CMA4CH 2010, Mediterraneum Meeting

Application of Multivariate Analysis and Chemometry to Cultural Heritage and Environment
3rd ed., Taormina, Sicily island, Italy, Europe, 26-29 September 2010

Characterization By XPS and Combined Techniques of (Copper-Based) Coloured Stains Formed on Limestone Surfaces of Outdoor Roman Monuments

A.M. Salvi[1], F. Langerame[1], A. Macchia[2], M.P. Sammartino[2], M. Laurenzi Tabasso[2]
1. University of Basilicata- Chemistry Department- Viale Ateneo Lucano- PZ-(I)
2. University of Rome La Sapienza-Chemistry Department- P.le A.Moro-RM-(I)

Abstract

Monuments where marble and stone elements are used along with bronze or other copper alloys artefacts such as sculptures, decorations and dedicatory inscriptions are rather frequently met. In outdoor conditions, such a combination implies the corrosion products of the copper based alloy[1], directly exposed to rainwater, to be drained off and migrate through the porous surfaces, forming stains of different colours and intensities.

In this work we have analysed samples from the limestone surfaces of two modern monuments in Rome, the 'Vittoriano' (G.Sacconi, 1885-1911- Piazza Venezia) and the 'Statua dello Studente' (A.Cataldi, 1920, La Sapeinza University city) and confirmed, with the aid of XPS and other analytical techniques, that the coloured stains are mainly due to copper and mixed calcium/copper compounds. We have also related the composition of these patches with their chromatic characteristics and with the different sampling location.

Introduction

Coloured patches on the surface of monuments not only represent an aesthetic problem but also reduce the legibility of the artefacts thus depriving those monuments of their intrinsic (historical, religious or political) value.

In order to eliminate or reduce the damage produced by these patches, suitable cleaning procedures are required that would assure the removal of the surface stain without being too aggressive towards the underneath stone components that, in the case of marble and limestone, are mostly calcite and dolomite (calcium carbonate and calcium and magnesium carbonate respectively).

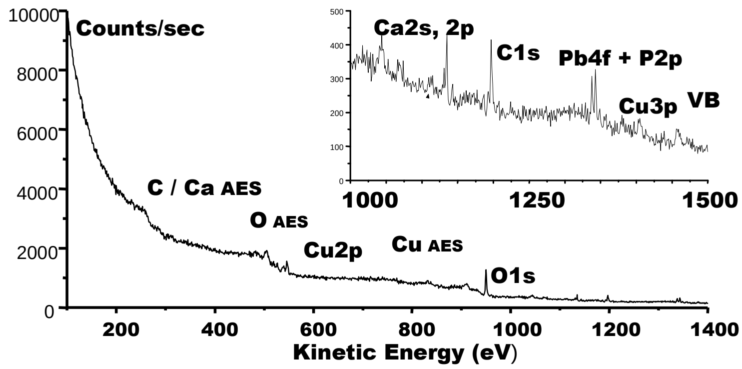
Experimental work built on specialist theses of the degree courses on cultural heritage at the University of Rome- was coordinated[2] with the aim of setting up a restoration project based on different operative phases: a) chemical characterization of the patches with combined analytical techniques; b) laboratory test; c) 'in situ' cleaning with selected procedures optimized in phase b).

In this paper our attention is focused on phase a) being an accurate physical-chemical characterization the necessary start also for the success of the subsequent phases.

In particular, some experimental details will be illustrated just for XPS (X-ray Photoelectron Spectroscopy) but the results will consider the outcome of the following analytical techniques: Optical Microscopy; X-ray diffraction; Electronic Microscopy combined with Fluorescence analysis (EDXRF); Micro-Raman and XPS spectroscopy.

Materials & Methods

The XPS spectra were acquired at UniBas- Chemistry Department- (PZ) using a Leybold spectrometer (LH X1) operating at 260 W with the acromatic AlKα (1486.6 eV) source. The figure shows a typical wide spectrum of one of the studied samples: once the elements composing the sample are individuated, the detailed region are then acquired at higher resolution for quantitative (peaks areas) and speciation (chemical state) analysis. The outcome data reported on tables (At% and Binding Energies, BEs) were elaborated with a curve-fitting program, NewGoogly[3].The peak assignments (uncertainty on BEs of +/- 0.2 eV) refer to literature data and to the NIST standard reference database available on line: http://srdata.nist.gov/xps/



XPS Table	C_{carb}- C-C	C_{Ox}	C ($CO_3^{=}$)	O1s
BE (eV)	282,5 *285,0*	287,4	289,6	531,7
At%	1,8 *29,3*	2,0	6,2	42,6
$Ca2p_{3/2}$	$Cu2p_{3/2}$	P2p	$Pb4f_{7/2}$	
347,1	935,0	133,2	139,0	
6,5	9,2	1,3	1,1	

Results

The most important outcomes can be summarized as the following:

- The major constituent of coloured stains on both travertine and Botticino limestone is copper, the presence, always in minor quantity, of the other elements in bronzes is dependent on their relative position with respect to the stone surface i.e. Zn was detected by XPS in the basement of the 'student statue' (travertine) but not in the wall surfaces of the 'Vittoriano' (Botticino limestone).
- the copper is mainly present in form of mixed compounds with calcium: hydroxysulfates, hydroxycarbonates, etc., the relative amount of counter-anions and different degrees of hydration being related to the location of the monuments in the city and, within the same monument, to the different sampling zones (fully exposed or partially protected areas)
- The colour of the stains (ranging from light blue-green to grey and dark black) is dependent on the relative amount of the mixed Cu compounds and on the presence of carbonaceous particulates, for example, black patches were found to be composed of tenorite (CuO) normally quite unstable, in this case, probably stabilized in joint zones made impermeable by carbon-containing contaminants.

Conclusions

The obtained results confirm the tendency of copper leaching from bronzes (transformed by corrosion to Cu(II)) to interact with calcium carbonate and form mixed compounds of variable compositions on the surface and sub-surface portions of stones. As reported[4], in depth analysis would show the slow formation of a solid solution $Ca_xCu_{1-x}CO_3$, very difficult to be removed without affecting the inner calcite structure. Moreover, the presence of CuO in black patches should be considered together with the likely influence of waterproof contaminants[5].

In perspectives the data will be statistically evaluated by PCA (Principal Component Analysis).

References

1) C. Chiavari, K. Rahmouni, H. Takenouti, S. Joiret, P. Vermaut, L. Robbiola, Composition and electrochemical properties of natural patinas of outdoor bronze monuments, *Electrochim. Acta*, 52(27), (2007) 7760-7769

2) M.L. Tabasso, A. Macchia, M.P. Sammartino, G. Visco, SEM/EDS analysis of incrustations coming from the "Fontana delle Tartarughe" (Turtles Fountain) located in Rome, Italy, *Proceedings of Chemometrics and Multivariate Analysis applied to Cultural Heritage and Environment 2006*, ISBN 8854807656

3) J.E. Castle, A.M. Salvi, Chemical state information from the near-peak region of the X-ray photoelectron background, *J. Electron Spectrosc. Relat. Phenom.*, 114-116, (2001) 1103-1113

4) P.M. Schosseler, B. Weahrli, A. Schweiger, Uptake of Cu by the calcium carbonates vaterite and calcite as studied by continuous wave (cw) an pulse electron paramagnetic resonance, *Geochim. Cosmochim. Acta*, 63(13-14), (1999) 1955-1967

5) U.S. Rai, R.K. Singh, Effect of polyacrylamide on the different properties of cement and mortar, *Mater. Sci. Eng. A-Struct. Mater. Prop. Microstruct. Process.*, 392(1-2), (2005) 42-50