

**CROSS-SECTION ANALYSIS TO ESTABLISH THE PENETRATION LEVEL OF ATMOSPHERIC POLLUTION IN MORTARS.** N. Prieto-Taboada<sup>1</sup>, O. Gómez-Laserna, I. Ibarrondo, I. Martínez-Arkarazo, M. A. Olazabal and J. M. Madariaga, University of the Basque Country (UPV/EHU), Department of Analytical Chemistry, Barrio Sarriena s/n, 48080, Bilbao, Spain. Tel.: +34 946018294. Email<sup>1</sup>: nagore\_prieto@ehu.es.

**Introduction:** The impact of the acid gases in buildings has been widely studied because of their notable and visible consequences in building materials [1-4]. Buildings are known to be pollutant repositories [5], but not always the penetration level of the pollutant is studied although it is an important factor to evaluate the real conservation state of building materials. Surface analysis do not allow to detect internal decaying processes that are the precursors of crackings and even material loss when soluble salts are formed. Cross-section analyses, however, are suitable to determine the depth reached by pollutants and thus, to determine the conservation state of the materials in order to preserve the integrity of the building. With this purpose, Raman spectroscopy was used in this work to analyse rendering mortars of a building located in an industrialized neighbourhood of metropolitan Bilbao.

**Experimental:** Two types of rendering mortars were analysed. Although they were collected from the same facade, the first (MF) belonged to the first floor of the building and was completely covered by a black crust, while the second one (MG, from the stone pillar of the groundfloor) showed almost the original appearance. The samples were analysed by two different Raman spectrometers: (i) an InnoRam<sup>®</sup> (B&WTEK<sub>INC</sub>) ultramobile spectrometer, equipped with 20x and 50x focusing lens and a 785 nm laser with a Peltier cooled CCD detector and (ii) an InVia Raman spectrometer (Renishaw), coupled to a Leica DMLM microscope provided with a 514 nm wavelength excitation source and CCD detector.

**Results:** The analysis of the internal part of the MF mortar revealed that it was a mixture including beach sand (bioclastic signatures), hematite and diverse silicates. The surface showed the typical composition of a black crust: carbon, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and occasionally anhydrite ( $\text{CaSO}_4$ ). However, coquimbite ( $\text{Fe}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$ ) was also detected as a result of a degradation process described elsewhere [5]. Moreover, the analysis of the cross section revealed subfrescences composed of calcite ( $\text{CaCO}_3$ ) at 3mm from the surface.

The second type of mortar, which was not black crusted, was indeed composed mainly by quartz and traces of anatase ( $\text{TiO}_2$ ), silicates, hematite and calcite in the surface (till 1mm depth). This layer suggested a high deterioration of the material by solubilisation of the cement and giving quartz as the final remaining compound. Besides, the analysis of the cross section of

the mortar sample revealed the widespread presence of nitrocalcite ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) at 4mm-11mm depth. The figure below shows the degradation products formed by the combined attack of  $\text{SO}_x$  and  $\text{NO}_x$  gases against calcite, giving gypsum and coquimbite, and nitrocalcite respectively.

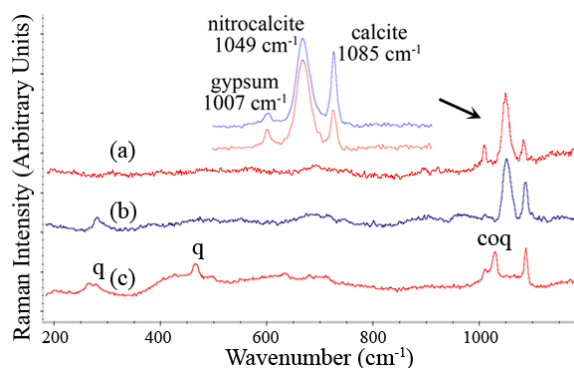


Figure: Raman spectra of MG mortar. (a) and (b) gypsum, nitrocalcite and calcite at different proportions at 11mm depth (c) quartz, q, belonging to the original composition together with gypsum, coquimbite, coq, and calcite at 2mm depth.

The nitrate band is quite broad to be related to a unique compound and thus the presence of other nitrates should not be ruled out. In the same way, the main Raman band of gypsum ( $1007\text{cm}^{-1}$ ) appeared also sometimes with a shoulder, shifted to higher wavenumbers corresponding to anhydrite ( $1017\text{cm}^{-1}$ ). Even more, coquimbite was also identified in this sample at 2mm depth joint to gypsum and calcite.

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