EVALUATION OF MONTE CARLO SIMULATION TECHNIQUE IN XRF QUANTITATIVE ANALYSIS OF METAL ALLOY STANDARDS

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PAPADOPOULOU DIMITRA
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EXAMINATION COMMITTEE:
ANDREAS G. KARYDAS
ALEXANDROS CLOUVAS
ARGYROPOULOS VASILIKI

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This is dedicated to my parents, Maria and Georgios,

who have been my rock and always been there for me.
Acknowledgments

I am most grateful for the support and guidance from my supervisor Andreas Karydas. He helped steer me in the right directions both professionally and scholarly to be able to accomplish my goals, and he is a source of inspiration for my future. He was always willing to help and never had a closed door for any of my small problems, and would dedicate as much time as he could to lending his guidance for experiments and problem solving. I thank him for his enthusiasm, encourage and for a great working relationship.

I would also like to thank my other advisor Vicky Kantarelou. The work presented here was only possible through her teachings, critiques, suggestions, and support.

Big thanks also to Dr. Tom Schoonjans, who provided extensive help and feedback concerning the XMI-MSIM program.

I would also like to thank my fellow lab members Eleni Kokiaomenou and Fatima Azzahra Rakhami for their kind cooperation and for the personal support. Also a big thank to my best friends for their support and encouragement.
Abstract

The strict requirement towards non-invasive compositional analysis of cultural heritage materials, has naturally motivated the application and evaluation of advanced modern Monte Carlo tools to simulate complex XRF spectra acquired by portable spectrometers (Schoonjans, et al., 2013), (Manso, 2015), (Schiavon, et al., 2016), (Brunetti, et al., 2015), (Bottaini, et al., 2015). In such cases, the analytical challenge relies on the holistic and accurate description of all spectral features, including the background shape, the intensity and shape of the scattered discrete lines of the tube anode material and of all detected elements emission lines. Each particular spectrum component projects useful analytical information on the sample elemental composition, stratigraphy, and roughness etc., usually ignored in conventional quantitative analysis based only on major peaks analysis.

The reliability of Monte Carlo tools, apart the subjective modelling of the sample composition and structure, depends on the embedded databases of the X-ray fundamental parameters (FPs), the adopted model for the analytical description of the X-ray source excitation spectrum, but also from the good knowledge of set-up geometrical parameters, hardware specifications and operational parameters. Obviously, relevant uncertainties and particularly the adaptation of the widely applied semi-empirical model of Ebel (Ebel, 1999) to describe the emission spectrum of modern low power X-ray tubes, can propagate inconsistencies in the simulated spectrum.

In the present work, the XMI-MSIM open source Monte Carlo tool (Schoonjans, et al., 2013), is employed for the systematic simulation of XRF spectra obtained from the analysis of certified gold, silver and copper alloys presenting compositional profiles that resemble the ones of the most common relevant archaeological alloys. The measurements were carried out using a portable XRF spectrometer equipped with an Rh anode, side window X-ray tube (50 Watt) and a Si-PIN detector. To optimize the use of the XMI-MSIM tool, scattered spectra from a certified material (PTFE) were measured at different high voltages (10 - 48 kV) and through comparison with the simulated ones, the description of the tube emission spectrum was optimized. The obtained results are critically evaluated and discussed.
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1 Introduction

Within this diploma thesis an analytical methodology was developed for the tube distribution and applications of this methodology in the field of cultural heritage.

More specifically, the first chapter is an introduction to the role of the X Ray Fluorescence (XRF) spectroscopy in the analysis of cultural heritage artifacts, the methodology followed and the objectives of this thesis as well.

In the second chapter the basic principles of the XRF technique are presented, as well as the interaction of X-Rays with the matter, the fundamental parameters method and the principle of the operation of the individual devices of an XRF spectrometer. The evolution of the XRF technique in the field of Cultural Heritage is also discussed.

In the third chapter, the reference materials used for the experimental part of the project are cataloged. The Monte Carlo method on which the XMI-MSIM simulation program is based, is extensively presented in the same chapter. The PyMca program, which is used in the analysis of the XRF spectra, and the experimental setup used in this work are also discussed in this chapter In chapter number four, a validation of the experimental parameters used is made, namely the accuracy of the high voltage settings, the current linearity, the thickness of the absorbers used in the excitation path, the estimation of the Si-PIN crystal thickness and the determination of the primary X-Ray intensity. A comparison is made between experimental measurements and Monte Carlo simulations of gold, silver and bronze alloys.

In the fifth chapter, the causations of the corrosion to metallic alloys, such as gold, silver and bronze alloys are discussed and the results of the Monte Carlo simulations of corroded metallic alloys are presented.

Finally, chapters six and seven present the conclusions from the present study and provide future directions towards this methodological approach on the analysis of CH artifacts using the XRF technique combined with the XMI-MSIM simulation program.
1.1 The role of XRF spectroscopy in Cultural Heritage scientific investigations

It is very important to maintain and preserve the objects of cultural heritage so that the next generations have the ability to admire them and also to study them, because it is a part of their history. Also, in order to avoid either speculation or historical counterfeiting, certification of the authenticity of these items is necessary. In order for these objectives to be achieved, their nature and composition and the alterations that they have suffered must be known. The application of non-destructive research methods is required, due to the uniqueness and often due to the small size of the objects under consideration. XRF spectroscopy is a widely used nondestructive analytical technique in the last decades. Furthermore, the development of portable devices (pXRF) ensured great flexibility since some artifacts can’t be moved because of their value or their size. XRF is an elemental technique which does not require sampling, keeping the material after its examination unchanged. Furthermore, measurements and analyses can be multiple and in a short time (Galli & Bonizzoni, 2014). To be more specific, the technique provides quick qualitative results of an analyzed spot, surface (area and line scans) or even of the whole object (macro-XRF). Spectra can be collected within a few seconds to minutes depending on the material to be analyzed and the measurement’s conditions. Therefore the technique’s use is suitable for a fast screening of an analyzed surface. It can be used for a large number of materials (obsidian, ceramics, coins, glasses, polishes, glazes, pigments, paintings, faience, etc.) by detecting chemical elements from Be-7 to U-238 and concentrations of certain trace elements up to the lower limit of 10-100ppm, which however depends on the type of material, while having automatic recording of the results, without detaching part of the object (Λυριτζής, 2005). The XRF is characterized as the most widespread method of analyzing cultural heritage items either in the laboratory or in in situ cases, by focusing on the development of analytical procedures for the characterization of glass or ceramics or pigments on painted surfaces and metal alloys in statues (Varella, 2013).

Of course, this method has some disadvantages. Firstly the XRF provides results on the elements present on the surface of a material. This means that compounds are not identified and the information of the detected elements is restricted to the upper surface (a few micro-meters in the case of metal alloys). Secondly, portable instruments
detect elements with an atomic number above 12 (Al). Finally, the quantification procedure is not straight forward, since it can be done by calibration curves that are produced by a proper set of standards or using the fundamental parameters approach. Nowadays it can also be done through the Monte Carlo simulation programs, as in the last two cases a good calibration of the instrument is necessary (Galli & Bonizzoni, 2014).

1.2 Objectives of this diploma work

In the X-ray fluorescence technique (XRF) an X-ray stimulating beam irradiates a multi-elemental sample by ionizing the inner atomic shells of the contained elements, thereby causing the emission of the corresponding characteristic X-rays. The whole process of X-ray fluorescence is accurately described by a mathematical formalism referred to as Sherman equations or fundamental parameters method and which forms the basis of quantification in the XRF technique. The reliability of the method depends significantly on the knowledge of the technical characteristics of the equipment being used (X-ray tube, X-ray detector) and its geometry which determines critical physical magnitudes such as the spectral distribution of the X-ray tube, the intrinsic yield of the X-ray detector, etc. In addition, it should be noted that basic atomic parameters such as mass X-ray attenuation factors in matter, K- or L- fluorescence yield have been registered in available databases with significant uncertainty, in some cases with an uncertainty of more than 10-20%.

These difficulties are largely addressed through the experimental calibration of an XRF spectrometer using mono-elemental or multi-element standard targets and application in the quantification process of corrective empirical factors.

In this thesis a new software tool based on the Monte Carlo simulation will be used to quantify analytical portable XRF spectrometer data in analyses of objects with interest in the Cultural Heritage. This software tool is XMI-MSIM, which is freely available at: https://github.com/tschoonj/xmimsim/wiki. In its use, the simulation feature that will be used to reproduce theoretical XRF spectra of multi-element reference materials will be evaluated and any discrepancies to be observed will be interpreted.

This study aims to develop a methodology using the XMI-MSIM tool for the accurate simulation of tube excited portable XRF spectra acquired from reference gold, silver and bronze alloys that imitate the elemental composition of archaeological ones.
The analytical procedure developed relies on the determination of various experimental and instrumentation parameters, namely by adjusting the x-ray tube emission spectrum of the XMI-MSIM tool to describe accurately the experimental one obtained by a low Z scatterer experiment.

1.3 Analytical methodology and expected results

The methodology to be developed includes the following phases:

i. Design and implementation of targeted experimental measurements of mono-elemental standard targets with the portable spectrophotometer (milli-beam spectrometer) provided by the XRF Laboratory of the Institute of Nuclear and Particle Physics (INPP), NCSR “Demokritos”,

ii. Determining the appropriate constructional and experimental parameters of the XRF spectrometers that achieve the optimal agreement of the simulated XRF spectra of mono-elemental standard targets with the corresponding experimental ones,

iii. Analyzing, with the p-XRF spectrometer, multi-element reference materials, which have certified concentrations and represent archaeological materials such as gold, bronze and silver metal alloys.

iv. Evaluation of simulation software in the reproduction of XRF spectra of multi-element reference materials and interpretation of any differences that will be observed.

v. Application on corroded gold, silver and bronze alloys and evaluation of the simulation results.

The proposed research will provide a systematic appraisal of the applicability of a very important and modern simulation tool software that is increasingly used by the non-destructive XRF science community to determine the elemental composition of materials of interest in the field of cultural heritage.
2 Theoretical background – The XRF analysis technique

2.1 X-ray interactions with matter

When a beam of X-ray photons is coming towards a material (fig. 1), a part of them will penetrate the material, another will be absorbed (causing fluorescent radiation) and another will be scattered either with energy loss (Compton scattering) or without energy loss (Rayleigh scattering). Fluorescence and scattering are influenced by thickness ($d$), density ($\rho$) and sample composition, and the energy of X-rays (Brouwer, 2010).

So, there are three possible interactions when an X-Ray beam passes through the matter.

1. The Photoelectric Effect
2. The Rayleigh Scatter (elastic scatter)
3. The Compton Scatter (inelastic scatter)

![Figure 1. X-ray interactions with matter. When an X-ray beam passes through the matter interacts by the Photoelectric Effect, Compton scattering and Rayleigh scattering.](image)

Each of the above mechanisms is more likely to occur than the other two in a certain area of photon energies. At energies up to $\sim 0.5 \text{ MeV}$ the photoelectric phenomenon is predominant. Whereas the Compton Effect dominates the intermediate energies ($\sim 0.1 \text{ MeV} \text{ to } \sim 5 \text{ MeV}$) (Ηλιόπουλος, 2014).
2.1.1 The photoelectric absorption

The description of the above phenomena is possible by adopting the simplistic atomic model of Bohr, where the atom consists of a solid nucleus (protons and neutrons) and a plurality of electrons that rotate around the nucleus in specific tracks, organized by shells and subshells. The shell closest to the nucleus is called K, the next L etc. Each shell retains a specific number of electrons determined by the Pauli prohibitory principle. Each electron is held in the shell having a certain energy, the binding energy $U_x$, which depends on the element and the shell to which it is located. For an electron to transit to another shell or for it to be distracted, it should obtain an energy level, equal to the binding energy or more than that (Serway, 1990).

Energy Level = binding energy = absorption edge

When a bonded electron reacts with a photon the transferred energy is equal to the difference of the photon energy ($E_0$) and the binding energy ($U_x$) (Ζαρκάδας, 2001).

A photon, as it penetrates a material, it interacts with it with a series of mechanisms as mentioned earlier, resulting in its attenuation, meaning the loss of a part of its energy within the material and the generation of secondary radiation. The thicker the sample the more radiation is absorbed. Assuming that there is a parallel, monochromatic X-ray beam, of intensity $I_0$ that passes vertically from a plate, a homogeneous and isotropic material of thickness $x$ (cm), if $dl$ is the reduction of intensity at a distance $dx$ from the surface of the plate and density $\rho$, the relative reduction of intensity will be proportional to $dx$:

$$\frac{dl}{I} = -\mu \rho dx$$

With integration, the intensity that passes through the plate is, according to Lambert-Beer law:

$$I = I_0 e^{-\mu \rho x}$$

The coefficient $\mu$, with dimensions (cm$^2$g$^{-1}$), is called the mass attenuation coefficient and expresses the fraction of energy absorbed by the mass of the material. At a certain energy, that is characteristic for each element, the value of $\mu$ rises sharply and the curve shows discontinuities, which are called absorption edges (Κόκκου & Χρηστίδης, 2000).
When the energy of the transmitted X – radiation from the material is equal to the energy which corresponds to an absorption edge, the energy of the photons is sufficient to extract electrons from the homonymous (toward the absorption edge) shell of the atom. As a result, there is a strong photoelectric absorption of the X-ray photons from the atoms of the material, the factor $\mu$ increases sharply and the intensity of the penetrating beam decreases immensely (Κόκκου & Χρηστίδης, 2000).

In the case of a matrix which consists of more constituents than one, the mass absorption coefficient $\mu(M)$ can be calculated from the following formula:

$$\mu(M) = \sum_{i=1}^{n} w_i \mu_i,$$

where $\mu_i$ is the mass attenuation coefficient of the $i$th pure element and $w_i$ is the mass fraction in the sample considered. The mass attenuation coefficient of an element is expressed by $\mu_i = \tau_i + \sigma_i$, where $\tau_i$ is the cross section for photo-electric ionization and $\sigma_i$ is the cross section for scattering interactions (Janssens, 2013).

**X-ray scattering**

As mentioned above, part of the radiation will be scattered either with energy loss (Compton scattering) or without any loss (Rayleigh scattering).

**Rayleigh Scatter (coherent)**

When a photon strikes an electron, which is strongly bounded, the electron remains in its shell, acquires reciprocating movement at a frequency, same as the frequency of the incoming radiation, resulting to the emission of radiation at the same
frequency of incoming radiation and giving the impression that incoming radiation is reflected by the atom. This phenomenon is called Rayleigh Scatter (Brouwer, 2010).

The Rayleigh cross-section is notable for low energy photons (<10keV) and when the target – material is of high atomic number.

*Compton Scatter (incoherent)*

A part of the X-ray, instead of producing characteristic radiation, is scattered from the sample. Scattering occurs when a photon impinges on an electron and loses part of its energy, taken up by the electron and bounces, having an energy greater than the allowable, for the shell it belongs to. The energy magnitude that the photon loses depends on the scattering angle and on the shell, to which the infected electron belonged. The difference in the wavelength of the incoming and outgoing photons can be calculated from the equation

$$\Delta \lambda = \frac{h}{mc} (1 - \cos \varphi).$$

A. Compton interpreted the X-ray scattering by electrons in 1923 and proved experimentally that the difference in the wavelength of the incoming and outgoing photons, scattered at an angle $\theta$, depends exclusively on that angle, according to the equation:

$$\Delta \lambda = \lambda_c(1 - \cos \varphi),$$

known as the Compton equation (Serway, 1990), where $\lambda_c$ depends on the electron resting mass and the constants $h$ and $c$, as shown in the following equation,

---

1For his work, which was an important support in quantum theory, confirming the particle nature of light, Compton was honored in 1927 with the Nobel Prize.
\[ \lambda_c = \frac{h}{m_e c}, \]

where \( \lambda_c \) is Compton’s electron wavelength, with a value of \( \lambda_c = 2.4263 \times 10^{-3}\text{nm} \) and length dimension (Ελευθεριάδης, et al., 2003).

The photons that interact with low bounding electrons in the atom are scattered by the electrons inelastic, due to the comparative mass of electrons compared to photon energy. These photons lose a part of their initial energy and impetus. As a result, they have lower energy than before scattering. The specific electron gains the energy that the photon loses, as kinetic energy and extracts it from the atom. This electron is called the Compton electron (Janssens & Van Grieken, 2004).

During the Compton scattering, the energy and the momentum conservation principle from which the energy of scattered photon arise are valid, following the Compton equation:

\[ E_c = \frac{E_0}{1 + \gamma (1 - \cos \phi)}, \]

where \( \gamma \) expresses the fraction of the photon’s incident energy and the electron’s rest energy: \( \gamma = \frac{h \nu_0}{m_e c^2} \) and \( \phi \) is the photon’s scattering angle (Van Grieken & Markowicz, 2001).

For \( \phi = 180^\circ \) the scattered photon’s energy becomes the lowest and in that case the phenomenon is called backscattering. The probability of the Compton scattering decreases with the atomic number and increases with energy, taking into account that the incident’s photon energy is significantly higher than the electron’s binding energy. The differential Compton cross-section depends on the scattering angle \( \phi \) according to the following equation:

\[ \frac{d\sigma(E,\phi)}{d\phi} = \frac{r_e^2}{2} \left( \frac{E}{E_0} \right)^2 \left[ \frac{E}{E_0} + \frac{E_0}{E} - (\sin \phi)^2 \right], \]

where \( r_e = \frac{e^2}{4\pi \varepsilon_0 m_e c^2} \) is the electron’s classic radius (Ελευθεριάδης, et al., 2003).

### 2.2 Emission of characteristic X-Rays

When an atom is irradiated by X-ray photons, it is possible to extract an electron resulting in the creation of a "hole" in the shell, from which the electron was extracted, placing the atom in an unstable and highly excited state with a higher energy level. In
order for the atom to return to its basic state an electron from a higher shell must be transited, completing the vacancy that was created. However, because the higher shell electrons have more energy than those of the lower shells, an excess of energy is produced, which is capable of emitting an X-ray photon or an Auger electron. In the case of a spectrum, this is perceived as a transition line and is observed as peaks on the X-Ray spectra.

The energy of the photon emitted depends on the difference in energy of the shell that had lost the electron and the one that offered the electron to fill the vacancy. And due to the fact that each element has a characteristic set of energy levels, the radiation emitted is characteristic for each element. Even in the same atom, "holes" can be created in different shells and filled with different electrons. This results in the creation of more than one transition lines in the spectrum, whose set is characteristic of the element that produces this set of spectral lines (Brouwer, 2010). The photon emission process in the above manner is called X-ray fluorescence. Moseley found that the relationship between the wavelength of the characteristic radiation $\lambda$ and the atomic number $Z$ from the atom being emitted is:

$$\frac{1}{\lambda} = K(Z - \sigma)^2,$$

$K$ and $\sigma$ are constants for a given spectral line (Van Grieken & Markowicz, 2001).

A second mechanism of de-excitation, antagonistic to the X-Ray emission, is the emission of atomic electrons, Auger electrons, or a special case of Auger the Coster – Kronig transition, where the created vacancy is filled by an electron from a higher subshell of the same shell (Heinrich & Newbury, 1991).

The fluorescence yield expresses this competition of two phenomena, X-Ray emission and Auger, and is defined as the ratio of the emitted X-Rays to the number of generated holes (Kantarélyou, 2016).

![Figure 5. Fluorescence /Auger electron yield versus atomic number (Karydas, 2014). For high Z elements a fluorescence phenomenon is more probable than Auger, while it is the opposite for low Z elements.](image)
As it can be observed from the figure, the fluorescence yield increases rapidly for items with an atomic number greater than 20, while conversely the Auger is predominant for items with an atomic number less than 20. The fluorescence yield depends on the atomic number of the element to which the atom belongs, but also on the shell in which the hole appears.

2.3 XRF instrumentation

The technique of the method consists of the fact that an X-Ray beam interacts with the sample and the characteristic X-Rays are detected by a detector. The principle of the method is based on the fact that in order to produce X-ray radiation from the sample, ionization of the inner shells of atoms must precede. This is accomplished by removing an electron from an inner shell, which is equivalent to an electron hole. The ionization of the target atoms occurs when the target – sample is bombarded with active particle beams, photons of energy capable of causing internal ionization of target atoms. Under these conditions, sample elements are stimulated by the absorption of the primary beam and emitting their own characteristic X-ray fluorescence spectra.

All XRF spectrometers are composed of three parts networked together. The first part is the primary source unit, which is an X-Ray tube, the second part is the spectrometer itself and the third part is the measuring electronics, so that the information can be analysed, processed, displayed and stored. There are two types of XRF systems: energy dispersive EDXRF and wavelength dispersive WDXRF, which differ in the detector (Brouwer, 2010).

X-ray tubes

Different X-Ray sources are used for XRF analysis such as sealed X-Rays tubes, rotating anode tubes and synchrotron radiation.
In sealed X-Ray tubes, the most common, thermionic electrons are produced by heating a tungsten filament in a vacuum chamber. Applying high voltage, the electrons are accelerated and then directed towards the anode, which is made of a high purity metal. The metals selected have energy which does not increase the background in the area of the important elements and provides the ideal stimulation of the sample components. Common metals used as anode material are Sc, Ti, Cr, Fe, Co, Ni, Cu, Mo, Rh, Pd, Ag, W. The electrons after hitting the anode they decelerate and is produced the bremsstrahlung continuum. On this continuum spectrum the characteristic lines of the anode material are superimposed when electrons hit the atoms in the anode and expel electrons from these atoms, resulting to the emission of characteristic radiation (Janssens, 2013).

The maximum power of the incident electron beam (~ 99%) is consumed as heat, making it necessary to cool the X-ray tube, by water cooling or by a metal fast spinning rotating water-cooled cylinder anode. The tubes has a Be window, most common a side window but there are also tubes with Be window at the end of the tube.

**X-ray optics**

X-ray optics are used to change the radiation distribution or the beam shape. Typically, these changes are made by using filters, monochromators or collimators.

Filters are usually metal or plastic and absorb X-rays immediately, even high-energy X-rays. The filters are often placed between the tube and the sample in order for the background to be reduced and to improve the fluorescence. There are also filters that are inserted between the detector and the fluorescent X-ray beam in order for the undesirable photons to be absorbed, for the photon recording rate to be reduced and for the saturation of the detector to be avoided.

Diffraction crystals are a set of thin layers of the same thickness. When a parallel X-Ray beam falls on the crystal, a fraction of X-Rays is reflected by the first layer.
Diffraction from the parallel layers occurs, when the difference in distance of the reflections, that are scattered from different parallel layers, is an integer multiple of the wavelength of the radiation. Then the scattered beam has maximum intensity as a result of a constructive contribution. According to Bragg’s law, a family of layers with a spacing d, receiving monochromatic radiation at a certain angle θ, will lead to constructive contribution when:

$$2d \sin \theta = n\lambda.$$ 

Collimators consist of parallel plates and the primary collimator is placed between the sample and the crystal to limit the angle of the beam that is required, in order to limit the photons that will be scattered outside the target and possibly directed to the detector and in order to obtain a parallel X-Ray beam. A secondary collimator can be placed between the crystal and the detector (Brouwer, 2010).

X-ray detectors

An X-Ray detector converts the energy of X-Rays into measurable and countable voltage pulses. Photo – ionization is the process under which the detectors are working. More specifically, a production of a number of electrons is a result of the interaction between the active detector material and the entering X-Ray photon. When an X-Ray photon enters the detector it produces an electrical pulse, whose height is proportional to the energy of the transmitted X-rays. Subsequently, the signal is amplified and is counted by a multi – channel analyser. Some of the types of detectors are Solid State Detectors (SDD), Silicon Lithium drift (Si (Li)), Silicon drift, PIN Diode. For EDXRF the Silicon Lithium drift Diode is commonly used, which allows the simultaneous detection of all elements above sodium (Janssens, 2013).

Some of the most important properties of the detection system are:

- Sensitivity (the efficiency of the incoming photons counting). An electromagnetic radiation detector may not be susceptible to the entire electromagnetic spectrum. The efficiency of the detector is determined by the window covering the photosensitive area as well as by the thickness of the Si-PIN diode. The efficiency of the detector is a function of the energy of the incident photon.
- Resolution (the degree of the ability to distinguish between many energies). The detector records a photon distribution, which is usually described by
a Gaussian function. The range of the spectral line is defined as the widening in the middle of the maximum height of the spectral line (FWHM, Full Width at Half Maximum). Energy resolution is determined by FWHM, which is given by the following formula: \( FWHM = 2.35 \left( \varepsilon FE \right)^{\frac{3}{2}} \), where \( \varepsilon = 3.81 \text{eV/pair} \), F is the Fano Factor and E is the photon energy. The range of the spectral line changes with the energy of the incident photon.

- Dispersion (the ability to distinguish different X-Rays with different energies).
- Dead time (the length of time required by the detector to record a photon and reset to count the following). Due to dead time, as the intensity of the incident beam increases, the measured intensity deviates from the actual value (Αναγνωστόπουλος, et al., 1993).

There are two possible detector setups: the energy dispersive EDSXF and the wavelength dispersive WDXRF detectors.

Wavelength dispersive spectrometers use a crystal to select which wavelength radiation actually enters the detector, by separating the X-Rays according to their wavelength. In these cases the X-Rays are scattered from different layers of atoms so the criteria of Bragg’s law are met at a certain angle, so that constructive interference may take place.

Energy dispersive X-ray (EDS)

An EDS separates the characteristics of X-Ray photons by their energy according to the number of electron – hole pairs that they manage to generate. A semi – conductor crystal (Si, Ge) is the heart of an ED – spectrometer. The detector crystal absorbs the incoming X-ray photons which ionize atoms resulting to the production of electron – hole pairs. The amount of those pairs is proportional to the energy of the X-Ray photons. The height of the pulse produced is proportional to the energy of the respective incoming X-Ray. In EDXRF spectrometry, the secondary radiation that leaves the sample and enters the detector does not underlie physical discrimination, which means that all photons of all energies in this secondary beam interact with the detector (Van Grieken & Markowicz, 2002). The most common element used as an ED detector is Si(Li), cooled to cryogenic temperatures with liquid nitrogen. A Be window allows the X-rays to pass and at the same time protect the detector from light.
Multichannel analyzer

The pulse is driven to a preamplifier, further amplified to a suitable amplifier and its height determined with the aid of a pulse height analyser. The detector’s count pulses are translated into counts per second (CPS). Finally, with the help of a multi-channel analyser that is stored in memory, depending on the pulse height, the pulses are segregated into channels according to energy, by MCA. The memory of the MCA is driven to the computer by means of a proper connection. The display of the contents of the memory is the measured spectrum (Brouwer, 2010).

2.4 Historical evolution of the XRF analysis in the field of Cultural Heritage

In 1895 W.C. Röntgen, with the discovery of X-rays, shook the waters of the scientific community. Except the fact that all physics laboratories were equipped with the appropriate devices for X-ray production and that physicists were persuaded in performing parallel research experiments, X-rays have, since then, charmed both the common and the philosophical and artistic world. Röntgen himself in his article (in Paris-Journal, 31/1/1906) stated that he had discovered rays with which one could see what was invisible, which caused confusion between the distinction of two and three dimensions, in the concepts interior – exterior, made the opaque transparent and shattered the foundations of positivism on the one hand and on the other hand he provoked the imagination of the writers of his time and influenced artistic trends such as the cubist tendencies of G. Braque, P. Picasso, M. Duchamp and artists such as V. Kandinsky and others (Miller, 2002). The first Nobel Prize, awarded in 1901, was given to W.C. Röntgen for this discovery. Accordingly, X-ray spectroscopy was used for elemental analysis after 1950, although it was known since 1909 by Charles G. Barkla, while the Moseley Law laid the foundation for X-ray spectroscopy. The importance of X-rays and their spectroscopy was considered particularly important, insomuch since 1914 to 1924 four
Nobel Prizes were awarded to scientists involved in the development of these subjects\(^2\). Since 1932, Hevesy, Coster and others have focused on fluorescence X-ray spectros-copy, exploring its potential in qualitative and quantitative elemental analysis (Van Grieken & Markowicz, 2002).

The first X-ray spectroscopy used, was in 1947 by Friedman and Birk, using electrons as an excitation source, with high vacuum requirements, electrically conductive samples and with volatility problems. To address these difficulties, the sample was placed under vacuum, outside the X-ray tube and under cooling conditions, a stimulation which led to the production of secondary fluorescence X-rays.

The first commercial spectrometers were wavelength dispersive, consisting of an X-ray tube, with a tungsten cathode, a crystal for the diffraction separation of the fluorescence wavelengths and a Geiger counter for the detector. With these, even today, the wavelength of the X radiation produced can be studied with high detection capability. Their disadvantage is their large size and high cost.

The energy dispersing spectrometers were available in the early 1970s. They were operated with a radioactive source or X-ray tube and an X-ray detector. The radioactive source spectrometers have the disadvantage of limited lifetime and the requirement for a special permit in case of their transportation (Κανταρέλου, 2016). Now, the evolution in XRF spectroscopy is important, because of the use of a new generation of semiconductor detectors and because of the use of new smaller X-ray tubes; also by using various anti-cathode materials, different geometries and are low-power air-cooled and with the possibility of measuring under atmospheric conditions and by allowing the use of computers. Analyses are carried out in depth, where information is obtained on the composition of the layers below the surface of the sample, while the stimulation of small areas of the sample allows the analysis of heterogeneous regions.

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2 1914, Von Lalue, Max, Germany, for his discovery of the diffraction of X-rays by crystals

1915, Bragg, Sir William Henry, Great Britain και Bragg, Sir William Lawrence, Great Britain, in the analysis of crystal structure by means of X-rays

1917, Barkla, Charles Glover, Great Britain, for their discovery of the characteristic Röntgen radiation of the elements

1924, Siegbahn, Karl Manne Georg, Sweden, in the field of X-ray spectroscopy
The XRF spectrometers can have different sizes and geometry, serving the applications for which they are intended. Some are tabletop instruments equipped with sample chambers and usually provide best energy and spatial resolution and allow, in vacuum analysis, the detection of light elements. However, the samples must be brought to the laboratory and for large objects sampling will be required. Portable versions are small and can be used also on great and geometrically elaborated objects, but usually have less excitatory power (Polese, 2015).

XRF spectrometry is an ideal analytical technique for a modern museum laboratory, since it can be used non-invasively, quickly and accurately to a wide variety of items in its collection, helping diagnose problems and therefore in determining the method of treatment. It can also be used in studying the history of objects, looking for deferred additions, or to determine the artist's material and to determine authenticity. At the same time, XRF is a constantly evolving technique and the scientific staff of the museum can use it according to the needs of the museum.
3 Experimental

3.1 Description of the portable milli-probe XRF spectrometer

The experimental apparatus that was used is a portable milli – XRF spectrometer, designed at the material analysis laboratory of INPP. The spectrometer consists of a low power X-ray tube with the following characteristics: Rh- anode side window (75mm), maximum power 50 W, maximum voltage 50kV, maximum current 1mA, spot size ~2.8 mm, model XTF5011, Oxford XTG, USA. A collimator focuses the beam of outgoing photons and a second one is located at the detector input. At the spectrometer’s head there is a filter selector to improve the quality of the spectral distribution of the source. The filters consist of different materials arranged in suitable ordinance. The other basic part of the spectrometer is the Silicon PIN detector, model XR-100CR Amptek Inc., with a nominal crystal thickness of 500-mm, FWHM 165eV at Mn-Kα. It also includes a photodiode Si-PIN cooled by a double step of a thermoelectric element Peltier and a preamplifier. The detector’s active area is 6 mm². The last part is a digital signal processor (PX4, Amptek Inc.). On the spectrometer’s head two laser spot pointers are aligned to enable the proper sample positioning. Depending on the used filter, the spectrometer offers the detection of Z>19 and trace elements 26 < Z < 50, Z > 72 (high voltage set at 40 kV), whereas in unfiltered mode it enables the analysis of all major and minor elements heavier than magnesium Z > 12 (high voltage set at 15 kV).
3.2 Reference materials

The development of the experimental methodology for the analysis of metallic objects requires the use of standard reference alloys. In this study gold, silver and bronze reference alloys were used, that resemble composition of the ancient ones.

Copper alloys

For the production of the bronze alloys a powder metallurgy technique was used, comprised of the following steps:

- Blending of S and Pb with Cu to minimize subsequent agglomeration.
- Mechanical blending of all components.
- Sieving to break down agglomerated particles.
- “Wet bag” cold isostatic pressing (CIPping) at 1500 bar.
- Welding of cold – compacted bars into 1.5mm thick stainless steel tubes and closure under vacuum.
- Hot isostatic pressing (HIPping) at 1000 bar, 820°C, 2h.

In the bronzes can be expected a micro – scale heterogeneity due to the immiscibility of the Cu and Pb phases, and because the Pb is molten during the HIPping operation, while the Cu remains solid. Because of a capillary action between the Cu grains and Pb, some Pb segregation cannot be excluded. In order to investigate the microstructure and elemental distribution, studies have been conducted by optical microscopy, electron microprobe analysis and nuclear microprobe on the candidate CRMs and on similar materials. These studies reveal grains of Cu – Sn composition with intergranular Pb – rich regions, also containing As, Zn, S and Mn, but no large agglomerations otherwise (Ingelbrecht, et al., 2001).

All standard alloys of the BCR-691 series were analyzed by different laboratories and as a result their typical concentrations (Table I) correspond to the average of the measurements of the individual laboratories.

Table I. Certified concentrations of copper alloys.

<table>
<thead>
<tr>
<th>Element</th>
<th>BCR – A</th>
<th>BCR – B</th>
<th>BCR - D</th>
<th>BCR – E</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.194±0.010</td>
<td>0.099±0.010</td>
<td>0.285±0.022</td>
<td>0.194±0.020</td>
</tr>
<tr>
<td>Pb</td>
<td>7.9±0.7</td>
<td>0.39±0.03</td>
<td>9.2±1.7</td>
<td>0.204±0.018</td>
</tr>
</tbody>
</table>
Silver alloys

The silver alloys used were manufactured at the Institute of Nanostructured Materials, CNR, Research Area of Rome, Italy, within the framework of the PROMET program (Protection of Metals) “Developing new analytical techniques for monitoring and protecting metal artifacts from the Mediterranean region”. According to the report sent by the Institute of Italy, for their preparation pure copper, silver and lead in powder form were used as starting materials. The materials were placed in a graphite crucible and melted in an electric oven. Standard samples were studied using the electron scan (SEM-EDS) X-ray microanalysis method. The electron backscattering technique has shown that in the alloys small accumulations of copper were created as this element does not completely dissolve in the silver. More specifically, it has been established that copper solubility in silver is 8-10% at 780 ° C resulting to these two metals being separated and forming tree structures. The certified elemental concentrations of silver alloys are presented in Table II. (Κανταρέλου, 2016).

<table>
<thead>
<tr>
<th></th>
<th>CNR – 91</th>
<th>CNR – 92</th>
<th>CNR - 141</th>
<th>CNR – 152</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>97±1</td>
<td>92±1</td>
<td>92.5±1</td>
<td>96.5±1</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5±0.1</td>
<td>6.5±0.3</td>
<td>7.5±0.4</td>
<td>3.5±0.1</td>
</tr>
<tr>
<td>Pb</td>
<td>1.5±0.1</td>
<td>1.5±0.1</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Gold alloys

The alloys of gold, supplied by Fischer-Helmut (www.fischer-technology.com), were developed as standard samples for application to X-ray micro – fluorescence (Helmut Fischer, 2012). The elemental concentrations of gold alloys are shown in Table III.

<table>
<thead>
<tr>
<th></th>
<th>ABKMF</th>
<th>ABLLI</th>
<th>ABSBL</th>
<th>ABQAQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>58.58±0.90</td>
<td>74.96±1.11</td>
<td>89.99±1.35</td>
<td>95.04±1.42</td>
</tr>
<tr>
<td>Ag</td>
<td>29.37±0.43</td>
<td>5.04±0.15</td>
<td>5.04±0.15</td>
<td>2.46±0.15</td>
</tr>
<tr>
<td>Cu</td>
<td>12.05±0.18</td>
<td>20.0</td>
<td>4.97±0.15</td>
<td>2.50±0.15</td>
</tr>
</tbody>
</table>
3.3 The Monte Carlo method

The method was introduced in 1949 with the publication of Nicolas Metropolis and Ulam Stan. For the first time though, it was proposed by John von Neumann (after studying the work of Ulam Stan) as a framework for a statistical approach to solve the neutron diffusion problem in fissile materials. Although, in the early 30s, Enrico Fermi - according to the testimony of Emilio Segre, student and partner - developed and applied the Monte Carlo method, without naming it or publishing anything about it, in order to solve many problems, with accurate predictions of experimental results (Metropolis, 1987). The method is used in many areas of physics, such as in the field of computational physics, of high energy physics and elementary particles, etc., but also in mathematics, in biology, in artificial intelligence, in engineering, in economics, etc.

3.3.1 General

The spirit of the method is eloquently recorded in the letters of John von Neumann (on 11/3/1947) to Robert Richtmyer, and (on 21/5/1947) to Ulam Stan (Eckhardt, 1987).

It is a set of numerical algorithms to solve problems of constructing numerical simulation models, such as neutron motion in the wall of a reactor or to study the properties of a large set of elements by a random subset, using random numbers, where random numbers mean numbers derived from a deterministic numerical method that fulfill some statistical randomness properties (Scheid, 1976), such as: speed, period length, uniformity.

The random numbers generators, depending on the application to be used, are distinguished in generators of physically random numbers (Physical Random-Number), the pseudorandom numbers generators (Pseudo-Random) and in nearly random number generators (Quasi-Random).

In the case of physically random numbers there is a difficulty in achieving and reproducing the same sequence, so that possible errors can be detected in the experimental procedure (Warnock, 1987).

In general, the problem to be solved is transformed into a similar probability problem, where the phenomena to be analyzed are characterized by a function, usually using a pseudo – random number generator.
The basic idea of a general Monte Carlo simulation of ED – XRF spectrometers is to predict the response of X – ray imaging and spectroscopy experiments. Monte Carlo can be used for optimizing and designing experimental setups in silico, for dose calculation, estimation of detection limits and quantification. Furthermore, it is useful for simulating the fate of individual photons, for modeling trajectories as consisting of a number of straight steps, and at the end of each step an interaction with the matter will occur, leading to a change in direction and energy (Schoonjans, 2014).

### 3.3.2 The XMI-MSIM software package

In the present work, the XMI-MSIM open source Monte Carlo tool, is employed for the systematic simulation of XRF spectra obtained from the analysis of certified gold, silver and copper alloys presenting compositional profiles that resemble the ones of the most common relevant archaeological alloys.

The reliability of Monte Carlo tools, apart the subjective modelling of the sample composition and structure, depends on the embedded databases of the X-ray fundamental parameters (FPs), the adopted model for the analytical description of the X-ray source excitation spectrum, but also from the good knowledge of set-up geometrical parameters, hardware specifications and operational parameters. Obviously, relevant uncertainties and particularly the adaptation of the widely applied semi-empirical model of Ebel (Ebel, 1999), to describe the emission spectrum of modern low power X-ray tubes, can propagate inconsistencies in the simulated spectrum.

The XMI – MSIM software (Schoonjans, et al., 2013), has been developed by Tom Schoonjans within his PhD. Is an open source tool designed for predicting the spectral response of ED X – ray fluorescence spectrometers based on Monte Carlo simulations.

The fate of individual photons can be simulated, following their paths, by this code and at the same time modeling the interactions that are likely to occur in a multi-layer sample, until they are discarded from the sample or until they escape from the sample and reach the detector. This type of simulation uses the “brute force” method.

The XMI – MSIM program utilizes the xraylib as the only database to retrieve physical parameters. The xraylib contains physical constants relevant to characterize x
– ray matter interactions, which were collected from a variety of datasets. The x-ray lib is used by the program for the following interactions:

- Photoelectric effect: cross-sections, fluorescence yields, transition rates and Coster-Kronig probabilities,
- Rayleigh and Compton scattering: atomic form factor, the incoherent scattering function (Bauters, 2013).

The interface of the XMI-MSIM consists of three pages, each one serve a well-defined purpose. The input files are generated at the first page, where the user defines a number of parameters. The execution of those files is made at the second page and the visualization of the results presents at the third and final page.

At the first page there is a number of frames, each designed to manipulate a particular part of the parameters that govern a simulation Figure 10.

Section General:

1. Output file: the results of the simulation will be saved to this file.
2. Number of photons per discrete line: determines how many photons are to be simulated per discrete line.
3. Number of photons per interval: determines how many photons are to be simulated per interval. Number of interactions per trajectory: determines the maximum number of interactions a photon can experience during its trajectory.

The calculation time is directly proportional to these three final values.
Figure 10. XMI - MSIM on startup – first page.
Section Composition.

In this section you can define the system that will make up your sample, as a stack of parallel layers (defining its composition, thickness and density), and its environment Figure 11.

For the following reasons it is important to add the atmosphere layer to the system:

- Attenuation of the beam and the X-ray fluorescence
- Influences the intensity of the Rayleigh and Compton scatter peaks
- Production of Ar-K fluorescence, a common artefact in X-ray fluorescence spectra, as a result of the excitation by the incident beam within the path seen by the detector.

The order of the layers is defined according to the distance from the X-ray source, so the closest to the source layer is the first layer and all the following have a position which is in an increasingly greater distance from the source.

The Reference layer is considered to be the first layer of the actual sample.

Figure 11. Composition section - adding a new layer.
The computational time will increase according to the number of the elements, especially when dealing with high Z – elements (L and M – lines).

Section Geometry

In this interface you can define the position and orientation of the system of layers, detector and slits. The coordinate system is as follows:

- It is right – handed Cartesian.
- Its origin corresponds to the position of the source.
- The z – axis is aligned with the beam direction and points from the source towards the sample.
- The y – axis defines, along with the z – axis, the horizontal plane.
- The x – axis emerges out from the plane formed by the y- and z – axes, as shown in the following figure.
- **Sample – source distance**: the distance between the source and the Reference layer

- **Sample orientation vector**: the normal vector that determines the orientation of the stack of layers that define the sample and its environment. The z component must be strictly positive
- **Detector window position**: the position of the detector window, the point where the photons are actually detected and terminated by the detector
- **Detector window normal vector**: the normal vector of the detector window, which should be directed towards the sample
- **Active detector area**: this corresponds to the area of the detector window that is capable of letting through detectable photons

![Figure 12. Geometry coordinate system.](image)
- **Collimator height**: is seen as the height of the cone, measured from the detector window to the opening of the collimator, along the detector window normal vector.
- **Collimator diameter**: diameter of the opening of the conical detector collimator. The base of the collimator corresponds to the *Active detector area*.
- **Source-slits distance**: corresponds to the *Sample – source distance*.
- **Slits size**: refers to the dimensions of the beam. These virtual slits do not reduce the beam intensity but they do impact the flux density, which increases when decreasing the Slits size parameters, and vice versa.

In the case of this project the coordinate system is the one shown in Figure 13.

![Figure 13. Coordinate system for this project.](image)

**Section Excitation**

Here is the definition of the X – ray beam that irradiates the sample. The corresponding excitation spectrum may consist of a number of discrete components, each with a horizontally and vertically polarized intensity, as well as a number of parameters that define the type and the aperture of the source. At this section it can be also added a number of continuous interval components, defined through a list of intensity densities, each with their horizontally and vertically polarized components.
For the determination of the number of photons that will be simulated per discrete component and continuous energy interval component at a runtime, the *number of photons per discrete line* and the *number of photons per interval* will be used by the code.

*Sections Beam and Detection absorbers.*

This section refers to the absorbers. Firstly the absorbers that are optionally placed in the excitation path and secondly the absorbers that are optionally placed in the detector path. The first ones will reduce the intensity of the incoming beam and the second ones will reduce the intensity of the photons that hits the detector.

*Detector settings section*

In this interface one can define the settings of the detector and its associated electronics, as follows:

- Detector type: depending on the response function, influenced by several detector and electronics parameters. XMI – MSIM provides two detector types: Si(Li) and Si Drift Detectors (SDD).
- Number of spectrum channels: the number of channels in the produced spectrum
- Live time: the actual measurement time of the simulated experiment, taking into account dead time.
- Detector gain: the width of one channel of the spectrum, expressed in keV/channel
- Detector zero: the energy of the first channel in the spectrum (channel number zero)
- Detector Fano factor: measure of the dispersion of a probability distribution of the fluctuation of an electric charge in the detector.
- Detector electronic noise: the result of random fluctuations in thermally generated leakage currents within the detector itself and in the early stages of the amplifier components. Plays a role in the Gaussian broadening.
- Pulse width: the time that is necessary for the electronics to process one incoming photon.
- Crystal composition: the composition of the detector crystal. Is used for the calculation of the detector transmission and the escape peak ratios.
Results interface

The results from the simulation appear in this interface in a plot canvas like in the following figure, which shows the different spectra obtained after an increasing number of interactions.

![Figure 14. Results panel. Displaying results from simulation of a gold alloy.](image)

X-Ray tube spectrum generator interface

The model that is used in simulations that use X-ray tube is the Ebel model. In the following figure is shown the X-ray tube dialog.

By changing the following parameters one can obtain an approximate model for the corresponding X-ray tube excitation spectrum.

- **Tube voltage**: the voltage in kV at which the X-ray tube is supposed to operate. This will determine the extent of the Bremsstrahlung contribution and through this which XRF lines (discrete energies) will be present in the spectrum.
- **Tube solid angle**: the solid angle in sr (steradian) under which the beam emerges from the X-ray tube. The default value here is determined by the Source-slits distance and the Slits size, taken from the [Geometry section].
- **Electron incidence angle and X-ray tube take-off angle**: X-ray tube geometry parameters
o **Interval width**: the width of the continuous energy intervals of Bremsstrahlung part of the spectrum.

o **Anode**: the material that the tube anode is made of.

o **Window and Filter**: tube filtration materials.

o **Transmission tube**: activating this option effectively places the tube exit-window on the opposite side of the anode with respect to the cathode, thereby operating in transmission mode.

o **Transmission efficiency file**: it is possible to load a two column ASCII file.

---

**Figure 15. X-ray tube (Ebel model).**

**Batching simulations**

In the need of simulating a number of unrelated input files one can use the batch tool, where there are options for each input file separately.

Another use of the batching tool is when one wants to variate one or two parameters in a single input file. Here the user can select either one or two parameters that will be varied during a series of simulations based on the initially selected input-file, as shown in the following figure:
In the results window of the batch simulation is possible to analyze specific elements, lines, regions of interest etc. for individual or cumulative interaction contributions (Schoonjans, 2017).

3.4 XRF spectrum analysis

3.4.1 General

Qualitative information can be provided by the energy of the fluorescence lines, due to that their intensities are related to the amount of the elements in the matrix. In simple cases, quite unequivocal assignments of spectral lines can be made based on $K\alpha$. 

Figure 16. Input parameters for batching mode.

Figure 17. Batching results.
or Lα lines or, in the case that an overlap exists, on Kβ or other L or M lines are checked to confirm or reject a line assignment. One can be informed by qualitative analysis about which elements are present in a sample.

By quantitative XRF analysis one can get information about the absolute quantity of an element present in a sample. Between intensity and concentration quasi linear relationships are found for cases where the concentrations are low. A quick and sufficiently accurate quantitative determination can be made by interpolation on standard curves, obtained in suitable standard samples. The basic principle for quantitative analysis is that the element concentration is proportional to the intensity of the fluorescence lines, which is influenced by many parameters that are taken into account (in the Fundamental Parameters method, FP). Some of these are the photoelectric cross-section, the secondary fluorescence effects, the matrix mass attenuation coefficient and the thickness of the sample.

The FP method consists of mathematical calculations based on theoretical expressions which relate all the above parameters to the fluorescence intensity. The relation between the intensity of an element and the composition of the sample is described by the Sherman’s mathematical equations.

Supposing that the exciting beam is monochromatic with energy $E_0$ and intensity $I_0$ and considering a narrow lane of the sample of surface thickness $dx$ at depth $x$ (g/cm²) from the surface, if the beam incidents on the surface at an angle $\phi_1$, its intensity will attenuate and becomes:

$$I = I_0 e^{-\frac{\mu(E_0)x}{\sin \phi_1}}$$

![Figure 18](image-url)
Where $\mu(E_0)$ is the mass attenuation coefficient for energy $E_0$, which depends on the concentrations of all the elements contained in the sample $\mu(E_0) = \sum_{j=1}^{n} w_j \mu_j(E_0)$. From the ionization of the element $i$ contained within the layer areal density $dx$, characteristic radiation of energy $E_i$ and intensity $dI_i$ is produced given by the following expression:

$$dl_0 = I_0 c_i \sigma_{Z_i}(E_0, E_i) e^{-\mu(E_0) \frac{x}{\sin \varphi_1}} \frac{dx}{\sin \varphi_1},$$

where $c_i$ the concentration of the $i$ element in the specimen, $\sigma_{Z_i}(E_0, E_i)$ is the fluorescence cross-section and is expressed by the following formula:

$$\sigma_{Z_i}(E_0, E_i) = \tau_Z(E_0) p_i(Z) \omega_i(Z) f_i(Z),$$

where $p_i = \frac{\tau_i(E_0)}{\tau_i(E)}$ and $\omega_i(Z)$ is the fluorescent yield for the line of element $i$ being measured. The radiation produced is subjected to further absorption until it reaches the surface of the sample and only the fraction that is contained in the solid angle of the detector ($\Delta \Omega$) and the final intensity of the detected radiation is:

$$dl_i = \frac{\Delta \Omega}{4\pi} \varepsilon_d(E_i) I_0 c_i \sigma_{Z_i}(E_0, E_i) e^{-\mu(E_0) \frac{x}{\sin \varphi_1}} e^{-\mu(E_i) \frac{x}{\sin \varphi_2}} \frac{dx}{\sin \varphi_1},$$

where $\varepsilon_d(E_i)$ is the intrinsic efficiency of the X-ray detector and $\varphi_2$ the angle between the detector and the sample surface. Integrating over the entire thickness of the sample for a monochromatic beam the total intensity of the detected X-rays is expressed by the formula:

$$I_i = \frac{\Delta \Omega}{4\pi} \varepsilon_d(E_i) I_0 c_i \sigma_{Z_i}(E_0, E_i) 1 - e^{-\mu_{tot}(E_0, i) x} \frac{\mu(E_0)}{\sin \varphi_1} + \frac{\mu(E_i)}{\sin \varphi_2},$$

(Kantarélov, 2016). To calculate the intensity emitted by a polychromatic primary radiation, the equation has to be integrated over the tube energy distribution that it is able to produce fluorescence emission from the element $i$ namely from element $i$ absorption edge up to the high voltage value.

In order to convert qualitative information into quantitative data, calibrations are created based on either FP method or empirical calibrations. Another point of interest in qualitative as well as in quantitative XRF analysis is the proper estimation of the spectrum background in order to obtain accurate net count rates. Further on, it is well known that by decreasing the level of spectral background the detection limits become lower (Van Grieken & Markowicz, 2002).
Semi-quantitative analysis can be used in cases where there is no existence of calibration or of a sample of known concentration and it allows the comparison of spectral data from samples in order to obtain information about the relative concentrations of elements from sample to sample.

Matrix effects, that cause secondary fluorescence, cascade effects and scattering of both primary and secondary fluorescence radiation can lead to an overestimation or underestimation of the concentration and the quantitative analysis may become much more complicated (Polese, 2015).

3.4.2 The PyMca software toolkit for XRF spectrum analysis

The PyMca (Python Multichannel Analyzer) is a friendly XRF analysis program, based on the Fundamental Parameters method and largely on instructions by Van Espen and Janssens for the evaluation of X-ray spectra. It was developed at the European Synchrotron Radiation Facility (ESRF), originally from a code that works with the Levenberg-Marquardt algorithm. The programming team with V. Armando Sole (PyMcaCH-ESS) was based on Python's dynamic programming language, which has efficient high-level data structures with a simple and effective approach to object-oriented programming. Basically PyMca Toolkit is a collection of Python tools, based on a set of libraries and development tools of C++. Data analysis routines can be used independently of any graphical interface (Linux, Windows, MacOS X, Solaris etc.) and are freely available for non-commercial use. In addition to the data files, PyMca can also access the shared memory SPEC for tracking extracted data. The mathematical model on which its simulation capacity is based is the Monte Carlo model (Solé, et al., 2007).

The creation of PyMca aims at:

a. Identification of individual elements in complex spectra and quantitative analysis of trace elements with good accuracy.

b. Interpretation of X-ray fluorescence spectra from a variety of samples.

c. Estimation of the concentrations of the elements used in an experiment (Anon., n.d.).

It allows interactive and batch processing of large data sets and of all experimental parameters required for data analysis and corrections for the attenuation. It can handle
many variables, describing the primary beam, the geometry of the installation, the various absorbers between the sample and the detector (such as air, Be window, etc.), the detector parameters and a first approach of the matrix composition to be analyzed. A multilayered object can also be defined in the matrix description. It can be used for monochromatic sources but also for polychromatic ones.

Various parameters can be defined in the configuration window by the Advanced Fitting interface, such as the region to fit, escape, pile-up, scattering peaks, the fitting function, the shape of the peaks. The absorbers, the matrix composition, the source and the detector parameters can be defined here as well. The fluorescence lines can be also selected for each element, in order to fit. The incident beam flux, which is one of the fundamental parameters as the fluorescence line intensities are linearly proportional to its value, can be defined in the tab Concentrations. By using the right configuration file, depending on the analysis case, one can fit the peaks of interest and get results about the net peak areas and the concentrations of the constituents of the sample.

**Figure 19.** PyMca fitting graph on ABKMF gold alloy.

PyMca can handle also a multilayered matrix. It is possible to select up to 10 layers in the MATRIX tab, and for each one to define a deferent composition, density and thickness (Polese, 2015).

### 4 Results

#### 4.1 Characterization of the pXRF spectrometer

Dedicated experiments were performed in order to evaluate different operational parameters and instrumentation characteristics of the XRF spectrometer. The purpose
of these experiments was to improve our knowledge about the portable XRF spectrometer apparatus so that the input data to the Monte Carlo simulation program are as accurate as possible.

4.1.1 High voltage setting

The operational voltage determines the absolute intensity and qualitative characteristics of the spectral distribution of the tube and therefore the intensity of the fluorescent radiation from the sample. Any inaccuracy between applied and displayed tube voltage will result in a systematic shift between theoretical and experimental data (Zarkadas & Karydas, 2004).

In order to test the accuracy of the displayed operational voltage, XRF measurements were carried out on specific samples composed by high purity rare earth element (La and Nd) compounds (oxides). The intensity of the characteristic X-ray peaks depends on the number of continuum photons that have energies just above their absorption edge in this case. In the present experiment the voltage was set to result primary photons with a maximum energy that equals the absorption edge of the element. Then the voltage was increased by 0.1 keV. The tube current was set according to detected counts per second to avoid pile up events at the end of the spectrum that could interfere with the bremsstrahlung scattered tube radiation. In the following figs 20a, b. some characteristic spectra of La and Nd compounds acquired at different voltages settings are presented.

After spectrum analysis by the PyMca software minimum La-K\(\alpha\) and Nd-K\(\alpha\) peaks were detected for the tube high voltages settings of 39.3 kV (for the La sample) and 44.0 kV (for the Nd sample), namely about 0.4-0.5 keV above the corresponding La and Nd K-absorption edges located at 38.894 and 43.538 keV, respectively. This method can’t provide more precision in the evaluation of the high voltage setting since by approaching the threshold K-absorption edge from larger values of the high voltage, less photons are produced capable to produce K-fluorescence emission of the rare earth elements and thus the scattered continuum dominates in the spectrum hamper the detection of their K\(\alpha\) characteristic x-rays. This experiment concluded that if there is tube voltage offset it would be less than about 0.4 kV.
Figure 20. The accumulated spectra of a La (a) and Nd (b) compounds at different high voltages settings are presented.

Figure 21. Intensity of La-K\(\alpha\) and Nd-K\(\alpha\) at different tube high voltages.
4.1.2 Tube current linearity

The variation of the intensity of the fluorescence radiation is affected by the change of the tube current in an analogous way. The expected linearity could be affected in micro-XRF (in particular) spectrometers due to variation of the micro-focusing of the electron beam on the tube anode, or generally due to systematic offset caused by the electronic control unit that was developed in-house. Measurements on a thin target of a Cu compound (CuSx) were conducted, in order to test the tube’s current linearity using unfiltered excitation at 40kV operational voltage. The characteristic copper intensities were recorded for different current values from 100 μA to 500 μA. The counts per second (cps) were normalized to the current of 100 μA.

Table IV. Counts and normalized cps of Cu-Kα at 100-500 μA.

<table>
<thead>
<tr>
<th>Current (μA)</th>
<th>Counts</th>
<th>Standard deviation</th>
<th>Time (s)</th>
<th>cps</th>
<th>Normalized cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>101241</td>
<td>239</td>
<td>1351</td>
<td>74.8 ± 0.2</td>
<td>1.000 ± 0.002</td>
</tr>
<tr>
<td>200</td>
<td>89535</td>
<td>225</td>
<td>601</td>
<td>148.7 ± 0.4</td>
<td>1.986 ± 0.005</td>
</tr>
<tr>
<td>300</td>
<td>89777</td>
<td>226</td>
<td>404</td>
<td>221.9 ± 0.6</td>
<td>2.964 ± 0.007</td>
</tr>
<tr>
<td>400</td>
<td>89779</td>
<td>303</td>
<td>307</td>
<td>291 ± 1</td>
<td>3.893 ± 0.013</td>
</tr>
<tr>
<td>500</td>
<td>89229</td>
<td>302</td>
<td>249</td>
<td>358.0 ± 1.2</td>
<td>4.781 ± 0.016</td>
</tr>
</tbody>
</table>

The normalized counts per second (cps) of Cu-Kα X-ray line versus tube current are presented in the graph below showing very good linearity, however, a slightly increased correction is needed from about 1% to 4% as the tube current increases from 100 μA to 500 μA.
Figure 22. The normalized counts per second (cps) of Cu-Kα X-ray line versus tube current exhibit very good linearity.

4.1.3 Filters characterization in the excitation channel

In the excitation path, a sandwich of two filters (Ni and V) was used. In order to estimate their thickness a scatterer (Polytetrafluoroethylene PTFE, by Goodfellow Cambridge Limited) was measured using filtered and unfiltered excitation. Their respective thicknesses were estimated by the following formula:

\[
\frac{I_{\text{filtered}}}{I_{\text{unfiltered}}} = e^{-\mu_N(E)\rho_N\xi_N} \ast e^{-\mu_V(E)\rho_V\xi_V},
\]

Where: \(I_{\text{filtered}}, I_{\text{unfiltered}}\): the detected intensity of characteristic X-rays using filtered and unfiltered excitation respectively, \(\mu_N, \mu_V\): mass attenuation coefficients (cm\(^2\)/g) of Ni and V and \(\rho_N\xi_N, \rho_V\xi_V\): Ni, V density (g/cm\(^3\)) and thickness (cm).

The ratio of filtered/unfiltered scattered tube radiation versus energy (14-20keV) is presented in the graph on fig.23. Through least squares fitting procedure using the OriginPro 2016 software, the thickness of Ni filter was determined to be equal to: 45.1 ± 0.5 μm. In the fitting procedure the V filter thickness was fixed equal to: 54.0 ± 1.0 μm (as determined before the application of the filters on the instrument through weighing and by measuring its dimensions). The simultaneous fitting of both thicknesses does not converge since their effect is strongly correlated. The measured Ni filter thickness by this method was found in good agreement to the value determined by measuring its areal density (~47.8 μm).
4.1.4 Thickness of the X-ray detector crystal

The detector’s intrinsic efficiency is affected by the thickness of its crystal, dead layer and atomic number and thickness of the contact material as well as for the characteristics of the entrance window. The later (beryllium entrance window) dominates the intrinsic efficiency at incident X-ray energies below ~2 keV, whereas at higher energies the Si crystal thickness plays the most important role. In order to check the reliability of the nominal value of 500 μm provided by the manufacturer (Amptek Inc.), a dedicated experiment was carried out.

XRF measurements of infinitely thin targets with an atomic number within the range 30-39, Zn, Br, Ga, Ge, Rb, Sr and Y, were carried out using an unfiltered tube exciting beam at 48kV operational voltage and 300μA tube current. The thin targets were chosen with an areal density of about ~50 μg/cm² in order to eliminate self- absorption effects that affect the relative efficiency of different emission lines that emanate after the ionization of the same (K) shell, such as the Kα and Kβ emission lines.

The intensity ratio of K- characteristic X-rays of an element, $\frac{i_{Kp}}{i_{Kα}}$, depends on the thickness of the Be window, the contact layer, the Si dead layer and the thickness of the
Si crystal, however for energies above 8 keV only the Si crystal affect the intrinsic efficiency of the Kα, Kβ emission lines detection.

\[
\frac{I_{K}\beta}{I_{K}\alpha} = \frac{f_{K}\beta}{f_{K}\alpha} \cdot \frac{1 - e^{-\mu_{Si}(E_{K}\beta)}\rho_{Si}\xi_{Si}}{1 - e^{-\mu_{Si}(E_{K}\alpha)}\rho_{Si}\xi_{Si}}
\]

where I: detected intensity of characteristic X-rays, \(\mu\): mass attenuation coefficient (cm\(^2\)/g), \(\rho\): Si density (g/cm\(^3\)), \(\xi\): Si thickness (cm), \(\frac{f_{K}\beta}{f_{K}\alpha}\) : the branching Kβ/Kα ratio of the relative radiative transition probabilities.

The above relationship can be rewritten as follows:

\[
F_{z}(\xi_{Si}) \equiv \frac{I_{K}\beta}{I_{K}\alpha} = \frac{f_{K}\beta}{f_{K}\alpha} \cdot \frac{1 - e^{-\mu_{Si}(E_{K}\beta)}\rho_{Si}\xi_{Si}}{1 - e^{-\mu_{Si}(E_{K}\alpha)}\rho_{Si}\xi_{Si}}
\]

The factor \(F_{z}(\xi_{Si})\) is determined experimentally for each target of different atomic number \(Z\) and presents a dependence only on the Si crystal thickness. The branching Kβ/Kα ratio of the relative radiative transition probabilities was calculated based on the xraylib database (Schoonjans, n.d.).

**Table V.** Analytical results from the XRF measurements of different atomic number pure elemental or compound infinitely thin samples (Kα=KL2+KL3 and Kβ=KM2+KM3+KN2+KN3).

<table>
<thead>
<tr>
<th>Element</th>
<th>(E_{K}\alpha) (keV)</th>
<th>(E_{K}\beta) (keV)</th>
<th>(I_{K}\alpha)</th>
<th>(I_{K}\beta)</th>
<th>(\frac{I_{K}\beta}{I_{K}\alpha})</th>
<th>(\frac{f_{K}\beta}{f_{K}\alpha})</th>
<th>(F_{z}(\xi_{Si}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>8.63</td>
<td>9.57</td>
<td>39373±201</td>
<td>5374±79</td>
<td>0.136 ± 0.002</td>
<td>0.137 ± 0.003</td>
<td>0.997 ± 0.025</td>
</tr>
<tr>
<td>Ga</td>
<td>9.241</td>
<td>10.263</td>
<td>39485±65</td>
<td>5595±27</td>
<td>0.142 ± 0.001</td>
<td>0.141 ± 0.003</td>
<td>1.01 ± 0.02</td>
</tr>
<tr>
<td>Ge</td>
<td>9.874</td>
<td>10.98</td>
<td>59584±78</td>
<td>8496±31</td>
<td>0.143 ± 0.001</td>
<td>0.146 ± 0.003</td>
<td>0.974 ± 0.020</td>
</tr>
<tr>
<td>Se</td>
<td>11.207</td>
<td>12.494</td>
<td>43511±156</td>
<td>6295±62</td>
<td>0.145 ± 0.002</td>
<td>0.158 ± 0.003</td>
<td>0.914 ± 0.021</td>
</tr>
<tr>
<td>Br</td>
<td>11.907</td>
<td>13.289</td>
<td>39023±64</td>
<td>5906±27</td>
<td>0.151 ± 0.001</td>
<td>0.164 ± 0.003</td>
<td>0.923 ± 0.019</td>
</tr>
<tr>
<td>Rb</td>
<td>13.373</td>
<td>14.959</td>
<td>95575±317</td>
<td>14643±136</td>
<td>0.153 ± 0.002</td>
<td>0.173 ± 0.003</td>
<td>0.883 ± 0.020</td>
</tr>
<tr>
<td>Sr</td>
<td>14.14</td>
<td>15.833</td>
<td>34036±188</td>
<td>5298±78</td>
<td>0.156 ± 0.002</td>
<td>0.178 ± 0.004</td>
<td>0.872 ± 0.022</td>
</tr>
<tr>
<td>Y</td>
<td>14.931</td>
<td>16.735</td>
<td>36509±194</td>
<td>5525±80</td>
<td>0.151 ± 0.002</td>
<td>0.183 ± 0.004</td>
<td>0.826 ± 0.021</td>
</tr>
</tbody>
</table>
In the following graph, the factor $F_z(\xi_{Si})$ was calculated for the measured elements and for different Si crystal thicknesses. The comparison of the theoretical curves obtained with the experimental results estimated that the Si crystal is according to its nominal value, equal to: 500 ± 25μm.

![Graph showing experimental and theoretical ratios of intensities for different crystal thicknesses.](image)

**Figure 24.** The experimental ratio of the intensities ($I_{K\beta}/I_{K\alpha}$) (stars in the graph) and their theoretical calculations (lines in the graph) for different crystal thicknesses.

### 4.1.5 Energy distribution of the X-ray tube excitation spectrum

Different certified materials, PTFE, PMMA, Plexiglas and Teflon were employed as samples in respective scattering experiments. The operational tube voltage was set equal to 40 kV. The experimental set-up conditions and samples characteristics are reported in detail in the table VI.

**Table VI.** Tube current and samples characteristics used for the scattering experiments (40kV, 2500s)

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Sample description</th>
<th>Current (μA)</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE, Polytetrafluoroethylene, (C2F4)n</td>
<td>square shaped sample thickness: 2.1mm</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td>PMMA, Polymethyl methacrylate, (C5O2H8)n</td>
<td>round shaped thickness: 1.62mm</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>square shaped</td>
<td>300</td>
<td>Yes</td>
</tr>
</tbody>
</table>

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From the different scattered spectra obtained from the samples described in the table VI, the better spectral quality was presented by the PTFE sample, namely has shown better purity and less diffraction peaks influencing the shape of the scattered continuum. Thus, the application of the simulation program XMI-MSIM was carried out with the PTFE sample and the various input parameters are displayed in the following screen shots (Figs 25-27), whereas Fig. 28 shows the calculated spectral distribution by the embedded plugin of the XMI-MSIM software.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample Description</th>
<th>Thickness (mm)</th>
<th>Energy (keV)</th>
<th>Acceptance</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA, Polymethyl methacrylate, (C5O2H8)n</td>
<td>thickness 2 mm</td>
<td>150</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>PTFE, Polytetrafluoroethylene, (C2F4)n</td>
<td>square shaped sample thickness: 1.62mm</td>
<td>30</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 25.** Input parameters at geometry settings.

**Figure 26.** Used absorbers.
The comparison of the simulated and experimental spectrum shown in Fig. 29 showed a rather good agreement. The ratio of the experimental measured continuum over the simulated one is presented in Fig. 30 however, it is also evidenced that an energy correction factor should be introduced. Similarly, the comparison of experimentally measured (using PyMca software) and simulated intensities of Rh-K and Rh-L discrete lines revealed deviations from an ideal matching.

In order to correct for the continuum part of the exciting tube radiation, a polynomial fit was applied on the measured/simulated ration versus energy from 5 to 13keV and a linear fit from 13 to 32 keV (details are shown in Figs. 31 and 32). The fitting relationships are the following:
• 5-13 keV: $y=2.98442-0.29426*E+0.01173*E^2$
• 13-32 keV: $y=1.0343+0.00362*E$

For the anode characteristic x-rays, the following correction factors were introduced: Kα line: 2.09, for the Kβ line: 1.51 and for the Rh-L lines: 2.99.

A modified x-ray tube distribution was introduced next to the XMI-MSIM program into the excitation section and the simulation was repeated. In Figs. 33 and 35 the comparison of measured and simulated spectra for unfiltered and filtered excitation are shown after the adjustment in the x-ray tube distribution. An excellent agreement is observed, whereas in Figs 34 and 36 the obtained ratio of experimental/simulated spectral data confirms the optimum agreement.

![Figure 29. PTFE unfiltered without correction at the distribution.](image1)

![Figure 30. PTFE experimental over simulated ratio before any correction.](image2)
Figure 31. Polynomial fit to the experimental over simulated ratio of the intensity of the continuum distribution (5-13 keV).

Figure 32. Linear fit to the experimental over simulated ratio of the intensity of the continuum distribution (13-32 keV). The spectra data that correspond to the discrete scattered peaks of the tube anode material were removed from the fitting procedure.

Figure 33. PTFE experimental over simulated at 40kV, unfiltered

Figure 34. PTFE experimental over simulated ratio at 40kV, unfiltered.
4.2 Comparison between pXRF measurements and MC simulations (charts, spectra)

Three sets of reference gold (4), copper (4) and silver (4) alloys were measured and respective simulations were performed by employing their respective nominal elemental concentrations as input. The graphs show selected experimental and simulated spectra without any scaling having been applied.

4.2.1 Gold alloys

As gold alloys was used the ABKMF, ABSBL, ABLLI and ABKMF. The chemical composition of the gold alloys is reported in detail at the Table III of the chapter 3.2 Reference materials.
In the following graph, the % difference between experimental and simulated net peak area intensities of the detected characteristic X ray lines are presented, as they were extracted by means of the PyMca Toolkit.
It can be concluded that the simulation overestimates systematically all elements’ major peak intensities between ~5-10%, however, the Au-M intensity is experimentally overestimated by ~10-15%.

4.2.2 Silver alloys

The silver alloys that was used are CNR-91, CNR-92, CNR-141 and CNR-152. The chemical composition of the silver alloys is reported in detail at the Table II of the chapter 3.2 Reference materials.
In the following graph, the % difference between experimental and simulated net peak area intensities of the detected characteristic X ray lines are presented, as they were extracted by means of the PyMca Toolkit.
In silver alloys, the Ag is the predominant component and the Ag-Kα lines are accurately simulated with differences below ~6% between the experimental and simulated intensities. The Cu-Kα lines are mostly overestimated. In CNR-91, where the Cu concentration is 1.5% the Cu-Kα intensity is overestimated by ~21%, whereas for other concentrations the observed differences are less than ~5%. The deviation observed for the Cu-Kα intensity for CNR-91 reference silver alloy could be attributed to a possible inhomogeneity of the Cu distribution within the alloy. Finally, the Ag-Lα lines are underestimated by the simulation for about 20%.

4.2.3 Copper alloys

As copper alloys was used the BCRA, BCRB, BCRD and BCRE. The chemical composition of the copper alloys is reported in detail at the Table I of the chapter 3.2 Reference materials.
In the following graph, the % difference between experimental and simulated net peak area intensities of the detected characteristic X ray lines are presented, as they were extracted by means of the PyMca Toolkit.
The elements Zn and As were analyzed and compared by their respective Kβ lines in order to avoid systematic errors in the analysis of their Kα peak areas due to spectral interferences (Cu-Kβ with Zn-Kα and As-Kα with Pb-Lα). In the cases where the concentration of both elements is below 1% (close to detection limits) the experimental measurements significantly overestimated the simulated counts by ~50-54% for Zn and ~26% for As. The Sn-Kα lines are overestimated by the simulation by ~9.7%. The differences observed regarding the intensity of Cu-Kα line is generally below ~10-14%.

4.3 Discussion

A comparison between the simulated versus experimental peak counts obtained from the analysis of the different reference gold, silver and copper alloys is shown in Fig. 43. The observed deviations at low peak statistics refer to the elements As and Zn which are detected close to the respective detection limits.
Figure 52. A comparison between the simulated versus experimental peak counts obtained from the analysis of the different reference gold, silver and copper alloys. The observed deviations at low peak statistics refer to the elements As and Zn which are detected close to the respective detection limits.

The present study proposed a universal way to optimize the description of tube emission spectrum without requiring dedicated set-up for direct measurements of the tube emission spectrum. The comparison of simulated and experimental characteristic X ray net peak area intensities has shown differences less than about ~20% for major and minor elements in gold, silver and copper alloys. However, it should be noted that for the three types of metal alloys there are rather systematic differences as far as the major elements are concerned. In more specific, the simulated peak areas of Au-La, Ag-Kα and Cu-Kα (in gold alloys), Ag-Kα, Cu-Kα and Pb-La (in silver alloys) and Cu-Kα, Sn-Kα, Pb-La (in copper alloys) are systematically higher up to 10% from the experimental ones. This fact strongly indicates that these differences might originate from a slight (few percent) underestimation of the geometrical parameters that account for incident and detection solid angle calculations. For the rest of detected minor elements, the differences observed can be mostly attributed due to the possible heterogeneity of these elements within the measured alloys (mostly in the case of the Cu and Ag alloys), to the inherent difficulties in the spectrum deconvolution due to various spectral interferences, but also in the relatively large statistical peak uncertainties which are associated with the simulation and spectrum analysis results of the minor elements (with concentration less than 1%).
This is a very promising result strongly indicating that the handling of secondary fluorescence and tertiary enhancement phenomena (which generally are quite significant in metallic alloys), cascade effects (L to M and K to L cascade excitation) are treated rather satisfactory by the XMI-MSIM tool.

5 Monte Carlo XRF simulations of corroded metallic alloys

5.1 Introduction (gold, silver, copper)

The corrosion of metals, a particularly complex phenomenon, is the destruction or the degradation of their properties, caused by the impact of the environment over time. The reactions that occur between a metallic material and its environment are electrochemical and thermodynamically spontaneous. Most of the metals in nature are chemically combined with other elements, such as oxides, sulphides, carbonates or other complexes such as Fe₂O₃, FeS, FeCO₃, FeOOH etc. The metals are in high energy states due to the fact that for their production it is necessary to separate the metal from the oxide with an energy supply. Therefore, the metals tend to return to a lower energy state by releasing energy. This tendency of the metals to return to their primary state, by reacting with the environment is called corrosion.

Corrosion occurs in the natural environment, in the air (existence of oxygen and humidity and in most cases the air is contaminated as well), in the water (the corrosive action is dependent on dissolved oxygen, dissolved salts and gases, microorganisms and dissolved or floating particles) and in the soil (the corrosive action depends on moisture, acidity, dissolved salts, microorganisms, electrical conductivity). Under intense corrosive environment, such as high temperature, chemical substances, humidity, anodic electric charge, contaminated air, etc., the corrosion accelerates. The phenomenon of corrosion takes part on the surface of the metallic object (Adler, et al., 2003).

The electrochemical reactions include reactions between ions and electrons. An anodic reaction is an oxidation, followed by the following reaction: \( M \rightarrow M^{n+} + e^- \), during which electrons are released and the metal dissolves. A cathodic reaction is a
reduction, followed by the following reaction: \( M^{n+} + e^- \rightarrow M \), in which electrons are consumed and metal deposition occurs.

Corrosion occurs in various forms such as:

- Uniform Corrosion
  
  A uniform layer of corrosion products of stable thickness appears throughout the material, as well as a uniform weight loss. It is the cause of the greatest destruction of metals, based on weight. However, it is not so dangerous because its results as well as the lifetime of the metal can be calculated. One type of uniform corrosion is oxidation.

- Localized Corrosion
  
  - Crevice (it can be caused due to the presence of hatches or gaps between metallic or non-metallic and metallic surfaces; the directional force is the difference in potential between the regions of the metal itself exposed to different environments)
  
  - Galvanic (occurs due to the contact of dissimilar metals in corrosive midst, this form of corrosion usually attacks the metal connections or areas where one metal succeeds another; humidity is a determining factor)
  
  - Pitting (autocatalytic process, localized formation of corrosion or selective local dissolution of the surface in depth)
  
  - Intergranular (the areas where the erosion develops are near the granule borders, where local galvanic elements are formed)
  
  - Erosion – Corrosion (the increasing rate of destruction of a material due to the relative movement between the corrosive fluid and the surface of the metal, occurs only in alloys where two or more metals form a solid solution)
  
  - De – alloying
  
  - Stress corrosion cracking (It refers to flaws caused by the simultaneous presence of tensile stress and the corrosive environment) (Adler, et al., 2003).
There are types of corrosion caused by the coordinated action of mechanical and chemical factors:

- Corrosion by abrasion
- Cavernous corrosion
- Corrosion by mechanical stress
- Damage by hydrogen without corrosive action
- Fatigue corrosion
- Thermo – galvanic corrosion
- Bacterial corrosion (biological or microbiological)
- Atmospheric corrosion

**Gold alloys**

Gold alloys are quite prone to corrosion, unlike pure gold. The degree to which they are affected depends on the percentage of gold in the alloy and the percentage of other constituent elements of the alloy. The less gold there is, the more the alloy is prone to corrosion. The gold alloys must be homogeneous, solid and not a mixture of two phases, so they can be more corrosion–resistant, as galvanic effects can be caused between the separated phases (Selwyn, 2004).

Gold alloys that are corrosion–resistant are those whose percentage of gold in the alloy is more than 50%, like the 14kt gold – copper alloy. Alloys with lower gold percentage are susceptible to tarnishing and corrosion, because the corrosion can selectively attack the alloying elements.

One of the reasons that can cause corrosion to a gold alloy is an air environment that consists of contaminants that contain reduced sulphur. If a gold alloy is exposed to outdoor conditions corrosion can be caused by moisture and oxygen that penetrate the gold layer due to some imperfections and affect the other constituents too and continue expanding. In burial conditions the less noble elements are selectively dissolved, which generates a residue rich in gold. The enrichment of the gold alloy in burial conditions is a process that is of interest when investigating archaeological finds, and for this reason a series of simulations is followed for the study of an enriched gold alloy. Moreover,
during those conditions stress corrosion cracking is very possible to occur (Selwyn, 2004).

Silver alloys

When Elemental Sulphur or Sulphur is in a reduced oxidation state, contained in gases or volatile organic sulphides, it can contribute to the tarnishing of silver alloys. Other causes responsible for corrosion are chloride contamination (sodium chloride), from fingerprints or if exposed to a marine environment, and residual chemicals that contain thiourea-based acid cleaning solutions.

During burial conditions, dissolved chloride ions can cause severe corrosion, while reacting with silver to form silver chloride, chlorargyrite. Decaying organic matter contains bromide ions that react with silver to form silver bromide.

Silver alloys can suffer from galvanic corrosion and may result to green corrosion products if it is a silver – copper alloy, referred to as “bronze disease” (Selwyn, 2004).

It has also been reported by many investigators that, in the silver coinage, a severe surface enrichment of silver appears, reaching differences up to 50% between the composition of the core and the surface of the silver alloy. Many hypotheses have been proposed to explain the silver surface enrichment phenomenon: (a) segregation during casting or annealing, (b) deliberate thermal and/or chemical post-treatment such as pickling in acids or blanching, (c) wearing and (d) corrosion. This list should also include post-exavation cleaning with diluted acids (e.g. H2SO4) that are used in order to identify and classify the coins, which can also affect the surface composition (Beck, et al., 2004).

Copper alloys

Cuprite (copper oxide) is the main compound that forms a thin film, too thin to be visible, above copper alloys when they are under indoor conditions. It is colorless unless it is heated, so it becomes red.

Tarnishing (dark colored copper sulphides) appears as the result of the reaction between copper and sulphur contained in the air. Chloride contamination can lead to the formation of green spots, while blue and green spots are formed due to exposure to volatile organic acids (Selwyn, 2004).
When fresh copper alloys are exposed to the air, the corrosion spreads rapidly, because of the water-soluble corrosion projects, which results in the formation of green staining on the adjacent surface. During one year of outdoor exposure, a soluble thin film of cuprite will cover the surface and by the time this film gets thicker, the surface will take purple and blue interference colors and gets darker. After several years, the development of the corrosion will gradually slow and the metal will remain with an adjacent layer of copper oxide on top and mainly with a green layer of copper compounds. More specifically, humid air combined with atmospheric pollutants can lead to a fast-developing corrosion. Bird droppings can also be dangerous for copper alloys. Whereas polluted air that contains sulphur dioxide contributes to the formation of brochantite (Cu₄(SO₄)(OH)₆), copper hydroxide sulphate, other sulphates and antlerite that requires more acidic conditions.

In burial conditions, copper corrosion products emerge, and the surface layer gets coarse. Moreover, red cuprite forms a thin inner layer next to the metal surface and there is also a possibility for copper chloride (nantokite) to appear. Beneath the cuprite layer the original surface of an archeological object may be preserved. Cuprite and malachite are the predominant corrosion products which are identified on copper alloys recovered from the soil. Simulations have been made to investigate the thickness of these corrosion products. Later studies show that the corrosion accelerates during moisture–retaining burial conditions and when the concentrations of soot are high, or phosphate is present in the soil (Selwyn, 2004).

Decuprification (the preferential corrosion of the copper) or destannification (the preferential corrosion of the tin), when copper tin alloys are under burial conditions and consequentially a smooth patina appears to their surface or the surface gets rough. Tin oxides can provoke a black patina.

Green malachite and blue azurite have been identified on many archeological copper alloys that were excavated from their burial environment, which are copper carbonate hydroxides. Also, many chloride containing compounds have been identified, such as nantokite, atacamite (Cu₂Cl OH)₃), paratacamite and many more. On the contrary, there were only two copper phosphate salts that were found on copper alloys of archeological interest: libethenite and sampleite (Selwyn, 2004).
After being excavated, copper alloys come in contact with air and moisture and get contaminated by chloride. Those copper alloys are referred to as “sick” or “diseased”, and this form of corrosion is called “bronze disease”, during which powdery light green spots (copper chloride hydroxides) appear on the surface.

Stress corrosion cracking or uniform corrosion can be caused to copper alloys because of ammonia, by forming soluble complexes with copper and copper ions. The zinc may selectively be removed (dezincification) in copper alloys that contain more than 15wt% zinc and those alloys will consequentially suffer from corrosion. The loss occurs uniformly over the entire surface (“layer – type” dezincification).

Galvanic corrosion can occur to copper alloys when they come into contact with other metals or fasteners (Selwyn, 2004).

5.2 Monte Carlo simulations of corroded metallic alloys

In order to simulate typical cases of corroded metallic alloys, the batching tool of XMI-MSIM program was used, which allows to apply a repeatable Monte Carlo simulation procedure. Various cases are examined and evaluated in order to show how the intensity of the characteristic x-rays’ changes in the presence of specific corrosion products. In the present adopted approach only one parameter of the corrosion product (thickness) varies. Despite the simplification of the hypothesis, the simulation results are expected to provide a deeper understanding on how the spectroscopic XRF signals differentiate from the ones of the un-corroded metallic alloy and to which degree will the non-invasive approach of quantifying the composition of a corroded alloy fail.

5.2.1 Gold alloys

In gold alloys, surface enrichment can take place in burial conditions resulting to a superficial enriched gold layer. As a test sample the gold reference alloy ABLL1 (75% Au, 5% Ag and 20% Cu) was employed in the calculation by assuming a superficial pure gold thin layer of variable thickness up to 20μm.
Observing the graphs, one can notice that from 2μm the Au-M intensity reaches a saturation value, whereas the Ag-Kα and Cu-Kα intensities decrease exponentially with different slopes being attenuated by several orders of magnitude.
If the surface of the alloy is enriched with gold and we proceed to analysis, without taking this enrichment into account, false quantitative XRF results will be obtained. More specifically, a surface enrichment of 0.5μm/1μm will result to a subsequent increase by 9%/16% for the Au-Lα intensity and decrease by 24%/45% for the Cu-Kα and 10%/20% for Ag-Kα intensities, respectively (with reference to the respective values obtained for thickness 50nm). Obviously, principal characteristic x-ray line intensities will be reflected, almost in a proportional manner, to the corresponding quantified elemental concentrations, as an effect of the changes in the intensity of the gold alloy elements.
5.2.2 Silver alloys

Silver alloy CNR-141 with 100% Ag surface layer from 0.005μm to 50μm.

**Figure 58.** The variation of the Ag-Kα counts with respect to the thickness of the silver pure layer formed on the surface of the silver reference alloy CNR-141.

**Figure 59.** The variation of the Ag-Lα counts with respect to the thickness of the silver pure layer formed on the surface of the silver reference alloy CNR-141.

**Figure 60.** The variation of the Ag-Kα/Ag-Lα intensity ratio with respect to the thickness of the silver pure layer formed on the surface of the silver reference alloy CNR-141.

**Figure 61.** The variation of the Cu-Kα counts with respect to the thickness of the silver pure layer formed on the surface of the silver reference alloy CNR-141.

From the graphs it can be observed that the Ag-Kα intensity increases with the increase of the Ag layer thickness, while the Cu-Kα intensity is attenuated exponentially.

An estimation was carried out, for 1.4 and 3.2μm thicknesses, in order to show how much the intensity of the characteristic lines change. The 50nm thickness was set as the reference value. In the case of the CNR-141 silver alloy, a superficial pure Ag layer of 1.4μm/3.2μm thickness will result to an increase by 2.8%/5.2% and 34.9%/63.7% for the Ag-Kα and Cu-Kα characteristic x-ray intensities, respectively. In terms of apparent concentrations, in the case of 1.4μm layer thickness, the XRF quantification will show that the alloy contains 95.1% of Ag (instead of 92.5%) and 4.9% Cu (instead of 7.5%).

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5.2.3 Copper alloys

Three different corrosion products of copper alloys, namely malachite, cassiterite and cuprite were chosen for investigating their influence on the XRF quantification results of the reference copper alloy BCR-E.

Malachite $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

Copper alloy BCR-E with malachite surface layer of thickness from 0.005\(\mu\)m to 100\(\mu\)m.

![Figure 62. The variation of the Cu-K\(\alpha\) counts with respect to the thickness of the malachite layer formed on the surface of copper reference alloy BCR-E](image1)

![Figure 63. The variation of the Sn-K\(\alpha\) counts with respect to the thickness of the malachite layer formed on the surface of copper reference alloy BCR-E](image2)

![Figure 64. The variation of the Sn-L\(\alpha\) counts with respect to the thickness of the malachite layer formed on the surface of copper reference alloy BCR-E](image3)

![Figure 65. The variation of the Sn K\(\alpha\)/L\(\alpha\) intensity ratio with respect to the thickness of the malachite layer formed on the surface of copper reference alloy BCR-E over malachite layer thickness.](image4)

The formation of a malachite layer influences at minimum the Cu-K\(\alpha\) intensity (only 13% increase over 100 \(\mu\)m thickness), whereas the Sn-K\(\alpha\) intensity is more affected showing a decrease of about 50%. However, it is interesting to note that the Sn-L\(\alpha\) intensity is drastically affected presented almost an order of magnitude decrease.
per 10 μm thickness of the malachite layer and subsequently this behavior is also reflected in the variation of the Sn Kα/Sn Lα intensity ratio.

**Cassiterite SnO₂**

In cases where bronzes contain high percentage of tin it can be observed a particularly form of a buried metal corrosion product, where the copper content may be progressively leached out resulting to the formation of cassiterite, i.e. stannic oxide SnO₂. The volume of alloy remains the same and the cassiterite film that is created acts as a protective layer for the alloy.

The simulations were performed for the copper alloy BCR-E with a cassiterite surface layer with thickness from 0.005μm to 100μm.
In the case of a copper alloy with cassiterite as a surface formed corrosion product, it can be observed that while the cassiterite layer thickness is increased, the Cu-Kα intensity is attenuated exponentially, while the Sn-Kα intensity is smoothly increased. The effect of 1.4 µm cassiterite thickness, is that the Cu-Kα counts are decreased by 4.5% producing an apparent Cu concentration of 88.3% instead of 92.4%, whereas the Sn-Kα counts are increased by 32%. What is very characteristic is that the Sn-Lα intensity is abruptly increased and then saturates above a thickness of 10 µm thickness. Thus, the intensity Sn-Kα/Sn-Lα ratio seems to be able to provide a discriminating parameter to identify and estimate the thickness of the cassiterite corrosion layer, in correlation with the net Sn-Kα and Sn-Lα intensities.
**Cuprite Cu₂O**

Copper alloy BCRE with Cuprite surface layer from 0.005µm to 100µm.

**Figure 70.** The variation of the Cu-Kα counts with respect to the thickness of cuprite layer formed on the surface of the reference copper alloy BCR-E

**Figure 71.** The variation of the Sn-Kα counts with respect to the thickness of cuprite layer formed on the surface of the reference copper alloy BCR-E

**Figure 72.** The variation of the Sn-Lα counts with respect to the thickness of cuprite layer formed on the surface of the reference copper alloy BCR-E

**Figure 73.** The variation of the Sn-Kα/Sn-Lα intensity with respect to the thickness of cuprite layer formed on the surface of the reference copper alloy BCR-E

In the case of cuprite as a surface corrosion layer product the overall increase of Cu-Kα intensity over a 100 µm thickness is only by 28%, whereas the Sn-Kα intensity is decreased almost by an order of magnitude (87.5%). Again, as in the case of the malachite corrosion layer, the Sn-Lα intensity is very sensitive to the presence of the surface cuprite corrosion layer showing a decrease of an order of magnitude for every
5 μm. Thus, the intensity Sn-Kα/Sn-Lα ratio seems to be able to provide a discriminating parameter to identify and estimate the thickness of the cuprite corrosion layer, in correlation with the net Sn-Kα and Sn-Lα intensities.

6 Conclusions

In the present diploma thesis, an X-ray fluorescent methodology was developed to determine the distribution of the tube intensity. The spectrometer’s operating parameters were validated: high voltage setting, tube current linearity, thickness of the filters and thickness of the detector. Using the X-ray tube excitation spectrum, that was determined, a comparison between the pXRF measurements and the simulated ones was made. The simulations were performed with the XMI-MSIM simulation program and evaluated shown differences that were less than ~15% for major elements, while for the minor elements or elements that are close to the detection limits the results showed greater deviations.

Concerning the corroded alloys, in the case of a gold alloy, if the surface of the alloy is enriched with gold and the analysis proceeds without taking this enrichment into account, then the wrong results will be obtained, and for example one would have assumed that it would have been a golden-rich alloy. So in order to be able to tell how much the thickness of the enrichment is, in the case of an enriched alloy, by identifying the percentage of decrease or increase of the concentrations of components, the simulations and the analysis that followed in chapter 5 should be performed. The same procedure can be followed in cases of corrosion layers on alloys.

7 Future directions

The validation of the tube emission spectrum and the set-up parameters to simulate accurately measured XRF spectra, through the XMI-MSIM tool, can lead to a more comprehensive input for the PyMca Toolkit for quantitative analysis purposes.

The present study can be extended in the analysis of other materials (Kokiasmenou, et al., 2018) and can be combined with PYMCA software for quantification procedure.
This project was presented in the EXRS conference in 2018 (Papadopoulou, et al., 2018) and another application using this methodology as a principle for Io, was presented in a second project of the laboratory at the same conference (Kokiasmenou, et al., 2018).

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Figure 2. Energy dependence of the mass absorption coefficient μ of several elements (Janssens & Van Grieken, 2004).

Figure 3. Compton scattering (Brouwer, 2010).

Figure 4. Geometry for Compton scattering of X-ray photons (Janssens & Van Grieken, 2004).

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