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# Multivariate Analyses as a Necessary Tool to Improve the XRF Data Treatment

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## Abstract

The use of portable instruments in the archaeometric study of ancient artefacts mostly fulfilled in a non invasive manner has become a very common practise over the past few years.

Among all the new instruments that are being used the Field Portable Energy Dispersive X Ray Fluorescence (FPEDXRF) spectrometers proved to be the most important.

In this paper we are going to show some cases in which multivariate statistics helped data mining and understanding the huge amount of data collected.

The FPEDXRF results and the statistical analysis of data show, sometimes unexpectedly, good results in the definition of the state of conservation of the monuments.

## Introduction

In the last decade, it has become common practice to carry out, during restoration, diagnostic exams with conservation finalities and/or archaeometric research. The sector of diagnostics in the Cultural Heritage area is growing up quickly with the development of many techniques and procedures that are now finding an established position in the restoration and maintenance of work of arts.

The EDXRF is gaining reputation as a useful technique in the monitoring the state of conservation of artefacts, but it is not well established the possibility to detect and follow the degradation processes using non-invasive procedures.

Many are the objects on which EDXRF can deploy his capabilities, in this manuscript we are going to focus on metals, but the issues introduced are replicable on other materials.

The main case we want to discuss of is the bronze burial monument of Pope Sixtus IV (1471-84) by Antonio del Pollaiolo, now in the Treasure Museum in the Vatican.

Before the restoration of the burial monument started, a series of non invasive analyses using a transportable EDXRF were carried out to map the composition of the alloy and evaluate the diagnostic capabilities for deterioration processes of the bronze surface. As a consequence of the first non invasive diagnostic campaign, a second campaign of micro invasive tests was planned and carried out. The samples were analyzed with SEM-EDS and XRF techniques.

## Materials & Methods

The results shown in this paper were obtained with different techniques such as Energy Dispersive X ray Spectrometry (EDS) and Scanning Electron Microscopy (SEM) with microanalysis.

A portable EDXRF system was assembled using an air-cooled X ray tube with an active spot of 1.5 mm, working with 38 kV high voltage and 0.2 mA current together with a Peltier cooled SDD (Silicon Drift Detector) detector with an energy resolution of 150 eV at 5.9 keV. A photo of the system at work on the monument is shown in Fig. 1.

For the SEM microanalysis was used a LEO 1450 VP, operating at 20 KV with a variable pressure (65 Pa), and a INCA 300 for the EDS. The samples were observed in back-scattered electrons mode to reveal differences in composition from the grey levels. The micro areas of homogenous composition, were selected manually to carry out the microanalysis.

## Results

The spectra were acquired on the surface, with a low HV, and were processed calculating the net area of the most intense peaks of the following elements: S, Cl, Ar, K, Ca, Mn, Fe, Cu. The counts were normalized with the copper peak in order to eliminate, in part, the variability due to the geometrical efficiency and instability of excitation source.

For a satisfactory sampling of all panels and visible alterations it was necessary to scheduled 111 measures. The identification of the points was performed in a way in which the colours, in the first case, can be used to classify the detected typologies. For each point, together with a picture of the sampled area and the XRF spectrum, it was added a short text describing the surface morphology.

The results of one way analysis of variance (between the five degradation typologies) gave good results on the significance of the found values.

## Conclusions

The possibility to use low energy element detection with portable EDXRF systems, that is, to detect elements such as Sulphur, Chlorine, Potassium and Calcium can increase significantly the surface information that non invasive portable systems can give.

The high number of analyses that it is possible to fulfil with a non invasive method, such as FP-EDXRF, can balance the limitations that the technique inherently has. This high number of results must be data-mined with statistical analysis to deploy all the right information.

Fig. 1; FPEDXRF analyses on the monument

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