Development of innovative analytical methodologies to catalogue the composition and evaluate the environmental impacts on mortars and concretes from Punta Begoña Galleries (Getxo, Basque Country)

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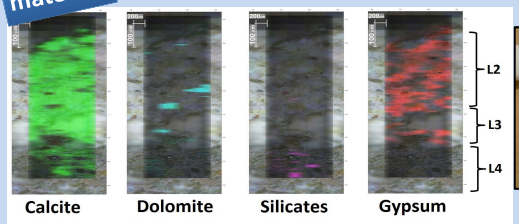
Aim of the PhD Thesis

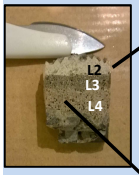
The aim of this PhD thesis is to study the advantages and usefulness of different X-ray fluorescence techniques (ED-XRF, TXRF, etc.) applied to the characterization of the mortars/cements and concretes and some of their decaying compounds (soluble salts, formations, black crusts) formed in Punta Begoña Galleries as a consequence of natural processes (e.g. Infiltration waters) and the impact of environmental stressors (acid gases, metallic particulate matter, etc.) coming from the surrounding atmosphere (road and maritime traffic, industry, etc.). In this work, different sample pre-treatments, quantification methodologies and measuring options (in situ and laboratory single point analysis and micro-imaging) were evaluated. In order to compare and complement the obtained results, other analytical techniques such as Raman microscopy, SEM-EDS, Ion Chromatography and ICP-MS were also employed. Although this PhD is focused on the study of Punta Begoña Galleries, and additional case study centred in a modern construction from the Bizkaia Science and Technology Park and a building from the 18th century (La Galea Fortress) was also considered in order to illustrate the possible role of biofilms acting as bioindicators of atmospheric heavy metal pollution.

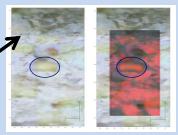
Characterization of building materials and evaluation of their conservation state in the laboratory

Building materials

Raman Imaging: Distribution of the components on each mortar layer







Calcite distribution in L2- Calcite aggregates

Aragonite ($CaCO_3$) in L3 and L4. Beach sand aggregate

Pathologies

Gypsum ($CaSO_4 \cdot 2H_2O$)
Thenardite (Na_2SO_4)
Calcite($CaCO_3$)
Natron ($NaCO_3 \cdot 10\ H_2O$)

FORMATIONS (STALACTITES)

Dissolution of the original material: Calcite Stalactites

BLACK CRUSTS

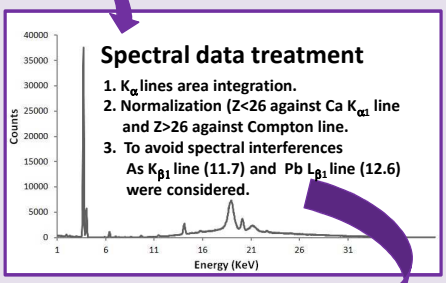
Gypsum matrix with metals trapped in its structure

In situ methodology to catalogue and classify different kind of mortars

Data acquisition using a hand-held ED-XRF (HH-ED-XRF) spectrometers

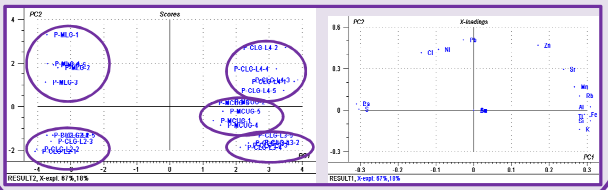
Spectral data treatment

1. K_α lines area integration.
2. Normalization (Z<26 against Ca $K_{\alpha 1}$ line and Z>26 against Compton line.
3. To avoid spectral interferences As $K_{\beta 1}$ line (11.7) and Pb $L_{\beta 1}$ line (12.6) were considered.



Semi-quantitative data given by the HH-ED-XRF instrument compared against a previously optimized WD-XRF method

Quantitative and qualitative data Principal Component Analysis (PCA) to classify the mortars according to their composition

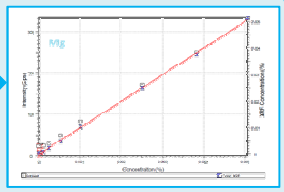


Development of different ED-XRF and TXRF quantification methodologies

dry 60 °C

Mutielemental standard solutions preparation and deposition on special sample retainers. External and standard addition calibrations.

ED-XRF measurements



Calibration curves for each element

Quartz reflector
Sample + Internal Standard

IR drying

TXRF measurements

Faster methodology No need of calibration, Rh as Internal Standard

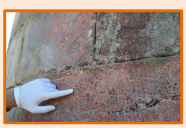
Some elements results	Concentrations comparisons (mg/L)			
	ED-XRF External Calibration	ED-XRF Standard Additions	TXRF	ICP-MS
Ti	N.Q	0.19	N.D	0.25
Mn	N.Q	2.37	2.63	2.70
Ni	N.Q	0.07	N.D	0.08
Cu	N.Q	0.44	N.D	0.07
Pb	2.00	1.81	2.38	1.91

✓ Improvement of quantitative values and Limits of Detection using Standard Addition calibration strategy.

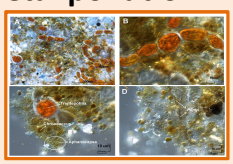
✓ TXRF → useful for some elements (e.g. Ca, Mn, Zn, Pb, Sr, etc.), specially at higher concentrations .

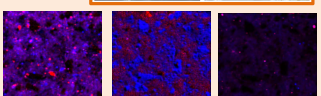
Alternative to other analytical techniques (e.g. ICP)

Biofilms acting as bioindicators of atmospheric heavy metal pollution

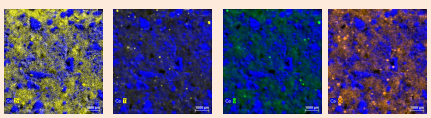


Trentepohlia algae, Chroococcus and Aphanocapsa cyanobacteria

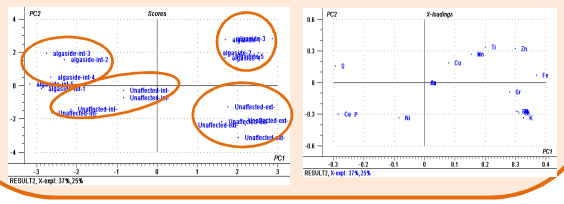




Metals distribution using µ-ED-XRF mapping



Elemental Composition comparisons between the biofilm area and unaffected building material using HH-ED–XRF methodology



Acknowledgments: This work has been financially supported by DISILICA-1930 project (ref. BIA2014-59124/p). Cristina is grateful to the University of the Basque Country (UPV/EHU) who funded her pre-doctoral fellowship.