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Use of Monte Carlo simulations for cultural heritage X-ray fluorescence analysis ☆

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The analytical study of Cultural Heritage objects often requires merely a qualitative determination of composition and manufacturing technology. However, sometimes a qualitative estimate is not sufficient, for example when dealing with multilayered metallic objects. Under such circumstances a quantitative estimate of the chemical contents of each layer is sometimes required in order to determine the technology that was used to produce the object. A quantitative analysis is often complicated by the surface state: roughness, corrosion, incrustations that remain even after restoration, due to efforts to preserve the patina. Furthermore, restorers will often add a protective layer on the surface. In all these cases standard quantitative methods such as the fundamental parameter based approaches are generally not applicable. An alternative approach is presented based on the use of Monte Carlo simulations for quantitative estimation.

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1. Introduction

XRF is a well-known technique for non-destructive analysis. In the field of Cultural Heritage, XRF may be used in several distinct ways depending of the kind of sample analyzed [1–5]. For example if a painting is analyzed, XRF will provide information about color composition and conservation state, and may deliver conclusive evidence in establishing the authenticity of artifacts. Another example of XRF applied to Cultural Heritage is the analysis of objects produced by the ancient civilizations of Peru [5–7]. Several of these artifacts consist of a very complex multilayered structure in which gold, silver and copper can be found in varying but high concentrations in each layer, accompanied by several trace elements. Under such circumstances, the determination of both composition and concentration becomes an onerous task for which several solutions, often customized for a specific application, can be found throughout literature [8–12].

When analyzing ancient corroded metallic objects, it becomes clear that any suitable quantification solution has to take into account the multilayered nature of the artifacts. This can be explained by the fact that the corrosion, as well as all other interactions with the environment, eventually lead to the emergence of a so-called patina layer, covering the original metallic layer(s). An additional protective layer (e.g. Paraloid) is sometimes applied during restoration.

Traditionally, quantitative XRF methodology was based on the so-called fundamental parameter method, which relies on the (complex) relation between the net-line intensities of the XRF lines and the corresponding elemental concentrations. Early versions of this method already included support for secondary and tertiary excitations occurring within (initially only binary and ternary) bulk samples [13,14], and were later extended towards the modeling of secondary inter- and intra layer effects [15,16]. This evolution in modeling corresponded to a simultaneous increase in complexity of the underlying algorithms, thereby making complete implementations challenging. For this reason, most (commercial) software packages will rarely venture beyond supporting the second interactions order when dealing with *single* layers [17,18], and even then one will only take into account XRF based enhancement, while ignoring scattering based enhancement.

The importance of the higher order interactions cannot be underestimated in many cases, in particular when dealing with samples that contain several major constituent elements. A typical example of such a case is stainless steel (with typically 18% Cr and 10% Ni) irradiated with monochromatic radiation: the contribution to the intensity of the Cr and Ni peaks from higher order interactions (2nd, 3rd and 4th) may reach up to 40% [19]. This enhancement effect also occurs between layers: primary XRF photons generated in a 'deep' layer may generate secondary XRF photons in a more superficial layer. Although such enhancement effects are less strong when using X-ray tube excitation compared to its (synchrotron based) monochromatic counterpart, a significant quantification error could be made when ignoring them, depending on the sample composition and the excitation conditions.

These limitations of the fundamental parameter method can be circumvented by using Monte-Carlo simulations of energy-dispersive

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spectrometers, which are well known for their trivial yet complete implementation of an arbitrary order of interactions in an arbitrary number of layers. Monte-Carlo simulations have also the advantage that they allow for highly complex experimental conditions as well as atypical sample layer boundaries such as rough surfaces due to corrosion, which are known to impact the XRF peak areas and therefore the concentration estimates [20].

2. Methods

The proposed methodology is based on the simultaneous use of portable X-ray equipment and fast Monte Carlo simulations. The experimental equipment needs to be portable since most of the Cultural Heritage samples are either located inside museums or are simply impossible to move, therefore rendering in situ measurements is the only remaining option. However, a portable X-ray system comes with several drawbacks: the current and the maximum operational voltage of the X-ray tube are low compared to a fixed laboratory XRF system leading to a lower sensitivity and a longer measurement time. This presents a problem for low concentration elements, since the corresponding lines in the X-ay spectrum will be very weak and difficult to distinguish from the background noise. Moreover, the standard approaches for quantification such as the fundamental parameter method, are based on an initial fit of the background and on area estimation. The fit of the background does not always follow the true profile of the background with sufficient precision and often it will either enter the base of the peak or remain far from it. In the former case this will lead to an underestimation of the area while in the latter case it will be overestimated. The influence of this error on the concentration estimate depends on the size of the peak: the smaller the area, the greater becomes the error. In order to overcome this problem, an alternative approach is needed. Our solution to this issue is to use Monte Carlo simulations. Monte Carlo simulations are probabilistic methods used for many parameter problems that cannot be solved with analytical methods. In the specific case of X-ray interactions with matter, Monte Carlo simulations are essentially based on an X-ray cross section database and a random number generator that is used to generate a large number of photons. The larger the number of photons, the lower the variance of the simulated spectrum. Generally speaking, a simulation of a large number of photons requires a considerable amount of time, in the order of several hours up to days, thereby imposing an insurmountable limitation for real time or in situ simulations. However, some specific strategies may be used in order to reduce the simulation time while simultaneously obtaining a simulated spectrum with lowered variance. These strategies are based on the so-called variance-reduction techniques, which force, in several ways, the interaction and/or the detection of the generated photons. This allows for the reduction of the simulation time by four to five orders of magnitude. Several papers describing Monte Carlo codes for the simulation of XRF spectrometers have been published over the last couple of decades [18–27]. For our kind of applications, two fast Monte Carlo codes have been developed within our group and by our collaborators of Ghent University and the European Synchrotron Radiation Facility, called *XMI-MSIM* and *XRMC* [23–26]. They are based on the database for X-ray interactions with matter called *xraylib* [28,29], which is being developed within the same collaboration framework. *XMI-MSIM* has been specifically developed targeting XRF applications while *XRMC* covers a larger set of X-ray simulations, such as radiography, tomography and phase contrast imaging. Both of them are able to produce satisfactory simulations in a couple of minutes, less than the time required by a real XRF experiment using X-ray tube excitation. Recently *XRMC* has been extended with the capability to simulate arbitrary rough surfaces. This feature is of great significance for Cultural Heritage analysis since rough surfaces are often encountered in the analyzed artifacts. It can be used for two distinct applications: the investigation of the effect of the real surface on the quantification outcome as well as the optimization of the experimental setup by minimizing the effects of the roughness. In this work we could not use the Monte Carlo codes for the former application since we are not yet able to record a reliable roughness profile of the surface. Fortunately the latter merely requires an approximate estimate of the surface roughness. With this information, one can simulate its influence on the XRF signal, while varying excitation parameters such as beam size and tube voltage [27].

After settling on a convenient experimental setup, the quantification step of the composition of the sample starts. Firstly, a measurement of the XRF spectrum emitted by the sample is recorded with satisfactory counting statistics. Subsequently the Monte Carlo code is run several times until the simulated and the experimental spectrum match almost perfectly. At the end of each iteration, the composition and/or the structure of the simulated sample are modified. Currently, this step involves considerable intervention by the user. An automated procedure is being developed, which should eliminate possible user errors as well as diminish its tedious and time-consuming nature.

In order to obtain a good simulation of the experimental measurement, several important parameters need to be carefully determined: the model of the X-ray spectrum emitted by the X-ray source, the response of the detector and its efficiency. A correct description of the geometry is also important, but it doesn't need to be as accurate since its influence on the simulation is comparatively lower. An accurate reproduction of the emitted X-ray spectrum is critical; ideally it is obtained by positioning an energy-dispersive X-ray detector directly into the beam. Recording such a spectrum is challenging since the detector, identical to the one used for the XRF measurements, will easily saturate. One possible solution entails positioning it sufficiently removed from the source, and correcting the recorded spectrum for air attenuation. This approach works quite well at high energies but the quality of the reproduced spectrum is poor at energies lower than about 4 keV. However, this is not necessarily a disadvantage since the XRF lines observed at these energies are often L-lines whose corresponding K-lines will also be present in the spectrum, for example silver or tin in the case of metallic alloys.

Modeling the detector response function may be the most challenging part in a Monte Carlo simulation of ED-XRF spectrometers due to its dependence on many parameters, many of which are either unknown or heavily influenced by settings of the detector and its associated electronics. Ideally one would obtain the detector response function for a given detector unit through a series of measurements: the required parameters that govern the response function can be obtained after comparison with the experimental counterpart. Scholze and Procop have obtained excellent results using a five-parameter response function based on this technique [30]. Both *XMI-MSIM* and *XRMC*, however, use a customized version of the detector model of He et al. with different values for some of the response function parameters in order to agree with the output of more recent detector types. It can be described by the following equation [31]:

$$R_{peak} = a \cdot G_{peak} + b \cdot (c + d \cdot \exp_tail)$$

where G corresponds to the Gaussian broadening of the peak and a, b, c and d are the parameters that will determine the peak tailing and the flat continuum formation. The detailed model can be found in He et al. [31]. Here, we have stripped the escape peak contribution from the original algorithm since it can be simulated by the Monte Carlo code itself as described in ref. [32].

In the next section the effects of changes to the parameters values that determine the peak tailing and the flat continuum as well as of other models on the simulation will be investigated and discussed. The last important parameter, the detector efficiency, can in most cases be obtained from the detector manufacturer who may provide the thickness and composition of both the crystal and window. Although *XRMC* initially did not target ED-XRF applications, and therefore did not come with a detector response function, this functionality was

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