars from Punta Begoña Galleries (Getxo, North of Spain), J. Raman Spectrosc. 47 (12) (2016) 1458–1466.
[21] E. Lama, N. Prieto-Taboada, I. Etxebarria, J. Bermejo, K. Castro, G. Arana, M. D. Rodríguez Laso, J.M. Madariaga, Spectroscopic characterization of xx century mural paintings of punta begoña's galleries under conservation works, Microchem. J. 168 (2021) 106423.
[22] P.N. Nesterenko, Simultaneous separation and detection of anions and cations in ion chromatography, TrAC 20 (6) (2001) 311–319.
[23] V.A. Sötz, S. Kochmann, Simultaneous separation and detection of anions and thiophilic cations using capillary-size anion exchange chromatography with suppressed conductivity detection, J. Sep. Sci. 38 (8) (2015) 1301–1309.
[24] A. Broggi, E. Petrucci, M.P. Bracciale, M.L. Santarelli, FT-Raman spectroscopy for quantitative analysis of salt efflorescences, J. Raman Spectrosc. 43 (11) (2012) 1560–1566.
[25] N. Prieto-Taboada, M. Maguregui, I. Martinez-Arkarazo, M. Olazabal, G. Arana, J. M. Madariaga, Spectroscopic evaluation of the environmental impact on black crusted modern mortars in urban–industrial areas, Anal. Bioanal. Chem. 399 (9) (2011) 2949–2959.
[26] A. Iturregui, N. Arrieta, X. Murelaga, J.I. Baceta, M.Á. Olazabal, I. Martínez-Arkarazo, J.M. Madariaga, The relevance of the analytical methodology in the geochemical study of beachrock outcrops: Arrigunaga Beach inside the Nerbioi-Ibaizabal estuary (Getxo, Basque Country), Anal. Methods 6 (20) (2014) 8247–8257.
[27] AOAC Official Methods of Analysis, (2016) p. 1-18.

[28] O. Gómez-Laserna, N. Prieto-Taboada, I. Ibarrondo, I. Martinez-Arkarazo, M.A. Olazabal, J.M. Madariaga, in: S.M. Rivera and A.L. Pena Diaz (Eds.), Brick and Mortar Research, Nova Science Publishers, 2012, p. 195-214.

[29] M.A. Kakakhel, F. Wu, J.-D. Gu, H. Feng, K. Shah, W. Wang, Controlling biodeterioration of cultural heritage objects with biocides: A review, Int. Biodeter. Biodegrad. 143 (2019) 104721.

[30] S. Sanchez-Moral, L. Luque, S. Cuezva, V. Soler, D. Benavente, L. Laiz, J. M. Gonzalez, C. Saiz-Jimenez, Deterioration of building materials in Roman catacombs: The influence of visitors, Sci. Total Environ. 349 (1) (2005) 260–276.

[31] N. Prieto-Taboada, O. Gómez-Laserna, I. Ibarrondo, I. Martinez-Arkarazo, M. A. Olazabal, J.M. Madariaga, in: Conference on Micro-Raman and Luminiscence Studies in the earth and planetary sciences (CORALS II), Lunar and Planetary Institute (LPI) y Consejo Superior de Investigaciones Científicas (CSIC), Houston, 2011, pp. 66–67.

[32] O. Gómez-Laserna, P. Cardiano, M. Diez-Garcia, N. Prieto-Taboada, L. Kortazar, M.Á. Olazabal, J.M. Madariaga, Multi-analytical methodology to diagnose the environmental impact suffered by building materials in coastal areas, Environ. Sci. Pollut. Res. 25 (5) (2018) 4371–4386.

[33] I. Martínez-Arkarazo, M. Angulo, L. Bartolomé, N. Etxebarria, M.A. Olazabal, J. M. Madariaga, An integrated analytical approach to diagnose the conservation state of building materials of a palace house in the metropolitan Bilbao (Basque Country, North of Spain), Anal. Chim. Acta 584 (2) (2007) 350–359.

[34] N. Prieto-Taboada, I. Ibarrondo, O. Gómez-Laserna, I. Martinez-Arkarazo, M. A. Olazabal, J.M. Madariaga, Buildings as repositories of hazardous pollutants of anthropogenic origin, J. Hazard. Mater. 248–249 (2013) 451–460.

[35] J. Aramendia, L. Gomez-Nubla, I. Arrizabalaga, N. Prieto-Taboada, K. Castro, J. M. Madariaga, Multianalytical approach to study the dissolution process of weathering steel: The role of urban pollution, Corros. Sci. 76 (2013) 154–162.

[36] L. Rampazzi, Calcium oxalate films on works of art: A review, J. Cult. Herit. 40 (2019) 195–214.

[37] O. Gómez-Laserna, M.Á. Olazabal, H. Morillas, N. Prieto-Taboada, I. Martinez-Arkarazo, G. Arana, J.M. Madariaga, In-situ spectroscopic assessment of the conservation state of building materials from a Palace house affected by infiltration water, J. Raman Spectrosc. 44 (9) (2013) 1277–1284.

[38] N. Prieto-Taboada, D.V. Fdez-Ortiz, M. Veneranda, E. Lama, K. Castro, G. Arana, A. Larrañaga, J.M. Madariaga, The Raman spectra of the Na2SO4-K2SO4 system: Applicability to soluble salts studies in built heritage, J. Raman Spectrosc. 50 (2) (2019) 175–183.

[39] A. Chabas, R.A. Lefèvre, Chemistry and microscopy of atmospheric particulates at Delos (Cyclades–Greece), Atmos. Environ. 34 (2) (2000) 225–238.

[40] F. Pintér, The combined use of ion chromatography and scanning electron microscopy to assess salt-affected mineral materials in cultural heritage, J. Am. Inst. Conserv. 61 (2) (2022) 85–99.

[41] W. Han, S. Pei, F. Liu, Material characterization of the brick in the Ming Dynasty heritage wall of Pianguan County: A case study, Case Stud. Constr. Mater. 19 (2022), e00940.

[42] M.F. La Russa, V. Comite, N. Aly, D. Barca, P. Fermo, N. Rovella, F. Antonelli, E. Tesser, M. Aquino, S.A. Ruffolo, Black crusts on Venetian built heritage, investigation on the impact of pollution sources on their composition, Eur. Phys. J. Plus 133 (9) (2018).