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SEM-EDS microanalysis in cultural heritage and archaeology: thickness effects and measurement strategy for ultrathin glass and metal fragments and particles

Daniele Moro[1], Gianfranco Ulian[1], Giovanni Valdrè[1]

[1] Centro di Ricerca Interdisciplinare di Biomineralogia, Cristallografia e Biomateriali, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna "Alma Mater Studiorum" Piazza di Porta San Donato 1, 40126 Bologna, Italy.

***Abstract* – Scanning electron microscopy (SEM) combined with energy dispersive X-ray spectrometry (EDS) is a powerful technique when both morphology and chemical information of a sample are desired at the microscale. However, when dealing with micrometre-scale materials, such as glass and metal fragments, as often found in cultural heritage and archaeology, several effects must be considered to avoid quantification errors. In the present work, a study of the thickness and shape effect on SEM-EDS microanalysis of ultrathin glass and metal alloys fragments by means of Monte Carlo simulations is presented. Different kind of glasses with elongated shapes, square section and thicknesses from 0.1 to 10 µm, and some gold metal alloys were simulated in realistic experimental conditions, using electron beam energies of 5, 15 and 25 keV. The strong influence of the fragments shape and thickness on the detected EDS X-ray intensity can be used to devise an appropriate measurement strategy.**

I. INTRODUCTION

Chemical, structural, morphological, and other analyses on cultural heritage manufacts are sometimes limited because of the hindered possibility of large sampling, which results in very small amount of available materials. In this case, analytical techniques at the micro- and nanoscales are of utmost importance to provide significant results for the purpose of the characterization that is restoration and preservation of the manufact. Among the different advanced methods for materials characterization [1-6], Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-ray Spectrometry (EDS) or SDD is a very effective technique to investigate both the morphology and the local composition of sample materials [7], even when their dimensions are on the micrometre and sub-micrometre scale. This is a typical situation when dealing with glass, ceramics and lithotypes fragments and particles, or extremely thin metal and alloys sheets and bits.

However, when the EDS detector/sample configurations and arrangements are not properly set, systematic errors could arise from the electron and X-Ray scattering in the thin materials and also adjacent ones. This effect is due to the elastic scattering of electrons in the finite size (mass) of the particle, which in turn is influenced by the average atomic number. The X-rays intensity revealed by the detector is mainly affected by the particle size with respect to the volume of electron penetration. To avoid these phenomena during the quantitative analysis of ultra-thin samples, the standard SEM/EDS routine operating conditions (*e.g.* electron beam energy of 15-20 keV) could be modified, devising specific analytical strategies that depend on both the size and the composition of the sample. A systematic study of the best material-instrumental setups is highly required to advise and route the reader to a simple, fast and significant procedure.

To this aim, in the present work, Monte Carlo simulation was proposed to simulate electron transport, X-ray generation and detection in two different kind of thin materials. Among other fundamentals computational tools for materials study, characterization and development [8-11], Monte Carlo method is particularly suitable to model electron transport. In the first case study here presented, the investigation of very small glass fragments was accounted, using an initial simple geometry made of elongated shapes and square section. In the second case, extremely thin metal sheets and bits, such as those found in glass mosaic tesserae, were employed as a substrate for analysis.

The simulations were performed considering realistic experimental conditions, such as typical glass sample chemistry, geometry, SEM set-up and EDS

detector physics. The effects related to the glass and metal fragments (thickness, composition), the electron beam/sample interaction physics (*e.g.*, electron beam energy, electron elastic/inelastic scattering, element ionization threshold levels) and the SEM-EDS chamber setups (*e.g.*, take-off angle of the sample, azimuthal angle of the probe, position of the electron beam) were here considered.

The results of this study are very helpful to researchers interested in using this micro-nanoanalytical methodology to provide detailed and accurate quantitative analyses of very thin materials in cultural heritage and archaeology. Indeed, it is a general, fast, accurate and consistent strategy useful whenever the dimensions of the object under investigation approaches those of the electron penetration volume, as it could happen in thin layers in paintings, surface protective treatments, contamination and alteration layers, micro- and sub-microscopic surface dishomogeneity, oxidized metal surfaces.

II. MATERIALS AND METHODS

Electron scattering, X-ray generation, absorption and fluorescence in various kind of materials must be studied in detail to perform accurate quantitative microanalysis of thin structures by X-ray spectroscopy. Monte Carlo method is a powerful tool for these purposes and was here used to model electron transport and X-ray generation (both characteristic and Bremmstrahlung) and transport, including primary and secondary fluorescence generation. The Monte Carlo method allows simulating electrons trajectories and X-rays through thin materials and to a realistic EDS X-ray detector. Electron trajectories are modelled considering the elastic scattering and a continuous energy loss (continuous slowing down approximation) [12]. The elastic scattering is modelled by a basic screened Rutherford model, the Mott scattering cross section of Czyzewski and co-workers [13], and the Mott cross section of Jablonski and co-workers [14]. The Joy-Luo expression, which is an empirical modification of the Bethe energy loss equation is used to model the energy loss. The ionisation cross-section is modelled using the expression of Bote and Salvat [15]. The mass absorption coefficients and the fluorescence yields are, respectively, those of Chantler and co-workers [16].

To model the physics of secondary fluorescence the emitted primary X-ray intensity (Bremsstrahlung and characteristic) is propagated from the point of generation in a direction selected at random from a uniform distribution of directions until it is absorbed by photoionization, after a computed mean free path for photoionization, or it escapes the system. Photoionization is then followed by relaxation with the associated probabilities of emitting the characteristic X-rays of the absorbing element.

The electron source was defined as a Gaussian beam. The effect of the sample thickness was investigated by simulating the acquisition of EDS spectra. To this aim, a response function that mimics the energy resolution of a Si(Li) EDS detector was convolved with the emitted X-ray events. Afterwards, peaks intensities were integrated and compared as a function of thickness, beam energy and position, detector position and orientation for all the model samples, after background subtraction. Sample coating with carbon conductive films was not considered in the simulations.

III. RESULTS AND DISCUSSION

In general, the characterization of the composition of very thin materials using SEM-EDS microanalysis, where the dimension of the objects is close to the one of the electron penetration volume, requires special care and different phenomena can affect the analytical results. The size of the interaction volume of the electron beam and the X-ray generation volume in conventional SEM-EDS microanalysis (with beam energy between 10 keV and 30 keV) are of the order of several μm^3 in most materials. For extremely thin materials, it is not uncommon to have a penetration depth of the primary electron beam greater than the particle size: in this case, a fraction of the electron beam escapes the fragment or particle before exciting X-rays (finite size effect), which may result in an excitation of X-rays from adjacent particles or even the substrate. Furthermore, it is worth remembering that the microchemical characterization standard is typically a bulk material (of infinite size for the electron scattering) of much larger size than the unknown sample. This leads to more X-rays generated in the standard respect to the micro-nanosized particle or material. Thus, the k-ratio (intensity ratio of X-rays emitted by the unknown fragment to those produced by a massive sample) is additionally diminished because the intensity of the element X-ray in the standard (denominator of the k-ratio) is larger. These phenomena must be carefully taken in account to improve the quality and consistency of the analysis.

A. Case study 1: glass fragments

Three different kind of glasses, one sodic, one magnesian and one calcic, were considered for simulating the SEM/EDS analysis of glass fragments. Each model was realized considering an elongated shape of square section, with thickness in the range 0.1 – 10 μm, above a bulk graphite substrate. The detailed elemental compositions of the three glasses are reported in Table 1.

Table 1. Oxide contents (wt. %) in the simulated glass fragments.

SiO_2	Fe_2O_3	Na_2O	CaO	MgO
53	35	8	-	4
53	40	-	-	7
62	2	-	14	22

The integrated intensities (counts), obtained from the simulated EDS spectra, as a function of electron beam acceleration energy, 5 keV, 15 keV and 25 keV, for different thicknesses, are reported, as an example, in Fig. 1 for Si and Na in the case of the sodic glass, and in Fig. 2 for Ca and Mg in the case of the calcic glass (Ca 14 wt. % and Mg 22 wt. %).

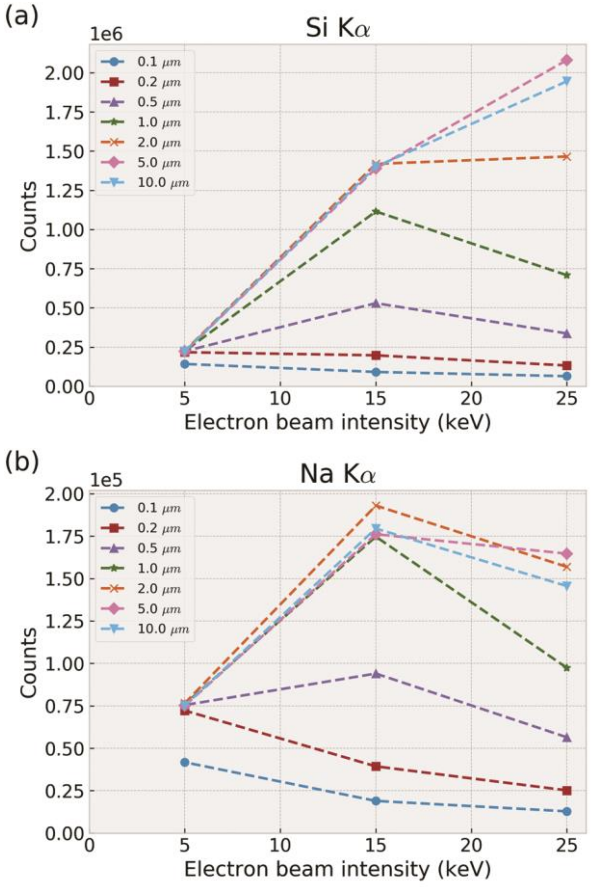

Fig. 1. Simulated SEM-EDS X-ray intensity, for the sodic glass in Table 1, as a function of electron beam acceleration energy, 5, 15 and 25 keV, for different thicknesses as reported in the inset. (a) Si and (b) Na.

The results show a strong dependence of the simulated X-ray intensity on the thickness of the glass model. In addition, the trends for the X-ray emissions of Si, Na, Mg and Ca are not linear. As a rule of thumb, when the thickness of the sample approached 10 μm, the calculated intensity values were similar to those for a massive sample. The integrated intensities of Si Kα, Na Kα, Mg Kα, Ca Kα and Ca Kβ started reducing below a sample thickness of about 5 μm at 25 keV, 2 μm at 15 keV and 0.5 μm at 5 keV. The same trend was observed for the Fe Kα, Fe Kβ, Fe L and O Kα, here not showed.

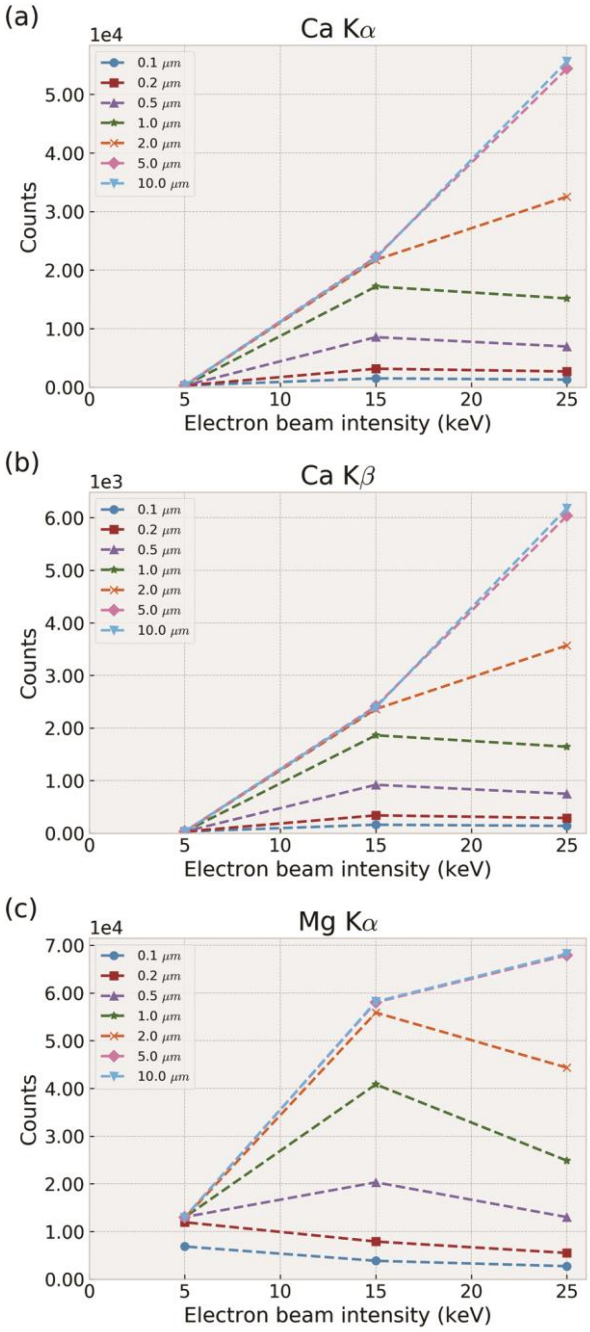

Fig. 2. Simulated SEM-EDS X-ray intensity, for the calcic glass in Table 1, as a function of electron beam acceleration energy, 5, 15 and 25 keV, for different thicknesses as reported in the inset. (a) Ca Kα, (b) Ca Kβ, and (c) Mg Kα.

An enhancement of the intensity, different for each specific X-ray emission line and electron beam energy, before the reduction starting point was also evinced by the simulations.

In terms of the previously cited effects related to the glass fragment thickness and shape, the reduced absorption effect (shape component) initially prevails on the finite size one (thickness), which in turn becomes predominant for smaller thicknesses. As a rule of thumb, in the case of "soft" X-rays, when there is high absorption, the magnitude of the reduced X-ray absorption effect is largest [17].

B. Case study 2: ultrathin metal layers

A very thin metal sheet of Au-Ag-Cu alloy, placed between two virtually infinite natron glass layers (mass density 2.5 g cm^{-3}), was modelled, resulting in a composite similar to mosaic tesserae [18]. The thickness of the metal sheet was set to 200 nm and 1 μm, and the investigated compositions of the simulated gold-silver-copper alloy are reported in Table 2.

The integrated intensity of the elements in the metal sheet was compared to reference calibration curves calculated on bulk standards, to characterize the influence of the sheet thickness in the chemical quantification.

Table 2. Chemical composition (wt% of the elements) of the simulated gold alloys in thin metal sheet models and respective mass density.

Au	Ag	Cu	Mass density [g/cm^3]
97.0	2.7	0.3	19.1
93.0	6.4	0.6	18.5

Gold alloy element analysis may be affected by secondary fluorescence, namely fluorescence generated when a primary X-ray (either characteristic or continuum) photoionizes an electron from a core shell. Indeed, the secondary fluorescence can come from a material with which electrons never interacted, since the mean free path of energetic X-rays far exceeds the range of electrons in most materials. When the sheets are extremely thin and the trace elements could be distributed in the surrounding material (in this case, glass), secondary fluorescence (*i.e.* XRF of the surrounding material) must be considered and properly addressed to obtain accurate quantification of the gold alloy composition, on the contrary misresults are obtained.

When using a standard SEM/EDS setup (a centred 25 keV electron beam) and the metal sheet is 1 μm thick, with the detector oriented in the same direction as the particle long axis, the integrated intensity is close to the reference bulk one. However, when the metal sample thickness is reduced to 200 nm, an underestimation of about 33% for Ag and 53% for Cu was observed.

It should be noted that the size of the electron interaction volume, and related X-rays generation, strongly depends on the energy of the incident electron beam and the material composition. The penetration depth is affected by electrons elastic and inelastic scattering within the specimen, which causes a lateral spreading ranging from hundreds of nanometres to several micrometres. Fig. 3 shows, as an example, images of detected X-ray emission for Cu ($K\alpha_1$ line) in a 200 nm thick gold leaf, Fig. 3a, and Si ($K\alpha_1$ line) in the adjacent support glass and cartellina, left and right part of Fig. 3b respectively. The beam energy was set to 25 keV. The images represent a three-dimensional distribution of the generation of detected X-rays, projected onto the x–z plane. The interaction volume in the gold leaf has a lateral size extended to the whole thickness of the gold leaf (Fig. 3a). Electron- and photo-ionization of Si in the glass layers takes place more than 3 μm apart from the gold leaf boundaries.

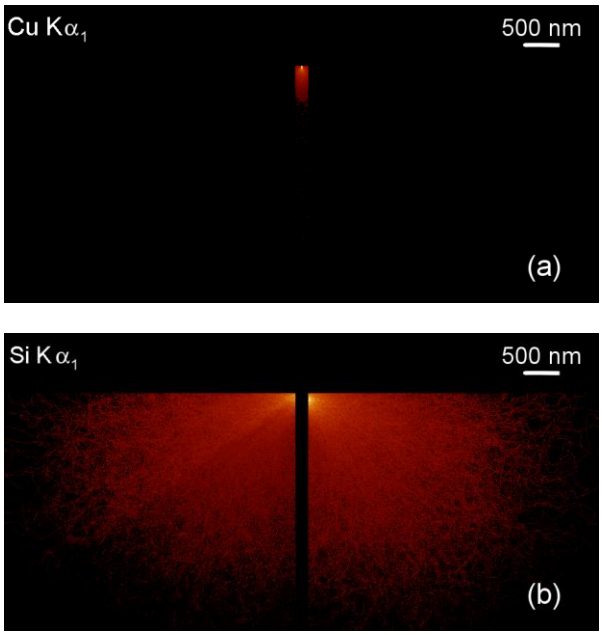

Fig. 3. Monte Carlo simulation of the X-rays interaction volume for 25 keV electrons in a 200 nm thick gold leaf (a) and adjacent glass layers (b). The intensity for Cu $K\alpha_1$ (a) and Si $K\alpha_1$ (b) is plotted using a colour scale where the brightest colours represent the highest X-ray intensity. The images represent a three-dimensional distribution projected onto the x–z plane.

To improve the analysis for a metal sheet with thickness of 200 nm, it is then suggested to reduce the electron beam energy to 7.5 keV, because the simulations showed that the X-ray signal generation is

confined within the ultrathin metal fragment. Indeed, with this setup, the thin metal sheet behaves like a bulk sample for a beam energy of 7.5 keV, enhancing the quantitative analysis of this kind of materials.

IV. CONCLUSIONS

The present study showed that several potential error sources can affect the quantitative SEM-EDS X-ray microanalysis of thin materials, such as glass fragments and metal sheets, which may have drastic repercussions on other, indirect analyses (*e.g.* the dating of the manufact or the type of material source used). The quantification errors may depend on several factors, such as the material thickness, the electron beam energy and other SEM-EDS experimental parameters, the material composition and the specific element considered. For this reason, it is of utmost importance to fully understand the limits of the methodology and the instrument parameters for the optimal measurement.

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