Development of a Methodology
for the Determination of a TXRF Spectrometer Sensitivity Curve

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Development of a Methodology for the Determination of a TXRF Spectrometer Sensitivity curve

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To my family
Abstract

The standard method for determining the sensitivity curve of a TXRF spectrometer relies on a calibration done using a set of vendor-certified values of reference calibration standards. These samples, which are certified by the provider, are costly and their quality cannot be verified. We propose the use of pure substances for calibration, along with a mathematical procedure that assures high precision and accuracy of the results. The method described herein is economically efficient and eliminates having to deal with some uncertainties related to the concentration of the standard used with the usual method, thereby improving the quality of the TXRF results.
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Chapter 1

Introduction and Motivation

Total-Reflection X-ray Fluorescence Spectroscopy (TXRF) is a technique for multi-elemental analysis that allows the identification of elements with an atomic number $Z > 12$. It is efficient, rapid, and can be applied to minimal sample quantities\footnote{mass $\sim 1\mu g$}. TXRF is based on the study of fluorescence emissions, which present characteristic energies of the elements that compose the analyzed sample. The emission intensity depends directly on the atomic concentration of the elements present in the sample. Since TXRF analyzes very little amounts of sample it is considered in practice as non-destructive [1].

One of the main characteristics of this process is the small incidence angle of the X-ray beam which is below a critical value. This condition allows the reflection of nearly 100% of the photons of the excitation beam, thereby reducing the effect of background noise [2]. Thus, the detection limit of the technique is decreased on the order of $10^{-8} \text{g/g}$.

For purposes of quantification, TXRF requires reference calibration standards. Therefore, the quantitative results obtained with this technique are as good as the patterns used to calibrate the instrument. TXRF is a metrological technique that ensures the quality of the results. The quantification of the uncertainties includes activities of normalization, testing, inter-comparison, among others. Therefore, the results can be used for certification purposes.

The relative sensitivity is a number that indicates how many times the signal of a given element is bigger compared with another element signal if both elements are in the same concentration in the sample. The sensitivity curve of a TXRF spectrometer is usually obtained through an analysis of a set of multi-elemental reference samples whose composition should be known with very high accuracy and precision (Fig. 1.1). The ensuing analysis with the spectrometer determines the abundance of each line (Fig. 1.2), resulting in the creation of a calibration curve. To find the composition of an unknown sample, the spectrum resulting from the analysis should be affected by the calibration curve. Fig. 1.3 shows a characteristic relative sensitivity curve.

Although this method is the most often used, it has many deficiencies [3]. The most significant are related to statistical fluctuations, uncertainties regarding concentrations and masses, the possible precipitation of elements in the standard sample, the time and
Figure 1.1: A set of reference multi-elemental solutions prepared with well known concentrations, in order to determine the sensitivity curve of a TXRF spectrometer.

Figure 1.2: The spectrum of the artificially prepared samples is measured with the spectrometer, and the abundance of each line should be determined.
Figure 1.3: Typical TXRF spectrometer sensitivity curve. Gallium is used as reference.

Figure 1.4: Spectrum of CuCl$_2$. This spectrum is simpler to analyze than the spectrum shown in Figure 1.2.
cost of the analysis, and the complexity of fitting a spectrum of a sample with many elements.

However, if the calibration sample to be used is a pure substance, its proportion in terms of atoms of the elements involved can be defined with perfect precision. Also, the purity of the substance can be verified with the spectrum resulting from the TXRF analysis.

In this thesis, a general methodology is described for obtaining the sensitivity curve of a TXRF spectrometer [chapter 3] based on the known stoichiometry of pure samples [3]. This will improve the quality of traditional results.

Besides, a mathematical procedure was adapted [4], with certain considerations that allow obtaining a high precision and accuracy, and an evaluated number for the uncertainty in the determination of the sensitivity curve of a TXRF spectrometer.

There is a general formulation [5] for the TXRF technique, which describes all of its uncertainties sources. The procedure proposed here eliminates many sources of uncertainties. In this sense, we consider that our procedure improves the quality of the results as much as we know about the technique.

First, in [chapter 2] the basic topics related to TXRF are expanded for giving to the reader a better understanding of the underlying processes.
Chapter 2
Fundamentals

In this chapter the key and core topics related to the physics of X-rays and TXRF will be covered. The contents are treated descriptively as a review, and for more depth please follow the references.

2.1 X-rays Physics

In 1895 Rontgen discovered a new kind of electromagnetic radiation that he called X-rays [6]. The X-ray photons have energies in the kilo-electronvolt range, from 0.01 to 100 keV, and in terms of wavelengths in the nanometer range in the interval 0.01-100 nm [1].

Some properties of X-rays are [7]:

- Invisibility;
- Propagated in straight lines at the velocity of light \((3 \times 10^8)\) m/s;
- Unaffected by electrical and magnetic fields;
- Differentially absorbed while passing through matter;
- Reflected, diffracted, refracted, and polarized;
- Capable of ionizing gases;
- Capable of affecting electrical properties of liquids and solids;
- Capable of blackening a photographic plate;
- Able to liberate photoelectrons and recoil electrons;
- Capable of producing biological reactions;
- Emitted in a continuous spectrum;
Figure 2.1: Radiative loss energy via bremsstrahlung. Image from [9].

- Emitted also with a line spectrum characteristic of the chemical elements;
- Found to have absorption spectra characteristic of the chemical elements.

2.1.1 Production of X-rays

2.1.1.1 Bremsstrahlung

The continuous bremsstrahlung or breaking radiation is the radiation emitted when a charged particle, generally electrons, lose energy in passing through the Coulomb field of a nucleus [7]. Roughly speaking, it can be defined as the emission of an X-ray photon in the scattering of an electron from an atom [8]. A schematic representation of the bremsstrahlung is presented in Fig. 2.1.

In general, as a procedure for generation of electron deflection (i.e bremsstrahlung), the electrons are accelerated by a high voltage, in an X-ray tube (Coolidge type [10], Fig. 2.2), and hit a solid piece of metal called the ‘target’.

The spectrum of the bremsstrahlung contains energies from zero up to the kinetic energy of the electrons [11]. Then, the maximum energy of the continuum is proportional to the voltage used in the X-ray tube.

However, during the process, sometimes an inner electron is removed from its orbit as a result of a collision, producing a vacancy, that is filled by another orbital electron radiating a characteristic X-ray quantum [12].

\[ E = eV, \] being \( e \) the electric charge and \( V \) the voltage.

\[ \text{Fluorescent photon, see section 2.2.1 on page 12} \]
Figure 2.2: X-ray tube of the Coolidge type used as an X-ray photon source. A metal–glass cylinder with a thin exit window (W). Tungsten-filament used as the cathode (C). The anode is a metal block with a slant plane (A). Reproduced from [1].

Figure 2.3: Spectra emitted by a Rh X-ray tube operated at various accelerating voltages. The characteristic lines of the anode material are superimposed (from [13]).
2.1.1.2 Radioactive sources

After de nuclear decay of a radioactive particle, photons in the X-ray range can be produced \[11, 14\]. A few radioisotopes are used as X-ray sources, they are \[14\]: $^{55}$Fe, $^{56}$Co, $^{109}$Cd, $^{125}$I, $^{155}$Eu, $^{153}$Gd, $^{170}$Tm, $^{238}$Pu, $^{241}$Am and $^{244}$Cm.

2.1.1.3 Synchrotron radiation

The Synchrotron is a particle accelerator, in which the charged particle is circulating in a stored ring \[13, 15\]. The synchrotron radiation was first observed in 1947 \[16\] (but it was previously derived theoretically \[17\]) and is the result of the movement of electrons, with velocities near to the light speed, forced to travel in the synchrotron path by strong magnets. As is listed in \[18\], some characteristics of the synchrotron radiation are the intensity of the primary beam with a continuous spectral distribution, the linear polarization in the orbit plane, the small source size, and its natural collimation.

More detail for this topic can be found in the Refs. \[19–22\] .

2.1.2 Interaction of X-rays with matter

The interaction between X-rays and matter results basically in the attenuation of the first by removed or deflected photons\[7\]. The attenuation of the intensity, upon a homogeneous medium with density $\rho$ and thickness $d$, can be expressed mathematically using the Lambert-Beer formula \[7, 13\]:

$$I = I_0 e^{-\mu \rho d} \quad (2.1)$$

where $I_0$ is the number of incident photons, $I$ the intensity after the transmission and $\mu$ the mass attenuation coefficient.

Three competitive types of events cause the attenuation of photons: absorption, scattering and pair production\[7\]. However, the pair production is considered insignificant for X-ray \[1\]. For the absorption type, we have the photoelectric interaction. For the other side, we have two kind of scattering: Compton (incoherent) or Rayleigh (coherent). A schematic representation of the attenuation and its causes is shown in Fig. 2.4.

2.1.2.1 Photoelectric Interaction

If an incident photon with energy $E_p$ strikes an inner electron with binding energy $\phi$, in an elastic collision, and $E_p > \phi$, the photon transfers all its energy to the electron. Instantly, the electron is expelled of the shell, the primary photon is annihilated and is generated a vacancy at the shell. All this interaction is called the Photoelectric Effect and the ejected electron is named Photoelectron \[23\]. The emitted photoelectron has characteristic kinetic energy given by incident photon energy minus the electronic

\[4\]The Inelastic Raman Scattering was ignored by its very low probability (1 in 10 million) \[1\].
binding energy or \( E_k = E_p - \phi \) \([7, 23]\). The measurement of these characteristic energies give rise to other spectroscopy technique: the Photoelectron spectroscopy \([24]\). The probability of occurrence of the photoelectric effect is given by the cross-section, \( \sigma \), which depends on \( Z \) and \( E_p \) \([25]\) (see Fig. 2.5). This effect predominates for \( E_p \) below 100 keV \([26]\).

2.1.2.2 Compton Scattering

The Compton scatter (incoherent scatter) is defined as the interaction (collision) of a photon with a single free (i.e., weakly bound) electron, where a portion of the photon energy is transferred to the electron \([27]\) leading to a change of direction of the photon. The energy (wavelength) of the scattered photon is lower (greater) than that of the incident photon.

This effect was first observed by Compton in 1923 \([28, 29]\) and derived a formula for the wavelength shift of the scattered photon (\( \lambda' \)):

\[
\Delta \lambda = \lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta)
\] (2.2)

being \( \lambda \) the wavelength of the incident photon, \( \lambda' \) the wavelength of the scattered photon, \( h \) the Planck’s constant, \( m_e \) the rest mass of the electron, \( c \) the velocity of light in vacuum and \( \theta \) the angle between the incident and the scattered photon (deflection angle). The term \( h/m_e c \) is known as the Compton wavelength (\( \lambda_C = 0.002426 \) nm). As we can see in the Eq. (2.2), on a Compton scattering, the shift of the wavelength, \( \Delta \lambda \) (named Compton shift), is independent of the wavelength of the incident photon and only dependent on the scattering angle \( \theta \).
Figure 2.5: Dependence of the photoelectric cross section on (a) photon energy and (b) atomic number. Adapted from [25].

With some algebra, the relationship (2.2) can be expressed in terms of the energy instead of the wavelength:

$$\frac{E'}{E} = \frac{1}{1 + (1 - \cos\theta)} \frac{E}{E_0}$$  \hspace{1cm} (2.3)

where $E_0$ is the rest energy of the electron with a value of 511 keV, $E$ the energy of the incident photon and $E'$ the energy of the photon after the deflection.

In terms of the intensity of the Compton scattering, we also have an angular dependence, with a minimum intensity around $90^\circ$.[30]

In Fig. 2.6, we can see a schematic representation of the Compton scattering.

2.1.2.3 Rayleigh Scattering

The Rayleigh scatter (coherent or elastic scatter) describe the collision of a photon with a bound atomic electron, without ionization of the atom and, in which the energy of the photon is the same before and after scattering, with changes only in the direction of the photon [1, 9, 13]. The Rayleigh scattering occurs mostly at the low energies and for high-Z materials [7].

\footnote{That is the reason why the geometrical arrangement of source-sample-detector have an angle around $90^\circ$ in XRF[11]}

10
2.1.3 Detection of X-rays

There is a wide range of instrumentation related to the detection of X-rays. One mechanism is to collect information on the counting of single photons (pulse-time systems); other is providing measurements of count rate or total flux (current-type systems) \[31\, 32\]. The most common types of X-ray detectors are:

- Gas-filled detectors \[33\]: based on the ionization (radiation through a gas).

- Scintillation detectors \[34\]: these produce sparks or scintillations (optical photons) when the X-ray radiation passes inside them, the NaI crystal scintillator activated with thallium, NaI(Tl) \[35\, 36\], is the most used of these type.

- Semiconductor detectors \[37\]: Working with generation of the electron-hole pairs by photonic interaction inside the material \[38\], and produce a voltage signal with amplitude proportional to the X-ray energies \[39\, 40\]; the most used is the silicon doped with lithium detector, or Si(Li), followed by the Ge(Li) detector. For this kind of detectors, simultaneous detection over a wide dynamic range of X-rays energies is allowed.

- Silicon drift detectors \[41\]: Called SDD or Si-drift, introduced in 1983 \[42\], is the new generation of detectors based on sideward depletion \[42\, 43\]. More information of them in Refs. \[38\, 43\, 46\].

Figure 2.6: Geometry for Compton scattering of X-ray photons. From Ref. \[13\].
These detection systems are completed with a multichannel analyzer [47], which accumulates an energy spectrum in a histogram memory [40].

2.2 X-ray Fluorescence

The beginning of the XRF as a spectrometric technique is fixed at the start of the XX century. In 1911 Barkla observed the characteristic X-ray emission spectra (called secondary emission) after excitation of X-rays (primary radiation) [48] showed for first the capability of X-ray in the chemical analysis. Later, in 1913, Moseley related the wavelengths (or frequency) of characteristic lines to the atomic numbers of the elements (Moseley’s Law) [49]. These facts established the basis of X-ray spectral analysis.

The emission of the characteristic secondary X-ray is called fluorescence [50] that has characteristic energy, allowing to identify the chemical composition of a sample.

2.2.1 The Fluorescence Process

After the primary X-ray exposure, a hole in the inner shell is generated by the ejection of the core electron (photoelectron). Later, an electron of a higher orbital, ‘fall’ (quantum leap) to the inner shell covering the vacancy, emitting with a certain probability (see section 2.2.1.1 on the next page) a secondary X-ray with characteristic energy, given by the difference of the electron binding energy at the two quantum levels [1, 39]:

\[ E_x = h\nu = \phi_1 - \phi_2 \]  \hspace{1cm} (2.4)

being \( \phi_1 \) and \( \phi_2 \) the energy of the orbitals involved, \( E_x \) the energy of the emitted X-ray, \( \nu \) its frequency and \( h \) the Planck’s constant.

Using the same notation of the Eq. 2.4 the transition from shell 2 to shell 1 produces a new hole in the shell 2. This vacancy can be filled by a more external electron (for example from the shell 3) generating a new fluorescent photon. In general, to identify the shells, capital letters are used; K for the most inner shell, L for the second and continue in this alphabetical sequence for the next upper shells.

However, the electrons of low energy shells are distributed into many sub-shells with nearby energies [39]. For example, the L shell is split into three sub-shells, M into five and N in seven. Thus, exist a lot of electronic transitions.

Siegbahn proposed a notation for to identify the transitions [51], based on the relative intensity of lines from different series, which consist in the letter of the ionized shell (K,L,M,...) follow of a greek letter that represent the origin shell of the electron involved in the fluorescence, and finally a subscript number for the sub-shell identification. The alpha letter indicates emission from the immediately upper shell, beta is for the second next shell and so in alphabetical order. The subscript is a qualitative indicator, related to the sub-shells: number one is reserved for the most intense energy emission, the two for the second intense emission and so. For example, \( K\beta_1 \) means the emission that relates a electron jump from the sub-shell 3 of M shell to the vacancy in the K shell.
This notation is widely used in X-ray spectroscopy but is non-systematic and indeed somewhat confusing [1].

The IUPAC recommends another kind of notation [52], which indicates the final level - initial level of the electron involved in the transition. Thus, for example, the transition $K\alpha_1, K\alpha_2 \text{ y } K\alpha$ from Siegbahn’s notation is replaced by K-L3, K-L2 y K-L, respectively, in the IUPAC’s notation [39]. The correspondence between the two nomenclatures can be found in the Refs. [1, 7, 52].

As an example (taken from the Ref. [39]), in Fig. 2.7 we can view a schematic drawing of the transitions of the iron (Z=26) and its intensities relative to the major line in each sub-shell.

The main transition is from the sub-shell L3 to K ($K\alpha_1$) with an energy of 6.404 keV. A second quantum leap occurs, with half of the intensity than the L3-K, from L2 to K ($K\alpha_2$ or L2-K). The transition from L1 to K (K-L1) doesn’t take place, being a ‘forbidden transition’. Besides, the jump down from the M shell (in specific from the M3 sub-shell) to K can take place (7.058 keV and low intensity). No more transitions appear.

The transitions from L3 and L2 to K have nearby energies, so is very difficult to separate these X-rays, even with a high-resolution detector. Commonly these two emissions are described in only one transition called $K\alpha$ with a mean energy of 6.40 keV.

According to quantum mechanics, and as we saw in the previous example, not all the electronic transitions are allowed for X-ray emission [1, 53], and thus, the emission follows selection rules [13]. In Fig. 2.8 the possible transitions for a heavy atom are shown.

**2.2.1.1 Auger effect and fluorescence yield**

As mentioned earlier, the fluorescent X-ray emission takes place only with a certain probability, because, after the transition from a higher shell to an inner shell, two mutually exclusive events can be achieved (see Fig. 2.9): The fluorescence (the excess of energy is released in a photon) with probability $\omega$ and the Auger effect with probability $a$. The Auger Effect occurs when the excess of energy is transferred to an electron of the external orbitals, which is ejected from the atom. The electron emitted is named Auger electron [55].

The Auger effect was observed for the first time in 1920’s years [56, 57], and given that the Auger-electrons have characteristic energies [57], is the basis of another kind of spectroscopy: The Auger Electron Spectroscopy [58, 59].

The X-ray photon emission and Auger electron emission are two competing but complementary effects [1]. Then the Auger probability of emission, $a$, and the fluorescence yield, $\omega$, are related by [53, 60]:

---

6The photon emission probability is called the "fluorescence yield", which is computed as the ratio between the number of emitted photon and the number of absorbed photons [54].

7The kinetic energy of the Auger electron is computed as the difference of the energy of the two orbitals involved in the transition minus the binding energy of the emitted electron [58].
Figure 2.7: Scheme of the energetic levels and characteristics X-ray relative intensities of the iron. Figure from Ref. [39].
Figure 2.8: Electron transitions (with the Siegbahn notation) that are possible in a heavy atom and that produce the principal lines or peaks within an X-ray spectrum. Figure from Ref. [1].
\[ a + \omega = 1 \]  \tag{2.5}

Fig. 2.10 shows the fitted values for the photon emission probability and the Auger emission probability for the K-shield in function of the atomic number. The Auger probability of emission dominates over the emission of fluorescent radiation in light elements. That is, in fact, the principal reason for the bad results (poor photon count rate) of XRF on elements with low atomic number\(^8\)[53].

### 2.3 Total Reflection X-ray Fluorescence Spectroscopy (TXRF)

TXRF, a geometrical variant of the classical Energy-Dispersive X-ray Fluorescence spectroscopy (EDXRF), can perform chemical analysis in the range of elements \(11 < Z < 92\)\(^6\)[62, 63] and with some instrumental modifications can be further extended for lower \(Z\)\(^6\)[64–66].

The technique is a recognized analytical tool with high sensitivity and low detection limits, under the femtogram range.

The main features of TXRF are listed in the following \[18, 67, 68\]:

- Performing both qualitative and quantitative elemental analysis
- Capability of simultaneous multi-elemental analysis;
- Large dynamic range;
- Practically non-destructive, because requires only small sample amounts (\(\mu\)L or mg);
- The excitation of the sample is produced by both the direct and the reflected beam, leading to a doubling in the intensity of the fluorescence signal;
- Almost no penetration of the primary radiation into the reflector, resulting in a reduced background contribution;
- The detector can be placed close to the reflector surface get a large angle solid for the fluorescence detection;
- The consequent improved signal/background;
- Low detection limits, below the picogram range or ng/mL;
- Relatively short analysis time (100–1000 s).
- No matrix-effect;

\(^8\)For example for carbon (Z=6), \(\omega_K \approx 1.4 \times 10^{-3}\)\[53\]
Figure 2.9: Photoelectric interaction, X-ray fluorescence and Auger Effect. After the photoelectric interaction (a) a photoelectron is generated (b) and in this case an electron from L shell fills the vacancy at the K shell emitting a X-ray photon (c) or an Auger electron (d). Figure reprinted from Ref. [23].
• Availability of mobile instruments for performing in-situ analysis.

• Simple calibration using an internal standard.

Despite these characteristics, some problems are associated with this technique [62, 68]: higher photon flux of excitation source, ultra-clean requirement of the reflector, unsatisfactory detection limits for light elements, high investment costs, and the inability to analyze the target X-ray source metal, among others.

The applicability of TXRF is divided into two branches: the chemical analysis (ultra-micro and ultra-trace analysis), where the sample is deposited on a polished reflector; and the surface analysis, where the analyzed sample is the reflector itself.

For chemical analysis purposes, the technique is applied in a wide variety of disciplines, as

• Environment: water [69, 72], air [73, 75], soil [76, 77];

• Food and Drinks: wine [78, 79], spirituous beverages [80, 81], soft drinks [82, 83], coffee [84, 85], tea and infusions [86, 88], tobacco [89], vegetables [90], honey [91, 92], candies [93];

• Biology [94, 95]

• Pharmacology [96, 98]

• Medicine: tissue [99, 100], blood [101, 102], fluid [103, 104];
• Polymer \[105\] [106];
• Forensic: ink \[107\], textile \[108\], firearm residues \[109\], fingerprints and sperm \[110\];
• Archaeology & Art: ceramics \[111\] [112], pigments, paintings and manuscripts \[113\] [117], varnishes \[118\] [119];
• Geology: \[120\] [122];
• Oil: \[123\] [124].

On the other hand, the capability of the technique for the analysis of thin films and semiconductor surfaces is often developed in the industrial field. A review of the fundamentals and applications in this topic can be found in \[62\] [63] [125] [131].

According to \[1\] competing method for TXRF, in terms of laboratory trace analysis, are electrothermal atomic absorption analysis (ET-AAS, variant of the standard AAS and also called GF-AAS) \[132\], inductively coupled plasma mass spectrometry (ICP-MS) \[133\], inductively coupled plasma optical emission spectrometry (ICP-OES) \[134\] and instrumental neutron activation analysis (INAA) \[135\]. Some publications compare these techniques in different scenarios \[63\] [136] [143]. In \[1\] are listing their main advantages and drawbacks of each one. In Fig. \[2.11\] is observed an overview of the detection limits of TXRF and some competitive techniques; although ET-ASS and ICP-MS have better detection limits (and other features), for both techniques the quantification process is very troublesome in comparison to TXRF \[63\], together with the time and cost favorable to TXRF.

Considering the capabilities of TXRF, some authors claim that the technique might even be considered as a primary method of measurement \[144\].

2.3.1 TXRF versus conventional XRF

TXRF and ‘classical’ XRF have the same fundamental principles and similar instrumentation (including the X-ray source, an energy dispersive detector, and pulse processing electronics \[145\] \[19\] and differ in the special geometrical arrangement of TXRF, which allow the total reflection of the photons and the consequently improving in the detection limits in several orders of magnitude in relation to conventional XRF \[18\]. In terms of uses, TXRF is suitable for both the ultra-micro and ultra-trace analysis, in contrast with the lack of sensitivity of XRF \[146\].

2.3.1.1 Experimental setup

In Fig \[2.12\] we can observe the basics differences between conventional XRF and TXRF. While in the classic XRF the incident angle is close to 45° and the detector is localized at

\[9\] In fact, TXRF is considered as a variant or particular case of XRF
Figure 2.11: Detection limits (in logarithmic scale) of TXRF and its competitive methods applied to trace analysis of pure aqueous solutions. A 50 μl sample was used for ET-AAS and TXRF, 3 ml were needed for FAAS, ICP-OES and ICP-MS. Image from Ref. [63].
45° of the sample; in TXRF the incident angle of the X-ray beam is very little (∼0.1°) and the detector is located above the sample. Another difference appears in the focus of the X-ray tube: the narrow or line focus for TXRF; in contrast with the extensive planar focus in conventional XRF leading to cylindrical or conical beam [146, 147]. The shape like a strip of paper of the incident beam, the beam incidence angle (below the critical angle, see section 2.3.3 on page 25) and the little sample amount, allow the reflection of almost 100% of the incident photons for TXRF [147].

2.3.1.2 Matrix Effect

One of the main strengths of TXRF over the conventional XRF is the removal of the “matrix effect” [148, 149], and in consequence, the correction methods are unnecessary [39, 150].

The matrix effects are produced mainly because of:

1. Attenuation of the X-ray exciting beam: As the thickness of the sample increases the outer atoms shield the inner atoms in the sample. The inner atoms protected become hidden for the incident excitation radiation.

2. The attenuation of the fluorescent emerging photons produced inside the sample, traveling outside the sample. The attenuation of the emerging radiation, in direction to the detector, is a different proportion for photons produced by different elements. This effect of self-absorption produces a distortion in the relative abundance of the radiation acquired.

3. Enhancements effects. The characteristic X-ray produced by excited atoms in the sample may act as a secondary excitation source for the rest of the atoms in the sample.

In the TXRF setting, if the mass of sample increases, limitations of the technique will occur owing to matrix effects [4, 13, 151]. Matrix effects may happen in particular samples, in the analysis of layer depositions, suspensions or small solids samples composed with high Z elements, but they are not expected in diluted ionic solutions in water [151]. A simple test to verify the proper and reliable utilization of the technique consists in a dilution process of the sample. In a correct application, the proportions in the abundances of the lines acquired (Ii/Ij) should remain unchanged in the original and in the diluted samples.

2.3.2 Historical background and growth of the technique

In 1923 Compton [29, 152] was the first to observe the phenomena of total reflexion in X-rays (three years before X-ray refraction and reflection phenomena were predicted in a doctoral thesis [153]) and thirty-one years later the formulas for X-ray reflectivity were presented [154]. However, only in 1971, TXRF was suggested as an analytical technique [155] in Japan, and implemented for first time in 1974 [156, 157] in Austria.
Figure 2.12: Comparison between conventional (a) and total reflection mode of excitation (b). Figure from Ref. [1]
However, the main boost of this technique was given in Germany (some years later) with the development of more precise portable spectrometers [158–160]. In 1983, was described the angular dependence of the fluorescence intensities below the critical angle of total reflection [161], allow the analysis of surfaces and surface layers. After that, in 1986, the synchrotron radiation was first used for excitation [162], bringing new benefits to the development of technique [163].

The continuous advances in both design and engineering have enabled a descend in the detection limits and better portability of the spectrometers. Some chronological highlights and the state of the art of the most recent spectrometers and instrumentation can be found in [68, 164, 165].

In the mid-80s, it was established a bi-annual meeting to discuss the capabilities and advances over TXRF, being carried out the first workshop in 1986 at Germany [10]. Through the years, many researchers have contributed to the growth of the TXRF technique, forming a stable community inside the analytical chemistry and applied physics, becoming in a well-established analytical technique (Figs. 2.13 and 2.14). At 2014, around 700 individual units are running in 57 countries, divided into 200 universities, 60 synchrotron-beamlines and 150 semiconductor fabs [166].

In this meeting the acronym TXRF was selected
Figure 2.14: Evaluation of the publications devoted to TXRF as a function of the corresponding literature sources using the subjects ‘TXRF’ (from Ref. [167]).
Figure 2.15: Schematic representation of refraction and reflection of a mono-energetic radiation beam, as a function of the incident critical angle. The refraction index of medium 1 (usually vacuum or air), \( n_1 \), is larger than the medium 2 (the reflector material), \( n_2 \). Case a) Refraction \((\phi > \phi_{\text{crit}})\), case b) Critical angle \((\phi = \phi_{\text{crit}})\) and case c) Reflection \((\phi < \phi_{\text{crit}})\).

### 2.3.3 Physical Background

At the interface of 2 different homogeneous media, a beam of mono-energetic radiation can be both refracted or reflected. In this way, there is an angle, called critical angle \((\phi_{\text{crit}})\), in which radiation is not refracted or reflected, remaining in the plane of the interface (see Fig. 2.15).

For the absorptive media (solid reflector) the refractive index has a complex value [145, 165]:

\[
n = 1 - \delta + i\beta
\]  

(2.6)

In the Eq. (2.7), the real term represents the dispersion and the imaginary term stands for the attenuation in the matter. These terms are \((\delta\) and \(\beta\)) are given by:

\[
\delta = \frac{N_a}{2\pi} r_0 \lambda^2 \frac{Z}{A} \rho
\]  

(2.7)

\[
\beta = \frac{1}{4\pi} \mu \lambda
\]  

(2.8)

being

- \(N_a\) = Avogadro’s number,
- \(r_0\) = classical electron radius,
- \(\lambda\) = the wavelength of the primary radiation,
- \(Z\) = the atomic number,
- \(A\) = the atomic mass,
- \(\rho\) = the density of the medium, and
• $\mu$ = the linear mass absorption coefficient.

The critical angle can be calculated using the Snell’s law, given in its basic form by:

$$n_1 \cos (\phi_{\text{inc}}) = n_2 \cos (\phi_{\text{out}})$$  \hspace{1cm} (2.9)

where $n_1$ is the refractive index of the air or vacuum, $n_2$ is the refractive index of the solid surface, and $\phi_{\text{inc}}$ and $\phi_{\text{out}}$ are the incident and output angle of the X-ray beam respectively. If $\phi_{\text{inc}} = \phi_{\text{crit}}$, the output angle is fixed to zero ($\phi_{\text{out}} = 0$). Taking in account that the refractive index of the vacuum is the unity\(^{11}\), and neglecting the imaginary term of the Eq. (2.6) we have:

$$\cos (\phi_{\text{crit}}) = 1 - \delta$$ \hspace{1cm} (2.10)

As $\phi_{\text{crit}}$ is closely to zero, the second order small-angle approximation for the cosine function is using\(^{12}\) yields to:

$$\phi_{\text{crit}} = \sqrt{2\delta}$$  \hspace{1cm} (2.11)

Replacing from (2.7), we have:

$$\phi_{\text{crit}} = r_0 \lambda \sqrt{\frac{N_a Z \rho}{2\pi A}}$$ \hspace{1cm} (2.12)

Given that the classical electron radius is a knowing expression defined by $r_0 = \frac{e^2}{m_e c^2}$, and the wavelength of the beam is related with its energy by the Planck–Einstein relation, the Eq (2.12) also be written as

$$\phi_{\text{crit}} = \frac{e h}{E} \sqrt{\frac{N_a Z \rho}{2\pi A m_e}}$$ \hspace{1cm} (2.13)

being $E$ the energy of the X-ray beam, $h$ the Planck constant, $e$ the charge of the electron and $m_e$ the mass of the electron.

In a common TXRF setting (Mo-K\(\alpha\) X-rays passing from vacuum to quartz glass), the critical angle takes a value of 0.00173 rad or 5.9 min of arc ($\sim 0, 1^\circ$) \(1^1\)165. \(11\)

In general, the critical angle grows with increasing medium density and drops with increasing primary X-ray radiation energy \(168\).

### 2.3.4 Experimental Matters for the Chemical Analysis

#### 2.3.4.1 Sample Pretreatment

Depending on the type or state of the sample, a pretreatment of it can be necessary to achieve the following goals \(167\):

\(^{11}\)If the medium is air, we can use the approximation $n_{\text{air}} \approx 1$

\(^{12}\)If $\theta \to 0$, $\cos (\theta) = 1 - \theta^2 / 2$
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- Thin-film formation;
- Homogeneous distribution of analyte and internal standard;
- To avoid spreading of organic solvents;
- Enrichment of analyte; and
- Separation from interfering elements.

These treatment include different types of digestion, slurry sampling, extraction, deposition, etc. One of the most used treatment is the acid digestion (i.e., wet digestion), which is based on the attack of the matrix with mineral concentrated acids and the release of the associated analytes to the liquid medium. The proceedings and strategies of sample pretreatment, according to the sample characteristics, are explained with details in the refs. [147, 167]. Fig. 2.16 shows the different procedures applied over the sample previous to the TXRF analysis. In this stage, for quantitative purposes, can be added to the sample a reference element in a fix concentration called the internal standard (see 2.3.4.3.2 on page 29 for more details).

2.3.4.2 Process of Analysis by Fluorescence

For the TXRF analysis, only a little specimen of the sample is needed. The best case is a few microliters of a liquid sample. After the pretreatment (if it was necessary), an aliquot is pipetted over the sample carrier and dried (in general a IR lamp is used). Follow that, a thin film is obtained with a mass in the range of $10^{-12} - 10^{-6}$ g, cover a surface of 5 mm diameter [39]. Given both the tiny thickness of the specimen and the high energy of the X-ray, the matrix effect is expected to be negligible [169].

For the fluorescence process, the sample carrier (typically made of quartz) is put inside the spectrometer and it is irradiated for around of $10^3$ seconds. A multichannel analyzer collects the counts as a function of the energy (or channel number), obtaining the X-ray fluorescence spectrum of the sample.

2.3.4.3 Spectral Analysis

2.3.4.3.1 Signal Intensity and Background The Energy Dispersive X-ray Fluorescence Analysis (EDXRF) in combination with a multi-channel analyzer collect the fluorescence radiation, separating the different energies, providing to the user a continuous X-ray spectrum of counts as a function of energy. The signal intensity of an element is determined by the integration of the counts of a region of interest (ROI) in which this element is defined.

Given that the background noise is present over all the energies, the signal needs to be distinguished from it. Thus, the detection limit (DL) is defined as the minimum intensity distinguishable over the background. Commonly the 3-$\sigma$ criterion for Gaussian noise is established as the critical level of the signal [31]. So, the probability that the
Figure 2.16: Diagram of the sample preparation procedures applied in the literature for solid, liquid and gaseous samples. Figure obtained from Ref. [167].
signal be a background fluctuation is less than 1%. The criterion results in the following condition to the intensity, \( I \), over a certain ROI [156]:

\[
I \geq 3\sigma_{Bg} \tag{2.14}
\]

where \( \sigma_{Bg} \) is the standard deviation of the background counts. If the intensity is proportional to the concentration \( C \), then the detection limit can be expressed as [1]:

\[
DL \geq \frac{C}{I} 3\sigma_{Bg} \tag{2.15}
\]

\[
\geq \frac{C}{I} 3\sqrt{Bg} \tag{2.16}
\]

The \( \sqrt{Bg} \) term is the integral in the ROI (under the signal) of the noise. The square root appear because the background obeys a Poisson statistics [31].

TXRF offers detection limits, for conventional excitation (X-ray tube), in the order of pg range [170]. These detection limits are improvement using synchrotron radiation as an excitation source and polymer film substrates [150, 171].

For the identification of elements present in the measured spectrum, both the X-ray library guidelines and user’s experience are needed for determine the ROI. Different software packages are developed for to deal with that issue [172, 173], given a more friendly data processing. Some problems, as superposition of signals [62, 174] (see Fig. 2.18) or spurious peaks [175], must be considered for an optimal analysis.

2.3.4.3.2 Quantitative Analysis For quantification in TXRF we need the help of an internal or external standard. For a formal definition of these terms in the context of the analytical chemistry, please see [176, 177].

The special configuration of TXRF leads to the linear conversion of the intensities into concentrations [68, 178]. Using that fact, an element of well-known concentration (called the internal standard) is artificially added to the specimen; then, the relative abundance of intensities of the different elements present in the sample is processed by
Chapter 2 Fundamentals

Figure 2.18: Theoretical spectrum of the superposition of the signals of arsenic and lead. From Ref. [174]

referring to one in particular (the internal standard) [3]. In some cases, there is no need to add an element as the internal standard because it is possible to use an element present in the sample itself [179] or the Compton peak standardization [180]. The elements selected as internal standard must be with very low concentration in the sample, and in general are used Ge, Ga, Co and Y [39].

The elements used as an internal standard must participate with very low concentrations in the samples. The Ge and Ga elements are commonly used for water samples and Co and Y for other types of samples.

The known concentration of the internal standard ($C_{std}$) allows to calculate the concentration of the element $i$ present in the sample following the next equation [11 68]:

$$C_i = \frac{I_i}{I_{std}} \frac{S_i}{S_{std}} C_{std}$$

(2.17)

where $C$ is the concentration, $I_i$ and $I_{std}$ are the intensities, and the ratio $S_i/S_{std}$ is the relative sensitivity of $i$ with respect to $std$. In Section 3.1 on page 32 on the following page, a better development is given arriving a Eq. (2.17).

The external standard calibration requires a previous analysis of the element $i$ present in a standard sample (with known concentrations of its elements), getting the response of the instrument concerning to a given concentration of $i$. In general, a curve of calibration (sensitivity curve) is obtained for a set of elements. For quantification, the obtained results are affected by the calibration curve in order to finally obtain the
element’s concentration in the sample [3].

The use of both the internal or the external standard calibration process is only justified under certain conditions [181, 182].
Chapter 3

A Methodology to Determine the TXRF Spectrometer Sensitivity Curve

3.1 Theoretical Considerations

The basic equation describing a line of a given element of a spectrum obtained with TXRF analysis is given by [7]:

\[ I_i = I_0 N_a k_i \sigma_i \omega_i m_i / A_i \]  

(3.1)

Where:

- \( I_i \) = Intensity of the line generated by element \( i \),
- \( I_0 \) = Intensity of the monoenergetic (\( E \)) source of excitation,
- \( N_a \) = Avogadro’s number,
- \( k_i \) = Experimental geometry and energy detection efficiency of the detector for element \( i \),
- \( \sigma_i \) = Total cross-section for the element \( i \), for photons with energy \( E \).
- \( \omega_i \) = Photon emission probability per ionization for the element \( i \) (fluorescence yield),
- \( m_i \) = mass surface density of the element \( i \),
- \( A_i \) = Atomic mass number of the element \( i \).

A property of equation (3.1) is the linearity, then, it is implicit that when doubling the acquisition time it will be doubled the acquired signal of each element, no matter the
nature of the sample. This property does not rely on specific characteristics of the X-ray source. In this sense, the procedure described here will be valid for any other technique, which its excitation source produce a signal linearly growing with time for each element, independent of the sample composition.

The traditional method used to obtain the concentration of an unknown sample consists of adding a small amount of element \( j (Z = j) \), known as the internal standard, to the sample. This element should not be originally present in the sample and its concentration, when added, should be defined as well as possible. Later, the concentrations of the original elements of the sample are determined in reference to the added standard.

If a small quantity of element \( j \) is added to the sample, the ratio between the intensities will be:

\[
\frac{I_i}{I_j} = \frac{k_i \sigma_i \omega_i m_i A_j}{k_j \sigma_j \omega_j m_j A_i}
\]  

(3.2)

Since the ratio of the masses \((m_i/m_j)\) is equivalent to the ratio of the concentrations \((C_i/C_j)\), Eq. (3.2) can be written as:

\[
C_i = \frac{I_i S_i}{I_j S_j} C_j
\]  

(3.3)

with

\[
S_i = k_i \sigma_i \omega_i / A_i
\]  

(3.4)

\[
S_j = k_j \sigma_j \omega_j / A_j
\]  

(3.5)

Later defining:

\[
S_{i/j} = \frac{S_i}{S_j}
\]  

(3.6)

we get

\[
S_{i/j} = \frac{I_j C_i}{I_i C_j}
\]  

(3.7)

where \( S_{i/j} \) is defined as the relative sensitivity of element \( i \) concerning the standard \( j \). This sensitivity will determine which of the two elements, given equal concentrations in the sample, is manifested with greater intensity in the spectrum. If the geometric parameters (position, shape, etc.) of the detector do not vary, then \( S_{i/j} \) depends exclusively on the atomic number \( Z \).

The intensities \( I_i \) and \( I_j \) have a certain absolute error \((\Delta I)\), as do the concentrations of the elements involved \((\Delta C)\). The error associated with \( S_{i/j} \) is determined by:
\[
(\Delta S_{i/j})^2 = \left(\frac{\partial S_{i/j}}{\partial I_i}\right)^2 (\Delta I_i)^2 + \left(\frac{\partial S_{i/j}}{\partial I_j}\right)^2 (\Delta I_j)^2 \\
+ \left(\frac{\partial S_{i/j}}{\partial C_i}\right)^2 (\Delta C_i)^2 + \left(\frac{\partial S_{i/j}}{\partial C_j}\right)^2 (\Delta C_j)^2 \tag{3.8}
\]

In the equation (3.8), the first two terms on the right-hand side are uncertainties related to the statistical fluctuations of the intensities and the background noise present in those intensities. The two last terms at the right-hand side are uncertainties related to the concentrations of the elements in the sample.

The formulation proposed in the following is similar to that used in previous publications[4, 184] and is intended to improve the results obtained with traditional methods. For the sake of simplicity, the spectrum of each element can be considered to be a function whose abscissa is the channel number (energy) and whose ordinate is the number of counts or events. Rather than being described by a Gaussian, Lorentzian, or other function, these can be obtained empirically through the analysis of each element by TXRF. Such functions are representative of each element and are normalized. The entire spectrum can be built using these normalized functions for each element. If the experimental parameters (detector, geometry of excitation, time, etc.) are not modified, and both the background noise \(B_g\) and statistical fluctuations are lower, the functions will be invariable for all spectra of the same element in different samples.

In the case of a multi-elemental sample, the intensity of each signal in the spectrum will be in direct relation to the parameters described in equation (3.1). Thus, the spectrum of the sample can be expressed as the product of two vectors:

\[
M = I_0 N_a \left( F_{Z=1} \cdots F_{Z=n} \right) \begin{pmatrix}
(k\sigma\omega m/A)_{Z=1} \\
\vdots \\
(k\sigma\omega m/A)_{Z=n}
\end{pmatrix} \tag{3.9}
\]

where:

- \(M\): spectrum of the sample,
- \(F_{Z=n}\): normalized function characteristic for element \(n\),
- \((k\sigma\omega m/A)_{Z=n}\): parameters of the spectrometer and the element \(n\), described in figure 1.1.

In the specific case of a TXRF analysis of a pure substance (well-defined proportion between atoms, see Fig. 1.4 and Table 3.1), with at least two elements that can be detected with the technique, in which the contributions of only two elements are quantified, the spectrum obtained \((M)\) can be expressed according to equation (3.9):
Chapter 3 A Methodology to Determine the TXRF Spectrometer Sens. Curve

\[ M = I_0 N_a \left[ F_{iN} \left( \frac{k \sigma \omega m}{A} \right)_i + F_{jN} \left( \frac{k \sigma \omega m}{A} \right)_j \right] \]  \hspace{1cm} (3.10)

where:

- \( i \): chemical element \( i \),
- \( j \): chemical element \( j \),
- \( F_{iN} \) and \( F_{jN} \): characteristic normalized functions of each element.

Later, defining:

\[ S_{i/j} = \frac{\left( \frac{k \sigma \omega}{A} \right)_i}{\left( \frac{k \sigma \omega}{A} \right)_j} \]  \hspace{1cm} (3.11)

and

\[ \phi = \frac{m_j}{m_i + m_j} \]  \hspace{1cm} (3.12)

It is possible to express (3.10) as:

\[ \frac{M}{I_0 N_a (m_i + m_j) \left( \frac{k \sigma \omega m}{A} \right)_j} = \phi F_{jN} + S_{i/j} (1 - \phi) F_{iN} \]  \hspace{1cm} (3.13)

where \( \phi \) is known as the relative proportion of element \( j \) in the pure sample. The \( S_{i/j} \) is defined as the relative sensitivity of element \( i \) respect to \( j \). This sensitivity is equivalent to that proposed in the Eq. (3.7) with the same considerations described therein.

Given that \( F_{iN} \) and \( F_{jN} \) are normalized functions, by integrating equation (3.11) along with all the energies of the spectrum, we have:

\[ \int_{E_i}^{E_f} \frac{M}{I_0 N_a (m_i + m_j) \left( \frac{k \sigma \omega m}{A} \right)_j} = \phi + S_{i/j} (1 - \phi) \]  \hspace{1cm} (3.14)

So, the spectrum of the sample can be normalized, obtaining:

\[ M_N = \frac{M}{I_0 N_a (m_i + m_j) \left( \frac{k \sigma \omega m}{A} \right)_j \left[ \phi + S_{i/j} (1 - \phi) \right]} \]  \hspace{1cm} (3.15)

We can define the parameter \( \alpha \) that links the amount of the element \( i \) and the element \( j \) in the sample:

\[ \alpha = \frac{m_j}{m_i} \]  \hspace{1cm} (3.16)
As we are analyzing pure substances, the parameter $\alpha$ is known and is perfectly defined (it has no uncertainty) and can be obtained easily by determining the quotient between the atomic masses rather than the total masses:

$$\alpha = \frac{A_j \# At_j}{A_i \# At_i}$$  \hspace{1cm} (3.17)

being $\# At$ the number of atoms either of the element $i$ or $j$. The ratio $(\# At_j/\# At_i)$ is obtained from the known stoichiometry of the used pure substance, it is considerate without error. For the case of water, this ratio has a value of 2 or 1/2. If the results obtained in the Eqs. (3.1) and (3.17) are substituted in (3.13), we obtain a normalized expression for the spectrum of the sample:

$$M_N = \frac{\alpha F_{jN} + F_{jN}S_{i/j}}{\alpha + S_{i/j}}$$  \hspace{1cm} (3.18)

Finally, by reordering the terms, the sensitivity can be described by:

$$S_{i/j} = \frac{\alpha F_{jN} - M_N}{M_N - F_{iN}}$$  \hspace{1cm} (3.19)

Here we can see that the sensitivity depends only on the statistical fluctuations of $M_N$, $F_{iN}$, and $F_{jN}$, since when dealing with the analysis of a pure substance, the parameter $\alpha$ is perfectly defined (it has zero uncertainty). The statistical fluctuations can be minimized with a longer measurement time. Nonetheless, if we consider that the functions $F_{iN}$ and $F_{jN}$ are representative of elements $i$ and $j$ in any spectrum and that they are obtained by averaging a high number of measurements, these functions can be considered to be free of error. Therefore, the only source of error to be considered would be the measurement of the spectrum of the sample ($M_N$).

The function $M_N$ has a given absolute error ($\Delta M_N$) composed of the statistical fluctuations of the function itself ($\Delta sf$) and those causing the background noise ($\Delta Bg$) present in said functions. Thus, the uncertainties that make up part of each function can be quantified as:

$$\Delta M_N = \sqrt{(\Delta sf)^2 + (\Delta Bg)^2}$$  \hspace{1cm} (3.20)

Where$^{13}$

$$\Delta sf = \sqrt{M_N}$$  \hspace{1cm} (3.21)

$$\Delta Bg = \sqrt{(Bg)_{MN}}$$  \hspace{1cm} (3.22)

Later, given the theory of the propagations of errors:

$$\left(\Delta S_{i/j}\right)^2 = \left(\frac{\partial S_{i/j}}{\partial M_N}\right)^2 (\Delta M_N)^2$$  \hspace{1cm} (3.23)

$^{13}$The square root is taken because the signal and noise obeys Poisson statistics$^{[5,31]}$. 

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If we compare the results obtained in the equations 3.23 and 3.8, we can see that the uncertainties referred to the concentrations vanished in the new formula. Only are considered the uncertainties related to the intensities (owing to statistical fluctuations and background).

### 3.2 Experimental and Instrumentation

The TXRF analytical system used in this study is an S2 PICOFOX Bruker spectrometer [185] that is enclosed in a suitably designed X-ray biological shield. The system includes:

- an X-ray metal-ceramic tube, with a molybdenum target, working at 50 W of maximum power, at 50 kV and 1 mA, air-cooled;

- a multi-layer monochromator;

- a Peltier-cooled high-resolution XFlash® Silicon Drift Detector, which does not need a liquid nitrogen cooling system, with 10 mm² active area, and energy resolution <140 eV at 100 kcps (Mn Kα line, 135.9 keV).

This equipment is highly versatile and allows the identification of traces of different types of samples. The instrument is connected to a computer with its own software (SPECTRA) that captures and processes the spectrum produced by the sample. All the specifications of the used spectrometer are available in the equipment’s brochure [185]. Fig. 3.1 shown the elements that the S2 PICOFOX spectrometer can to measure.

In Table 3.1 are listed the samples used for analysis. We chose two elements from each compound and we established their relative sensitivity, which is a characteristic of the TXRF spectrometer and it is calculated with Eq. (3.19). We used three different samples of the same compound, prepared in concentrations about 10-15 ppm, that is, the results obtained constitute an average. Samples that contain two cations like KMnO₄ were acidified with concentrated nitric acid (Merck Code 100456, with purity bigger than 65%). If the compound contains anions like Cl, S, Br or I, if the sample is acidified, those anions escape as ClH, SH₂, etc. The solubility of the salts was verified. Some salts cannot be used, like Cl₃Al, since the Al₃⁺ may precipitate as Al(OH)₃.

The volumes of solution analyzed were 2-5 μL. They were dried over sample holders made of SiO₂, in clean conditions under a IR lamp. The linearity between the relationship \( I_i/I_j \) was verified by successive dilution of the original sample, but these results are not included in the calculated sensitivity. We didn’t detect matrix effects in the samples analyzed. Our results are in complete agreement with those provided by other scholars [181] when they were studying quantification by internal or external standard in diluted samples. They were prepared and diluted in ultrapure water. Pure water was first obtained from a feeder 55 WG and subsequent purification by a Milli-Q SP Reagent Water System (Millipore) which yields ultrapure water with a resistivity of 18 MΩ. All the data was acquired by the same spectrometer and each measurement lasted 500 seconds.
Once all the measurements were processed, a sensitivity curve was elaborated (Fig. 3.2) for nine elements belonging to the K lines. We chose copper as the reference element for the calibration.

3.2.1 Data Treatment

The spectrometer acquires data through a multichannel analyzer, handing to the user the number of counts for given energy (channel number). Thus, $F_i$, $F_j$, and $M$ are a collection of numbers $(F_i)_{k_i}$, $(F_j)_{k_j}$, and $(M)_{k_M}$ respectively; where $k_i$, $k_j$ and $k_M$ are the ROIs in which each element are defined \[184\]. Then, the value of the normalized functions are \[184\]:

\[
F_{iN} = \frac{F_i}{\sum_{k_i} (F_i)_{k_i}} \quad \text{(3.24)}
\]

\[
F_{jN} = \frac{F_j}{\sum_{k_j} (F_j)_{k_j}} \quad \text{(3.25)}
\]

\[
M_N = \frac{M}{\sum_{k_M} M_{k_M}} \quad \text{(3.26)}
\]
### Table 3.1: Substances selected to determine the TXRF spectrometer sensitivity curve.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Merk code</th>
<th>Elements determined</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂Cr₂O₇</td>
<td>104864</td>
<td>K/Cr</td>
<td>≥ 99.9</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>106717</td>
<td>Ni/Cl</td>
<td>≥ 98.0</td>
</tr>
<tr>
<td>KCl</td>
<td>104936</td>
<td>K/Cl</td>
<td>≥ 99.5</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>105082</td>
<td>Mn/K</td>
<td>≥ 99.0</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>105153</td>
<td>K/S</td>
<td>≥ 99.0</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>818247</td>
<td>Cu/Cl</td>
<td>≥ 98.0</td>
</tr>
<tr>
<td>FeCl₃·6H₂O</td>
<td>103943</td>
<td>Fe/Cl</td>
<td>≥ 99.0</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>108816</td>
<td>Zn/Cl</td>
<td>≥ 98.0</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>105886</td>
<td>S/Mg</td>
<td>≥ 99.5</td>
</tr>
</tbody>
</table>

Assuming no overlapping, the spectrum can be express as the sum of each characteristic function:

\[ M = F_i + F_j \]  \hspace{1cm} (3.27)

Then, replacing (3.27) in (3.26), the normalized spectrum is expressed as:

\[ M_N = \frac{F_i + F_j}{\sum_{k_M} (F_i + F_j)_{k_M}} = \frac{F_i + F_j}{\sum_{k_j} (F_i)_{k_i} + \sum_{k_j} (F_j)_{k_j}} \]  \hspace{1cm} (3.28)

After that, using the Eqs. (3.24), (3.25) and (3.28) into (3.19), and some algebra, the sensibility is expressed by:

\[ S_{i/j} = \alpha \frac{\sum_{k_i} (F_i)_{k_i}}{\sum_{k_j} (F_j)_{k_j}} \]  \hspace{1cm} (3.29)

According to the Eq. (3.29), the sensibility of \( i \) with respect \( j \) can be interpreted as the ratio of the total net counts adjusted by the ratio of the masses.

### 3.3 Results and Discussion

Figure 3.2 shows the relative sensitivity curve obtained with the set of samples analyzed with respect to copper. In Table II, the different sensitivity values can be seen in more detail. According to the curve, the sensitivity of the spectrometer for the K lines
increased along with the atomic number. Although the spectrometer assigned very low sensitivity values to elements with a low $Z$, we were able to obtain the sensitivity for elements with a low $Z$ (Mg, S), which is very difficult to do using the standard calibration method. Upon comparison, we found potassium to be $0.070 \pm 0.002$ times less sensitive than copper.

### 3.3.1 Impact over accuracy and precision in standard measurements

To estimate the improvement of the sensitivity calculated using the proposed method over the values obtained from the methods which use commercially available multi-elemental standard solutions, we proposed a validation experiment and then we compared the results. The purpose is to determine by both methods the atomic proportions (stoichiometry) of two different elements, in a known substance, but considered as

Figure 3.2: Sensitivity curve for K-line X-ray emission determined with the proposed method. Cooper was selected as the reference element.
Chapter 3  A Methodology to Determine the TXRF Spectrometer Sens. Curve

<table>
<thead>
<tr>
<th>X</th>
<th>SX/Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.001 ± 0.003</td>
</tr>
<tr>
<td>S</td>
<td>0.026 ± 0.002</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0382 ± 0.0009</td>
</tr>
<tr>
<td>K</td>
<td>0.070 ± 0.002</td>
</tr>
<tr>
<td>Cr</td>
<td>0.272 ± 0.008</td>
</tr>
<tr>
<td>Mn</td>
<td>0.43 ± 0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.66 ± 0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>0.78 ± 0.02</td>
</tr>
<tr>
<td>Zn</td>
<td>1.10 ± 0.03</td>
</tr>
</tbody>
</table>

Table 3.2: TXRF spectrometer sensitivity curve relative to copper, calculated with the proposed methodology.

incognita. In particular, we have analyzed a K$_2$CrO$_4$ salt, which was evaluated first with the standard multi-elemental method. A Merck-XVI sample was used as a reference standard. The exact relation between K/Cr is 2. The relation obtained from a prepared K$_2$CrO$_4$ solution, using the Spectra software, provided by the fabricant, was 1.86 ± 0.04. To evaluate that relation with the proposed method, first we calculated the relative sensitivity S$_{K/Cr}$ from another compound, K$_2$Cr$_2$O$_7$, which have the same kind of atoms but with different stoichiometry. Then applying Eq. (3.19), the relationship between atomic abundances K/Cr from the K$_2$CrO$_4$ solutions, was 1.95 ± 0.03.
Chapter 4
Conclusions

In this thesis, a methodology that allows the determination of the sensitivity curve of a TXRF spectrometer with high accuracy and precision is developed. The established formulation eliminates some of the uncertainties of the typical methods used to calibrate a TXRF spectrometer and, therefore, improves the quality of the results. An experiment compares the results obtained by the proposed method with those provided by the standard method. The improvement in the quality of the results is due only to the data analysis proposed here.

For TXRF a general formulation is established [5], describing all the uncertainties sources. The procedure proposed here eliminates many of those sources of uncertainties. In this sense, we consider that our procedure improves the quality of the results as much as we know about the technique. The method proposed also offers benefits in terms of economics (pure substances are less expensive than certified samples), independence (a single provider of samples is not required), and complexity (sample preparation and analyses of the results are facilitated).

The information obtained here (the relative sensitivity) is a number that indicates how many times the signal of a given element is bigger compared with another element signal if both elements are in the same concentration in the sample. But the signal definition (“the region of interest in the spectrum where the signal appears, ROI”) for each element is quite an ambiguous definition. For low Z elements the Kα and Kβ signals are close, but for Z≈30 elements both signal are more separated (See Fig. 1.4). The signal finally processed is an “arbitrary” definition established by each user, based on its own criteria, looking for the signal maximization respect to the background or possible interferences. This variation is much more explicit when we work with L lines, which are much more complex and different criteria can be chosen even for the signal of the same element, depending on the characteristics of the sample [188, 189]. In that sense, the obtained results are not directly comparable with other results produced by different authors.

All of the mathematical procedures developed relay on the properties of Eq. (3.1), where we can see that the signal intensity of each element is a linear function of the time acquisition, with independency of the characteristics of the sample. Thus, the
methodology developed and its conclusions can be applied in the same form to other related techniques, based on the same analysis principle, like PIXE (Particle-Induced X-Ray Emission) \[190\]. Also, it is possible to extend this procedure not only to a system with a different X-ray source, also to any technique which the signal obtained grows linearly with time, no matter the characteristic of the sample; for example Rutherford Backscattering Spectroscopy (RBS) \[191\], Fast neutron Activation Analysis (FNAA) \[192\], etc. As we can see from Eq. 3.1 to the end of the formulation, it is never described the source characteristics.
References


References


