State of Art in the SIMS (Secondary Ion Mass Spectrometry) Application to Archaeometry Studies

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Summary: One of the main problems of cultural heritages in all the different forms (buildings, monuments, painting) is their deterioration caused by natural and artificial decay processes. To address the conservation issue specific studies are required to determine, for example, origin, date, materials composition, technology processes involved, etc. The use of microanalysis techniques, in particular secondary ion mass spectrometry (SIMS), in the cultural heritage area has been demonstrated extremely useful to approach and provide this kind of information and support the experts involved in studies within this area (art historians, archaeologists, curators etc.). In this work, an up to date overview of possible SIMS applications to archaeological topics is given, pointing out the peculiarity and the main limitations and drawbacks of this analytical approach. One example of SIMS application to archaeological glasses is reported. Moreover the wide technique flexibility and its strength in combination with other complementary techniques are remarked.

Keywords: amorphous; ESCA/XPS; Mass spectrometry

Introduction

Cultural heritages are an inestimable artistic wealth for any country. This is particularly true for Italy where their wide presence and historical relevance represent a great value not only from the cultural point of view, but also as an important economic source. Nevertheless cultural heritages in all the different forms (buildings, monuments, paintings) and archaeological sites are deteriorated by natural processes of decay such as environmental disasters, pollution, effects of enhanced public access, poor conservation measures and simple negligence. To address the conservation issue, specific studies are required to determine for example origin, date, materials composition, technology processes involved, etc. These studies can also help to address and support authentication issues. The use of microanalysis techniques in the cultural heritage area has been demonstrated extremely useful to approach and solve these kinds of problems and support the experts involved in studies within this area (art historians, archaeologists, curators etc.). SIMS (secondary ion mass spectrometry) is one of the main analytical techniques, developed in the microelectronic field. It consists in the bombardment of a sample surface with a primary ion beam followed by mass spectrometry of the emitted secondary ions. Recently SIMS has been widely applied to cultural heritage analysis demonstrating the capability to obtain useful information. Moreover it has been proved to be a suitable analytical technique that offers high atomic sensitivity (ppm or even ppb), high depth and lateral resolution and compositional information through analyses of small amount of material in a short time as required in the archaeological field. In fact SIMS was employed for many categories of materials: for example it was used to study the problem of deteriorating and degrading of the museum glasses [1], in a study of the tarnishing of museum

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silver [2] or for the examination of paint cross-sections to obtain simultaneous information about the nature and distribution of pigments. [3]

In this work SIMS technique and correlated methodologies, originally developed for their application in the semiconductor research, are used successfully in the cultural heritage area. In particular, the application of the technique to glasses found in the Altino archaeological site (Venice, Italy) is shown and the results are cross-related to complementary techniques like AFM, XPS and ToF-SIMS.

Experiment

SIMS analyses allow to obtain the compositional profile of materials from surface to several microns in depth. The sample is bombarded with a mono-energetic primary ion beam (energy in the range 0.25–20 keV), that sputters the first layers of the surface. The sputtering process consists in the implantation of the primary species into the sample and the consequent removal of surface atoms and many other particles like ionized secondary ions (tipically a fraction of 1% of the total atoms sputtered away), electrons, photons and resputtered primary ions. Positive and negative secondary ions are the species of interest, and are collected by an electric field and then analyzed by energy and by mass according to the mass/charge ratio. Different primary ion beam can be used: O_2^+ for electropositive species, Cs^+ for electronegative ones and Ga^+ to improve lateral resolution. In this work a Cameca SC-ULTRA instrument has been used for SIMS analysis. The MCs^+ methodology was selected: i.e. Cs^+ is the primary beam, while the positive secondary ions formed from the species of interest M and the Cs atoms resputtered from the surface are collected.[4,5] This methodology allows to reduce the matrix effects that can alter the results. The favourite mechanism of ions MCs^+ formation should be the recombination from the species of interest M (in neutral state) and the Cs^+ resputtered outside the surface. In this way there are two advantages: 1) the matrix effects are reduced, because the formation of polarized ions occurs outside the surface and consequently the intensity of secondary ions is not influenced from the state of the surface; 2) the intensity of MCs^+ ions is proportional to the number of neutral atoms M and so directly proportional to the material composition.

The analysis depth resolution depends also from the primary impact energy used.[6] In this case archaeological samples surface was very rough and a high depth resolution was not required then high primary impact energy was fixed (6 keV with an incident angle of 60°) in order to minimize the analysis time. The primary current intensity and the raster area were such that an adequate sputtering rate was assured. The conversion of sputtering time to depth was obtained by measuring the final crater depth and assuming a constant sputtering rate.

The SIMS results were cross-related with XPS and ToF-SIMS analytical techniques. For XPS a Gammadata Scienta ESCA-200 was used, setting an energy resolution of about 1 eV and an emission angle of 90°; a flood gun for the charge compensation was necessary. For Time of Flight-SIMS (ToF-SIMS) a Cameca IonToF-IV was used both for compositional map and depth profile. In the last case, a preliminary cleaning of the surface with an oxygen beam (energy of 5 keV) was performed; the depth profile was then aquired with a gallium beam at energy of 15 keV with a raster area of $500 \times 500\ \mu m^2$ and using a flood gun for charge compensation. In addition AFM characterization was performed to find the best area to be investigated with the other techniques using a UniSolver NT-MDT instrument in a non-contact mode.

Two artefacts from the Altino archaeological site (Venice, Italy) were studied: 1) a cup fragment with glass mosaic of the end of I or beginning of II century a. C. (Figure 1a); 2) a bottle neck fragment of the I-II century a. C. (Figure 1b).

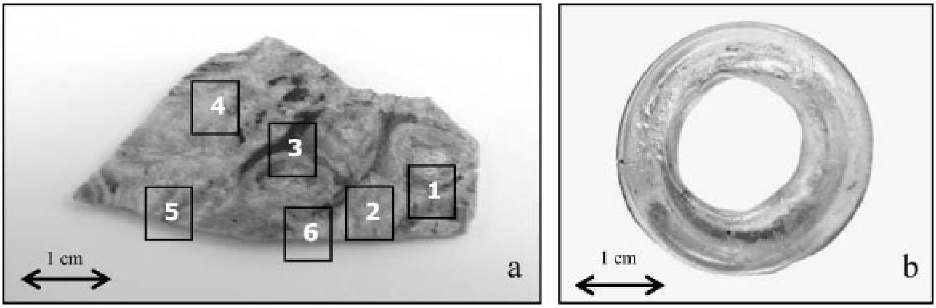

Figure 1.
a) Cup fragment with glass mosaic (the numbers mark the areas analyzed by XPS and ToF-SIMS); b) Bottle neck fragment.

To allow SIMS analyses samples must have shapes and dimensions suitable for the instrument sample holder, otherwise secondary ions cannot be efficiently collected. In particular lateral dimension must not exceed 1.5×1.5 cm. This request is very strict; at the present time the only solution is to cut selected sections from samples with unsuitable dimensions. Indeed SIMS technique have to be considerate an invasive tool. However the removed volume for the analyses is extremely limited (few microns), hence the technique is not destructive for the artefact integrity, or at least micro destructive.

SIMS data are in this kind of analyses only qualitative because specific standard are not available for archaeometric materials; therefore for quantitative analysis complementary techniques are needed.

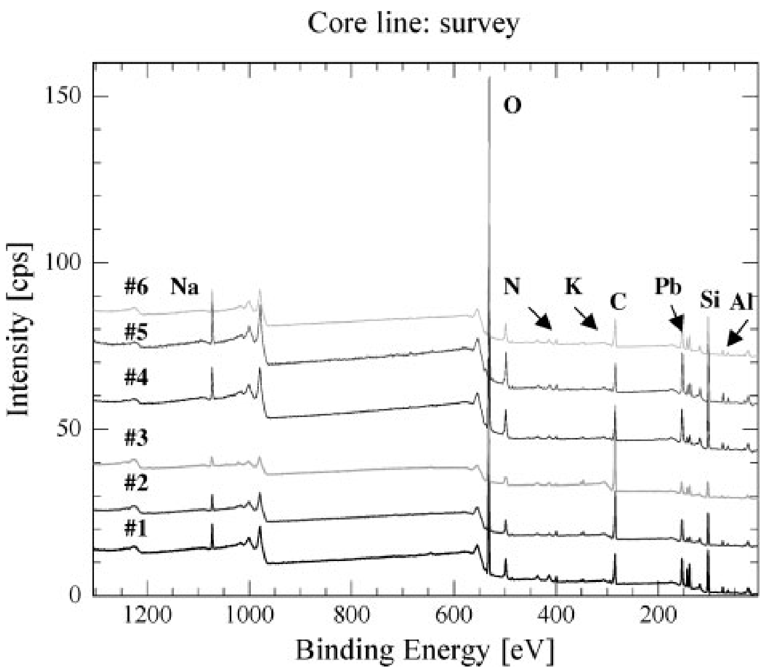

Figure 2.
XPS spectra on different areas of the cup fragment with glass mosaic.

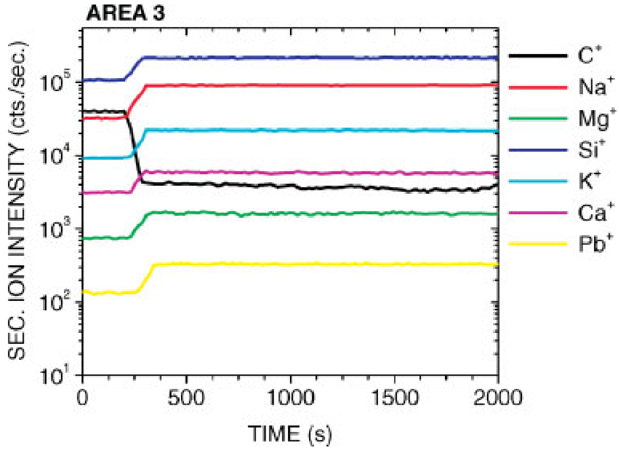

Figure 3.
ToF-SIMS depth profile of region 3 of the cup fragment with glass mosaic.

Results

Synthetic glasses with a chemical composition similar to the historical objects were analyzed, in order to set-up the sample preparation, avoid analytical errors and determine the accuracy and the reproducibility, with the aim of developing a complete methodology for the physical-chemical characterization of archaeological glasses using SIMS.

Concerning the cup fragment with glass mosaic, XPS analyses were done on different areas of the sample (marked in Fig. 1a) to obtain a chemical and compositional characterization of the surface with a sampling depth of about 10 nm. The spectra (Figure 2) collected in the six areas show the presence of different elements such as sodium, aluminium, silicon, potassium, oxygen and lead all in their oxidized form; these results were confirmed from compositional analysis obtained by ToF-SIMS [7]. Moreover, after a pre-sputtering of the analyzed area, a depth profile was performed to find out the uniform distribution of the elements also in depth. The profile obtained (Figure 3) shows that in the first

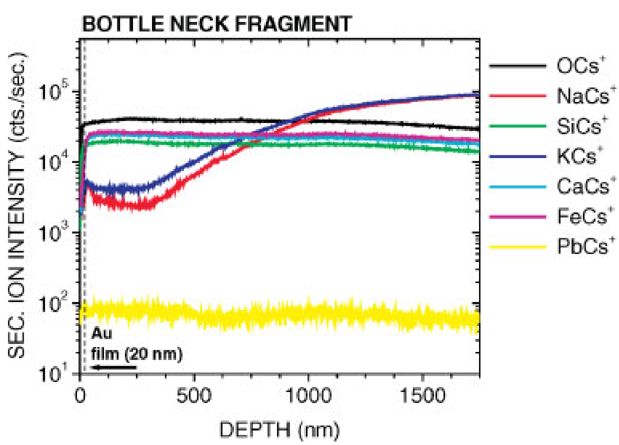

Figure 4.
SIMS depth profile of the bottle neck fragment.

nanometre there are modified values due both to interaction between glass and external atmosphere and to sample morphology. Increasing the depth in the sample, the intensity of each element reaches a constant value. The SIMS depth profile (Figure 4) of the bottle neck fragment shows a lower content of Na and K close to the surface, and a significant increase of these elements in the ''bulk''.

This distribution points out a probable interaction between the glass and the external environment. Furthermore, XPS analyses (not shown) are affected by a high concentration of carbon due to the contamination of the sample, in these conditions no quantitative evaluation can be done because most of the signals were covered. Finally, SIMS data were compared with XRF ones [8]: the determined chemical compositions are in good agreement, bearing in mind that light elements ($Z < 15$) are not detected by XRF in air. In particular, both analyses confirmed the absence of lead in the bottle neck fragment.

Conclusions

In this work SIMS technique has been proved to be a suitable and useful facility to analyse archaeological objects; in fact it is applicable in many fields and it provides answers to different kind of cultural heritage inquiries (authenticity, origin and provenance, degradation processes and conservation). Although it is a micro-destructive and invasive technique (constraints in sample dimensions and shapes), it is possible to do compositional analysis with high sensitivity to trace elements (ppm or ppb), high depth and lateral resolution in a short time and consuming small amounts of material.

The knowledge exchange between the expert scientist, needed for SIMS analysis, on one side and art historian, archaeologist on the other is necessary to develop new approaches for this study and to make the most of cultural heritage.

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