Universidade de São Paulo
Instituto de Física

Avaliação crítica da quantificação elementar
(incluindo hidrogênio, carbono e oxigênio) por
emissão de raios-X induzidos por prótons,
PIXE, e por fluorescência de raios-X, XRF.

MSc. Juan Manuel Restrepo Arteta

Orientador: Prof. Dr. Manfredo Harri Tabacniks

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Banca Examinadora:

Prof. Dr. Manfredo H. Tabacniks (IFUSP)

Prof. Dr. Nilberto H. Medina (IFUSP)

Prof. Dr. Augusto Câmara Neiva (EP/USP)

Prof. Dr. Javier Miranda Martín del Campo (UNAM/México)

Profa. Dra. Adriana de Oliveira Delgado Silva (UFSCar/Sorocaba)

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A critical evaluation on elemental quantification
(including hydrogen, carbon and oxygen) by
Proton-Induced X-Ray Emission, PIXE, and by
X-Ray Fluorescence, XRF.

MSc. Juan Manuel Restrepo Arteta

Supervisor: Prof. Dr. Manfredo Harri Tabacniks

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Examining Committee:

Prof. Dr. Manfredo H. Tabacniks (IFUSP)

Prof. Dr. Nilberto H. Medina (IFUSP)

Prof. Dr. Augusto Câmara Neiva (EP/USP)

Prof. Dr. Javier Miranda Martn del Campo (UNAM/Mexico)

Prof. Dr. Adriana de Oliveira Delgado Silva (UFSCar/Sorocaba)

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There will certainly be no lack of human pioneers when we have mastered the art of flight. Who would have thought that navigation across the vast ocean is less dangerous and quieter than in the narrow, threatening gulfs of the Adriatic, or the Baltic, or the British straits? Let us create vessels and sails adjusted to the heavenly ether, and there will be plenty of people unafraid of the empty wastes. In the meantime, we shall prepare, for the brave sky-travellers, maps of the celestial bodies – I shall do it for the moon, you Galileo, for Jupiter

*Johannes Kepler
Conversation with the Starry Messenger
An open letter to Galileo Galilei*

Nothing in this world can take the place of persistence. Talent will not; nothing is more common than unsuccessful men with talent. Genius will not; unrewarded genius is almost a proverb. Education will not; the world is full of educated derelicts. Persistence and determination alone are omnipotent. The slogan Press On! has solved and always will solve the problems of the human race.

*Calvin Coolidge
30th President of the United States*

Abstract

Among various analytical techniques, X-Ray Fluorescence (XRF) and Particle-Induced X-Ray Emission (PIXE) allow a highly sensitive, multi-elementary analysis, traditionally used in areas dealing with thin films, mineral, geological, archaeological and biological samples, etc. PIXE and XRF techniques allow quantifying the elemental composition of a sample measuring their characteristic X-rays. In thick homogeneous samples, the determination of the elemental mass concentrations requires prior knowledge of several parameters involved in the interaction of radiation with matter, such as the proton stopping power in the sample for PIXE and the X-ray mass absorption coefficients for both PIXE and XRF, which in turn depend on the elemental concentrations of the sample. In this work we will review and evaluate different methods for determining the mass concentrations that have been developed over the years, obtaining good accuracy in most cases, especially with geological and mineral samples. In samples with low-Z elements, like H, B, C, N, O and/or F, not detected in PIXE nor XRF, the methods to determine elemental concentrations do not have the same level of accuracy, except for major elements. Knowing the concentrations of these major elements, we can extract information of the undetected elements in the samples. We suggest a method for determining the concentrations of trace elements based on the knowledge of at least two major elements, constructing an equivalent sample-matrix constituted by hydrogen, carbon and oxygen with the same X-ray mass absorption coefficients and proton stopping power of the original sample-matrix made of hydrogen, carbon, nitrogen and oxygen, which are the major elements in biological and organic samples. Hence, the trace elements of the sample can be fully analyzed with an accuracy better than 1%. In PIXE analysis, under certain conditions, numerical calculations on thick and homogeneous samples show that on common materials, it is possible to retrieve the hydrogen amount in the sample with acceptable accuracy. The calculation of the uncertainties indicates that the method of determining hydrogen is quite sensitive to instrumental uncertainties, stressing the need for more precise PIXE measurements. A generalization of the method is also considered for all kinds of low-Z sample-matrix, not only biological or organic, having accuracies lower than 10%. Other applications and limitations are also discussed.

Keywords: Particle-Induced X-Ray Emission. X-Ray Fluorescence. PIXE. XRF. Elemental quantification. Hydrogen quantification.

Resumo

Entre várias técnicas analíticas, a fluorescência de raios X (XRF) e a emissão de raios X induzida por partículas (PIXE) permitem uma análise multi-elementar altamente sensível, tradicionalmente usada em áreas que trabalham com filmes finos, líquidos, amostras arqueológicas e biológicas, etc. Os métodos de PIXE e XRF permitem quantificar a composição elementar de um material medindo os raios X característicos. Em amostras homogêneas espessas, a determinação das concentrações de massa elementar requer o conhecimento prévio dos coeficientes de absorção de massa de raios-X e do poder de freamento de prótons na amostra, que por sua vez dependem das concentrações elementares da amostra. Diferentes métodos para determinar as concentrações de massa foram desenvolvidos ao longo dos anos, obtendo boa acurácia na maioria dos casos, principalmente em amostras geológicas e minerais. Em amostras com elementos com baixo número atômico, como H, B, C, N, O e/ou F, não detectados no PIXE nem no XRF, os métodos para determinar concentrações elementares não têm o mesmo nível de acurácia, exceto para os elementos majoritários. Conhecendo as concentrações desses elementos principais, podemos extrair informações dos elementos não detectados nas amostras. É proposto um método para determinar as concentrações de elementos traço com base no conhecimento de pelo menos dois elementos majoritários, construindo uma matriz equivalente para a amostra constituída por hidrogênio, carbono e oxigênio, porém, com os mesmos coeficientes de absorção de massa de raios-X e poder de freamento de prótons que na amostra original constituída por hidrogênio, carbono, nitrogênio e oxigênio, que são os principais elementos em amostras biológicas e orgânicas. Consequentemente, os elementos traço podem ser analisados com acurácia menor que 1%. No caso da análise PIXE, sob certas condições, cálculos numéricos em amostras espessas e homogêneas mostram que em materiais comumente analisados, é possível determinar a quantidade de hidrogênio na amostra com acurácia aceitável. O cálculo das incertezas indica que o método de determinação do hidrogênio é bastante sensível às incertezas instrumentais, enfatizando a necessidade de medidas PIXE mais precisas. Uma generalização do método também é considerada para todos os tipos de amostras com elementos de baixo número atômico, não apenas biológicas ou orgânicas, com acurácia inferior a 10%. Outras aplicações e limitações também são discutidas.

Palavras-chave: Emissão de Raios-X Induzidos por Prótons. Fluorescência de Raios-X. PIXE. XRF. Quantificação Elementar. Quantificação do Hidrogênio.

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Chapter 1

Introduction

*Don't be encumbered by history, just go out and do
something wonderful.*

*Robert Noyce
Intel's cofounder*

The applied physics group with accelerators, GFAA, of physics institute in the University of Sao Paulo has been working since 2000 with different characterization techniques provided by the interaction of positive ions with matter [1]. Particle Induced X-ray Emission (PIXE) is one of the methods belonging to the general Ion Beam Analysis (IBA) (figure 1.1a), which in turn comprises the Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Activation (NRA), Particle Induced-Gamma ray Emission (PIGE), Ion beam-induced luminescence (IBIL), Elastic Recoil Detection Analysis (ERDA), Scanning Transmission Ion Microscopy (STIM) and Secondary Electrons by Ions (SEI). The PIXE method [2] is based on the detection of the X-rays emitted by a sample, when the sample interacts with an incident ion beam. The obtained X-ray spectrum is processed to obtain the areas of the peaks corresponding to the elementary characteristic lines, which in turn are converted to mass concentrations.

The X-Ray Fluorescence (XRF) technique [3], is similar to the PIXE method for X-ray emission but differs from the latter by the excitation mode. In the PIXE method, the internal orbital ionization is due to the Coulomb interaction of an energetic ion with an electron in an electron shell, whereas the XRF ionization is due to the absorption of a photon with energy greater than the ionization energy of an electron shell. XRF is known and used for material analysis since the 1940s and the quantification methods started off with the seminal work of Sherman in 1955 [4], while PIXE is a newer analytical tech-

nique, introduced by Johansson in 1970 [5]. XRF is one of the main outcomes of various characterization techniques provided by the interaction of X-rays with matter, like X-Ray diffraction (XRD), X-ray for medical imaging and X-Ray Photoelectron Spectrometry (XPS) (figure 1.1b).

Figure 1.1: Analytical methods that can be obtained in the interaction of a) protons and b) X-rays with matter.

The PIXE method can use all kind of ions (H^+ , He^+ and also heavy ions, like Pb^+ [6]) but protons are preferably used, mostly due to its deeper penetration in materials and better theoretical understanding of the parameters involved in the interaction with matter (e.g. cross section and stopping power). In this work we limit our analysis to PIXE using a proton beam. Also, the XRF method uses all kind of X-ray sources, mostly polychromatic, like the X-rays given by electron tubes. In this work, we will focus only on monochromatic X-ray sources, like X-rays given by synchrotron light sources, or radioactive sources, which has a better understanding of the parameters involved in the excitation source than the parameters involved in the polychromatic X-ray source.

1.1 Purpose of research

The interaction of protons and/or X-ray beams with matter will produce elemental characteristic X-ray lines of the elements in a sample. Usually, elements with $Z > 10$ can be detected in vacuum conditions, or $Z > 12$ in air conditions. Figure 1.2 shows an X-ray spectrum obtained using 2 MeV of protons in PIXE and an X-ray spectrum taken with a 22 keV of monochromatic X-ray beam in x-ray spectroscopy [7] of a sediment sample. In these spectra we can see that every peak represents a characteristic X-ray line of an

element. Thus, PIXE and XRF can be used to identify the elements present in a sample.

Figure 1.2: X-ray spectra of sediment sample obtained by a) 2MeV protons and b) 22keV primary monochromatic X-ray beam. Figure taken from [7]

The X-ray peaks have a total number of counts N_i proportional to the elemental mass concentration C_i ¹ of the corresponding element and a function Y_i that also depends on C_i and the concentration of all other elements in the sample $C_j, C_k...$:

$$N_i \propto C_i Y_i(C_i, C_j, C_k...) \quad (1.1)$$

The $Y_i(C_i, C_j, C_k...)$ factor represents the correction effects due to the sample-matrix². There is no possible way to isolate, through simple algebraical methods, the mass concentration C_i from the sample-matrix effects, except for some simple cases in XRF. Along the years, many methods have been developed to determine the concentrations, dealing directly with the term $Y_i(C_i, C_j, C_k...)$, or trying to reduce its influence in order to maintain the proportionality between the total number of counts and the concentrations. In geological, mineral or alloy samples, these methods reached the objective with an accuracy of about 1%. In biological and organic homogeneous thick samples, or more general,

¹A concentration can be expressed in several units in X-ray spectroscopy. The mass concentration: elemental mass/total sample mass $\times 100$ is a common unit. Major elements in a sample are defined by all elements with a concentration larger than 1%, and trace elements are all elements with a concentration lower than 1%. A trace elements is commonly expressed in parts per million (ppm), where, 1000 ppm=0.1%. Ultratrace elements are expressed in parts per billion (ppb) where 1ppm=1000ppb. Other common unit of concentration is the atomic percentage which is the number of atoms of the analyte in a molecule divided by the total number of atoms of the molecule. For example, in H₂O the mass concentration of hydrogen is 11.1% and the atomic percentage is 66.6%

²A sample-matrix is the composition of the sample, sometimes expressed stoichiometrically, like H₂O or by its mass concentration H_{11.1%}O_{88.9%}. Different textbooks refers the sample-matrix with the simple term matrix, but we prefer to call it sample-matrix in order to avoid any confusion with the math expression.

in samples in which the presence of low-Z elements, defined as all elements with $Z < 11$ (not detected by X-ray detectors), is unknown, these methods have not improved their analytical accuracy in the last years. Recent textbooks [8], [9], [10], [11] refer to the same methods developed through the main 20th century textbooks, [2], [3], [12], [13], [14].

In this work we present an iterative method for determining an equivalent low-Z sample-matrix of a sample with the final purpose of reproducing the same $Y_i(C_i, C_j, C_k \dots)$ factor of the original sample-matrix, knowing the concentrations of the major elements and, then, allowing to determine the mass concentrations of the trace elements and analyzing other consequences of the method, like the possibility of obtaining the hydrogen concentration in PIXE.

1.2 Structure of the work

This work is divided into two parts. The first part describes the state of the art of the methods for determining the concentrations in PIXE and XRF. In chapter 2 we describe the fundamentals of the production of characteristic X-rays due to the interaction of protons and photons with matter, focusing on the fundamental parameters involved in these interactions. Then, we show several Matlab codes for the determination of the sample-matrix effects in PIXE and XRF in chapter 3. These codes, in chapter 4, are applied to evaluate the most referenced methods for elemental quantification, analyzing the accuracy of every one of these methods. Some contributions by the author are already shown in this first part, like the Matlab code for the analysis of the current methods of elemental quantification.

The core of this work begins in the second part, which constitutes the original contribution by the author. In the chapter 5 we suggest a method for the determination of trace elements in a sample with a high concentration of low-Z elements. Finally, in chapter 6 we present the application of this method to a large number of common samples, mostly standard reference materials, or organic samples, discussing the advantages and limitations.

Part I

Literature review

Chapter 2

Fundamentals of characteristic X-ray production by a radiation source

If it's a lie, then we fight on that lie

David Simon

The Wire (TV show)

X-ray and swift protons interact with atomic electrons in a sample primarily through photoelectric absorption, in the case of photons, and Coulomb forces, in the case of protons. In this chapter we will show how these interactions will produce X-ray fluorescence from a sample and how the energies and intensities of these X-rays are related with the elemental composition of the sample.

2.1 Characteristics X-rays

Quantum mechanics [15] states that the electrons in an atom, in their ground state, are ordered following a series of quantum numbers: The principal quantum number $n = 1, 2, 3, \dots$, also expressed with the letters $K, L, M, \dots$, the orbital quantum number, l , which varies from 0 to $n-1$, and the angular momentum number j which has the value $j = |l + s|$, where s is the electron spin $s = \pm 1/2$. The left side of figure 2.1 shows the order in decreasing binding energy followed by the electrons in an atom. The binding, or ionization energy is the minimum energy required to release an electron from its shell. Every shell

has a subshell called *s*, from *sharp* ($l = 0$), *p*, from *principal* ($l = 1$), *d*, from *diffuse* ($l = 2$) and *f*, from *fundamental* ($l = 3$).

An atom is in an excited state when an electron in any shell has been ejected from its shell, occupying a higher shell, or leaving the atom. Quantum theory of radiation [16] states that an atom in an excited state returns to its ground state spontaneously such that if an electron in a shell is ejected, some other electron from any other higher shell will occupy its vacancy.

Figure 2.1: Main electronic transitions, including their common designations. The most probable transition in every shell are shown in thick arrows.

2.1.1 Transition probabilities and transition energies

Not all electrons from a higher subshell can occupy a vacancy in a lower subshell. A transition, also called a line, between subshells follows the dipole transition rules, $\Delta l = \pm 1$ and $\Delta j = 0$ or ± 1 , in the dipole approximation, and its transition probability is calculated applying the Fermi golden rule to the electric dipole interaction [15].

The *K*, *L* and *M* transitions are all transitions from a higher subshell to some subshell of the *K*, *L* and *M* shells respectively¹. Figure 2.1 shows the most probable transitions

¹The spectroscopy notation adopted here is the Siegbahn notation introduced by [8] calling the most intense lines α transitions, followed by the less intense β transitions and so on. Modern spectroscopy,

for each shell. Other electric dipole transitions can occur (always satisfying the transitions rule) but its probability is lower than 1% of the most probable transition. Also, quadropole transitions and magnetic dipole transitions (with their own transition rules) can occur, but with a lower probability than the minor electric dipole transitions [17].

During a transition, an atom emits a photon with energy equal to the difference between the energy of the original subshell and the energy of the final subshell. These energy differences are calculated, in a first approximation by the Moseley law [18]. The most accepted X-ray energies² are given by Bearden in [19].

Some transitions emit photons with similar energies, and common solid state detectors detect these X-ray lines as a single line. So, the K_{α_1} and K_{α_2} lines are usually expressed as a K_{α} transition, and the L_{α_1} and L_{α_2} lines are expressed as a L_{α} transition and so on.

Figure 2.2 shows the X-ray energy of the most intense X-ray lines as a function of the corresponding atomic number. We can see that the X-ray energy region between 1 and 20 keV is the region where we can detect all K lines of elements from $Z= 11$ to 40, L lines of elements from $Z >30$ and M lines of elements from $Z >62$. This is the energy range mostly used in X-ray spectroscopy, since all elements can be measured with a common solid state detector, and also it is the range we will work in this thesis, unless otherwise stated. Also, we will focus on K transitions mostly. All biological and organic samples studied here have elements which K lines are the only lines detected, which are the $Z < 40$ ones. Heavier elements, which emit L lines in the same energy region than the K lines of those $Z < 40$ elements, could be presents but only in a few parts per million.

In general, the transition probabilities W are usually expressed in terms of the ratio between several of them. For example, we define the transition ratio b_i for a K transition of an element i :

$$b_i = \frac{W_{K_{\alpha}}}{W_{K_{\alpha}} + W_{K_{\beta}}} \quad (2.1)$$

This last term is obtained from [20] and [21]. This ratio increases with the atomic number Z .

like the notation given by the International Union of Pure and Applied Chemistry (IUPAC) recommends showing explicitly every subshell involved in the transitions. For example, K_{β_1} line is called the M_3K_1 line.

²Some works, due its historical application in crystallography, classify the X-ray lines according to their wavelength in angstroms ($\text{\AA}$). In this work we will use keV units, where the conversion follows the formula $E_x = hc/\lambda$, where E_x is the X-ray energy line, h is the Planck constant, c is the speed of light and λ is the wavelength of the X-ray line.

Figure 2.2: Energy of the most intense K , L and M lines as a function of the atomic number

2.1.2 Fluorescence yield

An emitted photon in the transition to the K shell can be absorbed by an electron of another L or M shell. If this electron is ejected it is called an Auger electron [22]. The vacancy generated by this Auger electron is filled by another electron from an upper shell emitting a new photon, called a satellite, or diagram, photon. As a consequence of the Auger electrons, the number of photons released by an atom is smaller than the photons produced by the ionizations. The probability that the photon produced in the ionization is released by the atom is known as the fluorescent yield. The fluorescence yield ω_i for K transitions of an element i , is:

$$\omega_i = \frac{I_K}{n_K} \quad (2.2)$$

where I_K is the total number of characteristic X-rays emitted by the atom and n_K is the total number of ionizations created in the K shell.

The fluorescent yield of an element i with atomic number Z_i for the K transition has been calculated by the Bambynek polynomial fit in [23] to experimental values:

$$\left(\frac{\omega_i}{1 - \omega_i} \right)^{1/4} = \sum_{k=0}^3 b_k Z_i^k \quad (2.3)$$

whose constants are $b_0 = (0.15 \pm 0.1) \times 10^{-2}$, $b_1 = (3.27 \pm 0.044) \times 10^{-2}$, $b_2 = 0$ and b_3

$=(0.64 \pm 0.07) \times 10^{-6}$. Different experimental b_k values have been published later, as in [24], in [25] and in [26].

In figure 2.3 we can observe the fluorescence yield of an element i as a function of Z for the K transitions. This fluorescence yield increases with the atomic number.

For L and M transitions, the ionization induces, in addition to Auger photons and electrons, non-radiative transitions, called Coster-Kronig [27], when an electron makes a transition from one subshell to another subshell without emitting radiation. Then, every subshell of L and M have its own fluorescence yield.

Figure 2.3: Fluorescence yield for the K line as a function of the atomic number. Calculated with equation (2.3).

2.2 Interaction of proton beams with matter

As described before, a proton passing through matter interacts with the bounded electrons in the atoms through the Coulomb forces. The energy transferred by the proton to the electrons (or the whole atom) makes the proton lose energy at every encounter, in such a way that the proton ends up losing all its energy at some point. The parameter that describes this energy loss is the stopping power.

2.2.1 Stopping power

The linear stopping power S of protons in a given material is defined as the energy loss rate of the proton, with energy E_p , with respect to the distance that it passes through:

$$S(E_p) = -\frac{dE_p}{dx} \quad (2.4)$$

This variable has units of force and has a negative sign, so it can be seen microscopically as a friction force acting on the proton inside the material.

The Bethe-Bloch equation, [28], describes the proton energy loss through the material and it is a good estimate for proton energies in the range of 1-5 MeV. Later on, successive corrections were made [28] and [29], letting the final form of the stopping power as:

$$S(E_p) = -\frac{4\pi e^4}{m_e v^2} N Z \left(\ln \frac{2m_e v^2}{\langle I \rangle} - \ln \left(1 - \frac{v^2}{c^2} \right) - \frac{v^2}{c^2} - \frac{C}{Z_2} - \frac{\delta}{2} \right) \quad (2.5)$$

where v is the velocity of the proton and e its charge, N and Z are the density and the atomic number of the atoms in the material, and m_e and e the rest mass and the electron charge, C and δ are factors dealing with shell corrections and density effects. The parameter $\langle I \rangle$ represents the average excitation and ionization energy of the target and it is obtained experimentally [28]. The stopping power increases with the atomic number of the target element.

The proton is stopped mainly due to the electrons of the material. There is still a small contribution to the stopping power due to the nucleus of the atoms, but the region in which we are working, $E_p > 100$ keV, the electronic stopping power is several orders of magnitude larger than the nuclear stopping power, making the nuclear stopping power negligible, as shown in figure 2.4.

Figure 2.4: Proton stopping power of a) carbon and b) titanium as a function of the proton energy. Data obtained from PSTAR [30]

2.2.2 Stopping power formulations

Various approaches and corrections of the proton stopping power have been developed along the past years. Many of these approaches focus on the low (<10 keV) or intermediate energy range (≈ 100 keV), such as the Lindhard-Scharff-Schiöt [31], or the Anderson-Ziegler [32].

For proton energies between 25 keV and 10 MeV the following parametrization of the proton stopping power of an element i , $S_i(E_p)$ can be used, based on a fit of the experimental data available [33]:

$$\begin{aligned}
 S_i(E_p) &= \frac{602.22}{A_i} \left(\frac{1}{S_L} + \frac{1}{S_H} \right)^{-1} \\
 S_L &= aE_p^b + sE_p^d \\
 S_H &= \frac{e}{E_p^f} \ln \left(\frac{g}{E_p} + hE_p \right)
 \end{aligned} \tag{2.6}$$

where $a - f$ are tabulated variables that depend on each element and A_i is the mass number of the element. Successive updates of these variables are comprised in the SRIM (The Stopping and Range of Ions in Matter) [34] program derived from a database of more than 27,000 experimental values for all proton energy ranges and also other ions on different targets.

Similar to SRIM database is the PSTAR code [30]. This code provides stopping powers for 74 materials, of which 25 are elemental targets, in the range from 1 keV to 10 GeV,

based on experimental fits as well. In this work we use the 1985 Ziegler polynomial and the PSTAR fit for calculating the proton stopping power in the range of 25 keV - 10 MeV. The discrepancies between these two databases are shown in figure 2.5. We can see that these discrepancies are higher in the low and intermediate proton energy region ($E_p < 100\text{keV}$), but in our region of interest $E_p > 500\text{keV}$, the discrepancies are less than 5%, especially when $E_p > 1\text{ MeV}$.

Figure 2.5: Relative deviation between PSTAR [30] and Ziegler [33] proton stopping power databases for different elements.

2.2.3 Bragg additive rule and units

Other stopping power units can be more convenient. Dividing the stopping power by the density of the sample, the mass stopping power is obtained:

$$S_\rho(E_p) = -\frac{1}{\rho} \frac{dE_p}{dx} \quad (2.7)$$

This unit can be used to calculate the stopping power for compounds and mixtures. For a chemical composition of N elements with mass stopping powers $S_{\rho i}$ and mass concentrations C_i the combined stopping power can be calculated:

$$S_\rho(E_p) = \sum_i^N C_i S_{\rho i} \quad (2.8)$$

If the stopping power is divided by the atomic density N_ρ :

$$\epsilon_S(E_p) = -\frac{1}{N_\rho} \frac{dE_p}{dx} \quad (2.9)$$

the stopping power of the compounds is obtained as a sum of its stoichiometric form:

$$\epsilon_S(E_p) = \sum_i^N n_i \epsilon_{Si} \quad (2.10)$$

where n_i is the stoichiometric weight of the element in the sample. This last expression is called the Bragg rule for the stopping power and has been proved experimentally for a large variety of cases in solid samples with discrepancies of less than 3% [35].

2.2.4 X-ray cross section by protons

The proton cross section for X-ray production, $\sigma_{pi_{K\alpha}}(E_p)$, for the K_α transition of an atom i is the product of three probabilities: The probability that the proton will produce an ionization in the K shell, called the ionization cross section $\sigma_{pi}(E_p)$; the probability that this ionization results in an emission of a photon, the fluorescence yield ω_i (Equation (2.3)) for the K line; and the probability b_i that this photon corresponds to the transition K_α (Equation (2.1)):

$$\sigma_{pi_{K\alpha}}(E_p) = \omega_i b_i \sigma_{pi}(E_p) \quad (2.11)$$

Several models are used to calculate the ionization cross section e.g. Born plane wave approximation (BPWA) [36], binary encounter approximation [37] and the semiclassical approximation [38] are among them. The most used model of the ionization cross section is the ECPSSR theory [39], which considers the deflection of the ions due to the Columbian field by the nucleus (C), Perturbed Stationary State (PSS), relativistic effects (R) and the loss of the proton energy (E).

Several semi-empirical functions fitted on experimental data as a function of the proton energy have been developed. All of them have the general polynomial form:

$$\ln \sigma_{pi}(E_p) u_i^2 = \sum_{k=0}^5 d_k (\ln(E_p/\lambda_m u_i))^n \quad (2.12)$$

where u_i is the ionization energy of the of the atom i for the K transitions, λ_m is the ratio between the proton mass and the electron mass and E_p is the proton energy. The first

experimental fit was proposed by Johansson in [40], having the advantage that it is valid for all elements. Subsequently, values of d_k have been parameterized as a function of the atomic number, as in [41], or [42]. This last reference is shown in figure 2.6. The ionization cross section continues to be intensively studied, adding new experimental data aiming better terms d_k of the polynomial in equation (2.12) [43] and the investigation of these data is still in progress, as shown in [44]. Figure 2.7 shows the difference, in percentage, between three common fitted polynomials and the ECPSSR theory for protons of 2 Mev, where we can see that for this energy, the discrepancies are lower than 18%. Notice that the fit provided by Kahoul shows discontinuities with respect to the atomic number. Previous ionization cross section fits also correct for the atomic number, but the Kahoul ionization cross section treats every atom separately.

Figure 2.6: Fitted cross sections on experimental values in the form σu_K^2 vs $E_p/\lambda u_K$ for different atoms. Figure taken from [42]

Figure 2.7: Relative deviations between the ionization cross section of different fitted polynomials [40], [41] and [42] and the ionization cross section calculated by the ECPSSR theory [39] for 2 MeV protons as a function of the K_α energy of the correspondent atom.

2.3 Interaction of X-ray with matter

Considering the energy range for X-rays between 1 keV and 20 keV defined in section 2.1.1, three main phenomena can occur in the interaction of X-rays with matter [45]. First, the photon can be totally absorbed by an electron in an electron shell, a phenomenon known as the photoelectric effect, being responsible for the electronic transitions. Also, the photon can be scattered by quasi-free electrons, so that the photon energy is partially absorbed by the electron and partially scattered with less energy than the incident photon, a phenomenon known as Compton effect, or inelastic scattering. Finally, the Rayleigh, or elastic, scattering occurs when the photons are scattered by the bounded electronic orbitals without ionizing the atom.

2.3.1 Photoelectric cross section

In the interaction of X-rays with matter, the phenomena responsible for the transition of an electron from an subshell to another subshell is the photoelectric effect, in which all the energy of the photon is totally absorbed by the atom, letting an empty vacancy. The production of this absorption is described by the photoelectric cross section $\tau(E_x)/\rho$, or

photoelectric coefficient, and the most simple approximation as a function of the element i with atomic number Z_i has the form [46]:

$$\frac{\tau_i(E_x)}{\rho_i} \propto \frac{Z_i^4}{E_x^3} \quad (2.13)$$

This relation shows that the photoelectric cross section decreases as the X-ray energy increases. When the X-ray energy reaches the ionizing energy of some atomic orbital, the photoelectric coefficient undergoes a discontinuity, the so-called absorption edge. The photoelectric coefficient depends on the sum of the probabilities of ionizing each orbital through the photoelectric effect. These effects are shown in figure 2.8.

The ratio between the ionization probability of the K shell with the probability of total ionization is called the jump ratio:

$$J_i = \frac{\tau_K}{\tau_{(K+L+M)}} \quad (2.14)$$

and can be parameterized, in the case of K transitions, as [47]:

$$J_i = 1 - \frac{1}{\frac{125}{Z_i} + 3.5} \quad (2.15)$$

The total cross sections of photons produced by a K_α transition of some element i is the photoelectric coefficient multiplied by the probability of ionizing that orbital, J_i (equation (2.14)), by the probability of emitting a particular suborbital b_i (equation (2.1)) and by the fluorescence yield ω_i (equation (2.3)), resulting in:

$$\sigma_{xi}(E_x) = \frac{\tau_i}{\rho}(E_x)\omega_i J_i b_i \quad (2.16)$$

This last term is the XRF equivalent to the proton cross section $\sigma_{pi}(E_p)$ defined in equation (2.11)³.

2.3.2 Compton and Rayleigh cross section

Photons, when interacting with a free electron, are scattered transferring a part of their energy to the electron such that the change in the photon wavelength $\Delta\lambda$ with respect to the initial photon wavelength λ_0 follows the Compton equation, $\Delta\lambda = \lambda_0(1 - \cos\phi)$ [15],

³Notice that the proton cross section units are in cm^2 while the photon cross section are in cm^2/g . We keep the units managed in both PIXE and XRF databases, and the conversion formula follows $\sigma_{\text{cm}^2/\text{g}} = N_0/A_i \sigma_{\text{cm}^2}$

where ϕ is the scattering angle.

The Compton cross section is calculated using the Klein-Nishina equation [12], whose cross section is calculated assuming photons reaching free electrons at rest.

$$\frac{d\sigma_{KN}}{d\Omega} = \frac{r_0^2}{2} \left(\frac{E_c}{E_0} \right)^2 \left(\frac{E_0}{E_c} + \frac{E_c}{E_0} - \sin^2 \phi \right) \quad (2.17)$$

where r_0 is the electron radius, E_c is the energy of the scattered photon and E_0 is the electron rest energy, 511 keV⁴.

Rayleigh scattering occurs when the photon are elastically scattered from bound electrons, the cross section is calculated by [12]:

$$\frac{d\sigma_{KN}}{d\Omega} = \frac{r_0^2}{2} (1 + \cos^2 \phi) F^2 \quad (2.18)$$

where F^2 is the atomic structure factor, dealing with phase differences between the waves scattered.

Rayleigh and Compton scattering are easily identified in a X-ray spectrum. Rayleigh scattering has an X-ray energy equal to the incident X-ray energy, E_{x0} , and Compton scattering has an X-ray energy equal to:

$$E_c = \frac{E_{x0}}{\frac{E_{0x}}{E_0}(1 - \cos\phi) + 1} \quad (2.19)$$

2.3.3 Mass absorption coefficient

The absorption of a radiation with intensity I_0 passing through a distance x in a sample is described by the Beer-Lambert equation [15]:

$$I = I_0 e^{-\frac{\mu}{\rho} \rho x} \quad (2.20)$$

where I is the final intensity of the radiation, ρ is the density of the sample and μ/ρ is called the mass absorption coefficient, whose value is the sum of the cross sections corresponding to the photoelectric coefficient (equation (2.13)), Compton cross section (equation (2.17)) and Rayleigh cross section.

$$\mu(E_x)/\rho = \tau(E_x)/\rho + \sigma_{Com}(E_x) + \sigma_{Ray}(E_x) \quad (2.21)$$

⁴The classical limit of the Compton cross section leads to the Thomson cross section in the framework of classical electrodynamics.

In our X-ray energy range $1 < E_x < 20$ keV, the mass absorption coefficient for the photoelectric effect $\tau(E_x)/\rho$ predominates, as shown in figure 2.8 in the case of lead. Compton and Rayleigh cross sections are negligible, except for energies $E_x > 15$ keV where the Compton cross section can reach 20% of the total mass absorption coefficient, especially in low-Z sample-matrices.

Figure 2.8: Mass absorption coefficients of a) carbon b) iron c) zirconium d) lead with their respective photoelectric, Rayleigh and Compton cross section, as a function of the X-ray energy. Notice the absorption edges of K, L and M shells. Data taken from [48]

2.3.4 Additive rule for the mass absorption coefficient

For a chemical compound or a mixture of n elements with mass absorption coefficients μ_i/ρ_i and mass concentrations C_i , the total mass absorption coefficient can be approximated using:

$$\frac{\mu}{\rho} = \sum_i^n C_i \frac{\mu_i}{\rho_i} \quad (2.22)$$

which is similar to the Brag rule for the stopping power. This additive rule is verified experimentally within 10% of agreement [49], [50].

2.3.5 Mass absorbtion coefficient databases

There are two widely used mass absorption coefficients databases: XCOM [51] and FFAST [24], which are based on interpolations of experimental data. The relative deviations between them can reach 15% in our range of elements and energies, especially near absorption edges, but, in most cases, the relative deviations are less than 5% as shown in figure 2.9. Both databases provide also photoelectric and Compton cross section separately.

Figure 2.9: Relative deviations in mass absorption coefficients between XCOM and FFAST Taken from [48]

2.4 X-ray detection efficiency

The probability that a photon passing through a detector will be counted is the intrinsic detector efficiency. Silicon detectors are the most common detectors used in X-ray spectrometry. Its efficiency can be calculated by the following equation: [2]:

$$\epsilon_i = \exp \left(- \sum_{k=1} \frac{\mu_k(E_i)}{\rho} t_k \right) [1 - \exp(-\frac{\mu_{Si}(E_i)}{\rho} t_{Si})] (1 - f_{esc}) \quad (2.23)$$

where $\mu_k(E_i)/\rho$ is the mass absorption coefficient of various materials k in front of the silicon crystal, absorbing the photons before it enters the detector, for the K_α line of the element i , with energy E_i , t_k is the thickness of these materials, which may be a beryllium window that separates the crystal from the ambient, a silicon dead layer that does not detect X-rays, the air that separates the sample from the detector, a gold contact layer (typically $\approx 200\text{\AA}$), a thin water layer condensed along the years of operation [2] and the filters that can be used between the sample and the detector. $\mu_{Si}(E_i)/\rho$ is the mass absorption coefficient of the silicon crystal for the energy E_i and t_{Si} is its thickness. f_{esc} is the probability of loss of events due to the silicon X-ray escape [52]. Other corrections to equation 2.23 can be added, like detector surface or dead time correction [45].

An example of a typical efficiency curve is shown in figure 2.10 of two silicon detectors: one detector with 100 μm crystal thickness and 50 μm beryllium window and other detector with 500 μm from the crystal and 12 μm from the beryllium window. A typical silicon death layer of 1 μm is considered. The smaller the beryllium window thickness, the greater the element detection efficiency with $Z < 20$. Also, the higher the thickness of the silicon crystal the higher the efficiency for elements larger than $Z > 30$. Notice the Si K absorption edge is clear between $Z=14$ and 15.

Figure 2.10: Calculated efficiency of two 500 μm and 100 μm thick silicon detectors and 12 μm and 50 μm beryllium windows respectively for the K_α line of the corresponding atomic number. The discontinuity is the effect of the absorption of Si K_α line due to a typical 1 μm dead silicon layer

2.5 X-ray primary production equations

Hitherto we showed how characteristic X-rays are produced on the interaction of proton beams and photons with matter. In the following subsections we will show how these X-rays are related to the elemental concentrations of a sample. Figure 2.11 shows a typical diagram of a proton or X-ray beam interacting with a sample, with beam incident angles ϕ_p or ϕ_x , and X-ray take-off angles θ_p or θ_x with respect to the surface. In this section, we will describe the general equations for the primary X-rays produced. The term primary refers to the production of X-ray due to the original beam. Other ways of X-ray production due to enhancement effects will be described in section 2.7.

From here on, unless otherwise stated, we will refer the detection of an element due to its K_α peak.

Figure 2.11: Geometry of a typical PIXE/XRF setup

2.5.1 PIXE primary equation

The general equation for the PIXE total number of counts⁵, N_{pi} , due to the X-ray production of an analyte i of its K_α line, with energy E_i , in a homogeneous and smooth sample due to a proton beam of energy E_{p0} is [2]:

⁵Old textbooks sometimes use intensity, count rate or total counts indistinctly. In this work there is a clear difference between these terms. Intensity is the energy transferred per unit area and time. Count rate is the total number of radiation detected per unit area, per unit time or per unit channel in the acquisition system. Total number of counts is the total number of radiation detected. Total number of counts is unitless.

$$N_{pi} = C_i \frac{\Omega}{4\pi} \epsilon_i b_i \omega_i \frac{N_0}{A_i} T_p \int_{E_{pf}}^{E_{p0}} \frac{\sigma_{pi}(E_p) \exp\left(-\frac{\mu(E_i) \sin \phi_p}{\rho \sin \theta_p} \int_{E_{p0}}^{E_p} \frac{dE'_p}{S_\rho(E'_p)}\right)}{S_\rho(E_p)} dE_p \quad (2.24)$$

where C_i is the mass concentration of the analyte, ϵ_i is the efficiency of the detector at the energy E_i , $\Omega/4\pi$ is the detector solid angle, N_0 is the Avogadro number, A_i the mass number of the analyte and T_p is the total number of incident protons. The parameters ω_i and b_i are the K fluorescence yield and the K_α transition probability of the analyte, respectively (equations (2.3) and (2.1)). The integral part contains the ionization cross section for the analyte $\sigma_{pi}(E_p)$, the proton stopping power $S_\rho(E_p)$ (in mass units, equation (2.7)) and the mass absorption coefficient $\mu(E_i)/\rho$ of the sample for the K_α . E_p is the proton beam energy crossing the sample and E_{pf} is its final energy. Finally, ϕ_p and θ_p are respectively the beam incident angle and the photon take-off angle relative to the surface (Figure 2.11). Equation (2.24) can be found in any standard textbook of PIXE, [2] and [13]. The term $\sigma_{pi}(E_p)/S_\rho(E_p)$ in the integral deals with the energy loss of the proton and the exponential part deals with the self-absorption of these emitted X-rays through the sample. Although the analyte concentration is explicitly outside the integral, the quantities $S_\rho(E_p)$ and $\mu(E_i)/\rho$ also depend on the concentrations of the elements, as shown in equations (2.8) and (2.22), requiring different algorithms to determine these elemental concentrations in the sample, as will be shown in chapter 4.

In the case of thin targets, with thickness⁶ usually less than 100 $\mu\text{g}/\text{cm}^2$, the beam energy loss and X-rays self-absorption can be neglected and equation (2.24) is reduced to:

$$N_{piThin} = C_i \frac{1}{\sin \phi_p} \frac{\Omega}{4\pi} \epsilon_i b_i \omega_i \frac{N_0}{A_i} \sigma_{pi}(E_0) T_p \rho_i t \quad (2.25)$$

where t is the thickness of the sample and ρ_i the analyte density. We can define the PIXE thin film factor as:

$$r_{pi} = \frac{1}{\sin \phi_p} \frac{\Omega}{4\pi} \epsilon_i b_i \omega_i \frac{N_0}{A_i} \sigma_{pi}(E_0) \quad (2.26)$$

and we have:

⁶A thickness of a sample is measured with two commons units in X-ray spectroscopy, besides the conventional SI units: in terms of areal density (Number of atoms per cm^2) or in terms of mass density (g/cm^2). This last unit is adopted here, where the thickness of the sample is multiplied by its density.

$$N_{piThin} = C_i r_i T_p \rho_i t \quad (2.27)$$

This last relation shows that for thin films⁷, the total number of counts of X-ray production is directly proportional to the elemental mass concentration in the sample and will be important to characterize thin samples or as a normalization factor.

For thick samples, the final energy is $E_{pf} = 0$ in (2.24) and the integral part in the same equation is called the thick target factor for PIXE [1]:

$$M_i = \int_0^{E_{p0}} \frac{\sigma_{pi}(E_p) \exp\left(-\frac{\mu(E_i) \sin \phi_p}{\rho \sin \theta_p} \int_{E_{p0}}^{E_p} \frac{dE'_p}{S_\rho(E'_p)}\right)}{S_\rho(E_p)} dE_p \quad (2.28)$$

and represents the sample-matrix effects of the sample, depending on the mass concentrations of each element present in the sample. This factor encompasses the three main variables we described in this chapter: the stopping power, the ionization cross section and the mass absorption coefficient. A complete knowledge of these variables is necessary to determine the elemental concentration of a sample.

A useful expression for the thick target factor, adopted here, is the division of the thick target factor by the ionization cross section at the initial proton energy E_{p0} [53], called the correction factor:

$$F_i = \frac{\sin \phi_p M_i}{\sigma_{pi}(E_{p0})} \quad (2.29)$$

$$F_i = \frac{\sin \phi_p}{\sigma_{pi}(E_{p0})} \int_0^{E_{p0}} \frac{\sigma_{pi}(E_p) \exp\left(-\frac{\mu(E_i) \sin \phi_p}{\rho \sin \theta_p} \int_{E_0}^{E_p} \frac{dE'_p}{S_\rho(E'_p)}\right)}{S_\rho(E_p)} dE_p \quad (2.30)$$

which is useful because we can express equation (2.24) for thick targets in a similar way to the thin film analysis (equation (2.27)):

$$N_{pi} = C_i r_{pi} T_p F_i \quad (2.31)$$

The PIXE correction factor, F_i ⁸, is the most important variable to take into account in thick target PIXE analysis and will be referenced several times through this work.

⁷Ideally, the total number of incident protons, T_p is included in the thin film factor, but it is not always possible to obtain the same number of incident protons in similar experimental conditions. An independent calculation of the number of incident protons through the measurement of the total integrated charge, or current must be done.

⁸This term is adopted from [53]

2.5.2 XRF primary equation

The main equation for the total number of counts of characteristics X-ray production due to a primary X-ray beam with energy E_{x0} is [3], [12]:

$$N_{xi} = C_i \frac{1}{\sin \phi_x} \frac{\Omega}{4\pi} \epsilon_i J_i b_i \omega_i \frac{\tau_i(E_{x0})}{\rho} T_x \frac{1 - e^{-\left(\frac{\mu(E_{x0})}{\rho \sin \phi_x} + \frac{\mu(E_i)}{\rho \sin \theta_x}\right) \rho t}}{\frac{\mu(E_{x0})}{\rho \sin \phi_x} + \frac{\mu(E_i)}{\rho \sin \theta_x}} \quad (2.32)$$

where C_i is the mass concentration of the analyte, ϕ_x and θ_x are the incident angle of the X-ray and take-off angle of the emitted X-ray, respectively. ϵ_i is the efficiency of the detector at the energy E_i , $\Omega/4\pi$ is the detector solid angle and T_x is the total number of incident protons. ω_i , b_i , and J_i are the K fluorescence yield, the K_α transition probability and the K jump factor of the analyte, respectively (equations (2.3), (2.1) and (2.14)). $\tau_i(E_{x0})/\rho_i$ is the photoelectric coefficient of the analyte for the incident energy and ρt the sample thickness. The last term:

$$\chi_i = \frac{\mu(E_{x0})}{\rho \sin \phi_x} + \frac{\mu(E_i)}{\rho \sin \theta_x} \quad (2.33)$$

is a factor dealing with the mass absorption coefficient of the sample for the X-ray incident energy, $\mu(E_{x0})/\rho$, and the mass absorption coefficient of the sample for the K_α line of the analyte, $\mu(E_i)/\rho$. This χ_i is called the XRF correction factor and is equivalent to the PIXE correction factor (equation (2.30)) for XRF and depends, in a similar way to PIXE, on the concentration of the elements. This factor will also be several times referenced through this work.

For thick targets, we have $e^{-\chi_i \rho t_s} \rightarrow 0$, then:

$$N_{xi} = C_i \frac{1}{\sin \phi_x} \frac{\Omega}{4\pi} \epsilon_i J_i b_i \omega_i \frac{\tau_i(E_{x0})}{\rho} T_x \frac{1}{\chi_i} \quad (2.34)$$

that is the XRF equivalent to (2.24). For thin samples, $e^{-\chi_i \rho t} \rightarrow 1 - \chi_i \rho t$

$$N_{xi\text{thin}} = C_i \frac{1}{\sin \phi_x} \frac{\Omega}{4\pi} \epsilon_i J_i b_i \omega_i \frac{\tau_i(E_{x0})}{\rho} T_x \rho t \quad (2.35)$$

that is the XRF equivalent to (2.25). Defining the thin film factor for XRF:

$$r_{xi} = \frac{1}{\sin \phi_x} \frac{\Omega}{4\pi} \frac{\tau_i(E_{x0})}{\rho} \omega_i J_i b_i \quad (2.36)$$

we can rewrite (2.34) and (2.35) in the forms:

$$N_{xithin} = C_i r_{xi} T_x \rho t \quad (2.37)$$

and

$$N_{xi} = C_i r_{xi} T_x \frac{1}{\chi_i} \quad (2.38)$$

Equations (2.37) and (2.38) are the XRF equivalents of equations (2.27) and (2.31) in PIXE analysis⁹.

2.6 Background radiation

Characteristic peaks are not the only X-ray energies that are detected. A continuous background is also seen in the background and has physical causes. In PIXE, four processes are the main contributors to the continuous background. At the moment a proton ejects an electron from the sample it passes through the sample losing energy due to the Coulomb force of the nuclei of the different elements. This process is known as Secondary Electron Bremsstrahlung (SEB) and is the main contributor to the background in PIXE [55]. Other contributions are the Quasi-Free Electron Bremsstrahlung (QFEB), when the proton velocity is higher than the orbital velocity of the electrons, hence the electrons can be considered almost free, from a point of view of the proton; atomic bremsstrahlung (AB), due to electron transitions to the continuum; and the nuclear bremsstrahlung (NB); due to the movement of the target nucleus [56]. Unfortunately, there is no general parameterizations formula valid for all kinds of targets and a case by case experimental fit is still necessary for every spectrum. Figure 2.12 shows the four types of processes of continuous emission by protons and their regions of predominance.

⁹Notice that in PIXE the total number of counts is proportional to the PIXE correction factor, while in XRF the total number of counts is inversely proportional to the XRF correction factor. We could define a XRF correction factor equal to $1/\chi_i$ but we prefer keeping the usual order in both PIXE and XRF. The XRF correction factor is also called effective or combined mass absorption coefficient [12], but, in this case, we adopt a similar word to the PIXE correction factor. The term χ is adopted from [54]

Figure 2.12: Continuous radiation by a 2 MeV of H^+ beam on carbon. Dashed line represents experimental values. Figure taken from [56]

In XRF, the Compton and Rayleigh scattering of the original beam are the main contributors to the background, as shown in figure 2.13. The broad shape in the incoherent peak is due to the range of scattering angles. The incomplete charge collection is also present due to the combination of holes and electrons produced in the detector. Also, peaks due to the gold contact in the silicon detector, like L lines of gold in this example, can appear. The incomplete charge collection and the peaks due to the gold contact also occur in PIXE and they have an origin in the detector, not in the sample.

Figure 2.13: Continuous background in a XRF spectrum of a water sample by a monochromatic primary beam excitation at 17.4 keV. Figure taken from [3]

Other artifact peaks occur in the X-ray spectrum Si-escape peaks usually are peaks at energy 1.74 keV to the left of characteristic peaks and are generated from the silicon crystal and usually total number of counts lower than 2% of the characteristic line. Sum peaks are produced when two X-rays arrive at the detector approximately at the same time. The energy value recorded of these two X-rays is the sum of these two X-ray energies.

In this work we assume that the total number of counts of characteristic peaks are properly measured, making a correct background fitting and taking into account overlapping between different characteristic lines and artifacts peaks.

2.7 Enhancement effects

Other effects can increase the X-ray production in a PIXE or XRF analysis. As we saw in the introduction, in figure 1.1, several other outcomes, like electrons and scattered beam radiation, can be obtained with the interaction of protons and X-rays with matter. Various of these outcomes can also interact with the electrons in a shell, producing new vacancies that will be filled by a electron from a higher shell, producing a new characteristic X-rays that will be added to the primary X-rays.

2.7.1 Enhancement by electrons

It can happen that an ejected electron produced by the absorption of a photon interacts with another electron generating a new photon. The probability of having this emission comparing to the primary emission is several orders of magnitude lower than the primary X-ray emission and its effects are negligible in PIXE [57] and XRF [10]. This effect can be noticed for low-Z elements like O or F, in setups specially designed for low-Z element detections.

2.7.2 Enhancement by scattering

In PIXE, the probability of having backscattered protons can be calculated using the Rutherford's equation [28]. In the center of mass, the probability of a proton with energy E_p being backscattered in an angle θ_R is determined by:

$$\frac{d\sigma_R}{d\Omega} = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{Z_1 Z_2 e^2}{4E_p} \right)^2 \frac{1}{\sin^4(\theta_R/2)} \quad (2.39)$$

where Z_1 and Z_2 are the atomic numbers of the proton ($Z_1=1$) and the target nucleus, e the electron charge and θ_R the scattering angle. For example, the number of backscattered protons is up to eight orders of magnitude, at $25 \mu\text{g}/\text{cm}^2$ of calcium, lower compared to the number of protons that are scattered in the front, which indicates that backscattered protons may be negligible in calculating this X-Ray production. The distribution of protons around the mean energy, called straggling is equally negligible [58]

In XRF, the enhancement effect due to Compton scattering and Rayleigh scattering is not usually taken into account, but it can contribute up to several tens percent to the primary fluorescence in the case of trace elements for low-Z sample-matrices [59], [60] because the cross section due to Compton scattering and Rayleigh scattering are comparable with the photoelectric cross section in the region of 10-20 keV for low-Z elements as shown in figure 2.8a for the carbon.

2.7.3 Secondary fluorescence

The photons generated by some element can be seen as a new X-ray beam that can be absorbed by electrons of other elements if their energy exceeds the ionization energy of these elements. For example, photons released by nickel atoms, with energy $E_i = 7.5 \text{ keV}$, in a Fe-Ni array, can interact with the electrons in the iron K shell, because the ionization

energy of iron is lower, $u_{Fe} = 7.1$ keV, producing an X-ray photon by the iron that will be added to the total number of counts of the primary beam.

Usually, the secondary fluorescence is expressed as the ratio between the total number of counts due to this secondary fluorescence, $N_{i_{sec}}$, and the total number of counts due to the primary fluorescence, $N_{i_{pri}}$, so that the total number of counts is expressed as follows:

$$N_i \propto C_i N_{i_{pri}} (1 + S_{ij}) \quad (2.40)$$

where $S_{ij} = \frac{N_{i_{sec}}}{N_{i_{pri}}}$, interpreted as the influence of the j element over the i element.

In PIXE, Various approaches for the X-ray production due to secondary fluorescence were made as in [61] and [62]. A complete formulation of the increment in total number of counts to secondary fluorescence is given by [63]. An element j produces a secondary X-ray fluorescence over the analyte i in the form:

$$S_{ijPIXE} = L_{pi} \frac{1}{M_i} \int_0^{E_0} \frac{\sigma_{pi}(E_p) \exp(-u'x\rho) F(x)}{S_\rho(E_p)} dE_p \quad (2.41)$$

where M_i is the PIXE thick target factor (equation (2.28)), $\sigma_{pi}(E_p)$ is the proton cross section of the element i for their K_α line and:

$$\begin{aligned} x &= \frac{\sin \theta_p}{\rho} \int_{E'_p}^{E_{p0}} \frac{dE'_p}{S_\rho(E'_p)} \\ F(x) &= \frac{1}{u'} \left(\ln \frac{u + u'}{|u - u'|} - G[(u - u')x\rho] + e^{u'x\rho} G(u'x\rho) \right) \\ u' &= \frac{\mu(E_i)}{\rho \sin \theta_p} \\ u &= \frac{\mu(E_j)}{\rho} \\ G(a) &= \int_1^\infty \frac{1}{a} e^{-at} dt \end{aligned} \quad (2.42)$$

where $\mu(E_i)/\rho$ and $\mu(E_j)/\rho$ are the mass absorption coefficients of the sample for the energies K_α of the i and j elements. The term $G(a)$ is called the exponential integral function and must be calculated numerically. Finally, L_{pi} is a constant related to fundamental parameters of the elements i and j :

$$L_{pi} = 0.5 C_j \frac{A_i}{A_j} \frac{\tau_i(E_j)}{\rho} \omega_j b_j J_i \quad (2.43)$$

where C_j is the concentration of the element j , A_i and A_j are the number mass of the elements i and j , $\tau_i(E_j)/\rho$ is the photoelectric coefficient of the element i for the K_α line of the element j , ω_j is the yield fluorescence of the element j , b_j is the ratio of the K_α over the total $K_\alpha + K_\beta$ of the j element and J_i is the jump factor of the i element. Derivation of equations (2.41) to (2.43) can be found in [63].

In XRF, the secondary fluorescence term has the exact form [12]:

$$S_{ijXRF} = L_{xi} \frac{\tau_i(E_j)}{\tau_i(E_{0x})} \left(\ln \left(1 + \frac{\mu(E_{0x})/\rho}{\mu(E_j) \sin \phi_x / \rho} \right) \frac{\sin \phi_x}{\mu(E_{0x})/\rho} + \ln \left(1 + \frac{\mu(E_i)/\rho}{\mu(E_j) \sin \theta_x / \rho} \right) \frac{\sin \theta_x}{\mu(E_i)/\rho} \right) \quad (2.44)$$

where $\tau_i(E_j)$ and $\tau_i(E_{0x})$ are the photoelectric cross section of the element i for the K_α energy of the element j and the incident beam energy respectively. $\mu(E_{0x})/\rho$, $\mu(E_i)/\rho$ and $\mu(E_j)/\rho$ are the mass absorption coefficient of the sample for the K_α energies of the elements i and j and the incident beam energy. Finally:

$$L_{xi} = 0.5 C_j \omega_j b_j J_j \quad (2.45)$$

where the constants in this equation are almost the same constants in equation (2.43). Derivation of equations (2.44) and (2.45) can be found in [12].

As we will see in section 3.5, the Secondary fluorescence effects are stronger when two elements are nearby in atomic number, like nickel ($Z=28$) and iron ($Z=26$), or calcium ($Z=20$) on potassium ($Z=19$) and the element with highest atomic number has a concentration higher than the lower element with lower atomic number, like a sample with 99% of nickel and 1% of iron. Also, these effects increase with the energy of the photon, or proton beam. The secondary fluorescence due to K_β energies must be also included, adapting the parameters of this section to the correspondent K_β energies.

Finally, the secondary fluorescence can also be absorbed again by other electrons of other lower elements forming a tertiary fluorescence, T_{ijk} . Thus, the photons produced by iron by secondary fluorescence of the nickel can also excite the chromium in a Fe-Ni-Cr array. This tertiary fluorescence has a maximum of typically 3-4/% but usually does not reach 1%, being usually neglected [12], [63]. In this work, we will consider secondary fluorescence only.

2.8 Comparison between PIXE and XRF

In general three parameters are important when comparing PIXE with XRF [8]. First, typical protons of 2-3 MeV have a low penetration range, of the order of 10 to 20 micrometers, while X-rays produced by a monochromatic X-ray source typically between 5-20 keV can penetrate several millimeters, making the methods with proton beams most suited for surface analysis. Second, the proton cross section as a function of the atomic number is a decreasing function; while in XRF, the photoelectric coefficient is an increasing function with respect to the atomic number, as shown in figure 2.14. Likewise, the continuous background is more prominent in the region of elements of $Z < 20$ for PIXE, due to secondary electrons, while in the XRF the background is more prominent near the incident energy of the primary beam, due to the Compton and Rayleigh scattering as shown in section 2.6.

Figure 2.14: Ionization proton cross sections of 1 MeV, 2.4 MeV and 5 MeV proton beam compared to photoelectric cross section of 5.9 keV, 22 keV and 60keV X-rays beam as a function of the K_{α} line of the correspondent element. Data taken from [41] and [51]

2.9 PIXE and XRF correction factor as a function of the element

In this chapter we showed that equation (1.1), in the introduction, has the actual form:

$$N_i = C_i r_i Y_i T (1 + S_{ij} + T_{ijk} + \text{OtherEnhancements}) + \text{background} \quad (2.46)$$

where T deals with the total number of incident radiation (T_p for PIXE and T_x for XRF) and Y_i is a factor depending on fundamental parameters, geometric setup and the elemental concentrations that provides the sample-matrix correction. For PIXE, $Y_i = F_i$ and for XRF, $Y_i = 1/\chi_i$.

Mathematically, we can generalize the PIXE or XRF correction factors for K_α energies of elements that are not present in the sample. This allows to determine elements that at some point have not been quantified (or even not detected), like trace elements. Also, we can focus on the major elements in the sample that are the main contributors to the correction functions. This means that the PIXE and the XRF correction factor are written as a function of any element i from $Z_i = 11$ to 40:

$$F_{PIXE}(Z_i) = F_i(S_\rho(E), \sigma_p(E_p), \mu(E_i)/\rho, \phi_p, \theta_p, E_{p0}, C_i, C_j, C_k, \dots) \quad (2.47)$$

$$\chi_{XRF}(Z_i) = \chi_i(\mu(E_{x0})/\rho, \mu(E_i)/\rho, \phi_x, \theta_x, C_i, C_j, C_k, \dots) \quad (2.48)$$

where E_i is the K_α energy for the analyte and the elemental concentrations are calculated for the major elements only.

Chapter 3

Matlab code for X-ray production in XRF and PIXE

Several programs for modeling and processing PIXE and XRF spectra have been developed. AXIL package [64] was one of the first programs to be widely used, together with the QXAS software [65]. In PIXE, GUPIX software [66] is the most used of them, allowing fitting spectrum and converting total number of counts of characteristic peaks to concentrations for thin, intermediate and thick samples. Other PIXE programs are the GEOPIXE [67], which focus on geological examples, and VibaLab [68] which simulates PIXE spectra from fundamental parameters. The program Clara [53] is a free software which calculates the PIXE correction factor in equation (2.30) for any sample-matrix or a mixture of two of sample-matrices. In XRF, the free software PyMca [69] is the most used for fitting spectra and determining elemental concentrations. For simulation from fundamental parameters, the free software XMI-MSIM [70] is suitable.

For this work, we wrote a code which focuses on the PIXE and XRF correction factors calculations, which are the main factors we are interested in this work. We used Matlab although the code can run on Octave, a free software, as well. Following sections show all the steps in the writing process.

3.1 Data bases

As we saw in chapter 2, many fundamental parameters are used for calculating the X-ray production, and the PIXE and XRF correction factors. For our codes, we organized these parameters in a database file as follows:

- **Atomic number.** For elements from $Z=1$ to 92
- **Atomic mass.** For elements from $Z=1$ to 92
- **K_α and K_β energies.** Taken from [19] for elements from $Z>10$ to 40
- **K Ionization energy.** Taken from [71] for elements from $Z>10$ to 40
- **K Fluorescence yield.** Evaluated from Bambynek polynomial (Equation (2.3)) for elements from $Z>10$ to 40 or taken from [24], [25] or [26].
- **W_{K_α} coefficients.** Choosing from [20], [21] or equation (2.1) for elements from $Z>10$ to 40
- **Jump ratio. (For XRF only)** Taken from equation (2.14) for elements from $Z>10$ to 40
- **Mass absorption coefficients and photoelectric cross section.** We can choose between XCOM or FFAST (section 2.3.5). The data is interpolated at the K_α and K_β energies. The photoelectric cross section is taken from the XCOM or FFAST as well.

These parameters are used for PIXE and XRF. For PIXE only, we must add the following parameters:

- **Stopping power.** We can select between the Ziegler polynomial (equation (2.6)) for the proton energy range indicated before, the PSTAR code, interpolated to our energy range, and the SRIM 2013 database [34].
- **Proton cross section.** We can choose between three polynomials based on equation (2.12): [40], [41] and [42].

The archive DataBase.m contains all these parameters and, in the incoming codes, it is always called.

3.2 Input parameters

With these database, we have to select the input parameters for the experimental setup.

- **Initial beam energies.** For PIXE, we use a range from any initial energy E_{0p} to any final energy E_{fp} with any number of steps. For XRF we use a K_α energy of some element from $Z=11$ to $Z=92$. In this work, we use $E_{p0} = 2.4$ MeV and $E_{0x} = E_{TcK_\alpha} = 18.4$ keV, but other set of values can be chosen.
- **Incident angle of the beam.** In this work, for PIXE and for XRF, we use $\phi_p = \phi_x = 90^\circ$,
- **Take-off angle of the photon.** In this work, for PIXE and for XRF, we use $\theta_x = \theta_p = 45^\circ$
- **Sample-matrix.** We can configure any sample-matrix for elements from $Z = 1$ to $Z = 92$ together with their concentrations, or stoichiometric values. Also, a second sample-matrix can be configured with a weight mass relative to the first sample-matrix. This second sample-matrix is important for the case that we dilute, or add, other composition to our samples.

3.3 PIXE Correction factor

The fundamental and input parameters are enough for calculating the thick target factor (equation (2.28)) and the PIXE correction factor (Equation (2.30)). The calculation of these factors as a function of every element from $Z = 11$ to 40 follows the path:

- Calculation of the total stopping power for our sample-matrix using the additive rule (equation (2.8)) as a function of the proton energy.
- Calculation of the mass absorption coefficient of the sample for the K_α energy of the element in the sample-matrix using the additive rule (equation (2.22)).
- With these two variables, we can calculate the exponential part of equation (2.28) corresponding to the absorption of the K_α line of the element through the sample.
- With the exponential part already calculated, we proceed to calculate the PIXE thick target factor in equation (2.28) using the ionization cross section and the stopping power. All these integrals are calculated with the trapezoidal rule using an enough number of steps in proton energies such that the differences between the PIXE correction factor of one number steps and another higher number of steps are

less than 1%. The trapezoidal rule is a sufficient integral method since the stopping power and ionization cross section as a function of the proton energy are continuous and smooth.

- We calculate the PIXE correction factor dividing the thick target factor by the ionization cross section in the initial energy (equation (2.30)). Figure 3.1 and 3.2 shows the calculations of the main code: The thick target factor and the PIXE matrix factor for different kind of targets: Pure elements, compounds, and mixtures.

The name of this code is PFactor.m and the output is the PIXE correction factor as a function of the K_α line of the correspondent element, from $Z = 11$ to 40. This code is detailed in the appendices.

Figure 3.1: Thick target factor for different samples at $E_{p0} = 2.4$ MeV, $\phi_p = 90^\circ$ and $\theta_p = 45^\circ$ as a function of the K_α line of the correspondent element.

Figure 3.2: PIXE Correction factor for different samples at $E_{p0} = 2.4$ MeV, $\phi_p = 90^\circ$ and $\theta_p = 45^\circ$ as a function of the K_α line of the correspondent element.

3.4 XRF Correction factor

Different from the PIXE correction factor, the XRF correction factor does not require an integration, making the calculation of this XRF correction factor more straightforward than the PIXE correction factor:

- Calculation of the mass absorption coefficient of the sample for the energy of the incident X-Ray beam in our sample-matrix using the additive rule (equation (2.22)).
- Calculation of the mass absorption coefficient of the sample for the K_α energy of the element in our sample-matrix using the additive rule (equation (2.22)).
- These two mass absorption coefficients are divided by the sine of the incidence and take-off angles following equation (2.33) and added up these two terms to obtain the XRF correction factor.

Because the incidence X-ray energy does not lose energy, only intensity, when passing through the sample, there is no need to divide by the initial photon cross section to obtain another XRF factor, like in PIXE. Figure 3.3 shows the XRF correction factor for the same samples showed in PIXE.

The name of this code is XFactor.m and the output is the XRF correction factor as a function of the K_α line of the correspondent element, from $Z = 11$ to 40. This code is detailed in the appendices.

Figure 3.3: XRF correction factors for different targets at incident X-ray energy of 18.4 keV as a function of the K_α line of the correspondent element.

3.5 Secondary fluorescence enhancement

Secondary fluorescence effects are a considerable enhancement in some situations. We have to enter the same database and input parameters that we worked in the previous codes, specifying which element j will cause secondary fluorescence in the element i . So, for PIXE, the code to calculate the secondary fluorescence of i due to j follow this order (File PSecondary.m):

- Calculation of the PIXE correction factor, following section 3.3.
- Calculation of the factor L_{pi} , using equation (2.43), the terms u , u' and x from equation (2.42) using the databases.
- These last terms are introduced in the function $F(x)$ of (2.42), and calculating the integral $G(a)$ through a Matlab command.

- Finally, all calculated parameters are used to calculate the integral in equation (2.41) using the trapeze rule.

For the XRF secondary analysis, there is no integration as in PIXE. We only need to evaluate equation (2.44) and including data from the database for every mass absorption coefficient and proton cross section. (File XSecondary.m).

Figure 3.4 shows the increment of the secondary fluorescence compared to the primary fluorescence of iron in a Fe-Ni sample-matrix as a function of the Nickel concentration (iron concentration is $100\% - C_{Ni}$). We observe that the enhancement due to secondary fluorescence for high concentrations of nickel in XRF is higher than the enhancement in PIXE. This enhancement is always higher in XRF for other pair of elements. The fluorescence enhancement of an element with atomic number Z with 0.1% mixed with 99.9% of an element with atomic number $Z + 2$ is shown in figure 3.5. Notice that, from $Z = 34$, the enhancement due to an atom with atomic number $Z + 2$ is due only to the K_β energy of this $Z + 2$ element, because the K_α energy of the latter element does not reach the ionization energy of the element Z .

Figure 3.4: Secondary fluorescence enhancement of iron in a Fe-Ni sample as a function of different concentrations of nickel.

Figure 3.5: Secondary fluorescence enhancement as a function of elements with atomic number Z due to another element with atomic number $Z + 2$. The composition of the sample is 0.1% of the element Z and 99.9% of the element $Z + 2$

3.6 Comparison with other programs and previous works

The four codes described in this chapter, PFactor.m, XFactor.m, PSecondary.m and XSecondary.m, have been tested and compared with other programs. For PIXE, the Clara software [53] is the only open software to date that calculates the PIXE correction factor for any kind of compound or a mixture of compounds. Table 3.1 shows a comparison between the PIXE correction factors obtained by Clara and our code. It is obtained that the results of these codes differ only by less than 1%.

Sample	Analyte	Correction Factor (10^{-3}g/cm^2)	
		Clara	PFactor
Fe_2O_3	Fe	5.16	5.11
TiO_2	Ti	4.34	4.33
Ge	Ge	6.35	6.30
50% Fe + 50% $\text{H}_{10}\text{C}_6\text{O}_5$	Fe	4.85	4.83

Table 3.1: Comparison between the PIXE correction factor obtained by Clara [53] and PFactor.m.

For XRF, there is no software that shows explicitly the XRF correction factor as a final result, so we compared our code with a combination of different results of another

software. The program XMI-MSIM [70] simulates the XRF spectrum for a given geometry and detector characteristics, calculating the total number of counts with equation (2.32). We compared our codes dividing two total number of counts of an element i of two different samples, simulated for the same initial primary X-ray intensity:

$$\frac{N_{isample1}}{N_{isample2}} = \frac{C_{isample1} \chi_{isample2}}{C_{isample2} \chi_{isample1}} \quad (3.1)$$

where $N_{isample1}$ is the total number of counts of the first sample with concentration of the analyte i of $C_{isample1}$ and XRF correction factor $\chi_{isample1}$. $N_{isample2}$ is the total number of counts of the second sample with concentration of the analyte i of $C_{isample2}$ and XRF correction factor $\chi_{isample2}$.

Table 3.2 shows a comparison between the total number of counts ratios obtained from the left part of equation (3.1) by program XMI-MSIM and those obtained from the right part of this equation obtained by our XFactor code. The results show an agreement better than 5% between the two results.

Sample 1	Sample 2	Analyte	$\frac{N_{isample1}}{N_{isample2}}$	
			XMI-MSIM	XFactor
CaCO ₃	CaO	Ca	0.853	0.845
CaCO ₃	CaF ₂	Ca	1.00	0.99
KI	K ₂ O	K	0.146	0.139
Fe ₂ O ₃	FeB	Fe	0.952	0.965

Table 3.2: Comparison between the XRF total number of counts ratios obtained by XMI-MSIM [70] and XFactor.

For the secondary fluorescence codes, we compared the codes PSecondary.m and XSecondary.m with published data. Table 3.3 shows the comparison between the ratio of secondary enhancement and primary production obtained by this work and the same ratio calculated by Campbell [63]. In some cases the differences are bigger than 20%, but in other cases, there is a good agreement between them. Table 3.4 shows the same comparison for XRF between this work and the calculations of Hawthorne [72] for different alloys, using an Ag, K_α , primary X-ray beam. It is shown a better agreement between the two calculations, with differences up to 2%.

Element i	Element j	Experimental conditions	$N_{sec}/N_{pri}(\%)$	
			Campbell	PSecondary.m
Cr	Fe	$E_{p0}=2.5$ MeV, $\phi_p = \theta_p = 45^\circ$	45	54
Ti	Fe	$E_{p0}=2.5$ MeV, $\phi_p = \theta_p = 45^\circ$	22	17
Ca	Fe	$E_{p0}=2.5$ MeV, $\phi_p = \theta_p = 45^\circ$	5.7	6.0
Cl	Fe	$E_{p0}=2.5$ MeV, $\phi_p = \theta_p = 45^\circ$	1.06	1.04
Fe	Ni	$E_{p0}=2$ MeV, $\phi_p = 90^\circ$, $\theta_p = 45^\circ$	50	53
Fe	Zn	$E_{p0}=2$ MeV, $\phi_p = 90^\circ$, $\theta_p = 45^\circ$	20	22
Si	P	$E_{p0}=2$ MeV, $\phi_p = 90^\circ$, $\theta_p = 45^\circ$	19	23
Si	S	$E_{p0}=2$ MeV, $\phi_p = 90^\circ$, $\theta_p = 45^\circ$	12	14

Table 3.3: PIXE Secondary fluorescence enhancement from a 99% element j over the 1% of analyte i , comparison between this work and data from Campbell [63].

NBS Sample	Concentrations (%)			$N_{sec}/N_{pri}(\%)$					
				Hawthorne			XSecondary.m		
	Ni	Fe	Cr	Ni-Fe	Ni-Cr	Fe-Cr	Ni-Fe	Ni-Cr	Fe-Cr
35324	19.3	52.8	26.9	9.6	11	45	9.3	11	45
35321	20	59.1	19.9	10	11	59	9.8	11	58
161	64	15	17	58	24	24	57	23	24

Table 3.4: XRF Secondary fluorescence enhancement for different alloy samples using a monochromatic Ag, K_α , beam. Comparison between this work and Hawthorne [72].

Chapter 4

Methods to determine the elementar mass concentrations of samples in PIXE and XRF. State of the art

As we saw in previous sections, the PIXE and XRF correction factors depend on the elemental concentrations of the sample. A complication arises when we don't detect the low elements ($Z < 11$) and they are major elements in our samples, as in the case of biological samples and organic samples. So, the composition of our sample is determined by:

$$\sum_i^n C_{i\text{Detected}} + \sum_j^n C_{j\text{Low-Z elements}} = 1 \quad (4.1)$$

Several methods of elemental quantification have been developed over the years to deal with these challenges. Usually [11], these methods are divided in three types: sample-matrix correction methods, where all the fundamental parameters are used for calculating theoretically the total number of counts and comparing with the measured total number of counts. If the sample is homogeneous, it does not require special treatment. The second type is the compensation methods, where additions to the samples are made and sample preparation is necessary. The third type is the minimization of the sample-matrix effects, where the sample is transformed into an intermediate or thin sample.

In this chapter, using the codes described in the previous chapter, we will discuss ev-

ery method for determining elemental concentrations from a measured total number of counts and discussing their advantages and drawbacks. We are going to use three ways to determine these advantages and drawbacks of a method: The simplicity, when few measurement steps are required, few measurement time or sample treatment is minimal¹; the accuracy, describing how the approximations required in the PIXE or XRF correction factors deviate from the real PIXE or XRF correction factors; and the precision, describing how sensitive is the uncertainty propagation from the measured, instrumental and fundamental parameters².

There are more methods for determining the elemental concentrations from a measured spectrum described in the literature, but the described here are the most common referenced methods [3].

4.1 The importance of calibration to known samples

If we entirely work with equations (2.31) and (2.38) for the analysis of bulk samples, we will have to deal with the uncertainties of every variable and the differences between databases. Most authors compare the total number of counts of the analyte in the sample with another total number of counts of the analyte in a sample of known composition. This procedure is called calibration, or normalization and the known composition is called a standard. The first advantage is the cancelation out of parameters like the fluorescence yield, the detector efficiency and the solid angle of the detector, contained in the term r_{pi} and r_{xi} , canceling out their uncertainties. The second advantage is the reduction of the uncertainty due to the other parameters inside the PIXE and XRF correction factors as we will see in the next subsections.

4.1.1 Calibration to known thin samples

An unknown sample can be analyzed comparing the total number of counts of the elements in the sample with the total number of counts of thin film standards containing the same elements. Typical thin standards have a thickness of about $50 \mu\text{g}/\text{cm}^2$ and they

¹ Nearly, all samples need a sample treatment because most samples are heterogeneous and require an homogenization procedure [73]. Some treatment methods includes dilution in liquids, briquetting-grinding-pressing method or fusion techniques. Every method has their own advantages and drawbacks, including particle size effects, surface irregularity effects and moisture effects. Some analysis are made *in situ* and it is not possible to eliminate all effects.

²These definitions are inspired by the definitions of accuracy and precision given in experimental physics, where accuracy refers to agreement of the measurements to a referenced value, and precision refers to the reproducibility of different measurements to each other.

are usually prepared via physical vapor deposition, chemical vapor deposition or atomic layer deposition [74].

In PIXE, we can determine the thin film factor measuring the total number of counts, N_{is} , when analyzing a single element i in a thin film standard:

$$r_{pi} = \frac{N_{is}}{C_i Q \rho_i t} \quad (4.2)$$

and calculate the concentration of the analytes replacing (4.2) in (2.27) and solving for C_i :

$$C_i = \frac{N_{pi}}{r_{pi} F_i Q} \quad (4.3)$$

The advantage of this last term is that all the possible uncertainties from the instrumental and fundamental parameters contained in r_i are reduced to the uncertainties of N_{id} , Q and t only, in the thin film analysis. On the other hand, equation (4.3) uses the PIXE correction factor (equation (2.30)) instead of the PIXE thick target factor (equation (2.28)) with the main advantage of reducing discrepancies between the databases of cross sections due to the ratio $\sigma_i(E_p)/\sigma_i(E_{p0})$. We modified the PFactor code for calculating the propagation of uncertainties due to the ionization cross section values as a function of the proton energy and the proton beam initial energy. This calculation is made simulating a Gaussian distribution with a given standard deviation of every coefficient of the polynomial (2.12) for the ionization proton cross section and a Gaussian distribution for the initial energy of the proton beam, calculating the thick target and PIXE correction factors for every value of the distributions obtaining, then, distributions for the PIXE thick target and correction factor. Thus, an average and a standard deviation are determined for the two last distributions. A relative uncertainty for these distributions is calculated using standard deviation/average $\times 100$ which will be the propagated relative uncertainty of the PIXE correction and thick target factors. Figure 4.1 shows the comparison between the uncertainty propagation of the PIXE matrix factor due to a 10% of relative uncertainties in every coefficient in the polynomial (2.12) and a 10% of relative uncertainty in the initial proton beam energy and the propagation of these uncertainties in the thick target factor for two kind of samples, a pure element, and the same element as a trace element in cellulose (See composition in table A.1). The calculations show that using the PIXE correction factor, with the aid of thin film standards, can reduce the relative uncertainties to various

order of magnitude comparing with the analysis of bulk analysis using the PIXE thick target factor. Still, the PIXE correction factor has relative uncertainties with the same order of magnitude of the relative uncertainty of the energy of the incident proton beam, increasing with respect to the atomic number of the element.

Figure 4.1: Assuming a 10% of relative uncertainty in every coefficient of the polynomial (2.12) in the proton cross section and a 10% of relative uncertainty in the energy of the incident proton we calculated the propagation of these relative uncertainties in a) the PIXE thick target factor for a pure element, b) the PIXE correction factor for a pure element, c) the PIXE thick target factor for a trace element in cellulose, d) a the PIXE correction factor for a trace element in cellulose. At first, the calculation is made separating the relative uncertainty of cross section from the relative uncertainty of incident proton energy. The combined line is the calculation with both relative uncertainties at the same time. All graphs are as a function of the K_α line of the correspondent element.

In XRF, the X-ray beam does not lose energy when it passes through a sample and the normalization to thin samples is more straightforward, cancelling out the photoelectric cross section of the analyte for the incidence X-ray energy and having the uncertainties in the measured r_{xi} by thin film standards and calculating the concentrations, similar to

PIXE:

$$C_i = \frac{N_{xi}\chi_i}{r_{xi}T_x} \quad (4.4)$$

4.1.2 Calibration to known thick samples

Calibration with thick samples is useful when there is some knowledge of the elemental composition of the sample. A known sample will have an elemental concentration followed by (4.3) and (4.4):

$$C_{iknown} = \frac{N_{pi}F_{iknown}}{r_{pi}T_{pknown}} T_{pknown} \quad (4.5)$$

$$C_{iknown} = \frac{N_{xi}F_{iknown}}{r_{xi}T_{xknown}} T_{xknown} \quad (4.6)$$

so that, the concentration of an element in an unknown sample is:

$$C_i = C_{iknown} \frac{N_{pi}}{N_{piknown}} \frac{F_{iknown}}{F_i} \frac{T_{pknown}}{T_p} \quad (4.7)$$

$$C_i = C_{iknown} \frac{N_{xi}}{N_{xiknown}} \frac{\chi_i}{\chi_{iknown}} \frac{T_{xknown}}{T_x} \quad (4.8)$$

In PIXE, The calibration with thick target has the advantage of reducing the propagation of uncertainties due to discrepancies between databases, not only for the ionization cross section, like in thin film calibration, as well as every other parameters inside the PIXE correction factor like the stopping power, mass absorption coefficients, initial proton energy and the incidence and take-off angles. To illustrate this, a relative uncertainty for every value of these parameters of 10% is simulated in a similar way that was made in section 4.1.1 and calculated a propagation of these uncertainties in the correction factor F_i in a sample of a pure element as a trace element. The same propagation is calculated for the quotient F_{iknown}/F_i where the known sample is the pure element itself. Figure 4.2a shows that the uncertainties in the PIXE correction factor are due mainly to the uncertainties in the incident proton energy, for elements with $Z > 20$ and the mass absorption coefficient and the incident angle for elements with $Z < 20$. Also, with 10% of uncertainties in every parameter involved in the PIXE correction factor, it propagates up to 20% to the PIXE correction factor of the sample. Figure 4.2b shows that if we normalize the

PIXE correction factor of cellulose with thick samples of pure elements, the uncertainties are reduced, especially for elements with $Z > 20$. This result shows the advantage of the normalization to known thick samples over the normalization to thin samples.

A common kind of calibration is the normalization to similar samples. Figure 4.3a shows the propagated relative uncertainty of the PIXE correction factor of a referenced tomato sample, NBS-1573a [75], compared with the propagated relative uncertainty of the quotient of the PIXE correction factor of the same sample with the PIXE correction factor of another similar biological sample, pine needle, NBS-1575 (see compositions in table A.1). This figure shows a reduction of uncertainties for all elements when the PIXE correction factor of the sample is normalized to a PIXE correction factor of a similar sample. Figure 4.3b shows the same reduction for metallic samples, when a Fe-Cr-Ni alloy, NBS-35324, is compared with a similar alloy, NBS-161 (see compositions in table 3.4).

Figure 4.2: Assuming a 10% of relative uncertainty in every coefficient of the polynomial (2.12) in the proton cross section, every mass absorption coefficient, every stopping power as a function of the proton energy, incident and takes-off angle and proton incident energy, it is calculated the propagated relative uncertainty in a) the PIXE correction factor for a trace element in cellulose and b) the quotient between the PIXE correction factor for a pure element with the PIXE correction factor for the same element as a trace element in cellulose. At first, the calculations is made separating the relative uncertainty of every parameter separately. The combined line is the calculation with all relative uncertainties at the same time. All graphs are as a function of the K_{α} line of the correspondent element.

Figure 4.3: Assuming a 10% of relative uncertainty in every coefficient of the polynomial (2.12) in the proton cross section, every mass absorption coefficient, every stopping power as a function of the proton energy, incident and takes-off angle and proton incident energy, it is calculated the propagated relative uncertainty in a) the PIXE correction factor of a tomato sample, NBS-1573a [75], and b) the quotient between the PIXE correction factor of a pine needle sample with the PIXE correction factor of the same tomato sample. All graphs are as a function of the K_α line of the correspondent element.

In XRF, the normalization to thick samples also has the advantage of reducing uncertainties. Figure 4.4a shows the propagated relative uncertainty in the XRF correction factor of the referenced tomato sample described above compared with the propagated relative uncertainty of the quotient between the XRF correction factor of the same sample with the XRF correction factor of the pine needle. Figure 4.4b shows the propagation of uncertainties for an alloy, NBS-35324, normalized with a similar alloy, NBS-161. These figures show the same reduction of uncertainties for all elements for the XRF correction factor as shown for the PIXE correction factor.

Figure 4.4: Assuming a 10% of relative uncertainty in every mass absorption coefficient, every incident and takes-off angle and in the photon incident energy, it is calculated the propagated relative uncertainty in a) the XRF correction factor of a tomato sample, NBS-1573a [75], b) the quotient between the XRF correction factor of the same tomato sample with the XRF correction factor of a pine needle sample . All graphs are as a function of the K_α line of the correspondent element.

4.2 Sample-matrix correction methods

In sample-matrix correction methods, or fundamental parameters methods, we measure all the total number of counts corresponding to every element in the sample. The first method to work with is the iteration method, when an initial concentrations of the detected elements are guessed and, then, an iteration is made around these concentrations to calculate the PIXE or XRF correction factors (sometimes including secondary and tertiary fluorescence), until the theoretical calculations and the experimental values are consistent. Usually, this method is developed for a binary or ternary sample-matrix, like Fe-Cr-Ni or Cr-Ag-Au in alloys. When more elements are present in a sample, the number of iterations also increases as does the computational time. These iterations can be made for both PIXE and XRF, although each technique has also its own sample-matrix correction methods. The main advantage of these sample-matrix corrections methods is that we can work with samples without previous treatments. As a constrain, the sum of the concentrations must be equal to one:

$$C_i + C_j + C_k + \dots = 1 \quad (4.9)$$

then, the number of iterations necessities are $N-1$, where N is the number of detected elements.

Equation (4.9) leaves space for the assumption of one element. In the case of geological samples, we can assume that all elements detected are presented in oxide forms, as SiO_2 , TiO_2 , FeO_2 and so on, in such a way that the undetected element in a sample is only oxygen [76], [77]. This assumption is valid for a large variety of minerals. In some cases, there are also the presence of other low- Z elements like carbon in the form of carbonates, like in siderite (FeCO_3) or calcite (CaCO_3), and hydrogen in the form of hydroxide or water, like goethite ($\text{FeO}(\text{OH})$) or Melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). How these low- Z elements change the correction factors if we suppose that all these elements are oxygen is shown in figure 4.5, calculated using our codes PFactor and XFactor. For carbonates and hydroxides, the discrepancies are lower than 5%, but in the presence of water, the discrepancies are higher. In the case of biological samples like cellulose, the assumption of oxygen as a low- Z element is not valid. In these biological samples, the major presence of hydrogen, carbon and oxygen, even nitrogen in the sample, cellulose is the usual assumption for the compositions of the low- Z sample-matrix, that can be written as an element with the same mass absorption coefficient and stopping power than cellulose [78], [79]. With these assumptions, the concentrations of the major elements detected are calculated based on comparison with thick reference samples. In PIXE, the assumption of cellulose as a sample-matrix of lower elements is a good approximation for some biological samples as leaves, but it can show major discrepancies for some other samples like, for example, tissues, especially for elements lower than $Z=20$. In XRF, the assumption of cellulose is not as accurate as in PIXE, and the comparison with standards has to be more specific, like leaves with other similar leaves, tissues with other similar tissues and so on.

Figure 4.5: Relative deviations between the correction factors for the assumption of low-Z elements of a) mineral samples and cellulose with the oxygen assumption in PIXE, b) biological samples with the cellulose assumption in PIXE, c) mineral samples and cellulose with the oxygen assumption in XRF and d) biological samples with the cellulose assumption in XRF, and the correction factor of the original sample as a function of the K_{α} line of the correspondent element.

4.2.1 Influence coefficient algorithms for XRF

Considering primary X-ray production, we can isolate the concentration of an element i in a sample in equation (2.38) and obtain:

$$C_i = R_i \chi_i \quad (4.10)$$

where $R_i = N_{xi}/r_{xi}T_x$. This means that the concentration of the analyte is proportional to the XRF correction factor, χ_i . Equation (2.33) shows that χ_i depends on the mass absorption coefficients of the sample for the incident and characteristic X-ray energy of the analyte. These mass absorption coefficients depend, in turn, on the concentrations of the elements, $C_i, C_k...$ in the sample. Following the additive law, equation (2.22), we

have:

$$\begin{aligned}
\chi_i &= C_i \left(\frac{\mu_i(E_{x0})}{\rho \sin \phi_x} + \frac{\mu_i(E_i)}{\rho \sin \theta_x} \right) + C_j \left(\frac{\mu_j(E_{x0})}{\rho \sin \phi_x} + \frac{\mu_j(E_i)}{\rho \sin \theta_x} \right) \\
&\quad + C_k \left(\frac{\mu_k(E_{x0})}{\rho \sin \phi_x} + \frac{\mu_k(E_i)}{\rho \sin \theta_x} \right) + \dots \\
&= C_i K_{ii} + C_j K_{ij} + C_k K_{ik} + \dots
\end{aligned} \tag{4.11}$$

where K_{ii} , K_{ij} , K_{ik} ... are the XRF correction factor for the analytes themselves, not for the sample, which are obtained from the database. Then, for every element in the sample we have a set of equations:

$$\begin{aligned}
C_i &= R_i (C_i K_{ii} + C_j K_{ij} + C_k K_{ik}) \\
C_j &= R_j (C_i K_{ji} + C_j K_{jj} + C_k K_{jk}) \\
C_k &= R_k (C_i K_{ki} + C_j K_{kj} + C_k K_{kk}) \\
&\vdots
\end{aligned} \tag{4.12}$$

This set of equations have the advantages of being linear, transforming the unknown parameters, χ_i , χ_k , χ_j ... into known parameters K_{ii} , K_{jj} , K_{kk} ... Also, we have the measured quantities N_i , N_j , N_k ... and the constants T_x and r_{xi} , r_{xj} , r_{xk} ..., which can be obtained by calibration. The set of equations (4.12) together with the constrain in equation (4.9) form a system of linear algebraical equations. The K terms are known as influence coefficients

Several other influence coefficient algorithms were developed over the years. The Lachance-Traill algorithm [80] uses a calibration with pure elements. We rearrange equations (4.12) and (4.9) in the form:

$$C_i = R_i^* \left(1 + \sum_{j \neq i} \alpha_{ij} C_j \right) \tag{4.13}$$

where the summation is made over all elements, except the analyte, R_i^* is the total number of counts measured with the analyte in the sample, N_i , divided by the total number of counts obtained from a pure analyte, and α_{ij} are the so-called alpha coefficients:

$$\alpha_{ij} = \frac{\frac{\mu_j(E_{x0})}{\rho \sin \phi_x} + \frac{\mu_j(E_i)}{\rho \sin \theta_x}}{\frac{\mu_i(E_{x0})}{\rho \sin \phi_x} + \frac{\mu_i(E_i)}{\rho \sin \theta_x}} - 1 \quad (4.14)$$

where $\mu_j(E_{x0})/\rho$ is the mass absorption coefficient of the element j for the incident X-ray energy, $\mu_j(E_i)/\rho$ is the mass absorption coefficient of the element j for the K_α line of the element i , $\mu_i(E_{x0})/\rho$ is the mass absorption coefficient of the element i for the incident X-ray energy and $\mu_i(E_i)/\rho$ is the mass absorption coefficient of the element i for the K_α line of the same element. These parameters are obtained directly from the database.

We see that equation (4.13), together with similar equations for the other detected elements C_j , $C_k...$ form a linear set of algebraical equations that depend on measured quantities, like R_i^* , R_j^* , R_k^* and known mass absorption coefficients from the database like the coefficients α_{ij} .

Other algorithm methods, taking into account secondary and tertiary enhancement, standardless analysis and, even, a polychromatic excitation [12] [14] have been developed. The main disadvantage is that these methods need the detection of, at least, N-1 elements in the sample, and the methods do not work in presence of low-Z elements, like biological samples. The constrain expressed in (4.9) leaves a space for the assumption of only one low-Z element that can be oxygen, as seen before.

4.2.2 Approximation methods for PIXE

Different than the XRF correction factor, the PIXE correction factor can not be written as a linear combination of the PIXE correction factor of every analyte. There are no influence coefficient algorithms for PIXE. Instead, some approximations can be developed for the PIXE correction factor. Smit et al [81] suggested an approximation for the PIXE correction factor, using an approximation of the stopping power [82] and the cross section:

$$S_\rho(E_p) = (E_p/E_{p0})^{q_S} S_\rho(E_{p0}) \quad (4.15)$$

$$\sigma_{pi}(E_p) = (E_p/E_{p0})^{q_\sigma} \sigma_{pi}(E_{p0}) \quad (4.16)$$

where q_S varies from -0.7 to -0.5, $S_\rho(E_0)$ is the stopping power at the proton initial energy E_0 , q_σ varies from 1 to 3 depending on the element and $\sigma(E_{p0})$ is the cross section at the same proton initial energy E_{p0} . Then, the PIXE thick target factor (equation (2.28)) can

be transformed into:

$$M_i = D\sigma_i \int_0^1 (1-t)^m e^{-kt} dt \quad (4.17)$$

where $\sigma_i = (1 - x/D)^{q_\sigma/(1+q_S)}$, $D = E_{p0}/(1 + q_S)S_\rho(E_{p0})$, $x = \int 1/S_\rho(E'_p)dE'_p$, $m = q_\sigma/(1 + q_S)$ and $k = \mu(E_i)/\rho \tan \phi_p D$. At this point, the parameters q_S and k depend on the target composition, showing the advantage of this approximation: an iteration is necessary with only these two parameters. Using the approximations (4.15) and (4.16), we obtain a PIXE correction factor (4.17) differing from the original PIXE correction factor by less than 5% for metal alloys. For biological and organic samples the differences increase because, for the elements lower than $Z=20$, the approximation (4.16) is less precise.

Another approach for bulk analysis is found in the work of Aloupogiannis et al [83]. They define the alpha parameter as:

$$\alpha_1 = \frac{\mu(E_i)}{\rho S_\rho(E_r)} \quad (4.18)$$

where E_r is a reference energy of the same order of E_{p0} and $\mu(E_i)/\rho$ is the mass absorption coefficient of the sample for the K_α line of the analyte. Using the approximation for the stopping power (4.15) the thick target factor (equation (2.28)) results in:

$$M_i = \frac{1}{S_\rho(E_r)} \int_0^{E_{p0}} \frac{\sigma_i(E_{p0} - U)}{(E_{p0} - U/E_r)_S^q} \exp\left(-\frac{\alpha_1 U \sin \phi_p}{\sin \theta_p} \left(1 + \frac{q_S}{2} \frac{U}{E_0}\right)\right) dU \quad (4.19)$$

where $U = E_{p0} - E_p$. We can see that this function depends on two parameters, α and $S_\rho(E_r)$, depending on the element

$$M_i = \frac{1}{S_\rho(E_r)} f(\alpha_1, E_{p0}, \theta, \phi) \quad (4.20)$$

Varying the beam energy, a second intensity, N_2 , can be measured, obtaining two simultaneous equations that can be transformed into only one equation, using $\alpha_2 = \alpha_1(E_{p1}/E_{p2})^{q_S}$.

Errors associated with the approximation (4.15) are in the order of 1% for biological samples and 3% for metal alloys. We still have to know $S_\rho(E_r)$. This parameter is estimated depending if the sample is biological, geological, metallic or other kind, and a theoretical average must be calculated, with standard deviations of around 10% calculated

from the tables shown in [83].

4.3 Compensation methods

The objective of the compensation methods is reducing the effects of the correction factors, dealing with the direct relationship between concentrations and total number of counts. Most of these methods need the addition or comparison with standard samples to the sample itself. Except for the external standard method, all these methods require the manipulation of the sample and are not valid for *in situ* analysis, adding systematic errors in the sample treatment.

4.3.1 External standard methods

When we have knowledge of the main elemental constituents of the sample and we only want to know the trace elements so that the sample-matrix effects are canceled out, a comparison method with known samples is applied. Examples of these methods are the analysis of trace elements in steel when we know that the main element is iron. In the analysis of contamination in biological samples, we compare the X-ray spectrum of a sample with the spectrum of an uncontaminated sample. In these cases, the correction factors of the known and the unknown samples are similar and equations (4.7) and (4.8) are transformed to:

$$C_i = C_{i\text{known}} \frac{N_i}{N_{i\text{known}}} \quad (4.21)$$

and the determination of the elemental concentrations is straightforward. This method is limited to the accurate knowledge of the composition of the sample, and sometimes we are only capable of assuming their composition.

4.3.2 Internal standard addition method

In this method, an element or a compound with the same element is added with the same quantity to the sample and to a standard, in a fixed percentage over the total [12]. It is added this internal standard so that the correction effects on the analyte and on the internal standard varies with the same proportionally constant. Usually, this addition is made with elements with atomic number of $Z + 1$ or $Z - 1$. The main drawback is

that several additions must be made, as there are the number of elements detected in the sample, and additions must be made to the standards, not only to the sample.

4.3.3 Dilution method

This method consists in diluting a sample into a known homogeneous sample of low-Z elements [53]. Common diluents are boric acid, graphite, urea, starch, and cellulose due to the ability of these materials to form sturdy and compact tablets. The method consists of mixing the sample homogeneously with the diluent in a ratio of less than 5%. For example, 5% of sample+95% of diluent, or 1% of sample+99% of diluent. Thus, we can calculate the PIXE and XRF correction factors assuming that all the elements in the samples are constituted by this diluent and the concentrations are obtained by:

$$C_i = \frac{1}{\Delta} \frac{N_{pi}}{F_i r_{pi} T_p} \quad (4.22)$$

for PIXE, or

$$C_i = \frac{1}{\Delta} \frac{N_{xi} \chi_i}{r_{xi} T_x} \quad (4.23)$$

for XRF. Δ is the ratio of the dilution. Figure 4.6 shows the accuracy we obtain changing the real PIXE and XRF correction factors of a Boric acid + sample to different percentages with the PIXE and XRF correction factors of the total boric acid in three kinds of samples. We see that in the case of biological samples the differences between them are the lowest, especially for PIXE. For heavier sample-matrices like glass and iron, the differences increase, especially in XRF.

Figure 4.6: Relative deviations between the correction factors for three samples with different dilutions in boric acid in proportions of a) 1% in PIXE b) 5% in PIXE c) 1% in XRF d) 5% in XRF and the correction factor of the boric acid as a function of the K_{α} line of the correspondent element.

An advantage of the dilution method is the reduction of the secondary fluorescence effects. Using our codes PSecondary.m and XSecondary.m we can see some examples. In a sample-matrix of 99.9% Fe and 0.1% Cr, the secondary fluorescence due to iron over chromium produces a 57% yield over the primary yield in PIXE and 176% in XRF. If this sample is diluted in boric acid in a 5% proportion over the total, this secondary fluorescence is 9% in PIXE and 32% in XRF; in 1% proportion, the secondary fluorescence is 1% in PIXE and 7% in XRF. In biological samples, when the secondary fluorescence is not as higher as the last example, the secondary fluorescence is reduced to negligible levels. In the tomato sample, for example, the calcium induces a secondary fluorescence of 1% in PIXE over the primary yield and 3.5% in XRF. In a 5% dilution with boric acid, we obtain secondary fluorescence of 0.1% in PIXE and 0.24% in XRF. Also, the dilution method only adds uncertainty in the Δ value with respect to a measurement in the undiluted sample.

Lets focus this dilution method on biological and organic samples, figure 4.7 shows the comparison between the correction factor of boric acid and the correction factors of 1% of biological or organic samples + 99% of boric acid. Cortical bone and polyethylene are one of the heaviest and lightest, respectively, kind of biological and organic samples. Any other sample of these kinds, like those shown in figure 4.5b and 4.5d, will have mass absorption coefficients and stopping power between these same parameters of cortical bone and polyethylene. Then, the differences in the correction factors will be between the two curves shown in figure 4.7 for PIXE and XRF. If we compare this figure with figure 4.5b and 4.5d we note that the dilution method provides better accuracy compared with the correction methods with the assumption of cellulose. In PIXE, these accuracies are lower than in XRF, especially for elements with atomic number of $Z > 20$. Still, we can improve these accuracies with dilutions of any value lower than 1%.

Figure 4.7: Relative deviation between the PIXE or XRF correction factors for different samples with dilutions of 1% cortical bone + 99% boric acid and 1% polyethylene + 99% boric acid, and the PIXE or XRF correction factors of boric acid as a function of the K_{α} line of the correspondent element.

The disadvantage of diluting the sample in a known sample-matrix is the loss of trace element information from the original sample since the peak intensities of these trace elements are further reduced in the dilution and some of them will be below the limit of detection. Having a 1% dilution the total number of counts are reduced to almost 100

times from the original sample, requiring a measurement time 100 times longer.

4.4 Addition methods

We can add, now, a small quantity of the analyte to the sample and comparing the total number of counts of the original sample with the total number of counts obtained with the small analyte plus the sample. Let's add a Δ percentage of the analyte over the total. Considering primary production, the ratio of the total number of counts of the sample and the total number of counts of the added sample, $N_{s/a}$ is, now:

$$N_{s/a} = \frac{C_i}{C_i - C_i\Delta + \Delta} \quad (4.24)$$

which we have a simple linear equation for C_i :

$$C_i = \frac{\Delta N_{s/a}}{\Delta N_{s/a} - N_{s/a} + 1} \quad (4.25)$$

Equation (4.25) is valid as long the ratio between the PIXE and XRF correction factors do not change significantly. In figure 4.8 we calculate, with our PFactor and XFactor codes, the differences between the PIXE and XRF correction factors of the sample and the PIXE and XRF correction factors of the sample plus the 5% of the analyte over the total. We examine two samples, one with 50% of iron +50% of the analyte, and another one with cellulose + 100 ppm of the analyte. The first sample is an example of the determination of major elements in mineral samples. The second sample is an example of the determination of trace elements in biological and organic samples. We see that in PIXE, as in XRF, for the first example, these differences are lower than 5% and, in most cases, the differences are lower than 2%. For the analysis of trace samples in biological samples, there is a quite different result if comparing PIXE with XRF: PIXE method provides better differences, of less than 5%, while in XRF these differences are higher, especially for high-Z elements, of up to 70%.

Figure 4.8: Relative deviation between the PIXE or XRF correction factors for a 5% addition of the analyte over the total of two different samples a) 50% Fe and 50% analyte and b) Cellulose+100 ppm analyte, and the PIXE or XRF correction factors of the original sample, as a function of the K_α line of the correspondent element.

If we analyze the uncertainty of C_i due to the propagation of uncertainties of $N_{s/a}$ we can find the relative uncertainty of C_i using the common propagation of error formula:

$$\frac{dC_i}{C_i} = \frac{dN_{s/a}}{N_{s/a}} \frac{1}{1 + \Delta N_{s/a} - N_{s/a}} \quad (4.26)$$

that is a function of the relative uncertainty of $N_{s/a}$ by a factor $1/(1 + \Delta N_{s/a} - N_{s/a})$ calculated from (4.24). If $C_i = 0.5$ and $\Delta = 0.05$, like in the first example, the relative uncertainty of C_i have a 10 times the relative uncertainty of the measured ratio $N_{s/a}$. Thus, the addition method is very sensitive to uncertainties of the major elements. On the other hand, for trace elements, we can make $C_i \ll \Delta$, then:

$$\frac{dC_i}{C_i} = \frac{dN_{s/a}}{N_{s/a}} \quad (4.27)$$

and the relative uncertainty obtained is the same relative uncertainty of the measurements. This means that the addition method is suitable, in precision, for trace elements analysis, but with low accuracy in XRF. In XRF, a double dilution method is usually suggested for improving this accuracy [12].

4.5 Thin film and intermediate thick samples.

Some samples can be transformed into thin films via chemical or physical procedures. The main advantage of this method is to allow canceling out every instrumental and

physical parameter of the experimental setup by comparing two measurements, for PIXE and XRF we have similar relationships for thin samples:

$$\begin{aligned} N_i &= C_i r_i T \rho t \\ N_{is} &= C_{is} r_i T \rho t_s \end{aligned} \quad (4.28)$$

then:

$$C_i = C_{is} \frac{N_i}{N_{is}} \frac{t}{t_s} \quad (4.29)$$

Thus, the concentration of an analyte in a sample is directly proportional to the total number of counts, making the analysis straightforward. The main drawbacks are the loss or contaminations of some quantities of trace elements in the sample in the process of conversion to a thin film and the low total number of counts that thin films have compared to thick samples, lowering the detection limit up to 100 times as shown in figure 4.9. This means we need a measuring time 100 times longer, like the dilution method, to achieve the same total number of counts as the original sample.

Figure 4.9: Ratio between the total number of counts of a thin sample of $50 \mu\text{g}/\text{cm}^2$ of a pure element and the total number of counts of a thick sample of the same element as a function of the K_α line of the correspondent element.

We can also transform a sample into intermediate thick samples. With these kinds of samples, we can measure the final energy of the proton or final intensity of the X-ray incident beam, when passing through the entire sample and, then, we can determine the proton stopping power and mass absorption coefficients of the sample at that point. Using other proton or X-ray beam energies we can determine the proton stopping power and the mass absorption coefficient for those energies, and then, calculate directly equations (2.24) and (2.32) for the determination of the analyte concentrations. The solution is exact, but several measurements must be made. Also, the intermediate thickness kind depends on the incident energy of the X-ray and proton beam. For example, calculations using equation (2.20) show that a K_α Zn line loses 87% of intensity passing through a $10\mu\text{m}$ of target. When a K_α Si line passes through the same target, it almost loses all its intensity. Then, for K_α Zn line, the target is intermediate, and for a K_α Si the target is thick and the measurement of the target mass absorption coefficient can not be made.

4.6 Backscattering methods

The Compton and Rayleigh scattered radiation, in XRF, can be used to calculate the mass absorption coefficient of the sample at the energy of these scattered photons. The models of the total number of counts for Compton and Rayleigh have the structure ??:

$$\begin{aligned} N_{Com} &\propto \frac{\sigma_{Com}}{\mu(E_{x0})/\rho} \\ N_{Ray} &\propto \frac{\sigma_{Ray}}{\mu(E_{x0})/\rho} \end{aligned} \tag{4.30}$$

The proportionality constants are more complex than the total number of counts for XRF fluorescence and the Compton and Rayleigh cross section, σ_{Com} and σ_{Ray} and the modeling of these peaks is more complex than the total number of counts of the characteristic X-rays. The main advantage of knowing correctly these total number of counts is that let us more equations for the evaluation of two more low-Z elements representatives of the sample, together with equations (4.9) and (4.12), forming a full set of equations with N detected elements and 3 undetected elements. So, the backscattering method is suitable for biological and organic samples if we know the exact form of the equations (4.30). The complication increases when the Compton and Rayleigh peaks are overlapped for incident X-rays energies $E_{x0} < 10$ keV, when there is no much difference between the Compton

X-ray energy and the Rayleigh X-ray energy, following equation 2.19, when the quotient E_{x0}/E_0 is less than 2%.

Backscattering protons, on the other hand, are detected by another method known as Rutherford Backscattering Spectrometry (RBS), where the proton energy reduction rate of the scattered particle depends on the mass ratio of the incident proton and the atoms in the sample and, then, allowing to determine the elemental concentrations in the sample, detecting low-Z elements like carbon, nitrogen and oxygen. The combined use of the PIXE and RBS allows us to be used for elemental identification and quantification of elements from biological and organic samples. Modern ion beam analysis programs are trying to make PIXE and RBS compatible in a single measurement [84]. There are softwares making self-consistent analysis of multiple ion beam techniques like a simultaneous RBS and ERDA in [85]. But there is still a need of making self-consistent analysis of simultaneous RBS and PIXE.

Part II

A new method for the determination of trace elements in low-Z sample-matrices

Chapter 5

Equivalent HCO sample-matrix

*Señores guardias civiles:
Aquí pasó lo de siempre.
Han muerto cuatro romanos
Y cinco cartagineses.
(Honourable Civil Guards:
The same as usual
Four Romans dead
And five Carthaginians.)*

*Federico García Lorca
Reyerta*

In previous chapters, we showed that determining all major elements in a sample using dilution methods or preparing thin samples is possible for biological and organic samples in PIXE and XRF with accuracies lower than 1%. A method to determine the trace elements not characterized in these methods with the same level of accuracy is still to be found. In this chapter we will show that, taking advantage of the knowledge of at least two major elements, we can determine the remaining trace elements. As a complementary consequence, the determination of the concentration of hydrogen in the sample is possible in a PIXE analysis.

5.1 Insight of the method.

The main idea of the method is to assume that all low-Z in a sample are in the form of an equivalent HCO sample-matrix, since the mass absorption coefficients of all low-Z

elements (except hydrogen) as a function of X-ray energy E_x , alike the stopping power, as a function of the proton energy E_p , have about the same functional dependence as shown in figure 5.1.

Because the PIXE and the XRF correction factors depend on the mass absorption coefficients and the stopping power (for PIXE only), the correction factor of the equivalent HCO sample-matrix will have the same PIXE and XRF correction factors of the original HCNO sample-matrix for K_α energies of all elements. The equivalent HCO sample-matrix is seen as a true effective sample-matrix and has no particular physical meaning.

Figure 5.1: a) Mass absorption coefficient of H, C, N and O as a function of the K_α line of the correspondent element. b) Proton stopping power of H, C, N and O as a function of the proton energy.

5.2 Approximate equivalent HCO sample-matrix for the stopping power and the mass absorption coefficient

Element	q_μ	q_S
H	Not linear	-0.75
Li	-2.7	-0.71
Be	-2.9	-0.69
B	-3.0	-0.69
C	-3.0	-0.69
N	-3.0	-0.64
O	-3.0	-0.63
F	-2.9	-0.63
Na	-2.9	-0.68
Mg	-2.8	-0.62
Al	-2.8	-0.63

Table 5.1: Exponents q_μ and q_S from equations (5.2) and (5.9), respectively. Parameters obtained from a fitting of the XCOM database [51] for X-rays energies from 1 keV to 15 keV for the mass absorption coefficient, and the SRIM2013 database [34] for proton energies from 0.5 MeV to 5 MeV

5.2.1 Approximation for the mass absorption coefficient

As shown in equation (2.13), the photoelectric cross section $\tau(E_x)/\rho$ as a function of the X-ray energy is, for an element i , approximately:

$$\frac{\tau_i(E_x)}{\rho} = B_i E_x^{q_\mu} \quad (5.1)$$

where $q_\mu \approx -3$ for elements from $Z > 2$, as shown in table 5.1, and B_i is a constant that depends on every element. For hydrogen, the mass absorption coefficient follows a different function, $\mu_H(E_x)/\rho$, which is not linear. As shown in figure 2.8 The mass absorption coefficient is approximately equal to the photoelectric absorption coefficient, $\tau(E_x)/\rho$, for X-ray energies between 1keV and 15 keV, then, it is expected that the mass absorption coefficient follows the same function:

$$\frac{\mu_i(E_x)}{\rho} = B_i E_x^{q_\mu} \quad (5.2)$$

The absorption edges of the low- Z elements are below 1keV, thus, in the X-ray energy region from 1keV to 20 keV, the mass absorption coefficients of these low- Z elements are continuous functions, without noticeable absorption edges.

Let us consider a sample-matrix of low elements $H_{C_H}C_{C_C}N_{C_N}O_{C_O}$, where C_H , C_C , C_N and C_O are the mass concentrations of H, C, N and O, respectively. The mass absorption coefficient as a function of the X-ray energy can be calculated using the additive law (equation (2.22)):

$$\frac{\mu(E_x)}{\rho} \approx C_H \frac{\mu_H(E_x)}{\rho_H} + C_C B_C E_x^{-3} + C_N B_N E_x^{-3} + C_O B_O E_x^{-3} \quad (5.3)$$

where B_C , B_N and B_O are proportionality constants. We define an equivalent HCO sample-matrix, with concentrations C_{Heq} , C_{Ceq} and C_{Oeq} of hydrogen, carbon and oxygen, respectively, with mass absorption coefficient of:

$$\frac{\mu(E_x)}{\rho} = C_{Heq} \frac{\mu_H(E_x)}{\rho_H} + (C_{Ceq} B_C + C_{Oeq} B_O) E_x^{-3} \quad (5.4)$$

which reproduce the same mass absorption coefficient of the original sample-matrix:

$$C_{Heq} \frac{\mu_H(E_x)}{\rho_H} + (C_{Ceq} B_C + C_{Oeq} B_O) E_x^{-3} = C_H \frac{\mu_H(E_x)}{\rho_H} + C_C B_C E_x^{-3} + C_N B_N E_x^{-3} + C_O B_O E_x^{-3} \quad (5.5)$$

We need to find these C_{Heq} , C_{Ceq} and C_{Oeq} concentrations, having one equation with three unknowns, C_{Heq} , C_{Ceq} and C_{Oeq} . Thus, we need some restrictions for finding one unique solution to this last equation. The first restriction is that this equation must be valid for all X-ray energies, E_x . Thus, we have to separate the $\mu_H(E_x)/\rho_H$ term from the E_x^{-3} terms, finding the trivial solution:

$$C_{Heq} = C_H \quad (5.6)$$

and reducing (5.5) to:

$$C_C B_C + C_N B_N + C_O B_O = C_{Ceq} B_C + C_{Oeq} B_O \quad (5.7)$$

The second restriction is the condition (4.9):

$$C_{Heq} + C_{Ceq} + C_{Oeq} = 1 \quad (5.8)$$

having, now, a set of two equations, (5.7) and (5.8), with two unknowns C_{Ceq} , C_{Oeq} .

We showed here that, for the approximation (5.2), we can find an HCO sample-matrix with the same mass absorption coefficient of an HCNO sample-matrix. Also, we find that the equivalent concentration of the hydrogen must correspond to the original concentration of hydrogen.

5.2.2 Approximation for the proton stopping power

In equation (4.15) we showed that the stopping power as a function of the proton energy has the form:

$$S_{\rho i}(E_p) = M_i E_p^{q_S} \quad (5.9)$$

where $q_S \approx -0.7$, as shown in table 5.1, and M_i is a constant that depends on the element. The additive rule (equation (2.8)) shows that the stopping power of a sample-matrix $H_{C_H}C_{C_C}N_{C_N}O_{C_O}$ as a function of the proton energy can be written as:

$$S_{\rho}(E_p) \approx C_H S_H(E_p) + C_C M_C E_p^{-0.7} + C_N M_N E_p^{-0.7} + C_O M_O E_p^{-0.7} \quad (5.10)$$

where M_C , M_N and M_O are proportionality constants. Using the same argument that we used for the mass absorption coefficient, we must find the equivalent concentrations C_{Heq} , C_{Ceq} and C_{Oeq} that reproduce the stopping power of the original sample-matrix:

$$S_{\rho}(E_p) = C_{Heq} S_H(E_p) + (C_{Ceq} M_C + C_{Oeq} M_O) E_p^{-0.7} \quad (5.11)$$

Then, we can find an HCO sample-matrix with the same proton stopping power coefficient as an HCNO sample-matrix, with the same solution for the hydrogen concentration, $C_{Heq} = C_H$, and an equation for the carbon and oxygen equivalent:

$$C_C M_C + C_N M_N + C_O M_O = C_{Ceq} M_C + C_{Oeq} M_O \quad (5.12)$$

Notice that the two equations (5.12) and (5.7) turn out to have different equivalent concentrations of carbon and oxygen for mass absorption coefficient and stopping power, since the constants M_C , M_N and M_O are different from the constants B_C , B_N and B_O . Also, we can not add another equation for the determination of the equivalent concentration of nitrogen, C_{Neq} , in searching for the complete determination of the real concentration of carbon, nitrogen and oxygen, because we can obtain multiple solutions. For example, an equivalent sample-matrix for the salammoniac, NH_4Cl ($H_{7.5\%}N_{26.2\%}Cl_{66.3\%}$), can

have two possible sample-matrices that reproduce the same mass absorption coefficient or stopping power than the original one: The sample-matrix itself, $\text{H}_{7.5\%}\text{N}_{26.2\%}\text{Cl}_{66.3\%}$, and those obtained by solving the system of equations described before, (5.8), (5.6) and (5.7), for the mass absorption coefficient, or (5.8), (5.6) and (5.12) for the stopping power

Figure 5.2: a) Mass absorption coefficient of H, C, N and O as a function of the K_α line of the correspondent element. b) Proton stopping power of H, C, N and O as a function of the proton energy.

5.2.3 Equivalent HCO sample-matrix for real values from the database

Currently, the functions $\mu(E_x)/\rho$ and $S_\rho(E_p)$ for N, C and O do not have the equations expressed in (5.3) and (5.10) as shown in equations (2.16) and (2.6). Table 5.1 shows the values of the exponents q_μ and q_S from equations (5.2) and (5.9), respectively, fitted from the XCOM database [51] and SRIM database [34] for different low-Z elements, plus Na, Mg and Al. In this table is shown that the exponents q_μ and q_S are different from the approximations $q_\mu = -0.3$ and $q_S = -0.7$. Thus, the equalities in equations (5.6), (5.7) and (5.12) do not necessarily hold on. In the next section we will see how these approximations, affect the results of the PIXE and XRF correction factors.

5.3 Determination of an equivalent HCO sample-matrix using PIXE and XRF

In PIXE and XRF we do not determine the mass absorption coefficients and stopping power directly from the measurement. In this work we showed that these parameters are part of the PIXE and XRF correction factors as described in equations (2.30) and

(2.33). In XRF we deal with formulas combining the mass absorption coefficients while the stopping power is added to the formulation in PIXE.

Consider a sample containing the elements H, C, N and O, and two major elements with concentrations C_i and C_j . We can define a set of three equations with three unknowns, the equivalent concentration of hydrogen, carbon and oxygen, C_{Heq} , C_{Ceq} and C_{Oeq} :

$$\begin{aligned} F_i(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= F_i(C_H, C_C, C_N, C_O, C_i, C_j) \\ F_j(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= F_j(C_H, C_C, C_N, C_O, C_i, C_j) \\ C_{Heq} + C_{Ceq} + C_{Oeq} + C_i + C_j &= 1 \end{aligned} \quad (5.13)$$

for PIXE, or

$$\begin{aligned} \chi_i(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= \chi_i(C_H, C_C, C_N, C_O, C_i, C_j) \\ \chi_j(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= \chi_j(C_H, C_C, C_N, C_O, C_i, C_j) \\ C_{Heq} + C_{Ceq} + C_{Oeq} + C_i + C_j &= 1 \end{aligned} \quad (5.14)$$

for XRF.

At least, the concentration of two major elements are required to construct a set of three equation with three unknowns. Other elements, $k, l...$ can be included to increase the precision of the results, as we will show in section 6.4.2. For now, in the next section, we will show the numerical solution for the system of equations (5.13) and (5.14) for different compounds and mixtures.

5.4 Numerical solution for theoretical compositions.

5.4.1 Solution for PIXE

Solving for the equivalent oxygen concentration in the system of equations 5.13:

$$C_{Oeq} = 1 - C_{Heq} - C_{Ceq} - C_i - C_j \quad (5.15)$$

the system of equations (5.13) is now a system of two equations with two unknowns:

$$\begin{aligned}
F_i(C_{Heq}, C_{Ceq}, C_i, C_j) &= F_i(C_H, C_C, C_N, C_O, C_i, C_j) \\
F_j(C_{Heq}, C_{Ceq}, C_i, C_j) &= F_j(C_H, C_C, C_N, C_O, C_i, C_j)
\end{aligned} \tag{5.16}$$

Equation (5.16) is a system of two nonlinear equations, since the two unknowns to find, C_{Heq} and C_{Ceq} , are inside two integrals, as shown in equation (2.30).

We can express (5.16) in the vectorial form:

$$\mathbf{F} \begin{pmatrix} C_{Heq} \\ C_{Ceq} \end{pmatrix} = \mathbf{F}_0 \tag{5.17}$$

where $\mathbf{F} = \begin{pmatrix} F_i(C_{Heq}, C_{Ceq}, C_i, C_j) \\ F_j(C_{Heq}, C_{Ceq}, C_i, C_j) \end{pmatrix}$ and $\mathbf{F}_0 = \begin{pmatrix} F_i(C_H, C_C, C_N, C_O, C_i, C_j) \\ F_j(C_H, C_C, C_N, C_O, C_i, C_j) \end{pmatrix}$ or simply:

$$\mathbf{F} = \begin{pmatrix} F_i \\ F_j \end{pmatrix} \tag{5.18}$$

and:

$$\mathbf{F}_0 = \begin{pmatrix} F_{0i} \\ F_{0j} \end{pmatrix} \tag{5.19}$$

There are several methods for solving systems of two nonlinear equations. A common algorithm consists in the transformation of a system of equations into an optimization problem [86], [87]. This means, a minimum of a function of two variables [88], [89]:

$$R(C_{Heq}, C_{Ceq}) = \|\mathbf{F} - \mathbf{F}_0\| \tag{5.20}$$

where R is a norm of the vector, is a solution of the system of equations (5.16). Several norms can be chosen, depending on the vectorial space we are working with. A common norm, chosen here, is the sum of squared differences:

$$R(C_{Heq}, C_{Ceq}) = (F_{0i} - F_i)^2 + (F_{0j} - F_j)^2 \tag{5.21}$$

Transforming a system of nonlinear equations (5.16) into an optimization problem allows having more equations than the unknowns [88]. Having more than two major elements in a sample, let's say $i, j, k...$ allows us to construct a set of several equa-

tions $(F_i(C_{Heq}, C_{Heq}), F_j(C_{Heq}, C_{Heq}), F_k(C_{Heq}, C_{Heq})...) = (F_{i0}, F_{j0}, F_{k0}...)$ with two unknowns. A set of more independent equations than unknowns does not have roots, but it has an optimal solution¹, which it is a minimum of:

$$R(C_{Heq}, C_{Ceq}) = (F_{i0} - F_i)^2 + (F_{j0} - F_j)^2 + (F_{k0} - F_k)^2 + ... \quad (5.22)$$

Several numerical methods can be applied to find a minimum of a function of several variables. Since the hydrogen and carbon equivalent concentrations vary between 0 and 1 we can make an iteration with incremental searches in that range of values. We wrote a code in Matlab with the same input parameters and databases we used in the chapter 3 and, in the next sections, we will show the iteration process.

5.4.2 Solution for XRF

We saw in section 4.2.1 that the XRF correction factor is a linear combination of the XRF correction factor for every element in the sample. For a sample with a HCNO configuration with additional elements $i, j, k..$ we calculate the XRF correction factor for an element i with equation (4.11):

$$\chi_{i0} = C_H K_{iH} + C_C K_{iC} + C_N K_{iN} + C_O K_{iO} + C_i K_{ii} + C_j K_{ij} + C_k K_{ik}... \quad (5.23)$$

and for an element j :

$$\chi_{j0} = C_H K_{jH} + C_C K_{jC} + C_N K_{jN} + C_O K_{jO} + C_i K_{ji} + C_j K_{jj} + C_k K_{jk}... \quad (5.24)$$

An equivalent HCO sample-matrix with the same XRF correction factor than equations (5.23) and (5.24) has an XRF correction factor:

$$\begin{aligned} \chi_i &= C_{Heq} K_{iH} + C_{Ceq} K_{iC} + C_{Oeq} K_{iO} + C_i K_{ii} + C_j K_{ij} + C_k K_{ik}... = \chi_{i0} \\ \chi_j &= C_{Heq} K_{jH} + C_{Ceq} K_{jC} + C_{Oeq} K_{jO} + C_i K_{ji} + C_j K_{jj} + C_k K_{jk}... = \chi_{j0} \end{aligned} \quad (5.25)$$

¹This method of solution is inspired by the least square problem of experimental data. For one point in a plane, infinite straight lines pass through the point. For two points, only one straight line passes through the two points. For three or more non collinear points there is no straight line passing through them, but there is a unique line minimizing the sum of squared distances

Remembering that the equivalent concentration of oxygen is given by $C_{O_{eq}} = 1 - C_{Heq} - C_{Ceq} - C_i - C_j - C_k...$ we have:

$$\begin{aligned}
C_{Heq}K_{iH} + C_{Ceq}K_{iC} + (1 - C_{Heq} - C_{Ceq} - C_i - C_j - C_k...)K_{iO} \\
+ C_iK_{ii} + C_jK_{ij} + C_kK_{ik}... = \chi_{i0} \\
C_{Heq}K_{jH} + C_{Ceq}K_{jC} + (1 - C_{Heq} - C_{Ceq} - C_i - C_j - C_k...)K_{jO} \\
+ C_iK_{ji} + C_jK_{jj} + C_kK_{jk}... = \chi_{j0}
\end{aligned} \tag{5.26}$$

and rearranging terms:

$$\begin{aligned}
(K_{iH} - K_{iO})C_{Heq} + (K_{iC} - K_{iO})C_{Ceq} &= P_i \\
(K_{jH} - K_{jO})C_{Heq} + (K_{jC} - K_{jO})C_{Ceq} &= P_j
\end{aligned} \tag{5.27}$$

where:

$$\begin{aligned}
P_i &= \chi_{i0} - K_{iO}(1 - C_i - C_j - C_k...) - C_iK_{ii} - C_jK_{ij} - C_kK_{ik}... \\
P_j &= \chi_{j0} - K_{jO}(1 - C_i - C_j - C_k...) - C_iK_{ji} - C_jK_{jj} - C_kK_{jk}...
\end{aligned} \tag{5.28}$$

Showing that, different from the solution for PIXE, the system of equations (5.14) was transformed into the simple set (5.27) of two linear equations with two unknowns, which has an exact solution.

Eventually we can add more equations in case we have more than two major elements:

$$\begin{aligned}
(K_{iH} - K_{iO})C_{Heq} + (K_{iC} - K_{iO})C_{Ceq} &= P_i \\
(K_{jH} - K_{jO})C_{Heq} + (K_{jC} - K_{jO})C_{Ceq} &= P_j \\
(K_{kH} - K_{kO})C_{Heq} + (K_{kC} - K_{kO})C_{Ceq} &= P_k \\
&\vdots
\end{aligned} \tag{5.29}$$

where:

$$\begin{aligned}
P_i &= \chi_{i0} - K_{iO}(1 - C_i - C_j - C_k...) - C_i K_{ii} - C_j K_{ij} - C_k K_{ik}... \\
P_j &= \chi_{j0} - K_{jO}(1 - C_i - C_j - C_k...) - C_i K_{ji} - C_j K_{jj} - C_k K_{jk}... \\
P_k &= \chi_{k0} - K_{kO}(1 - C_i - C_j - C_k...) - C_i K_{ki} - C_j K_{kj} - C_k K_{kk}... \\
&\vdots
\end{aligned} \tag{5.30}$$

The system of equations (5.29) with two unknowns does not have a solution but, similar to the PIXE solution in equation (5.22), it has an optimal solution, which is a minimum of:

$$R_x(C_{Heq}, C_{Ceq}) = (\chi_{0i} - \chi_i)^2 + (\chi_{0j} - \chi_j)^2 + (\chi_{0k} - \chi_k)^2 + ... \tag{5.31}$$

An iteration using and incremental search in the hydrogen and carbon equivalent concentrations between 0 and 1 will be made as we will describe in the next sections.

5.4.3 Calculation constrains

- Sample composition. The sample-matrix must contain at least one low-Z element and two known elements. In case there are no known elements, two elements can be added in a separate sample-matrix with its corresponding dilution factor.
- Supply the concentrations of the elements $C_i, C_j, C_k...$ up to 8 elements, from $Z = 11$ to 40.
- The number of steps varying the concentrations of hydrogen (m) and carbon (n). The number of steps will define the size of the minimization sample-matrix and the precision of the number of iterations for the hydrogen concentrations, m , and for the carbon concentrations, n . For oxygen concentrations we use the constrain $C_{Omn} = 1 - C_{Hm} - C_{Cn} - C_i - C_j - C_k...$
- As we will see later, this same procedure will also work with any HAB equivalent sample-matrix, where A and B are two elements between $Z=2$ and $Z=10$.
- Select the lowest atomic number of an element that can be detected. $Z_{min}=10$ in vacuum conditions, and $Z_{min}=11, 12$ or 13 in the case of in-air conditions, where elements like Na, Mg or even Al can not be detected and must be considered low-Z elements.

- Select the minimum and maximum hydrogen concentration. We can iterate around a region of hydrogen concentration if we partially know this value. For example, there is no solid sample in nature having more than 20% of hydrogen, so we can limit our iterations of hydrogen from 0% to 20%, to reduce computing time.

5.4.4 Determining the equivalent HCO sample-matrix in PIXE

With the constrains, physical parameters and database, we proceed to find the equivalent HCO sample-matrix. In PIXE we follow the steps:

- Determine the PIXE correction factor for all detected elements F_{0i} , F_{0j} , F_{0k} ... using the code PFactor.m described in chapter 3 by equation (2.30).
- Calculate the PIXE correction factor for all possible combination of concentrations of hydrogen, carbon and oxygen, as a function of the known elements, F_{mni} , F_{mnj} , F_{mnk} ... In other words, F_{mn} is the correction factor for a HCO sample-matrix tested of hydrogen, carbon and oxygen concentrations $H_{C_{Htested}} C_{C_{tested}} O_{C_{Otested}} i_{C_i} j_{C_j} k_{C_k}$..., calculated using equation (2.30), so that $C_{Htested}$ is the m subdivision from $C_{Htested} = 0$ to $C_{Htested} = 1 - C_i - C_j - C_k$... and $C_{Ctested}$ is the n subdivision from $C_{Ctested} = 0$ to $C_{Ctested} = 1 - C_{Htested} - C_i - C_j - C_k$ The oxygen concentration in every element of the sample-matrix is $C_{Otested} = 1 - C_{Htested} - C_{Ctested} - C_i - C_j - C_k$ The values of m and n can be as big as desired precision.
- Calculate the norm defined in equation (5.22) for every m and n . We define a matrix $\mathbf{R}$ with matrix element:

$$R_{mn} = (F_{0i} - F_{mni})^2 + (F_{0j} - F_{mnj})^2 + (F_{0k} - F_{mnk})^2 + \dots \quad (5.32)$$

Matlab determines the position (m,n) containing the minimum of this matrix. The equivalent hydrogen concentration is, then, calculated by $C_{Heq} = \min(m)/m$, the carbon equivalent concentration is $C_{Ceq} = \min(n)/n$ and the oxygen equivalent concentration is $C_{Oeq} = 1 - C_{Heq} - C_{Ceq} - C_i - C_j - C_k - \dots$.

- Finally, compare the PIXE matrix factor of the equivalent sample for all elements from Z=11 to 40 with the PIXE matrix factor of the original sample for these same elements. The accuracy of the method is calculated using the relative deviation

D_{iPIXE} :

$$D_{iPIXE} = \frac{F_i - F_{i0}}{F_{i0}} \times 100 \quad (5.33)$$

which is calculated for all elements between $Z=11$ and 40. The name of this code is HCOPIXE.m

5.4.5 Determining the equivalent HCO sample-matrix in XRF

A code for the determination of the HCO sample-matrix equivalent in XRF was written as described previously for PIXE, changing F for χ , so that we must find an equivalent HCO sample-matrix reproducing the same XRF correction factor as the original XRF correction factor knowing a minimum of two major elements. Thus, the matrix to minimize has the matrix element:

$$R_{mn} = (\chi_{0i} - \chi_{mni})^2 + (\chi_{0j} - \chi_{mnj})^2 + (\chi_{0k} - \chi_{mnk})^2 + \dots \quad (5.34)$$

and the minimum of this matrix will determine the hydrogen, carbon and oxygen equivalent concentration. The accuracy, then, is calculated:

$$D_{iXRF} = \frac{\chi_i - \chi_{i0}}{\chi_{i0}} \times 100 \quad (5.35)$$

In case we have only two major elements, Matlab can solve the linear system of two equations with two unknowns expressed in equations (5.27) and (5.28) calculating the parameters K directly from the database of the mass absorption coefficients.

In the next chapter we will apply these codes to several kinds of organic, biological or other kind of samples with high composition of low-Z elements, to see how the PIXE and XRF correction factors of the equivalent matrix agrees with the original PIXE and XRF correction factors, and in what cases the equality between the equivalent hydrogen concentration and the actual hydrogen concentration (equation (5.6)) holds up.

Chapter 6

Results and discussion for several compounds and mixtures.

The numerical solution described in the previous chapter was applied to several known samples. The composition of these samples are obtained from the National Bureau of Standards Publications (NBS) at the National Institute of Standards (NIST) [75] and the International Commission on Radiation Units and Measurements (ICRU) [90]. Other common organic samples are also considered. We calculated the PIXE and XRF correction factors for the known major elements like, for example, the ordinary concrete (composition shown in table A.1, in the appendix), and calculated the PIXE and XRF correction factors for the major elements $Z=13,14,19,20$. Then, we apply the iteration described in the previous chapter for determining the equivalent concentrations C_{Heq} , C_{Ceq} and C_{Oeq} .

There are uncontaminated samples where no element can be detected in PIXE or XRF analysis, e.g. organic samples like kapton, mylar, urea, cellulose (see concentrations in table A.1), or samples where the detected elements have concentrations lower than 1% that can not be considered major elements. In these cases we suggest an addition¹ of 10% of Si and 10% Zn over total which enables the calculation of the PIXE or XRF correction factors for these elements.

¹All additions described in this work are hypothetical and it is not always possible to find pure elements to add to the sample.

6.1 Example of a determination of an equivalent HCO sample-matrix

We illustrate how the code works with an example in PIXE. We want to find an equivalent HCO sample-matrix of a urea sample, $\text{CH}_4\text{N}_2\text{O}$ ($\text{H}_{6.7\%}\text{C}_{20\%}\text{N}_{46.7\%}\text{O}_{26.7\%}$). This sample does not have major elements to be detected in PIXE or XRF. We can add a known quantity of silicon and zinc to form a sample-matrix of 80% ($\text{H}_{6.7\%}\text{C}_{20\%}\text{N}_{46.7\%}\text{O}_{26.7\%}$) and 20% ($\text{Si}_{50\%}\text{Zn}_{50\%}$) for a total of $\text{H}_{5.4\%}\text{C}_{16\%}\text{N}_{37.3\%}\text{O}_{21.3\%}\text{Si}_{10\%}\text{Zn}_{10\%}$. Then, we construct a sample-matrix for every possible HCO configuration for a giving number of steps. Consider $m=11$ and $n=11$, forming a 11X11 sample-matrix, in such a way that we consider all 2% steps of possible hydrogen concentrations, from 0% to 20%:

$$\begin{bmatrix} \text{H}_{0\%}\text{C}_{0\%}\text{O}_{80\%}\text{Si}_{10\%}\text{Zn}_{10\%} & \text{H}_{0\%}\text{C}_{8\%}\text{O}_{72\%}\text{Si}_{10\%}\text{Zn}_{10\%} & \dots & \text{H}_{0\%}\text{C}_{80\%}\text{O}_{0\%}\text{Si}_{10\%}\text{Zn}_{10\%} \\ \text{H}_{2\%}\text{C}_{0\%}\text{O}_{78\%}\text{Si}_{10\%}\text{Zn}_{10\%} & & \ddots & \text{H}_{2\%}\text{C}_{78\%}\text{O}_{0\%}\text{Si}_{10\%}\text{Zn}_{10\%} \\ & \vdots & & \vdots \\ \text{H}_{20\%}\text{C}_{0\%}\text{O}_{60\%}\text{Si}_{10\%}\text{Zn}_{10\%} & \dots & \dots & \text{H}_{20\%}\text{C}_{60\%}\text{O}_{0\%}\text{Si}_{10\%}\text{Zn}_{10\%} \end{bmatrix} \quad (6.1)$$

Then, we calculate the PIXE correction factor for every matrix element, for the elements Si and Zn using equation (2.30):

$$F_{Si} = \begin{bmatrix} 0.57 & 0.60 & \dots & 0.93 \\ 0.58 & & \ddots & 0.94 \\ \vdots & & & \vdots \\ 0.69 & \dots & \dots & 1.04 \end{bmatrix} \times 10^{-3}\text{g/cm}^2 \quad (6.2)$$

and

$$F_{Zn} = \begin{bmatrix} 4.91 & 4.89 & \dots & 4.73 \\ 4.74 & & \ddots & 4.58 \\ \vdots & & & \vdots \\ 3.58 & \dots & \dots & 3.50 \end{bmatrix} \times 10^{-3}\text{g/cm}^2 \quad (6.3)$$

Then, we compare the matricial elements with the PIXE correction factor, calculated by equation (2.30), of the original composition $\text{H}_{5.4\%}\text{C}_{16\%}\text{N}_{37.3\%}\text{O}_{21.3\%}\text{Si}_{10\%}\text{Zn}_{10\%}$:

$$F_{Si} = 0.74 \times 10^{-3}\text{g/cm}^2 \quad (6.4)$$

and

$$F_{Zn} = 4.39 \times 10^{-3} \text{g/cm}^2 \quad (6.5)$$

and the matrix K has the matrix element:

$$R_{mn} = (F_0(15) - F_{mn}(15))^2 + (F_0(30) - F_{mn}(30))^2$$

$$K = \begin{bmatrix} 3.00 & 2.7 & \dots & 1.52 \\ 1.48 & \ddots & & 0.76 \\ \vdots & & \ddots & \vdots \\ 0.659 & \dots & \dots & 0.882 \end{bmatrix} \times 10^{-7} \text{g}^2/\text{cm}^4 \quad (6.6)$$

The minimum matrix element will correspond to the equivalent mass concentrations of the hydrogen, carbon and oxygen in the sample. In this case, in position $m = 4$ and $n = 6$ we found an equivalent sample-matrix of $\text{H}_{6\%}\text{C}_{37\%}\text{O}_{37\%}\text{Si}_{10\%}\text{Zn}_{10\%}$. Eventually, we can improve this result increasing the values of m and n or iterating, again, the PIXE correction factor around this first result to find a better result. The final equivalent sample-matrix obtained from a 200X200 iteration is $\text{H}_{5.4\%}\text{C}_{37.3\%}\text{O}_{37.3\%}\text{Si}_{10\%}\text{Zn}_{10\%}$. The equivalent hydrogen concentration corresponds to the original hydrogen concentration, of 5.4%.

In XRF, we have to solve the system of equations (5.27) for finding an HCO sample-matrix equivalent for the same sample described in PIXE. Obtaining the parameters from the database in (5.27), the system of equations to solve is:

$$\begin{aligned} 1.46C_{Heq} + 0.81C_{Ceq} &= 377 \\ 0.0132C_{Heq} + 0.0085C_{Ceq} &= 3.89 \end{aligned} \quad (6.7)$$

The solution of this equation is provided by Matlab, which results in an equivalent sample-matrix of $\text{H}_{1.8\%}\text{C}_{43\%}\text{O}_{35.2\%}\text{Si}_{10\%}\text{Zn}_{10\%}$ where the hydrogen equivalent concentration does not correspond to the original hydrogen concentration. If we apply the iteration process for finding the minimum of (5.31), we obtain the same sample-matrix, which is expected. An equivalent sample-matrix must be determined easily for two known major elements solving the system of equations (5.27), but it only can be solved minimizing (5.31) for more than two known major elements.

6.2 Application to several known samples

The example showed in the last section is applied to several known samples from the NBS [75], ICRU [90] and common organic samples, as described in table A.1, where the composition of these samples are organized from the lowest hydrogen concentration to the highest hydrogen concentration.

6.2.1 Accuracy of the equivalent HCO method

The PIXE correction factors of any HCO sample-matrix equivalent, F_i , changes less than 1% with respect to the PIXE correction factor, F_{0i} , of the original sample for all samples shown in table A.1, as shown in figure 6.1 for six different samples from that table. Figure 6.2 shows that the relative deviations obtained between the XRF correction factor, χ_i , equivalent and the original XRF correction factor, χ_{i0} , are still lower than PIXE, with 0.2% of maximum relative deviations.

The concentrations of trace elements depend on the PIXE and XRF correction factors. This means that the concentrations of these trace elements can be obtained with accuracies lower than 0.5%. These percentages are an improvement of the typical 5-10% accuracies obtained in the methods described in the chapter 4 for trace elements.

In both PIXE and XRF, when the original sample is composed of only hydrogen, carbon and oxygen, like mylar, cellulose or other samples (written in *italic* in table A.1), the equivalent HCO sample-matrix is, in fact, the original sample-matrix, as expected as a trivial solution of our method. Notice that when having only nitrogen and hydrogen, like salammoniac (in underline in the same table), there is an HCO solution, even when the sample does not contain carbon and oxygen.

Figure 6.1: Relative deviations of the PIXE correction factor F_i of an equivalent HCO sample-matrix from the PIXE correction factor F_{i0} of the original sample-matrix for six different samples as a function of the K_α line of the correspondent element..

Figure 6.2: Relative deviations of the XRF correction factor χ_i of an equivalent HCO sample-matrix from the XRF correction factor χ_{i0} of the original sample-matrix for six different samples as a function of the K_α line of the correspondent element.

6.2.2 Hydrogen concentration

As observed in the bold values in table A.1, in every sample the equivalent hydrogen concentration corresponds to the real hydrogen concentration in PIXE. The equivalent concentrations of hydrogen in XRF, instead, do not correspond to the original hydrogen, especially when there is a high concentration of nitrogen in the sample, like in urea. These results show that the HCO method in PIXE can be used to determine indirectly the hydrogen concentration in any biological or organic sample.

6.2.3 Uniqueness of solutions

Having a unique solution for our equivalent HCO sample-matrix is important because, if we can obtain the hydrogen concentration, we must ensure that this hydrogen concentration is unique. Figure 6.3 shows all possible values of the function $R(C_{Heq}, C_{Ceq})$ (equation (5.22)) for every iteration of the equivalent hydrogen concentration and equivalent carbon concentration for three different samples. The surface obtained, in PIXE, is a smooth surface with an absolute minimum and no relative minimums indicating that there is always a unique equivalent HCO sample-matrix. In XRF, instead, the surface $R(C_{Heq}, C_{Ceq})$, this time calculated using equation (5.31), has an irregular shape with several relative minimums, although also with a unique absolute minimum.

We can take advantage of having an absolute minimum and no relative minimums in the surfaces in PIXE. Only one minimum means that we can make a small iteration, around all domain in $\mathbb{R}^2$ finding a minimum. Next, the region around that minimum is split into equally sized sub-domains, making new iterations and repeating again until get a more precise minimum. Thus, the computational time is reduced compared to the computational time spent in an iteration around all the original domain. For example, at the time this work is written, an Intel(R) Core(TM)2 Duo CPU, 2.00GHz was used to run the codes. A complete 200x200 of C_{Heq} and C_{Ceq} iteration, as described in section 6.1, spends 140 s. Three 10X10 iterations around a minimum spend 3 s. This result shows one of the advantage of the equivalent HCO method: A short iteration is required with only two parameters, C_{Heq} and C_{Ceq} .

In XRF, with several relative minimums, it is not possible to make the same subdivisions than in PIXE. However, the computational time spent in XRF is lower than in PIXE because there are no integrals to make in the XRF correction factor, as in the PIXE correction factor. A 200X200 iteration require 2 s in the computer used for this work.

Figure 6.3: R function for a 200X200 possible iterations of C_{Heq} and C_{Ceq} for three different samples in PIXE and XRF.

6.3 Comparing equivalent HCO sample-matrix with other softwares.

Using the program XMI-MSIM [70] we can simulate an X-ray spectrum of any sample with a given instrumental XRF conditions. Figure 6.4 shows the spectra of two different samples: Cortical bone and their equivalent HCO sample-matrix, showed in table A.1. The figure shows an agreement between the total number of counts lower than 1% for the elements P, S and Ca for an X-ray incident beam with an energy of 5 keV. Calculations using the CLARA software for the PIXE correction factor shows also an agreement between the PIXE correction factor of the cortical bone, and the PIXE correction factor of their equivalent HCO sample-matrix of less than 1%. These results are checked with other samples showed in table A.1 with the same agreement. These results prove, with independent softwares, that the equivalent HCO sample-matrix method provides good accuracies.

Figure 6.4: Comparison between the net total number of counts of a cortical bone XRF spectrum with the equivalent cortical bone spectrum obtained in table A.1. A 5 keV monochromatic beam is used. Simulation using the program XMI-MSIM [70]. Default settings for geometry array and detection on the software were applied.

6.4 Propagation of uncertainties

Until now, we assume that the concentrations of the major elements are known with absolute precision. Experimentally, these concentrations can have uncertainties and, thus, are propagated to the PIXE and XRF correction factors for these elements. Also, the calculation of the PIXE and XRF correction factors have uncertainties due to the database, instrumental parameters and acquisition process, as discussed in section 4.1.

To determine the precision of the HCO method, we modified our HCOPIXE code to take into account these uncertainties, simulating Gaussian distributions for the PIXE and XRF correction factors F_{0i} , F_{0j} ..., χ_{0i} , χ_{0j} ... of the original samples assuming unbiased and independent parameters, similar to the calculations made in section 4.1. The standard deviations of these distributions will propagate to the final F_i and χ_i and the equivalent hydrogen concentration. Finally, the average and the standard deviation of these distributions are calculated and, thus, their relative uncertainty of the PIXE and XRF correction factor for every calculated element.

6.4.1 Uncertainties of PIXE and XRF correction factors

Figures 6.5 and 6.6 show the relative uncertainties of F_i and χ_i respectively, assuming 1%, 5% or 10% of relative uncertainties in the PIXE and XRF correction factors of a urea sample with an addition of 10% of silicon and 10% of zinc over the total. The relative uncertainties propagated in the PIXE and XRF correction factor of the equivalent HCO sample-matrix conserve the same order of magnitude of the relative uncertainties of the PIXE and XRF correction factor of the original sample, with better precision in XRF. Then, the HCO method is a convenient method to determine trace elements maintaining approximately the same relative uncertainties that the relative uncertainties of all the experimental array, for both PIXE and XRF.

Figure 6.5: Propagation of the relative uncertainty of F_i when having 1%, 5% and 10% relative uncertainties in F_{0i} and F_{0j} of a urea sample with an addition of 10% of silicon and 10% of zinc over the total as a function of the K_α line of the correspondent element.

Figure 6.6: Propagation of the relative uncertainty of χ_i when having 1%, 5% and 10% relative uncertainties in χ_{0i} and χ_{0j} of a urea sample with an addition of 10% of silicon and 10% of zinc over the total as a function of the K_α line of the correspondent element.

The addition in a sample of two different elements than Si and Zn, like Si and Ca or

Zn and Zr, or the addition of more than two elements, like Si, Ca, Fe and Zn, does not improve the accuracies showed in figures 6.1 and 6.2, but it can affect the precision of the PIXE and XRF correction factors of the equivalent HCO sample-matrix. Figure 6.7 and 6.8 show the propagation of 5% of relative uncertainties in the original PIXE and XRF correction factors for different added elements in urea to the relative uncertainties of the PIXE and XRF factor of the equivalent HCO sample-matrix. It is shown that the addition of elements with $Z > 20$, like Zn and Zr, propagates more than an addition of, for example, Si and Zn. Also, adding more elements can improve the precision of the PIXE and XRF correction factors. The addition of 12 elements can improve the precision to better than 1%.

Figure 6.7: Propagation of the relative uncertainty of F_i when having 5% of relative uncertainties in F_{0i} and F_{0j} of urea sample with an addition of 20% of equally distributed elements over the total as a function of the K_α line of the correspondent element. a) Si and Ca, b) Si and Zn, c) Al and Si, d) Zn and Zr, e) Si, Ca, Fe and Zn, f) Si, P, Ca, Fe, Ni, Zn, and Se and g) Si, P, S, K, Ca, Fe, Ni, Zn, Se, Sr and Zr.

Figure 6.8: Propagation of the relative uncertainty of χ_i when having 5% of relative uncertainties in χ_{0i} and χ_{0j} of a urea sample with an addition of 20% of equally distributed elements over the total as a function of the K_α line of the correspondent element. a) Si and Ca, b) Si and Zn, c) Al and Si, d) Zn and Zr, e) Si, Ca, Fe and Zn, f) Si, P, Ca, Fe, Ni, Zn and Se and g) Si, P, S, K, Ca, Fe, Ni, Zn, Se, Sr and Zr.

6.4.2 Uncertainties for hydrogen concentration in PIXE

In PIXE, where we obtain the hydrogen concentration, the distribution of this hydrogen concentration has a relative uncertainty varying 10 times the relative uncertainty of these F_{0i} and F_{0j} as shown in figure 6.9 where the Gaussian distribution is maintained. This result shows that with good relative uncertainties in F_{0i} and F_{0j} of around 1% the determination of the hydrogen concentration with around 12% of relative uncertainty is possible. Notice that sometimes the equivalent hydrogen concentration in the distribution can be negative because when the equivalent hydrogen concentration is zero, we can still explore negative solutions to improve accuracy in the PIXE correction factor. As stated in section 5.1, the equivalent HCO sample-matrix does not have physical meaning and the only physical requirement is that the total mass absorption of the sample must be positive.

The uncertainty in the hydrogen concentration in a sample can be minimized taking into account more known elements in the sample or adding several elements to the sample, and calculating F_{0i} , F_{0j} , F_{0k} ... In figure 6.10 we show an example, simulating the addition

of up to 12 different elements to urea like the example given in figure 6.7, in which a 5% of relative uncertainty can propagate to a relative uncertainty with values up to 30% of relative uncertainty in our hydrogen concentration.

Figure 6.9: Propagation of the Gaussian distribution of F_{0i} and F_{0j} with relative uncertainties of 1%, 5% and 10% to the hydrogen concentration in a urea sample with an addition of 10% of silicon and 10% of zinc over total. The standard deviation of every distribution are 12%, 60% and 120%.

Figure 6.10: Relative uncertainties of the mass concentration of hydrogen, propagated from a mixture of 80% urea and 20% of equally distributed elements, with 5% of relative uncertainty in their correspondent PIXE correction factor. a) Si and Ca, b) Si and Zn, c) Al and Si, d) Zn and Zr, e) Si, Ca, Fe, Zn, f) Si, P, Ca, Fe, Ni, Zn, Se and g) Si, P, S, K, Ca, Fe, Ni, Zn, Se, Sr, Zr.

6.5 In air conditions

In PIXE or XRF analysis in atmospherical conditions, elements like sodium and magnesium and, sometimes, aluminum, are difficult to detect due to the strong absorption of their characteristics X-ray lines through the air. Even so, there are other compositions showed in table A.1 with considerable concentrations of these elements, like ordinary concrete, with 1.5% and 2% of sodium and aluminum respectively, or, moreover, MS20 tissue, with 12% of magnesium. In both cases, if we consider Na, Mg and Al low-Z elements, we can find an equivalent HCO sample-matrix. In other words, we can find an equivalent HCO sample-matrix with the same PIXE and XRF correction factors than an HCNON-aMg or an HCNONaMgAl sample-matrix. This is possible because the exponents q_μ and q_S from equations (5.2) and (5.9), showed in table 5.1, for Na, Mg and Al are close to the q_μ and q_S of the other low-Z elements. The PIXE and XRF correction factors deviates from the original as much as 5% as we see in figure 6.11 and 6.12, which equivalent sample-matrices are shown in table A.2.

Minerals samples with high quantities of Na, Mg and Al, have an equivalent HCO sample-matrix with discrepancies in their PIXE and XRF correction factors higher than

10% like magnesium carbonate, in the hydrate form of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), or crystal carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), in the hydrate form of thermonatrite. Therefore, the equivalent HCO method provides better results with organic samples than with mineral samples for PIXE and XRF analysis in air conditions. However, there is still less than 10% of relative deviation in the PIXE correction factors for elements from $Z > 20$, where, in minerals, finding traces elements is common. In all samples, both in PIXE and XRF, the equivalent hydrogen concentration does not correspond to the original hydrogen concentration, as shown in table A.2.

Figure 6.11: Relative deviations of the PIXE correction factor F_i of an equivalent HCO sample-matrix from the PIXE correction factor F_{i0} of the original sample-matrix for five different samples containing Mg, Na or Al as a function of the K_α line of the correspondent element.

Figure 6.12: Relative deviations of the XRF correction factor χ_i of an equivalent HCO sample-matrix from the XRF matrix factor χ_{i0} of the original matrix for five different samples containing Mg, Na or Al as a function of the K_α line of the correspondent element.

6.6 A most general equivalent sample-matrix

This work focus on biological, organic samples or other samples which low-Z elements are in the form of HCNO. We can apply the same ideas for other kind of samples with other low-Z elements, like lithium, boron or fluorine. We still can find an equivalent HCO sample-matrix in most of these samples, as shown in table A.3, and calculate the relative deviations between their PIXE and XRF correction factors as shown in figure 6.13 and 6.14. For most samples, these relative deviations are lower than 3%, but for others, like boron carbide (B_4O) or Teflon (see table A.3 for composition), the relative deviations are higher.

Figure 6.13: Relative deviations of the PIXE correction factor F_i of an equivalent HCO sample-matrix from the PIXE correction factor F_{0i} of the original matrix for seven different samples containing Li, B or F as a function of the K_α line of the correspondent element.

Figure 6.14: Relative deviations of the XRF correction factor χ_i of an equivalent HCO sample-matrix from the XRF matrix factor χ_{0i} of the original sample-matrix for seven different samples containing Li, B or F as a function of the K_α line of the correspondent element.

The reason why we have higher differences in the correction factors in samples like

boron carbide or teflon in figure 6.13 is because the equivalents HCO sample-matrix shown in table A.3 are usually a mean sample-matrix between the carbon and oxygen, but in the case of boron carbide or teflon, the solutions are not a mean between carbon and oxygen, but a 100% carbon or 100% oxygen, respectively, which are absurd results.

Figure 6.15: a) Mass absorption coefficient of different low-Z elements as a function of the K_α line of the correspondent element. b) Proton stopping power of different low-Z elements as a function of the proton energy.

The most general equivalent sample-matrix that includes all possible low-Z elements is the HLiF sample-matrix. Figure 6.15 shows that the similarity between the mass absorption coefficient and the stopping power of all low-Z elements is comparable with the mass absorption coefficient and the stopping power of C, N and O, as shown in table 5.1, which follows equations (5.2) and (5.9). Then, we can follow the same reasoning shown in sections 5.2.1 and 5.2.2 to show that for every sample-matrix in the form of HLiBeBCNOF there is an equivalent HLiF sample-matrix with the same mass absorption coefficient or the same stopping power. Then, we have an equivalent HLiF sample-matrix reproducing the same PIXE or XRF correction factors than the original HLiBeBCNOF sample-matrix. To find this equivalent HLiF sample-matrix, we have to solve:

$$\begin{aligned}
 F_i(C_{Heq}, C_{Lieq}, C_{Feq}, C_i, C_j) &= F_i(C_H, C_{Li}, C_{Be}, C_B, C_C, C_N, C_O, C_F, C_i, C_j) \\
 F_j(C_{Heq}, C_{Lieq}, C_{Feq}, C_i, C_j) &= F_j(C_H, C_{Li}, C_{Be}, C_B, C_C, C_N, C_O, C_F, C_i, C_j) \quad (6.8) \\
 C_{Heq} + C_{Lieq} + C_{Feq} + C_i + C_j &= 1
 \end{aligned}$$

for PIXE, or

$$F_i(C_{Heq}, C_{Lieq}, C_{Feq}, C_i, C_j) = F_i(C_H, C_{Li}, C_{Be}, C_B, C_C, C_N, C_O, C_F, C_i, C_j)$$

$$F_j(C_{Heq}, C_{Lieq}, C_{Feq}, C_i, C_j) = F_j(C_H, C_{Li}, C_{Be}, C_B, C_C, C_N, C_O, C_F, C_i, C_j) \quad (6.9)$$

$$C_{Heq} + C_{Lieq} + C_{Feq} + C_i + C_j = 1$$

for XRF. Again, we need at least two major elements to solve these equations

Table A.4 shows that for every low-Z element, there is an HLiF equivalent sample-matrix in PIXE and XRF. The PIXE correction factor deviates up to 15%, but lower than 5% for elements from $Z > 14$, as shown in figure 6.16. In XRF, however, these same elements show higher relative deviations in the XRF correction factors up to 20% as shown in figure 6.17. Notice that, as shown in table A.4, written in bold, there is an equivalent hydrogen concentration even when the original sample does not have hydrogen in the sample. The reason is that, as shown in table 5.1, the exponents in equations (5.2) and (5.9) are not all the same, especially if comparing lithium with fluorine. Then, the separation of terms in equations (5.6) and (5.7) does not hold up.

Figure 6.16: Relative deviations of the PIXE correction factor F_i of an HLiF equivalent sample-matrix from the PIXE correction factor F_{0i} of the original matrix for seven different pure low-Z elements as a function of the K_α line of the correspondent element.

Figure 6.17: Relative deviations of the XRF correction factor χ_i of an HLiF equivalent sample-matrix from the XRF correction factor χ_{0i} of the original sample-matrix for seven different pure low-Z elements as a function of the K_α line of the correspondent element.

We apply this HLiF method for the same samples analyzed in figure 6.13. Differences between the PIXE and XRF correction factors for these materials and their HLiF equivalents are shown in figures 6.18 and 6.19. In PIXE, these differences are lower than 7%, but from $Z > 14$ the differences are lower than 5%. In XRF these differences are higher, especially for light compounds like boron carbide, but for the other samples, the differences are lower than 8%.

The tomato sample shows higher relative deviations using the HLiF equivalent sample-matrix than using the equivalent HCO sample-matrix comparing the relative deviations showed in figures 6.18 and 6.19 with the deviations showed in figures 6.1 and 6.2. But, in the case we do not actually know the biological origin of the sample, it is still a deviations lower than 5% for most elements.

The HLiF sample-matrix is a good equivalent sample-matrix, especially in PIXE, for all kind of samples with a considerable amount of unknown low-Z elements and it is the best method to determine trace elements of these kind of samples since there is no other method in the literature providing lower relative deviations that those shown in figures 6.18 and 6.19 for a complete unknown sample-matrix of low-Z elements.

Eventually, we can choose another equivalent sample-matrix having some information

of the sample. If we know that there are considerable amount of boron in the sample, an equivalent HBO sample-matrix can give better results. If there is a considerable amount of fluorine in the sample, an equivalent HCF sample-matrix will be also a good choice. Even for external samples we can select an equivalent HONa or HOMg sample-matrix for mineral samples. We must remember than the hydrogen must be always in the equivalent sample-matrix because this element is the one which has a different equation for the mass absorption coefficient and stopping power as shown in table 5.1.

Figure 6.18: Relative deviations of the PIXE correction factor F_i of an HLiF equivalent sample-matrix from the PIXE correction factor F_{0i} of the original sample-matrix for eight different samples as a function of the K_α line of the correspondent element.

Figure 6.19: Relative deviations of the XRF correction factor χ_i of an HLiF equivalent sample-matrix from the PIXE correction factor χ_{0i} of the original sample-matrix for eight different samples as a function of the K_α line of the correspondent element.

6.7 L lines for elements from $Z > 40$.

In common Si detectors, the K lines of elements from $Z > 40$ have low efficiency, but the L lines of these elements can be detected with better efficiency. We can define a PIXE and XRF correction factors for the L lines in the same way we defined for the K lines in equations (2.30) and (2.33), changing the ionization cross section $\sigma_{pi}(E_p)$ for the K line, for the ionization cross section for the L line, $\sigma_{piL}(E_p)$, in PIXE, and changing the mass absorption coefficients of the sample for the K_α lines by the mass absorption coefficients of the sample for the L_α line, in both PIXE and XRF:

$$F_{iL_\alpha} = \frac{\sin \phi_p}{\sigma_{piL}(E_{p0})} \int_0^{E_{0p}} \frac{\sigma_{piL}(E_p) \exp\left(-\frac{\mu(E_{iL_\alpha}) \sin \phi_p}{\rho \sin \theta_p} \int_{E_{p0}}^{E_p} \frac{dE'_p}{S_\rho(E'_p)}\right)}{S_\rho(E_p)} dE_p \quad (6.10)$$

where $\sigma_{piL}(E_p)$ is calculated using the parametrization given by Johansson in [5] and:

$$\chi_{iL_\alpha} = \frac{\mu(E_{x0})}{\sin \phi_x} + \frac{\mu(E_{iL_\alpha})}{\sin \theta_x} \quad (6.11)$$

In both equations (6.11) and (6.10) the mass absorption coefficients for the L_α lines are calculated using the XCOM database.

6.7.1 Heavy elements as known elements

We determine an equivalent HCO sample-matrix using the same procedure described in section 5.4, but now using the PIXE and XRF correction factors in equations (6.10) and (6.11). Results are shown in table A.6.

Figure 6.20 shows the relative deviations we obtain between the PIXE and XRF correction factors of the equivalent and original sample, for two kinds of photographic emulsion: nuclear ($H_{1.4\%}C_{7.2\%}N_{1.9\%}O_{6.6\%}S_{0.1\%}Br_{34.9\%}Ag_{47.4\%}Cs_{0.3\%}$) and Kodak(R) ($H_{3\%}C_{21\%}N_{7.2\%}O_{16.3\%}Br_{22.2\%}Ag_{30\%}$) [90]. We used the L_{α} lines of Br and Ag for the determination of the equivalent HCO sample-matrix and, then, calculated the PIXE and XRF correction factors for all elements. Figure 6.20 shows accuracies lower than 0.3%. In PIXE, as in the other biological samples, the equivalent hydrogen concentration is equal to the real hydrogen concentration for both Kodak(R) and nuclear photographic emulsion.

Figure 6.20: Relative deviations between the PIXE or XRF correction factors of the equivalent HCO sample-matrix from the original sample for two kinds of photographic emulsion [90] as a function of the K_{α} line of the correspondent element.

6.7.2 Heavy elements as trace elements

Common heavy elements from $Z > 40$ can be present in biological and organic samples in ppm, like iodine, cadmium, mercury and lead [75]. Using the equivalent HCO sample-matrix found for the tomato sample, we calculate the PIXE and XRF correction factor

calculated for the L_α lines of these heavy elements and calculated the relative deviations with the PIXE and XRF correction factor of the original sample. Figure 6.21 shows that this relative deviation is lower than 1%. Then, the HCO method also provide good accuracy for trace elements of heavy elements.

Figure 6.21: Relative deviations between the PIXE or XRF correction factors of the equivalent HCO sample-matrix from the original tomato leave sample for the L_α lines of the heavy elements Ag, Cd, Hg and Pb as a function of the K_α line of the correspondent element.

6.8 Secondary fluorescence considerations

In some cases, we must consider enhancement effects when the possible trace element that we want to characterize is near a major element and the fluorescent X-ray line of this major element can excite this trace element causing secondary fluorescence, as described in section 2.7.3.

Table A.7 shows the comparison between the ratio secondary/primary fluorescence of the original sample and the same ratio for the equivalent HCO or HLiF sample. We obtain that these ratios maintain similar levels of relative deviations to those shown in primary fluorescence for the equivalent HCO and HLiF sample-matrix methods. In the case of the HCO method, the relative deviations are lower than 1%, and in the case of the HLiF method, the relative deviations can be higher up to 20%, making the HLiF method sensitive for secondary fluorescence.

6.9 Other input parameters

Examples of every case were shown in table A.1 and all other following tables and figures, but we can test any HCNO sample-matrix with additional major elements to find an equivalent HCO sample-matrix reproducing the same PIXE and XRF correction factors for checking the limits of the method. Also, we can check if the equivalent hydrogen concentration corresponds always to the original hydrogen concentration. The input parameters described in chapter 3 were used in these examples, but we can vary the principal parameters also.

Figures 6.22 and 6.23 show the relative deviation obtained between the PIXE and XRF correction factors for some common trace elements, like Mg, P, Fe, Zn or Rb, as a function of the incident energy beam, in the tomato leaves (see composition in table A.1).

In Figure 6.22 we can see that the region between 2 MeV and 5 MeV in the proton beam is the most suitable region to obtain relative deviations in the PIXE correction factor lower than 1% for all trace elements. Also, this region provides the hydrogen concentration with relative deviations lower than 1%

In Figure 6.23 we can see that the variation in the X-ray incident energy beam does not affect the relative deviations obtained in figure 6.2 for all incident X-Ray energies, keeping the relative deviations of less than 0.5% in the XRF correction factor. Also, The equivalent HCO sample-matrix found for the tomato sample is equal to the equivalent HCO sample-matrix shown in table A.1 for all incident X-ray energies. This last result shows that this method can be applied to polychromatic XRF analysis in further researches.

All calculations shown in this work are also verified for different databases, changing from XCOM to FFAST, for the mass absorption coefficient; from Ziegler to SRIM, for the proton stopping power; and from Johansson to Kahoul for the proton ionization cross section. Also, the variation of the incident and take-off angles are checked, obtaining relative deviations of the XRF and PIXE correction factors in the same order than the original parameters.

Figure 6.22: Relative deviations of the PIXE correction factor F_i of an equivalent HCO tomato sample from the PIXE correction factor F_{i0} of the original tomato leave sample for different elements and the relative deviation of the equivalent hydrogen concentration from the actual hydrogen concentration as a function of the proton incident energies.

Figure 6.23: Relative deviations of the XRF correction factor χ_i of an equivalent HCO tomato sample from the PIXE correction factor χ_{i0} of the original tomato leave sample as a function of monochromatic X-ray incident energies.

6.10 An experimental suggestion for the determination of trace elements in a low-Z sample-matrix

Hitherto we were calculating the equivalent sample-matrices knowing the major elements *a priori*. Experimentally, we can take advantage of the previous determination of at least two major elements discussed in chapter 4 with dilution methods or thin film preparations and makes a new measurement with the original sample.

6.10.1 Experimental determination of sample-matrix equivalents

Knowing at least two major elements in a sample, we can determine the PIXE or XRF correction factors, solving for F_i or χ_i in equations (4.3) and (4.4):

$$F_i = \frac{N_{pi}}{C_i r_{pi} T_p} \quad (6.12)$$

$$\chi_i = C_i \frac{r_{xi} T_x}{N_{xi}} \quad (6.13)$$

with the total number of counts, N_{pi} and N_{xi} of these elements and a calibration for r_{pi} and r_{xi} . An equivalent HCO sample-matrix reproducing the PIXE or XRF correction factors obtained from equations (6.12) and (6.13) for two elements i and j satisfies the equations:

$$\begin{aligned} F_i(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= \frac{N_{pi} r_{pi}}{C_i T_p} \\ F_j(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= \frac{N_{pj} r_{pj}}{C_j T_p} \\ C_{Heq} + C_{Ceq} + C_{Oeq} + C_i + C_j &= 1 \end{aligned} \quad (6.14)$$

for PIXE, or

$$\begin{aligned} \chi_i(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= C_i \frac{r_{xi} T_x}{N_{xi}} \\ \chi_j(C_{Heq}, C_{Ceq}, C_{Oeq}, C_i, C_j) &= C_j \frac{r_{xj} T_x}{N_{xj}} \\ C_{Heq} + C_{Ceq} + C_{Oeq} + C_i + C_j &= 1 \end{aligned} \quad (6.15)$$

for XRF. Equations (6.14) and (6.15) are a system of three equations with three unknowns which have a similar form of equations (5.13) and (5.14). A solution of these systems of equations follows the same path described in section 5.4, which also follows the constrain $C_{Heq} + C_{Ceq} + C_{Oeq} + C_i + C_j = 1$. Then, we transform these systems of three equations with three unknowns into a systems of two equations with two unknowns. For PIXE, we must minimize the function:

$$R = (F_{0i} - F_i)^2 + (F_{0j} - F_j)^2 + (F_{0k} - F_k)^2 + \dots \quad (6.16)$$

where, this time, F_{0i} , F_{0j} , $F_{0k}...$ is obtained experimentally using equation (6.12). For XRF, we must solve the system of equations:

$$\begin{aligned} (K_{iH} - K_{iO})C_{Heq} + (K_{iC} - K_{iO})C_{Ceq} &= P_i \\ (K_{jH} - K_{jO})C_{Heq} + (K_{jC} - K_{jO})C_{Ceq} &= P_j \\ (K_{kH} - K_{kO})C_{Heq} + (K_{kC} - K_{kO})C_{Ceq} &= P_k \\ &\vdots \end{aligned} \quad (6.17)$$

where:

$$\begin{aligned} P_i &= \chi_{i0} - K_{iO}(1 - C_i - C_j - C_k...) - C_i K_{ii} - C_j K_{ij} - C_k K_{ik}... \\ P_j &= \chi_{j0} - K_{jO}(1 - C_i - C_j - C_k...) - C_i K_{ji} - C_j K_{jj} - C_k K_{jk}... \\ P_k &= \chi_{k0} - K_{kO}(1 - C_i - C_j - C_k...) - C_i K_{ki} - C_j K_{kj} - C_k K_{kk}... \\ &\vdots \end{aligned} \quad (6.18)$$

where, this time, χ_{0i} , χ_{0j} , $\chi_{0k}...$ is obtained experimentally using equation (6.13).

The codes described in section 5.4 are modified. Instead of calculating the values F_{i0} , $F_{k0},...$ or χ_{i0} , χ_{j0} , $\chi_{k0}...$ from equations (2.30) or (2.33) we determine these values from the experimental values using equations (6.12) or (6.13).

6.10.2 Concentration of trace elements in a sample.

The HCO method for a complete determination of all elements from $Z > 11$ of a sample requires two measurements (after a calibration process): The first measurement using the dilution method, or thin film transformation, for the determination of major elements as

described in chapter 4. The second measurement is a single measurement with the original sample, detecting the major elements, and calculating the PIXE or XRF correction factors with equations (6.12) or (6.13). With these correction factors is determined the equivalent HCO (or HLiF) sample-matrix and, next, we calculate the PIXE or XRF correction factors for the trace elements detected, using equations (2.30) or (2.33). The final concentrations of these trace elements is obtained using equations (4.3) and (4.4).

Part III

Conclusions

Chapter 7

Conclusions and future perspectives

*Si nous ne trouvons pas des choses agréables, nous
trouverons du moins des choses nouvelles.
(If we do not meet with agreeable things, we shall at least
meet with something new.)*

Voltaire

Candide

In the first part of this work, we summarized all the most important parameters that PIXE and/or XRF have to deal with for the elemental analysis of homogeneous samples. For XRF, the mass absorption coefficient plays the major role and in PIXE we have to add the ionization cross sections and the proton stopping power. We showed the importance of these parameters because they are part of the PIXE or XRF correction factors and how there are still deviations between the databases. Other parameters like detector efficiency, detector solid angle, fluorescence yield, jump ratio, transition rates photoelectric cross section at initial X-ray energy and proton cross section at initial proton energy do not contribute to the PIXE or XRF correction factors and they are usually gathered in a unique term and can be canceled out through a calibration process.

We developed several Matlab codes for calculating sample-matrix effects including the secondary fluorescent in PIXE and XRF when analyzing thick target samples. With these codes, we did a critical evaluation of the main methods for determining the mass concentrations of the elements based on fundamental parameters, assumptions about the samples and for different sample treatments.

Most methods for determining elemental concentrations based on the total number of counts in an X-ray spectrum provide approximations that disagree by less than 10%, being suitable for common experimental setups, when the instrumental uncertainties are of the same order of magnitude. Most of these methods are suitable for mineral, geological and alloy samples. For biological and organic samples, we found that the dilution method is the best procedure for low analytical discrepancies for major elements, of about 1% (with a dilution factor of 1% in PIXE and 0.5% in XRF), and the reduction to a thin films gives exact solutions, with a proper calibration, but depends on laborious and a potentially contaminated laboratory work. Both methods may present systematic errors in the sample preparation process and also worsen the detection limits, reducing the chances of detecting and determining the concentration of trace elements. For these trace elements we found that the addition method in PIXE can give good accuracies and precisions for the analysis of low-Z samples, but it needs several sample additions and sample treatments.

In the second part of this work, we presented the equivalent HCO sample-matrix method for elemental quantification of low-Z sample-matrix samples under the usual formulation of PIXE and monochromatic XRF with the available databases up to date and we analyzed the consequences and applications of this method. We showed that, for all sample-matrices in the form HCNO, there is an equivalent HCO sample-matrix with similar PIXE or XRF correction factors. This result allows the elemental quantification of homogeneous thick samples for trace elements knowing the mass concentration of at least two major elements without any previous assumption of the composition of the low-Z elements in the sample, while needing only two single measurements: the analysis of a diluted sample with a low-Z additive for the determination of major elements, and another measurement of the original sample for the determination of trace elements. For biological and organic samples, the equivalent HCO method has a theoretical accuracy better than 1%, lower than any other method for the determination of trace elements of these kind of samples. It was shown also that this equivalent HCO method has a relative uncertainty at the same order of magnitude of the relative uncertainties of the experimental setup. Another advantage of this method is that an iteration with two parameters, C_{Heq} and C_{Ceq} is enough to determine the equivalent HCO sample-matrix and there is no need of adding more parameters, like C_{Neq} or C_{Oeq} to the iteration, which can delay the iteration process.

An interesting consequence of the determination of an equivalent HCO sample-matrix

is that the equivalent hydrogen concentration in PIXE is close to the hydrogen concentration with an accuracy better than 1% for an HCNO sample-matrix, for PIXE analysis between 2 MeV and 5 MeV. Thus, obtaining the hydrogen concentration in an organic or biological sample analyzed by PIXE is theoretically possible. Nevertheless, the calculation of the uncertainties shows that the hydrogen concentration obtained has a relative uncertainty up to 10 times the relative uncertainties of the experimental setup, showing that there is still the need of reducing the PIXE uncertainties to make the hydrogen determination by PIXE possible. The database of ionization cross section, stopping power and mass absorption coefficients still have significant differences among them. Thus, Setup uncertainties, databases discrepancies and spectrum processing must be improved. We still have to make a comparison with other Ion Beam Analysis techniques for the determination of hydrogen in samples, like ERDA or NRA [91] [92].

For other low- Z samples, we showed that we can generalize the HCO method to an HLiF method or other low- Z combinations like HBF, HLiC, etc. with a theoretical accuracy of less than 5% in PIXE and 10% in XRF. This result is promising since there is no a general method for these kind of samples. Also, we showed that for in-air conditions, an HCNa or HCMg can be used.

The equivalent HCO sample-matrix method can be extended to L and M lines. We showed some particular cases but we still need a general code including a complete database of mass absorption coefficients for L and M lines and ionization cross section for those lines. While considering secondary fluorescence effects we showed the limits in which these effects could be disregarded yielding acceptable levels of accuracy.

Finally, the equivalent HCO method opens a window of extending this method to polychromatic XRF [12], PIXE with alpha beams [2] or electron-induced X-ray emission [93]. We showed that the equivalent HCO sample-matrix is similar for any energy of the incident X-ray beam. Thus, we expect extending the equivalent HCO method from monochromatic to polychromatic XRF.

Appendices

Appendix A

Tables from chapter 5

Table A.1: Equivalent HCO sample-matrix for different samples in PIXE and XRF. Added elements refers to a 10%Si+10%Zn+80% sample when there is no major elements in the sample, or 10% of Zn when there is one major element in the sample. Italic rows show samples without nitrogen concentration. Bolt columns show the hydrogen concentration. Underlined row shows a sample without carbon and oxygen.

Sample	Reference	Major elements	Low-Z elements composition (%)					Equivalent HCO				
			PIXE (%)					XRF (%)				
			H	C	N	O	H _{eq}	C _{eq}	O _{eq}	H _{eq}	C _{eq}	O _{eq}
<i>Siderite</i>	<i>FeCO₃</i>	<i>Fe_{49%} + Added</i>	0	10	0	41	0	10	41	0	10	41
<i>Ordinary concrete</i>	<i>[90]</i>	<i>Al_{2%}Si_{90%}K_{1%}Ca_{4.3%}</i>	2.2	0.2	0	57.5	2.2	0	57.5	2.2	0.2	57.5
	[90]	Added	2.6	69	7.3	21	2.6	73	24.4	1.2	74.8	24
Cortical bone	[90]	P _{10%} Ca _{22.5%}	3.4	15.5	4.2	43.5	3.4	17.7	45.5	2.8	19	44.8
Coal	[75]	Added	4.0	64.3	1.3	29	4.0	65.3	29.3	3.6	65.7	29.3
<i>Mylar</i>	<i>[90]</i>	<i>Added</i>	4.1	62.5	0	33.3	4.2	63	32.8	4.1	62.5	33.3
Tomato leaves	[75]	Cl _{1%} K _{4.5%} Ca _{3%}	5.1	37.8	5	42.5	5.1	41	44.3	4.5	41.7	44.2
Spinach	[75]	Na _{1.4%} K _{3.6%} Ca _{1.4%}	5.6	40.8	5.8	40.8	5.5	44	43.5	4.8	45.4	42.8
Orchard leaves	[75]	K _{1.5%} Ca _{2.1%}	5.8	46.2	2.7	41.3	5.7	47	43.3	5.3	48.6	42.1
<i>Cellulose</i>	<i>C₆H₁₀O₅</i>	<i>Added</i>	6.2	44.4	0	49.3	6.1	45	48.9	6.2	44.4	49.3
Compact bone	[90]	P _{7%} Ca _{14.7%}	6.4	27.8	2.7	41	6.4	28	43.5	6.4	27	44.5
Pine needle	[75]	Added	6.5	51	1.2	40.3	6.5	51.8	40.7	6.2	52.1	40.7
Urea	CH ₄ N ₂ O	Added	6.7	20	46.7	26.7	6.7	46	47.3	1.6	54.4	44
Bovine liver	[75]	P _{1%} Ca _{1.1%}	7.0	50.6	11	29.3	6.9	56	35	5.5	59.5	32.9
Salammoniac	NH ₄ Cl	Cl _{66%} +Added	7.48	0	26.2	0	7.5	14.7	11.5	4.3	20	9.3
<i>Polystyrene</i>	<i>C₈H₈</i>	<i>Added</i>	7.7	92.3	0	0	7.7	92.3	0	7.7	92.2	0.1
Alanine	C ₃ H ₇ NO ₂	Added	7.8	40.4	15.7	35.9	7.8	50	42.2	5.5	53	41.5
Povidone	C ₆ H ₉ NO	Added	8.1	64.9	12.6	14.4	8.1	72	19.9	7.0	73.8	19.2
MS20 Tissue substitute	[90]	Mg _{13%} +Added	8.1	59.3	1.8	18.6	8.1	59	12.2	7.9	60	11.4
Eye lens	[90]	Added	9.6	19.5	5.7	64.6	9.6	22.4	67.4	8.7	24.3	66.4
Nylon type 6 and type 6/6	[90]	Added	9.8	63.7	12.4	14.1	9.8	70.4	19.8	7.8	47.1	45.1
Blood, whole	[90]	Added	10.2	11	3.3	74.5	10.1	12	76.9	9.5	14	76.5
Lung tissue	[90]	Added	10.3	10.5	3.4	74.9	10.2	12.3	76.3	9.8	13.1	75.9
Adipose tissue	[90]	Added	11.4	59.8	0.7	27.8	11.4	60	28.3	11.3	60	28.4
<i>Polyethylene</i>	<i>C₂H₄</i>	<i>Added</i>	15.3	84.7	0	0	15.3	84.7	0	15.3	84.7	0

Table A.2: Equivalent HCO sample-matrix for different samples in PIXE and XRF containing sodium, magnesium and aluminium.

Sample	Reference	Major elements	Low-Z elements composition (%)					Equivalent HCO		
			H	C	N	O	Na, Mg and Al	PIXE (%)	XRF (%)	
Thermonatrite	Na ₂ CO ₃ H ₂ O	Added	1.6	9.7	0	51.2	Na _{37%}	H_{eq}	O_{eq}	C_{eq}
Ordinary concrete	[90]	Si _{30%} K _{1%} Ca _{4.3%}	2	0.2	0	57.5	Na _{1.5%} Al _{2%}	24	0	76
Nesquehonite	MgCO ₃ ·3H ₂ O	Added	4.3	8.7	0	69.4	Mg _{17%}	2.2	0	57.5
Spinach	[75]	K _{3.6%} Ca _{1.4%}	5.6	40.8	5.8	40.8	Na _{1.5%}	20	0	80
MS20 Tissue substitute	[90]	Added	8.1	59.3	1.8	18.6	Mg _{13%}	5.8	40.8	47.8
								11.2	14.2	74.5
								19	0	80

Table A.3: Equivalent HCO sample-matrix for different samples in PIXE and XRF containing lithium, boron or fluorine.

Sample	Reference	Major elements	Low-Z elements composition (%)			Equivalent HCO		
			H	Other		PIXE (%)	XRF (%)	
Pyrex glass	[90]	Na _{2.8%} Al _{1.1%} Si _{38%}	0	B _{4%} O _{54%}		0.5	4.6	52.9
Carbon boride	B ₄ O	Added	0	B _{78.3%} C _{21.7%}		0	100	0
Teflon	[90]	Added	0	C _{24%} F _{76%}		0	0	100
Lithium tetraborate	[75]	Added	0	Li _{14%} B _{21.7%} O _{64.3%}		0	51	49
C-552 Air equivalent plastic	[90]	Added	2.5	C _{50%} F _{46.5%}		2.2	26.3	71
Boric acid	H ₃ BO ₃	Added	4.9	B _{17.5%} O _{77.7%}		4.4	24.9	70.7
Bone equivalent plastic	[90]	Ca _{17.6%} + Added	6.5	C _{53.7%} N _{2.2%} O _{3.2%} F _{16.7%}		6.4	46.3	29.6
							30	15.8
							37	

Table A.4: Equivalent HLiF sample-matrix for different elements.

Sample	HLiF Equivalent				
	PIXE (%)			XRF (%)	
	H_{eq}	Li_{eq}	F_{eq}	H_{eq}	F_{eq}
Lithium	0	100	0	0	0
Beryllium	0.1	95	5	1.5	18.7
Boron	0.2	84.8	15	2.5	15.5
Carbon	3	65	32	1.2	32.1
Nitrogen	3	45	52	0.1	51.9
Oxygen	2.5	20.5	77	1.6	76.8
Fluorine	0	0	100	0	100

Table A.5: Equivalent HLiF sample-matrix for different samples.

Sample	Reference	Major elements	Low-Z elements composition (%)		Equivalent HLiF				
					PIXE (%)			XRF (%)	
			H	Other	H_{eq}	Li_{eq}	F_{eq}	H_{eq}	F_{eq}
Pyrex glass	[90]	Na _{2.8%} Al _{1.1%} Si _{38%}	0	B _{4%} O _{54%}	1.2	16.5	40	0	16
Carbon boride	B ₄ O	Added	0	B _{78.3%} C _{21.7%}	0.1	81.4	18.5	1.5	80
Teflon	[90]	Added	0	C _{24%} F _{76%}	1.9	17.7	80.4	0.5	15.9
Lithium tetraborate	[75]	Added	0	Li _{14%} B _{21.7%} O _{64.3%}	0.1	81.4	18.5	1.4	73
C-552 Air equivalent plastic	[90]	Added	2.5	C _{50%} F _{46.5%}	2.7	33	63.5	1.8	35
Boric acid	H ₃ BO ₃	Added	4.9	B _{17.5%} O _{77.7%}	5.1	32.3	62.6	1.4	37
Tomato leaves	[75]	Cl _{1%} K _{4.5%} Ca _{3%}	5.1	C _{37.8%} N _{5%} O _{42.5%}	5.7	37.3	47.4	0	43.8
Bone equivalent plastic	[90]	Ca _{17.6%}	6.5	C _{53.7%} N _{2.2%} O _{3.2%} F _{16.7%}	7.1	37.6	37.6	0	45

Table A.6: Equivalent HCO sample-matrix for different samples calculated from the L transitions of heavy elements.

Sample	Reference	Major elements	Low-Z elements composition (%)					Equivalent HCO			
			H	C	N	O	H _{eq}	C _{eq}	O _{eq}	H _{eq}	C _{eq}
Nuclear standard photographic emulsion	[90]	Br _{22.3%} Ag _{30.1%}	1.4	7.2	1.9	6.6	1.4	8	7.7	1.6	8
Kodak photographic emulsion	[90]	Br _{34.9%} Ag _{47.4%}	3.2	21.1	7.2	16.3	3.2	24.9	19.6	2.2	26.6
											18.9

Table A.7: Comparison of the ratio secundary/primary fluorescence between the original sample and the equivalent HCO or HLiF sample.

Sample	Composition	Elements $j-i$	N _{sec} /N _{pri} (%)			
			PIXE		XRF	
			Original sample	Equivalent sample	Original sample	Equivalent sample
Urea	Table A.1	30-28	9.6	9.5	50.8	50.9
Tomato leave	Table A.1	20-19	1.5	1.5	3.5	3.5
MS20 Tissue substitute	Table A.1	12-11	0.59	0.59	1.33	1.33
Cortical bone	Table A.1	20-19	9.9	9.9	21.3	21.2
Bone equivalent, plastic	Table A.5	20-19	12.5	12.3	32.7	31.7
Pyrex glass	Table A.5	14-13	3.9	3.3	6.7	5.9
Lithium tetraborate	Table A.5	30-28	9.6	13.2	51	49

Appendix B

Matlab codes

In this appendix, we are going to show the PFactor and XFactor codes. For other codes, like Database.m, PSecondary.m, XSecondary.m, HCOPIXE.m or HCOXRF.m please contact the author.

B.0.1 PFactor

```
1 %Program calculating the PIXE Correction Factor
2 tic
3 clear all
4
5 DataBase %Open the data base
6
7 %Initial conditions
8 E0=2400; %Initial proton beam energy
9 phy=90; %Incident angle of the proton
10 theta=45; %Take-off angle of photon
11 k=1000; %Number of integration steps
12 VE=(100:(E0-100)/k:E0); %Forming a vector of energy varying from
    100keV to E0
13
14
15 %First sample
16 Concen=1; %Concentration of this matrix over total.
17 target1=[ %Can be stecheometry or by concentrations (sum must be
    1)
18 6 1
19 ];
20
21 %Secondary matrix (In case there is a mixture)
22 target2=[
23 26 1
24 ];
25
26 %Sin of every angle
27 senp=sin(pi*phy/180);
28 sent=sin(pi*theta/180);
```

```

29
30 %Program assumes the samples are expressed in stecheometric form
    .
31 if target1(1,2)<1 %If it is not stecheometric, transform to
    stecheometric
32 Restriction=1000000; %Free restrain
33 Stecheome=target1(:,2)./A(target1(:,1)).*Restriction;
34 target1=[target1(:,1), floor(Stecheome)];
35 end
36
37 if target2(1,2)<1
38 Restriction=1000000; %Free restrain
39 Stecheome=target2(:,2)./A(target2(:,1)).*Restriction;
40 target2=[target2(:,1), floor(Stecheome)];
41 end
42
43 %Mass absorption coefficient and stopping power on the specific
    elemental array
44
45 elements=target1(:,1);
46 stecheometry=target1(:,2);
47 MassMatrix=A(elements).*stecheometry;
48 TotalMass=sum(MassMatrix); %M=n1M1+n2M2+...+
49
50 elements2=target2(:,1);
51 stecheometry2=target2(:,2);
52 MassMatrix2=A(elements2).*stecheometry2;
53 TotalMass2=sum(MassMatrix2); %M=n1M1+n2M2+...+
54
55 %Calculation of stopping power
56 for z=1:92 %Ziegler polynomial
57 SL(z,:)=Ziegler(z,1)*VE.^Ziegler(z,2)+Ziegler(z,3)*VE.^Ziegler(z
    ,4);
58 SH(z,:)=Ziegler(z,5)./(VE.^Ziegler(z,6)).*log(Ziegler(z,7)./VE+
    Ziegler(z,8).*VE);
59 SZ(z,:)=602.22/A(z)*(1./SL(z,:)+1./SH(z,:)).^(-1);
60 end
61
62
63 SMatrixZ=SZ(elements,:); %S1, S2... Sn
64 SMassZ=10^3*SMatrixZ.*A(elements).*stecheometry/TotalMass; %
    n1M1S1+n2M2S2+.../M
65 [filesZ columnsZ]=size(SMassZ);
66 if filesZ==1;
67 SZi=SMassZ;
68 else
69 SZi=sum(SMassZ);
70 end
71

```

```

72 SMatrixZ2=SZ(elements2,:); %S1, S2... Sn
73 SMassZ2=10^3*SMatrixZ2.*A(elements2).*stecheometry2/TotalMass2;
    %n1M1S1+n2M2S2+..../M
74 [filesZ2 columnsZ2]=size(SMassZ2);
75 if filesZ2==1;
76 SZi2=SMassZ2;
77 else
78 SZi2=sum(SMassZ2);
79 end
80
81 SZiegler=Concen*SZi+(1-Concen)*SZi2;
82
83 %Integral inside term
84 InvS=1./SZiegler;%Same SZiegler
85 for iS=1:k+1
86 IntInvS(iS)=trapz(VE,InvS);
87 InvS(iS)=0;
88 end
89
90 for kaline=11:1:40 %Construct the vector CorrectionFactor vs Z
91
92 %Calculation of mu
93 MuMatrix=muka(:,elements);
94 MuMatrixKaline=MuMatrix(kaline-10,:)' ; %mu1 mu2 mu3...
95 mu=sum(MuMatrixKaline.*MassMatrix)/TotalMass; % (M1mu1+M2mu2
    +...+)/M
96
97 %Calculation of mu from second sample
98 MuMatrix2=muka(:,elements2);
99 MuMatrixKaline2=MuMatrix2(kaline-10,:)' ; %mu1 mu2 mu3...
100 mu2=sum(MuMatrixKaline2.*MassMatrix2)/TotalMass2; % (M1mu1+
    M2mu2+...+)/M
101
102 mu=Concen*mu+(1-Concen)*mu2; %Final mu
103
104 %Cross section of element kaline for every energy on VE
105 sigmakVE=10^(-20).*(1./uk(kaline-10)).^2.*exp(CrossSection(
    kaline-10,1)*(log(VE./(uk(kaline-10)*1836.15))).^0+
    CrossSection(kaline-10,2)*(log(VE./(uk(kaline-10)*1836.15)))
    .^1+CrossSection(kaline-10,3)*(log(VE./(uk(kaline-10)
    *1836.15))).^2+CrossSection(kaline-10,4)*(log(VE./(uk(kaline
    -10)*1836.15))).^3+CrossSection(kaline-10,5)*(log(VE./(uk(
    kaline-10)*1836.15))).^4+CrossSection(kaline-10,6)*(log(VE./(
    uk(kaline-10)*1836.15))).^5);
106
107 TZiegler=exp(-mu.*IntInvS*senv/sent); %Exponential part of
    integral
108
109 %Cross section/Stopping *Transmission part

```



```

110 sigmaSZ=sigmakVE.*TZiegler./SZiegler;
111
112 %Integral primary
113 IntegralprimaryZ=trapz(VE,sigmaSZ);
114
115 %Integral total
116 ThickTargetFactor=trapz(VE,sigmaSZ);
117 PIXEMatrixFactor=IntegralprimaryZ/sigmakVE(k+1)*1000;
118
119 ThickTargetFactorZ(kaline-10)=ThickTargetFactor;
120 kalineVector(kaline-10)=kaline;
121 PIXEMatrixFactorZ(kaline-10)=PIXEMatrixFactor;
122 end
123
124 ThickTargetFactorZ=(ThickTargetFactorZ*10^20)';
125
126 CorrectionFactorvsZ=[kalineVector',PIXEMatrixFactorZ'*10^3] %
    PIXE Matrix Factor Vs Z
127 PIXEMatrixFactorZ'*10^3';
128
129 figure
130 plot(kalineVector',PIXEMatrixFactorZ'*10^3)
131 grid on
132 toc

```

B.0.2 XFactor

```

1 clear all
2 DataBase %Open the data base
3
4 %Program calculating XRF Correction Factor in a matrix
5
6 psix=90; %Incident angle
7 thetax=45; %Outside angle
8 Ep=43; %K $\alpha$  line of the incident energy
9
10
11 Concen=1;
12
13 target1=[ %Target in weight mass of composition 1
14 9 0.4867
15 20 0.5133
16 ];
17
18 target2=[ %Target in weight mass of composition 2 (If exists)
19 1.0000 0.0617
20 6.0000 0.4447
21 8.0000 0.4936
22 ];
23

```

```

24 for Ef=11:Ep-1
25
26 if target1(1,2)>1 %Stechometry
27
28 %Transform to weight mass
29 AMass=A(target1(:,1)); %Mass of every element in the sample
30 TotalMass=AMass'*target1(:,2); %Total molar mass of the sample
31 TargetMass=target1(:,2).*A(target1(:,1))/TotalMass; %Weight mass
    of every element
32 target1=[target1(:,1),TargetMass]; %New target in mass
33
34 elements=target1(:,1); %Elements of the Sample
35 Weightmass1=target1(:,2); %Weight mass of every sample
36 MuMatrix1=muka(:,elements); %Mass absorbtion coefficient for
    every element in the sample
37 TotalMu1=MuMatrix1*Weightmass1; %Total Mass absorbtion
    coefficient of the sample
38
39 else
40 elements=target1(:,1); %Elements of the Sample
41 Weightmass1=target1(:,2); %Weight mass of every sample
42 MuMatrix1=muka(:,elements); %Mass absorbtion coefficient for
    every element in the sample
43 TotalMu1=MuMatrix1*Weightmass1; %Total Mass absorbtion
    coefficient of the sample
44 end
45
46 if target2(1,2)>1
47 AMass=A(target2(:,1)); %Mass of every element in the sample
48 TotalMass=AMass'*target2(:,2); %Total molar mass of the sample
49 TargetMass=target2(:,2).*A(target2(:,1))/TotalMass; %Weight mass
    of every element
50 target2=[target2(:,1),TargetMass]; %Transform to weight mass
51
52 elements2=target2(:,1); %Elements of the Sample
53 Weightmass2=target2(:,2); %Weight mass of every sample
54 MuMatrix2=muka(:,elements2); %Mass absorbtion coefficient for
    every element in the sample
55 TotalMu2=MuMatrix2*Weightmass2; %Total Mass absorbtion
    coefficient of the sample
56
57
58 else
59
60 elements2=target2(:,1); %Elements of the Sample
61 Weightmass2=target2(:,2); %Weight mass of every sample
62 MuMatrix2=muka(:,elements2); %Mass absorbtion coefficient for
    every element in the sample
63 TotalMu2=MuMatrix2*Weightmass2; %Total Mass absorbtion

```

```

        coefficient of the sample
64
65 end
66
67
68 TotalMu=Concen*TotalMu1+(1-Concen)*TotalMu2;
69
70 muin=TotalMu(Ep-10); %Mass absorbtion coefficient of incident
    photon
71 muout=TotalMu(Ef-10); %Mass absorbtion coefficient of outside
    photon
72
73 X(Ef-10)=muin/sin(pi/180*psix)+muout/sin(pi/180*thetax); %Chi
    coefficient for XRF
74 end
75
76 for i=1:Ep-11
77     kalinevector(i)=i+10;
78 end
79 MatrixFactor=[kalinevector',X']
80 X=X'
81
82 figure
83 plot(kalinevector',X')
84 grid on
85
86
87 %Comparing with thin film:
88
89 rhot=50;
90 rhot=rhot*10^(-6);
91
92 Comparisonthin=X*rhot;

```

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