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Characterization of cultural heritage objects is challenging. It requires being adapted to the object dimensions or limit deterioration by sampling, not damage samples during manipulation, preparation and by the analyses techniques employed themselves. Non-invasive techniques are then preferred. At first sight, electron spectroscopies (XPS and AES) are of particular interest as they give information about the composition and chemical environments (oxidation degree) at the material surfaces (depth probed < 10 nm) from micrometric to nanometric scale. Copper compounds analysis by XPS and AES is a routine when they are issued from microelectronic processes but radical different behaviour are observed for atmospheric corrosion products. The present work deals with the implementation of XPS and nano-AES on different compounds constitutive of atmospheric corrosion product layers of heritage copper objects. We propose here a complete study made on commercial (Cu_2O, CuO, $CuSO_4$ $5H_2O$), synthetized and natural ($Cu_4SO_4(OH)_6$) references. The literature is rare but instability during prolonged irradiation has been previously mentioned in some cases. So, spectra are recorded during increasing UHV exposition and/or irradiation times enabling to determine the dynamic, ultimate irradiation doses and nature of the changes (reduction process). This conditions the analysis time to obtain reliable information but also the optimised analyse pathway when multi-techniques analyses are implemented.