ENERGY DISPERSIVE X-RAY FLUORESCENCE:

Measuring Elements in Solid and Liquid Matrices

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Final Degree Project - Outgoing Erasmus Students
June 2006

Degree Course: Enginyeria Tèc. Ind. Química Industrial

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Preface

The subject of this project is about "Energy Dispersive X-Ray Fluorescence" (EDXRF).
This technique can be used for a tremendous variety of elemental analysis applications.
It provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials.

The purposes of this project are:

- To give some basic information about Energy Dispersive X-ray Fluorescence.
- To perform qualitative and quantitative analysis of different samples (water-dissolutions, powders, oils,..) in order to define the sensitivity and detection limits of the equipment.
- To make a comprehensive and easy-to-use manual of the 'ARL QUANT'X Energy Dispersive X-Ray Fluorescence' apparatus.

RAQUEL SALAMÓ CLAPERA

Antwerpen, June 2006

Abstract

Since a new ARL QUANT'X Energy Dispersive X-Ray Fluorescence apparatus was delivered to the chemistry-biochemistry department of Karel de Grote Hogeschool, my task was to find out the methodology, so that afterwards this technique could be used for education and research.

This project is roughly divided in three parts:

The first part refers to the general theory of XRF and specific theory of EDXRF, including a description of the main parts of the ARL QUANT'X equipment.
The second part consists of three different experiments performed with the ARL QUANT'X:

- The approach of the 1st experiment consists of determining unknown components from the SIS sample (powder).
- The purpose of the 2nd experiment is to determine the lowest concentration of metals in water detected by ARL QUANT'X using different nitrates dissolved in water.
- The 3rd experiment's goal is to reveal the detection limit for phosphorus by adding lecithin to sunflower oil and finally, performing a quantitative measurement of a palm oil sample.

The third part of this project is a comprehensive and easy-to-use manual, including the minimum requirements which are needed for someone who wants to perform a qualitative or a quantitative analysis with the ARL QUANT'X apparatus by using the WinTrace software. (This part will be included in a separate book).

As a general conclusion, the ARL QUANT'X Energy Dispersive X-Ray Fluorescence apparatus can be used for a tremendous variety of elemental analysis applications, because almost every element from Na to Pu in the periodic table can be measured, in concentrations ranging from a few ppm to nearly 100 percent.

1.   Introduction

There are several research projects at the department of industrial sciences of Karel de Grote-Hogeschool. For some of those projects, elemental analysis is a very interesting technique.

One of those projects, for example, is the HAGAR-project. The purpose of the HAGAR-project is to give waste fats and oils a second life by transforming them into alkali-esters. These esters can be used as a biofuel, but also as biocleaning agents. In the transesterification reaction, triglycerides (oil or fat) and an alcohol react with each other in the presence of an alkali catalyst (contains Na or K) to form the alkali-esters. After the reaction is completed, there is a natural separation between the glycerol and the esters that are formed. At that time, most of the catalyst that is used in the reaction should be in the glycerol layer, but a small part of the catalyst will still be situated in the ester layer. After the reaction, the catalyst is neutralised and the ester layer is washed several times with water. It is possible to follow up the concentration of catalyst by measuring the concentration of sodium or potassium in the glycerol layer and in the washing waters by using ion-chromatography. If you want to measure the sodium or potassium concentration in the ester layer, the ester sample has to be burned into ashes and the ashes have to be dissolved in water. This kind of analysis is very time-consuming and it is therefore not practical to use this technique to follow up the concentration of sodium or potassium in the esters layer during the washing steps. In this case, the use of an x-ray fluorescence system would be more appropriate since it requires no sample preparation and the measurements take only a few minutes.

Another example of a project in which the use of x-ray fluorescence is a very useful technique, is the SIS-project. SIS stands for Sick Installation Syndrom and the purpose of the project is to analyse central heating systems. Sometimes these systems are malfunctioning due to the precipitation of metals, most of the time in their oxide or hydroxide form, in the system. By analyzing the precipitated material from the central heating system by means of x-ray fluorescence, one can get an idea about what the cause of the malfunction could be.

Because of the usefulness of an x-ray fluorescence system in those two projects and in other situations, like the determination of heavy metals in wasted water and the determination of the composition of certain powders, the department of industrial sciences of Karel de Grote-Hogeschool purchased a Quant'X Energy Dispersive X-Ray Fluorescence system from Thermo Electron. The purpose of this thesis work is to start up the XRF-system, to make an easy-to-use manual for anyone who wants to use the apparatus and to try to get an idea of the possibilities of the apparatus by performing measurements in several matrices (water, powders, oil,...).

2. Basic theory

2.1 Electromagnetic Spectrum

The electromagnetic spectrum is the distribution of electromagnetic radiation according to energy (or equivalently, according to frequency or wavelength).

The following table gives approximate wavelengths, frequencies, and energies for selected regions of the electromagnetic spectrum.

Spectrum of Electromagnetic Radiation				
Region	**Wavelength (Angstroms)**	**Wavelength (centimeters)**	**Frequency (Hz)**	**Energy (eV)**
Radio	$> 10^9$	> 10	$< 3 \times 10^9$	$< 10^{-5}$
Microwave	$10^9 - 10^6$	$10 - 0.01$	$3 \times 10^9 - 3 \times 10^{12}$	$10^{-5} - 0.01$
Infrared	$10^6 - 7000$	$0.01 - 7 \times 10^{-5}$	$3 \times 10^{12} - 4.3 \times 10^{14}$	$0.01 - 2$
Visible	$7000 - 4000$	$7 \times 10^{-5} - 4 \times 10^{-5}$	$4.3 \times 10^{14} - 7.5 \times 10^{14}$	$2 - 3$
Ultraviolet	$4000 - 10$	$4 \times 10^{-5} - 10^{-7}$	$7.5 \times 10^{14} - 3 \times 10^{17}$	$3 - 10^3$
X-Rays	**$10 - 0.1$**	**$10^{-7} - 10^{-9}$**	**$3 \times 10^{17} - 3 \times 10^{19}$**	**$10^3 - 10^5$**
Gamma Rays	< 0.1	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^5$

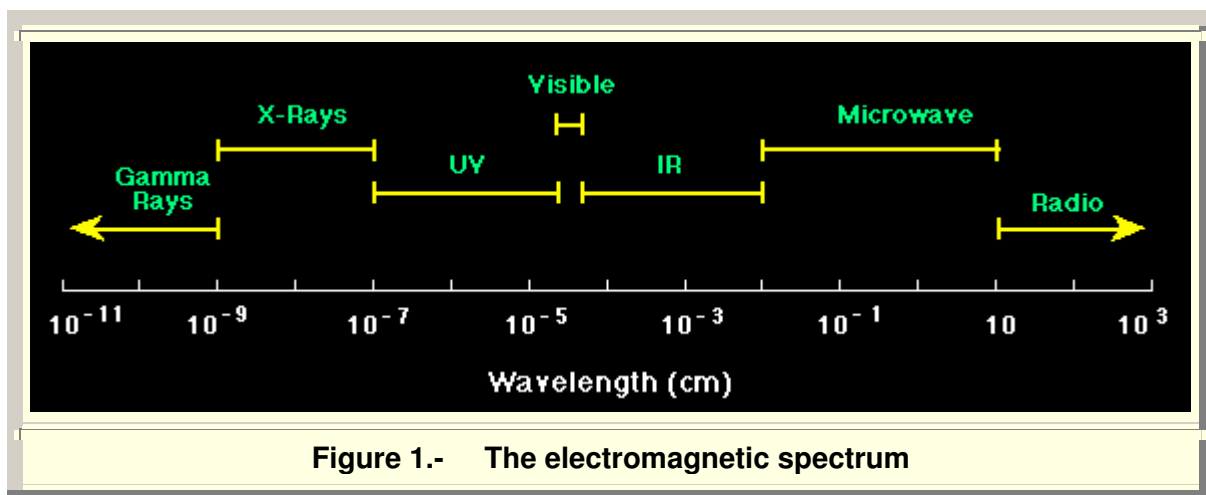A graphical representation of the electromagnetic spectrum is shown in the figure below.

Figure 1.-   The electromagnetic spectrum

2.2 About X-rays

2.2.1 Introduction

The x-ray region is that part of the electromagnetic spectrum between about 0.1 and 200 Å (Ångstrom units) where $Å=10^{-10}$ m.

Only a relative small part of the total x-ray region is covered by the conventional x-ray spectrometer, about 0.2^{-20} Å, this being referred to as the analytical x-ray region. That is why most applications use x-rays of between 0.1 Å to 25 Å.

In general, x-rays have an extremely short wavelength but wavelengths shorter than a few tenths of an Ångstrom are difficult to excite and even more difficult to disperse or separate.

X-rays, like all other electromagnetic waves, travel in straight lines at the same speed in vacuum. They are not deviated by electric fields or magnetic fields. They are reflected and refracted in accordance with the same laws, and they can be superimposed to set up interference patterns. In addition to these, x-rays have certain special properties not shared by the lower end of the electromagnetic spectrum:

They expose photographic films.
They cause emission of electrons from metals.
They ionize gases.
They penetrate matter.

2.2.2 X-ray Spectra

When an element is bombarded with primary photons, electrons from the atomic subshells may be excited to unfilled orbital levels. The element regains its initial or "ground" state by transference of outer orbital electrons to the unfilled inner levels and the energy surplus following each transference may be emitted as characteristic radiation. The energy of the emitted x-ray photon is equal to the absolute energy difference between the binding energies of the initial and final states of the transferred electron. Thus the wavelength of the photon is dependent upon the distribution of electrons in the excited atom and hence upon the atomic number of that atom. Since, under a given set of circumstances, many such electron transferences take place simultaneously, several characteristic lines are emitted at the same time and we refer to this total emission as the characteristic emission spectrum of the element. A fairly simple set of selection rules covers the normal transitions (diagram lines) but certain lines are observed which do not apparently fit the selection rules. These lines are categorized as forbidden and satellite lines and, although they are generally weak, they do have significance in analytical x-ray spectroscopy.

2.2.3   Basic Units

In x-ray spectrometry, it is necessary to utilize both wavelength and energy terminology to explain the properties of x-ray radiation. The most common units utilized are the Ångstrom unit for wavelength and the kilo electron volt for energy.

The basic unit for wavelength is the Ångstrom (Å) which is 10^{-10} m.
The basic unit for energy is the kiloelectron volt (KeV) which is 1000 electron volts. Energy is also measured in joules, and 1 eV=1.60219 x 10^{-19} J
Energy and wavelength are related in the fundamental equation which gives a very useful relationship for the conversion of wavelength to energy.

$$E = hv = \frac{hc}{\lambda}$$

where E is the energy, λ the wavelength, v the frequency, c the velocity of light and h is Planck's constant. Thus the energy equivalent of a 1 Å x-ray photon would be

$$E = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{10^{-10}} J = 2 \times 10^{-15} J$$

or

$$\frac{2 \times 10^{-15}}{1.6 \times 10^{-19}} eV = 12.4 \text{ KeV}$$

2.3 X-rays Production

X-rays are produced when the electrons are suddenly decelerated - these rays are called bremsstrahlung radiation, or "braking radiation".

X-rays are also produced when electrons make transitions between lower atomic energy levels in heavy elements. X-rays produced in this way have definite energies just like other line spectra from atomic electrons. They are called characteristic x-rays since they have energies determined by the atomic energy levels.

2.3.1 Bremsstrahlung X-rays

"Bremsstrahlung" means "braking radiation" and is retained from the original German to describe the radiation which is emitted when electrons are decelerated or "braked" when they are fired at a metal target. Accelerated charges give off electromagnetic radiation, and when the energy of the bombarding electrons is high enough, that radiation is in the x-ray region of the electromagnetic spectrum.
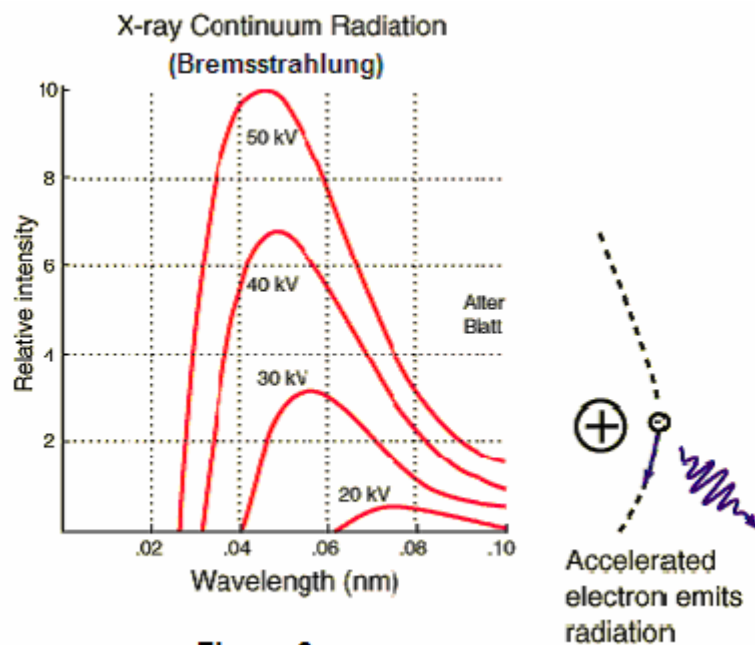
Figure 2

It is characterized by a continuous distribution of radiation which becomes more intense and shifts toward higher frequencies when the energy of the bombarding electrons is increased. The curves above are from the 1918 data of Ulrey, who bombarded tungsten targets with electrons of four different energies.

The bombarding electrons can also eject electrons from the inner shells of the atoms of the metal target, and the quick filling of those vacancies by electrons dropping down from higher levels gives rise to sharply defined characteristic x-rays.

2.3.2   Interaction of X-ray Radiation with Matter

In interactions with matter, x-rays are ionizing radiation and produce physiological effects which are not observed with any exposure of non-ionizing radiation, such as the risk of mutations or cancer in tissue.

Since the quantum energies of x-ray photons are much too high to be absorbed in electron transitions between states for most atoms, they can interact with an electron only by knocking it completely out of the atom. That is, all x-rays are classified as ionizing radiation. This can occur by giving all of the energy to an electron (photoionization) or by giving part of the energy to the photon and the remainder to a lower energy photon (Compton scattering). At sufficiently high energies, the x-ray photon can create an electron positron pair.
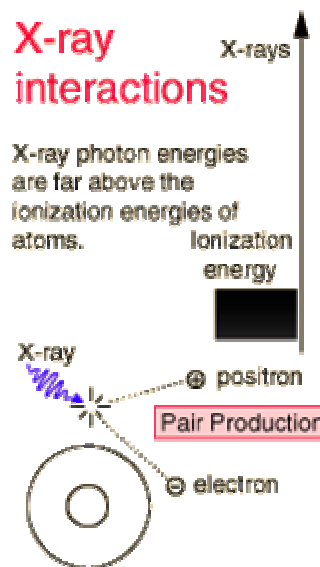
Figure 3

2.3.3   Ionizing Radiation

Ionization is the ejection of one or more electrons from an atom or molecule to produce a fragment with a net positive charge (positive ion). The classification of radiation as "ionizing" is essentially a statement that it has enough quantum energy to eject an electron. This is a crucial distinction, since "ionizing radiation" can produce a number of physiological effects, such as those associated with risk of mutation or cancer, which non-ionizing radiation cannot directly produce at any intensity.
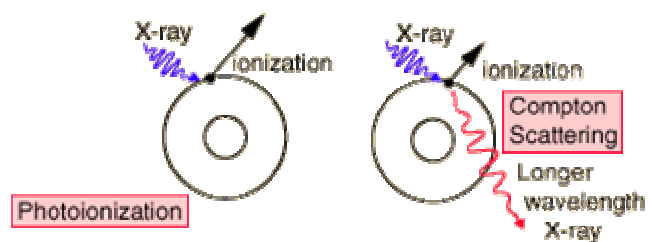
Comparison with non-ionizing radiation

Figure 4

The mechanisms of interaction for ionizing radiation in the form of x-rays and gamma-rays include the photoelectric effect, Compton scattering and at high enough energies, electron positron pair production.

Although the precise ionization energy differs with the atom or molecule involved, a general statement is any radiation with quantum energy above a few electron volts is considered to be ionizing radiation. The threshold for ionization lies somewhere in the ultraviolet region of the electromagnetic spectrum, so all x-rays and gamma-rays are ionizing radiation.

2.3.4 Scattering of X-rays

Scattering of primary x-rays by the sample results in two processes:

Coherent scattering (without loss of energy) and Compton scattering (with a little loss of energy). As not all of the incident x-rays participate in the photoelectric absorption because some of them do not reach the inner shells and thus they do not give rise to absorption. Instead, they are deflected by the atoms in two ways:

a) The incident x-ray photon is deflected without loss of energy.
b) The x-ray photon is deflected with a slight loss in energy and thus with an increase in wavelength.

In a) the sample scatters primary x-rays with exactly the same energy. This scattering is thus called coherent or elastic scattering.

In b), as shown in Figure 5, some of the photons collide with a loosely bound electron
in an outer shell of the atom. The electron recoils under the impact and leaves the atom carrying with it some of the energy of the incident photon. Thus the primary photon is scattered with a slightly lower energy. This phenomena is called Compton scattering.

The difference in energy between the incident photon and the compton photon depends only on the angle (φ) between the unscattered and the scattered x-rays.

It is given by the following equation:

$$\Delta\lambda = \lambda' - \lambda = h/m_o c \ (1 - \cos \varphi)$$

where λ and λ' are wavelengths (cm) of the incident and inoherently scattered x-rays, respectively; h is Planck's constant $(6.6 \times 10^{-34}$ J·s); m_o is the rest mass of the electron $(9.11 \times 10^{-28}$ g); c is the velocity of light (3×10^{10} cm/s); and φ is the angle (deg) between unscattered and scattered x-rays. Substitution of these values and intersection of the conversion factor 10^8 Å/cm gives:

$$\Delta\lambda = 0.0243 \ (1 - \cos \varphi) \qquad \text{where } \Delta\lambda \text{ is in angstroms.}$$

Thus $\Delta\lambda$ is independant of both x-ray wavelength and the atomic number of the scatterer. On the other hand, the intensity ratio of the coherent to the Compton scattering depends on the atomic number of the scatterer.

In practical x-ray spectrometry, we are confronted with scattered x-rays: coherently scattered x-rays contribute to the background in the x-ray spectra. Since they fall exactly at the same energy as the measured line of a given element, they can't be discriminated in general. Thus background in XRF can largely be attributed to scattering of primary x-rays by the sample. Since heavier elements absorb more and scatter less, the background level in the spectra from heavy elements is almost insignificant.

On the other hand, it becomes the limiting factor for measuring light elements at low concentrations.
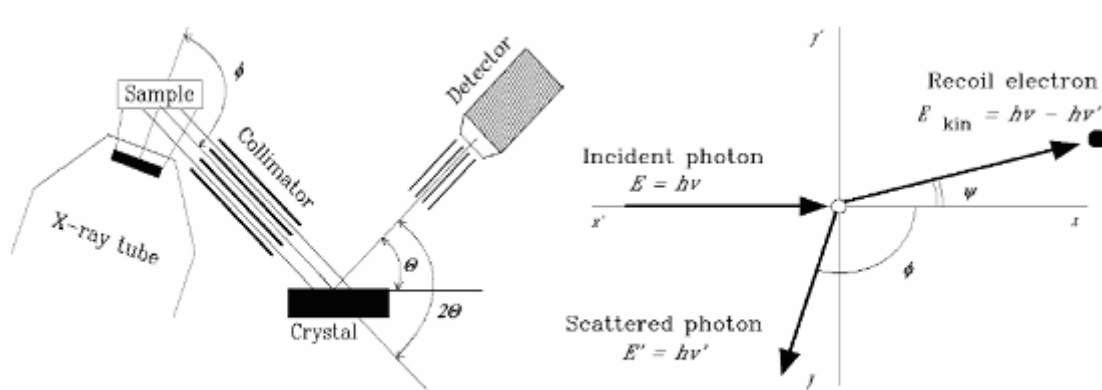
Figure 5

2.4 The Physics of X-rays

As it is said before, x-rays are high-energy photons that are produced when electrons make transitions from one atomic orbit to another. These transitions can be generated via the photoelectric effect as illustrated in Figure 6.

If you send a photon into an atom with an energy greater than the binding energy of an electron in that atom, the photon can knock that electron out of its orbit, leaving a hole (or vacancy). This hole can then be filled by another electron in the atom, giving off an x-ray in the transition to conserve energy. This process is known as fluorescence. Many different atomic electrons of different binding energies can fill this hole, so you would expect to see many energy peaks in an x-ray spectrum.

The figure 6 below, is a pictorial representation of x-ray fluorescence using a generic atom and generic energy levels. This picture uses the Bohr model of atomic structure and is no to scale.
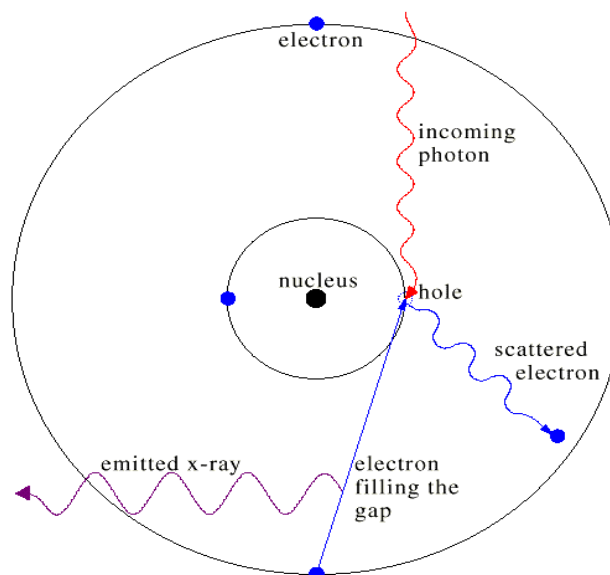
Figure 6

2.5 Emission Spectrum

The kinetic energy of an electron arriving at the target is given by,

$$\frac{1}{2}mv^2 = E_{kin}$$

Where: m = mass (Kg)
                v = velocity (m/s)
                E_{kin} = kinetic energy (J)

This kinetic energy is lost due to rapid deceleration on striking the target and is released as electromagnetic waves of varying frequencies as shown in the figure below. This radiation of continuously varying frequencies is called the background radiation or "white" radiation.
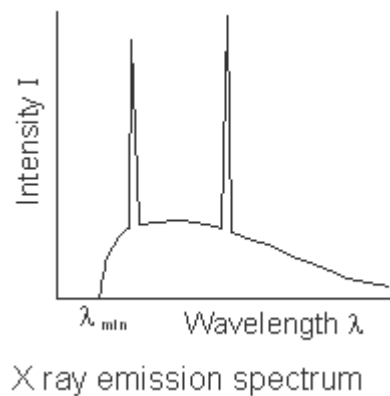
Figure 7

The highest frequency of electromagnetic wave released in this manner is that resulting from the greatest loss of kinetic energy in a single collision with a target atom.

Therefore, $hf_{max} = E_{coll}$

Where: h = Planck constant = $6.6260755 \cdot 10^{-34}$ J·s
                f_{max} = frequency $(1/s)$
                E_{coll} = loss of kinetic energy in a collision between 2 atoms

Lower frequencies are released when the decelerating electrons make multiple collisions losing energy in stages. Thus the minimum wavelength λ_{min} emitted by the x-ray tube is given by:

$$\frac{hc}{\lambda_{min}} = E$$

Where: h = Planck constant = $6.6260755 \cdot 10^{-34}$ J·s
c = velocity of light = 2.998×10^{10} cm/s
λmin = wavelength minimum (cm)
E = energy

In addition to this background radiation, there are also some pronounced spikes seen in the sketch graph of the emission spectrum. These are called the characteristic lines and are generated from re-radiation after excitation of orbiting electrons from lower to higher permitted shells in atoms of the target material.

2.6 Nomenclature Used

The electrons in an atom do not all follow the same orbit but arrange themselves in well defined shells around the nucleus; these shells are known as K, L, M, N, O, P and Q; the K shell being nearest to the nucleus.

Each shell represents an energy level, composed of different sub-levels. The K shell has the lowest energy and the Q shell the highest, but it is important to note that the largest energy difference between any two shells is between the K and L shells; the smallest difference is between the outermost shells.

The energy of a given electronic shell depends on the atomic number and thus, it varies from element to element.

X-ray spectral lines are grouped in series: K, L, M, N etc. All the lines in a series result from electron transitions from various higher levels to the same shell.

When a K shell vacancy is filled by an electron from the L shell we get the Kα line radiation, whereas when an electron from the M shell fills this vacancy, we get the Kβ line radiation. Similarly, if a vacancy in the L shell is filled by an electron from the M shell we get the Lα line radiation, if it is filled by an electron from the N shell, we get the Lβ line radiation and if it is filled by an electron from the O shell we get the Lγ line radiation.

Every element has its characteristic K, L and M series. Thus, light elements give rise to only K lines, mid range elements can emit both K and L series while the heavy elements produce K, L and M series. Thus, the spectra get increasingly complex when we go towards heavier elements. In practical XRF, we select the principle lines of K and L series to measure an element although there may be other lines present.

The selection of an analysis line depends mainly on the type of sample, the elements present in it, the concentration range of the elements and the excitation conditions.
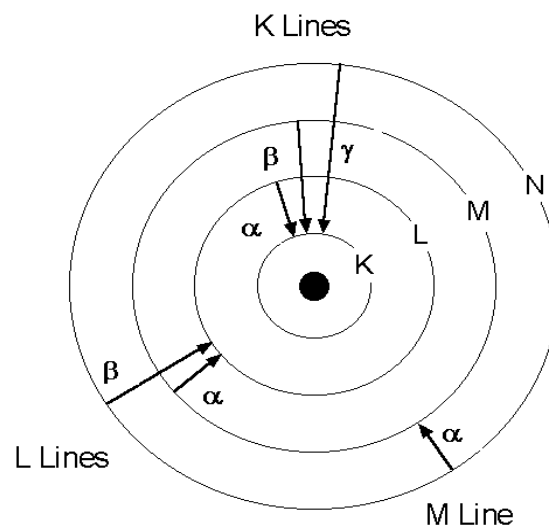

Figure 8

2.7 Emission of X-rays

X-ray production typically involves bombarding a metal target in an x-ray tube with high speed electrons which have been accelerated by tens to hundreds of kilovolts of potential. The bombarding electrons can eject electrons from the inner shells of the atoms of the metal target. Those vacancies will be quickly filled by electrons dropping down from higher levels, emitting x-rays with sharply defined frequencies associated with the difference between the atomic energy levels of the target atoms.

As it is said before, x-rays are generated by large energy transition of electrons within an atom from outer orbitals to core orbitals. Most x-rays are created by bombarding a metal target with energetic electrons. The electron beam typically ejects core electrons from the target metal, making the atoms unstable. The atoms relaxes from this position by dropping an outer valence electron to the core level. This large decrease in energy required for an electron to be able to drop to the core level requires the emission of the excess energy in the form of a photon. These photons have the energy of x-rays.

An electron can be ejected from its atomic orbital by the absorption of a light wave (photon) of sufficient energy. The energy of the photon (hv) must be greater than the energy with which the electron is bound to the nucleus of the atom.
When an inner orbital electron is ejected from an atom, an electron from a higher energy level orbital will be transferred to the lower energy level orbital. During this transition a photon maybe emitted from the atom.

This fluorescent light is called the characteristic x-ray of the element.

The energy of the emitted photon will be equal to the difference in energies between the two orbitals occupied by the electron making the transition. Because the energy difference between two specific orbital shells, in a given element, is always the same (i.e. characteristic of a particular element), the photon emitted when an electron moves between these two levels, will always have the same energy. Therefore, by determining the energy (wavelength) of the x-ray light (photon) emitted by a particular element, it is possible to determine the identity of that element.
For a particular energy (wavelength) of fluorescent light emitted by an element, the number of photons per unit time (generally referred to as peak intensity or count rate) is related to the amount of that analyte in the sample.
The counting rates for all detectable elements within a sample are usually calculated by counting, for a set amount of time, the number of photons that are detected for the various analytes' characteristic x-ray energy lines.
It is important to note that these fluorescent lines are actually observed as peaks with a semi-Gaussian distribution because of the imperfect resolution of modern detector technology. Therefore, by determining the energy of the x-ray peaks in a sample's spectrum, and by calculating the count rate of the various elemental peaks, it is possible to qualitatively establish the elemental composition of the samples and to quantitatively measure the concentration of these elements.

Inside the Atom

An atom has a nucleus, which contains particles of positive charge (protons) and particles of neutral charge (neutrons). Surrounding the nucleus of an atom are shells of electrons - small negatively charged particles. Each shell has a specific energy associated with it. Within these shells the electrons move around the nucleus of the atom.
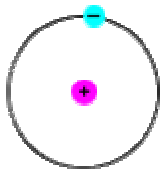
The ground state of an electron, the energy level it normally occupies, is the state of lowest energy for that electron. (Note that electron doesn't actually move about the nucleus in a circle. See The Quantum Story below.)

Ground State

When an electron occupies an energy shell greater than its ground state, it is in an excited state. An electron can become excited if it is given extra energy, such as when it absorbs a photon or if collides with a nearby atom or particle.

Photon

Ground State

Excited State
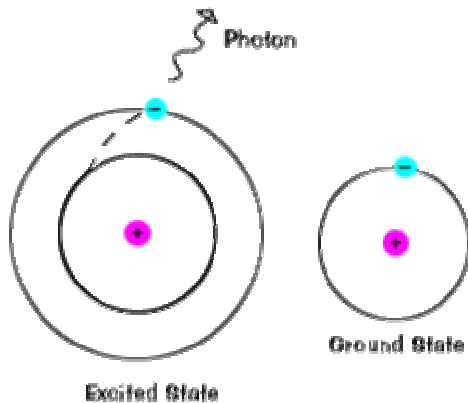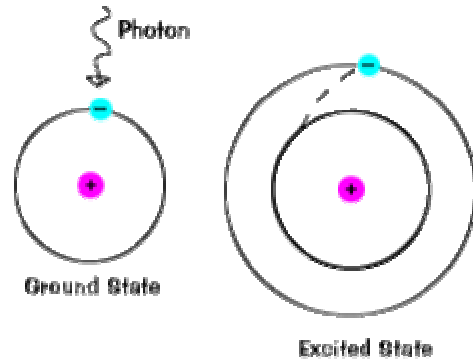
Photon

An electron does not stay in an excited state for very long - it soon returns to the ground states. When it does so, a photon is emitted that has the same energy as the difference in the energy level between the excited state and the ground state.

Excited State

Ground State

So an electron moving from one energy shell to a lower one emits a photon of a specific energy. Since the energy and wavelength of the photon are related, we see this photon at a specific wavelength in the spectrum. We refer to these as a "line" in the spectrum. Because there are many energy shells in any particular atom, there are many different possible energies with different initial and final values. When an atom is in an excited state, the electron can drop all the way to the ground state, or stop in an intermediate level.

2.8 Characteristic X-rays

We know that when orbiting electrons change from a higher permitted energy level to a lower one, the energy content of the atom drops and this excess in energy is emitted from the atom in a photon whose frequency is given by

$$E_{high} - E_{low} = hf$$

Where: E_{high} = energy of higher energy level
E_{low} = energy of lower energy level
h = Planch constant
f = frequency

Such changes between the states of the outer electrons involve small amounts of energy and result in radiation of the longer wavelengths of the infra red, visible and ultraviolet parts of the spectrum. But the innermost electrons being much closer to the nucleus experience larger forces. The corresponding larger changes of energy involving these electrons result in radiations of higher frequencies.
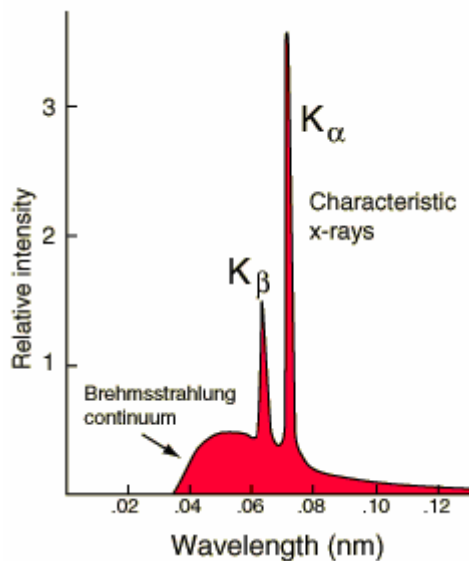

The energy associated with any permitted level is proportional to Z^2, where Z is the atomic number of the element. Thus for an element of Z = 42, the frequencies are $(42)^2$ times those obtained for the Lyman series of lines in the hydrogen spectrum which have frequencies of the order of 10^{15} hertz. Thus the characteristic frequency emitted from an element of Z=50 would be in the range of 10^{18} hertz. Such high frequencies correspond to the x-ray region of the electromagnetic spectrum. ($\lambda \sim 10^{-10}$ m).

Figure 9

X-rays from a molybdenum target at 35 kV

All methods of analysis based on x-ray spectrometry involve the excitation of characteristic wavelengths from the elements making up the sample being analysed, separation of these wavelengths by means of a spectrometer, measurement of the intensities of the individual characteristic wavelengths and estimation of elemental composition by use of the measured intensities.

3. X-Ray Fluorescence (XRF)

3.1 Introduction

X-Ray Fluorescence (XRF) is the phenomenon where a material is exposed to x-rays of high energy, and as the x-ray (or photon) strikes an atom (or a molecule) in the sample, energy is absorbed by the atom. If the energy is high enough, a core electron is ejected out of its atomic orbital.
An electron from an outer shell then drops into the unoccupied orbital, to fill the hole left behind. This transition gives off an x-ray of fixed, characteristic energy that can be detected by a fluorescence detector. The energy needed to eject a core electron is characteristic of each element, and so is the energy emitted by the transition. The transition of an L shell electron dropping into the K shell is termed a Kα transition, while an M shell electron dropping into the K shell is a Kβ transition.
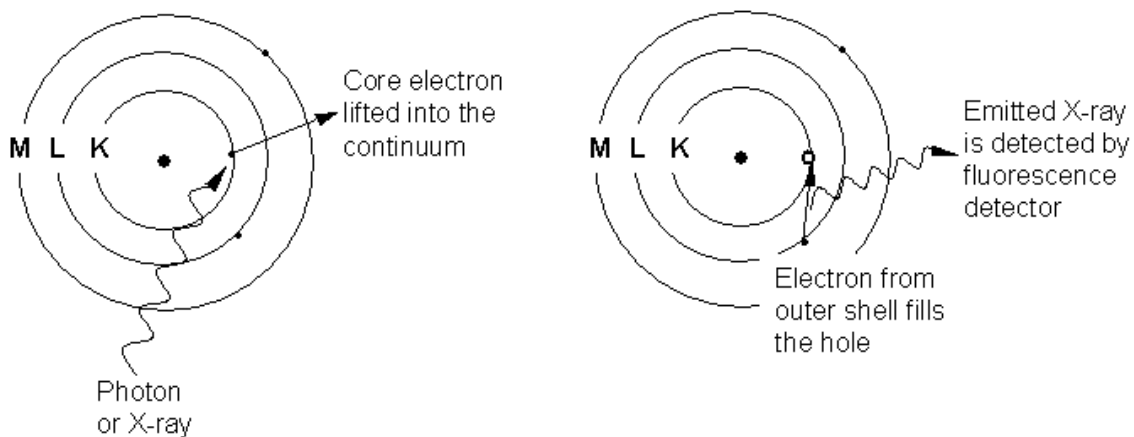

Figure 10

Typically the lightest element that can be analysed is beryllium (Z=4), but due to instrumental limitations and low x-ray yields for the light elements, it is often difficult to quantify elements lighter than sodium (Z=11).

There are two types of spectrometer:

- Wavelength dispersive spectrometers (WDX or WDS): the photons are separated by diffraction on a single crystal before being detected;
- Energy dispersive spectrometers (EDX or EDS): the detector allows the determination of the energy of the photon when it is detected; the EDX spectrometers are smaller (even portable), cheaper, the measurement is faster, but the resolution and the detection limit is far worse than the WDX spectrometers

EDXRF spectrometer is the one that we will focus later on.

3.2 Principles of X-Ray Fluorescence

3.2.1 X-ray Excitation

X-ray excitation is produced when a primary x-ray photon has sufficient energy to eject electrons from inner shells and therefore vacancies are created. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells in the X-Ray Fluorescence process.
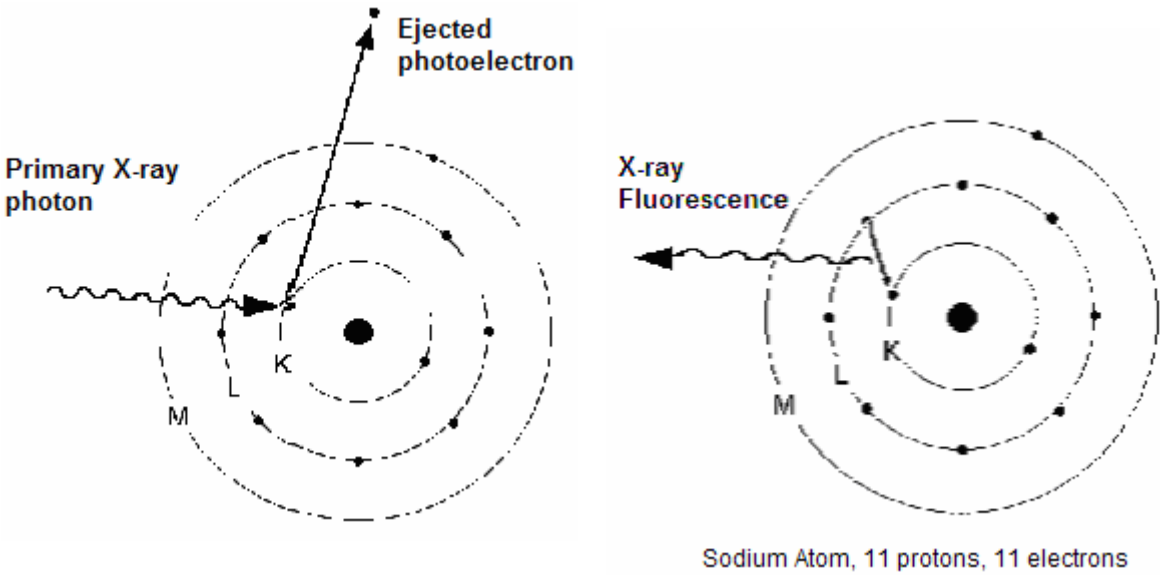

Figure 11

3.2.2 Electron Excitation

Electron excitation is the movement of an electron to a higher energy state.
When a high-energy electron is deflected from its original trajectory it becomes a scattered electron. Thus a secondary electron is generated as ionization product. It is called 'secondary' because is generated by other radiation (the primary radiation). This radiation can be in the form of ions, electrons, or photons with sufficiently high energy.
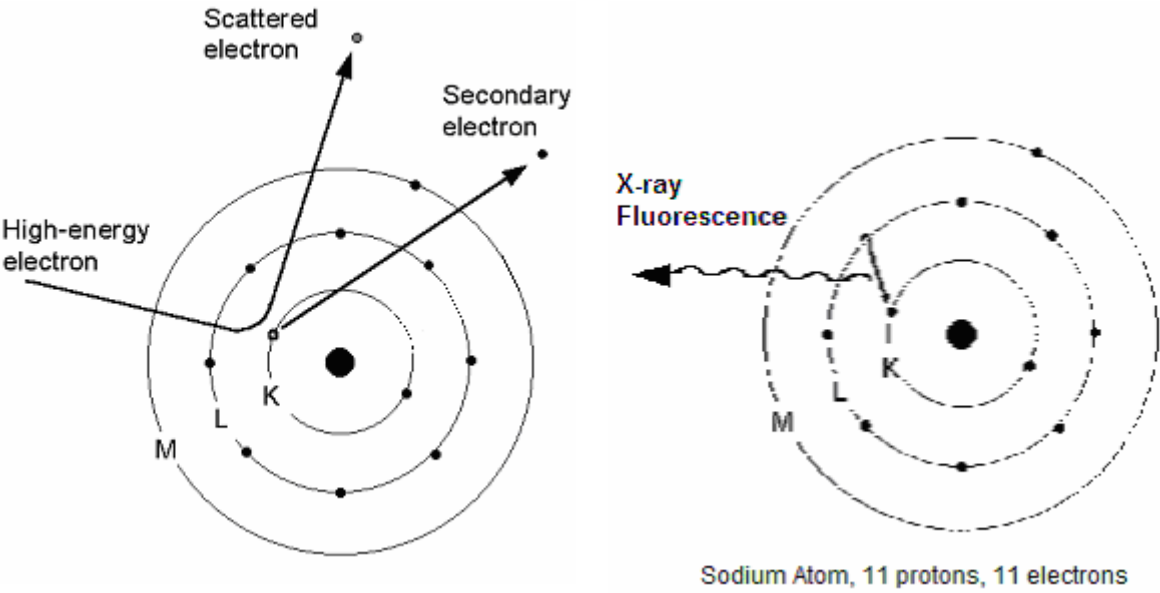

Figure 12

3.2.3 Auger Electron Emission

Auger emission is a phenomenon in which the emission of an electron from an atom causes the emission of a second electron. This second ejected electron is called an Auger electron.

The Auger process occurs in excited atoms which have a core electron removed. Thus, when an electron is removed from a core level of an atom, leaving a vacancy, an electron from a higher energy level may fall into the vacancy, resulting in a release of energy. Although sometimes this energy is released in the form of an emitted photon, the energy can also be transferred to another electron, which is then ejected from the atom.

Upon ejection the kinetic energy of the Auger electron corresponds to the difference between the energy of the initial electronic transition and the ionization energy for the shell from which the Auger electron was ejected. These energy levels depend on the type of atom and the chemical environment in which the atom was located.

Auger electrons are of very low energy and are only emitted from the extreme surface of the sample. This is exploited by etching the surface of the sample with an ion beam, exposing progressively deeper layers into the sample. An electron beam is then directed onto the exposed regions. The Auger electrons produced by the beam come from each new layer exposed, allowing depth profiling to be achieved.
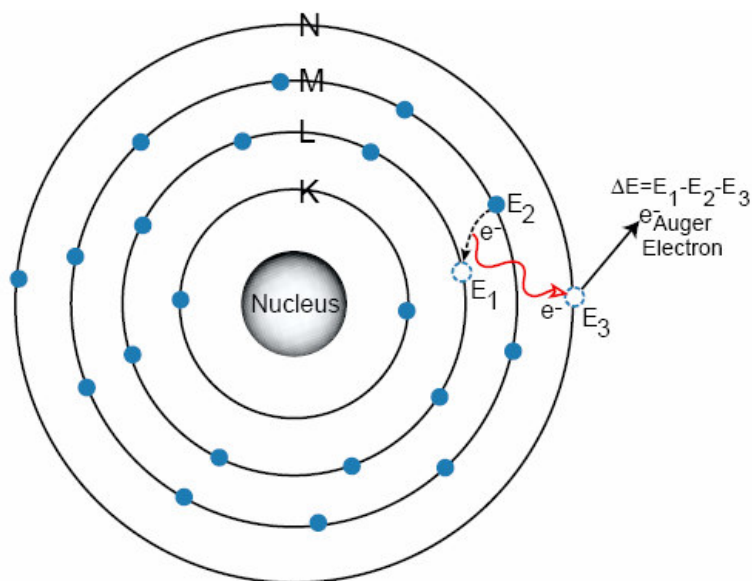

Figure 13

The reason why the Auger effect is more common in elements of low atomic number (Z) is because their atomic electrons are more loosely bound and their characteristic x-rays more readily absorbed

It should also be noticed that because of the Auger effect in the higher levels two or more vacancies could be created. The creation of double vacancies is responsible for the appearance of satellite peaks.

3.2.4 Fluorescence Yield

The probability that an x-ray photon will be emitted (instead of an Auger electron) is called Fluorescence Yield.

The figure 14 shows the fluorescence yield as a function of atomic number.

The K lines are more probable than the L lines which explains the difference in the yield for the K and L type transitions.

In practical x-ray spectrometry, we use the K lines to measure elements with low to medium atomic number while we switch over to measure L lines for the heavy elements, or even to the M lines.
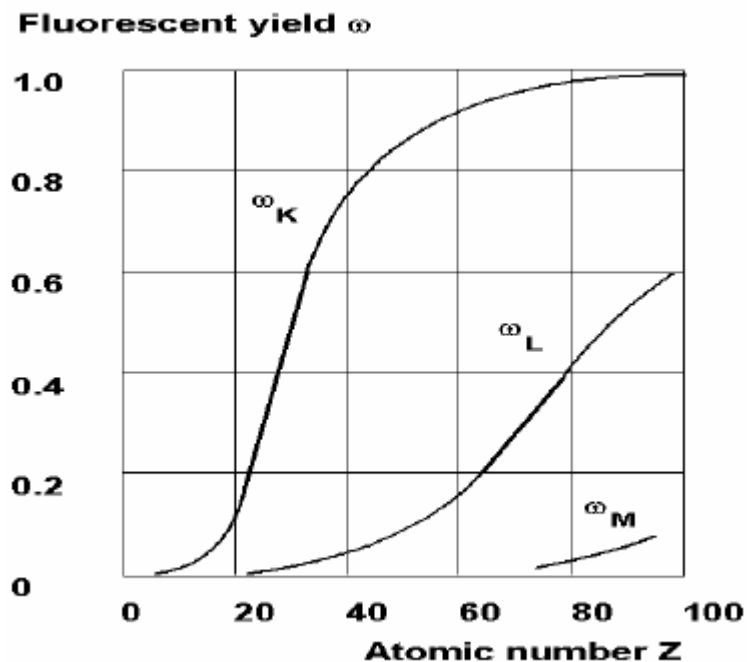
Figure 14

3.3 Matrix Effects

3.3.1 Introduction

The wavelength (λ) of the spectral line is a function of the atomic number of the element (Z). One can therefore associate each observed spectral line with an element. Thus, qualitative analysis can be accomplished. The intensity (I) of the spectral line is a function of the concentration of the element (C) present in the sample. Thus, quantitative analysis can be done if this function is determined.

$\lambda = f(Z)$ Qualitative analysis (Moseley's law)
$I = f(C)$ Quantitative analysis

This intensity/concentration relationship can be a rather complicated function since it not only depends on the concentration of the element responsible but also the concentrations of the other elements present in the sample. The effects of other elements on the analyte intensity is usually referred to as matrix effects.

In general, we can distinguish between the following effects:

- Line Overlaps of lines with the same diffraction order.
- Line Overlaps of lines higher diffraction orders.
- Line Overlaps by x-ray tube lines.
- Inter-element effects.
- Effects due to sample morphology (inter- and intra-particle effects).

Because the first three effects can be eliminated by the choice of a different crystal, detector, element line or by the use of a primary beam filter or by energy discrimination or by a suitable correction; and the last could be eliminated by a different sample preparation, they are not always referred to as matrix effects.

3.3.2 Types of Matrix Effects

In XRF absorption-enhancement effects arise from the following phenomena:

1. The matrix absorbs primary x-rays (primary-absorption effect); it may have a larger or smaller absorption coefficient than the analyte for primary source x-rays.

2. The matrix absorbs the secondary analyte x-rays (secondary-absorption effect); it may have a larger or smaller absorption coefficient for the analyte-line radiation.

3. The matrix elements emit their own characteristic lines, which may lie on the short wavelength side of the analyte absorption edge, thereby exciting the analyte to emit additional radiation to that excited by the primary source of x-rays alone (enhancement)

3.4 Wavelength Dispersive and Energy Dispersive XRF Compared

In X-Ray Fluorescence we basically distinguish between two types of instruments:
the wavelength dispersive (WDX) and the energy dispersive spectrometer (EDX).
Both WDX and EDX employ an x-ray source for exciting the sample.
Essentially, energy-dispersive x-ray spectrometry differs from wavelength-dispersive only in the means used to disperse (separate) the several spectral lines emitted by the specimen. So basically they differ in the way the x-ray spectra emitted by the sample is detected.

In wavelength-dispersive spectrometers (WDX), the fluorescence spectrum is dispersed into discrete wavelengths using a dispersion device (e.g. a crystal).
The several wavelengths are dispersed spacially on the basis of their wavelengths prior to detection; thus, in principle at least, the detector receives only one wavelength at a time which is detected using a gas proportional or scintillation counter.

In energy-dispersive spectrometers, one measures the entire fluorescence spectrum directly using a solid state detector which is then processed using a multichannel analyser to obtain the information on an energy scale.
The detector receives all excited lines of all the specimen elements at once. For each incident x-ray photon, the detector generates a pulse of electric current having height proportional to its photon energy. The detector output is amplified and subjected to electronic pulse-height analysis to separate the pulses arising from the several detected wavelengths on the basis of their heights and thereby on the basis of the photon energies of the incident x-ray lines.
By appropriate setting of the operating parameters, the pulses of each line of interest can be measured individually.

Advantages of Energy Dispersion

- simplicity of instrumentation - no moving parts
- simultaneous accumulation of the entire x-ray spectrum
- qualitative analysis can be performed in 30 s, or so
- a range of alternative excitation sources can be used in place of high-power x-ray tubes with their large, heavy, expensive and power-consuming supplies
- alternative sources include, low power x-ray tubes, secondary monochromatic radiators, radioisotopes and ion beams.

Advantages of Wavelength Dispersion

- resolution is better at wavelengths longer than 0.08 nm
- higher individual intensities can be measured because only a small portion of the spectrum is admitted to the detector
- lower detection limits are possible

3.5 Advantages and Disadvantages of X-ray Spectrometry

Advantages of X-ray Spectrometry

- Simple spectra
- Spectral positions are almost independent of the chemical state of the analyte
- Minimal sample preparation
- It is non-destructive
- Applicable over a wide range of concentrations
- Good precision and accuracy
- Can be used to measure solid, powdered and liquid samples

Disadvantages of X-ray Spectrometry

- X-ray penetration of the sample is limited to the top 0.01 - 0.1 mm layer
- Light elements (below Na) have very limited sensitivity although C is possible on new instruments
- Inter element (MATRIX) effects may be substantial and require computer correction
- Limits of detection are only modest
- Instrumentation is fairly expensive

3.6 Typical XRF Applications

- Qualitative and quantitative elemental analysis of organic and inorganic compounds and materials such as:

  - ores, minerals, ceramics, cement, construction materials and soils
  - chemicals, pharmaceuticals, biomaterials and plastics
  - corrosion products, environmental contaminants and hazardous materials
  - metals and alloys

- Control of raw material composition, technological processes and finished products.
- Determination of the content of heavy metals in soil, food and other materials.
- Authenticity verification of canvas, paint, metal objects, paper, pottery, etc.
- Forensic and medical studies.
- Analysis of precious metals.

4.   Energy Dispersive X-Ray Fluorescence (EDXRF)

4.1 Introduction

Energy Dispersive X-ray Fluorescence technology (EDXRF) provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials.
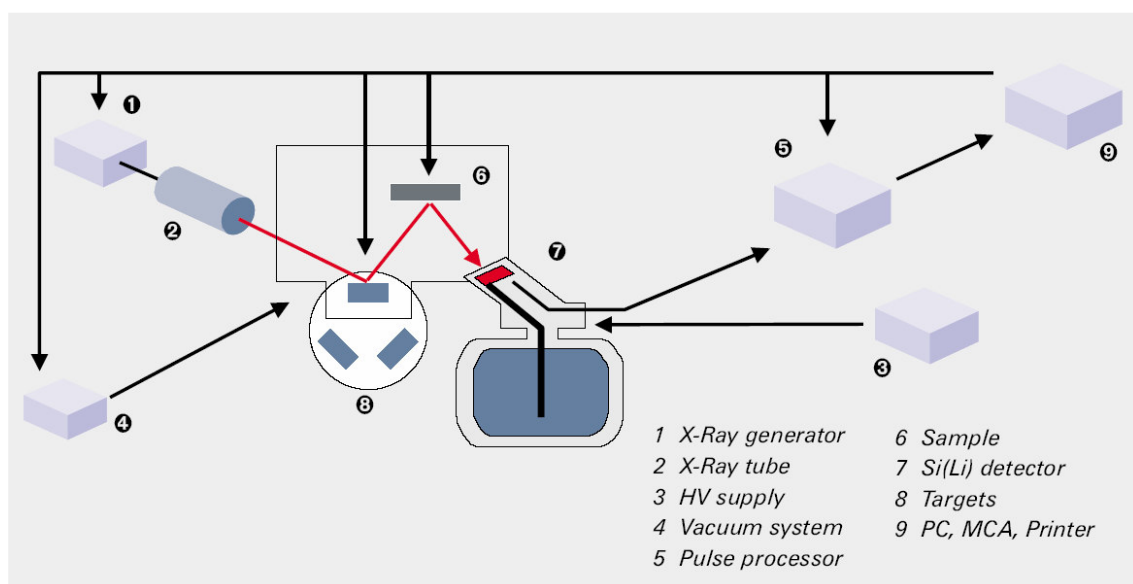
It can be used for a wide range of elements, from sodium (11) to uranium (92), and provides detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously.

4.2 Working Principle of an EDXRF Spectrometer

The atoms in the sample material are excited by x-rays emitted from a x-ray tube or radioisotope. For increasing sensitivity the primary excitation radiation can be polarised by using specific targets between the x-ray tube and the sample (ED-P (Polarisation)-XRF).

All element specific x-ray fluorescence signals emitted by the atoms after the photoelectric ionisation are measured simultaneously in a fixed mounted semi-conductor detector or sealed gas-proportional counter.

The radiation intensity of each element signal, which is proportional to the concentration of the element in the sample, is recalculated internally from a stored set of calibration curves and can be shown directly in concentration units.

1 X-Ray generator
2 X-Ray tube
3 HV supply
4 Vacuum system
5 Pulse processor

6 Sample
7 Si(Li) detector
8 Targets
9 PC, MCA, Printer

Analysis by EDXRF involves use of ionizing radiation to excite the sample.

This excitation ejects electrons from the atomic shells of the elements in the sample. When a given atom replaces the ejected electron, by taking another electron from an outer atomic shell, x-ray energies are emitted.

Since each element generates a specific energy level in this replacement process, these energies are known as characteristic x-rays.

For example, if an electron in the K shell of a manganese atom is ejected, an energy of 5.894 kilo-electron volts (keV) is generated when an electron from that atom's L shell is moved to the K shell.

EDXRF spectrometers use a semiconductor material (an x-ray detector) to convert characteristic x-rays into electrical signals. The spectrometer's electronics digitize the signals produced by the detector, and send this information to a PC or internal electronics for display and analysis.

The Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer makes use of the fact that the pulse height of the detector signal is proportional to the x-ray photon energy, which is correlated with the wavelength.

These x-rays can be detected and displayed as a spectrum of intensity against energy: the positions of the peaks identify which elements are present in the sample (qualitative analysis) and in counting and comparing the number of energies at the same energy level reaching the detector (peak heights), we can determine percentages and so identify how much of each element is present in the sample (quantitative analysis).

One limitation of the technique is that only a thin layer, less than 0.1mm, is actually analysed. This can sometimes give misleading results on corroded or plated metals unless the surface is cleaned.
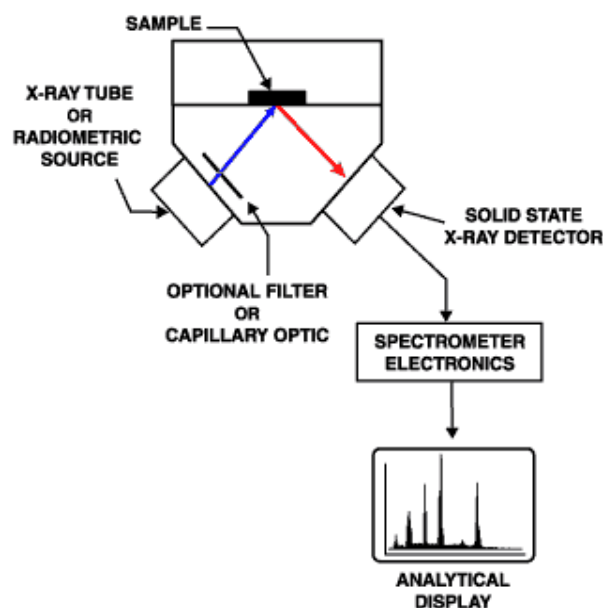

Figure 15

The EDXRF analyzer also uses an x-ray source to excite the sample but it may be configured in one of two ways.

The first way is direct excitation, where the x-ray beam is pointed directly at the sample. Filter made of various elements may be placed between the source and sample to increase the excitation of the element of interest or reduce the background in the region of interest.

The second way uses a secondary target, where the source points at the target, the target element is excited and fluoresces, and then the target fluorescence is used to excite the sample. A detector is positioned to measure the fluorescent and scattered x-rays from the sample and a multichannel analyzer and software assigns each detector pulse an energy value thus producing a spectrum. Note that there is absolutely no reason why the spectra cannot be displayed in a wavelength dependant graph format.

The apparatus we work with uses direct excitation.

4.3   Description of the Apparatus

4.3.1   Introduction

The Thermo ARL QUANT'X Energy Dispersive X-ray Fluorescence (EDXRF) uses an x-ray tube excitation source and a solid state detector to provide simultaneous spectroscopic analysis of elements ranging from sodium to uranium in atomic number and in concentrations ranging from a few parts per million to 100 percent.
Instrument control and data analysis are performed by a personal computer that is connected to the system.

The instrument contains the x-ray generating elements, sample chamber, detector, detector electronics, embedded microprocessor controller and associated power supplies.

The personal computer (PC) includes a second Ethernet Interface board and other standard PC elements.
Spectral data transfer and Instrument Control are established through a dedicated Ethernet cable. The PC sends commands (x-rays on, vacuum pump on, etc.) to, and receives status from, the Instrument embedded microsprocessor located in the QuanX-EC.

Figure 16.- External view of the ARL QUANT'X EDXRF

4.3.2   Important Components

The most important component of the apparatus is the x-ray tube in order to produce an x-ray source.

The second major component is the detector, which is designed to produce electrical pulses that vary with the energy of the incident x-rays.
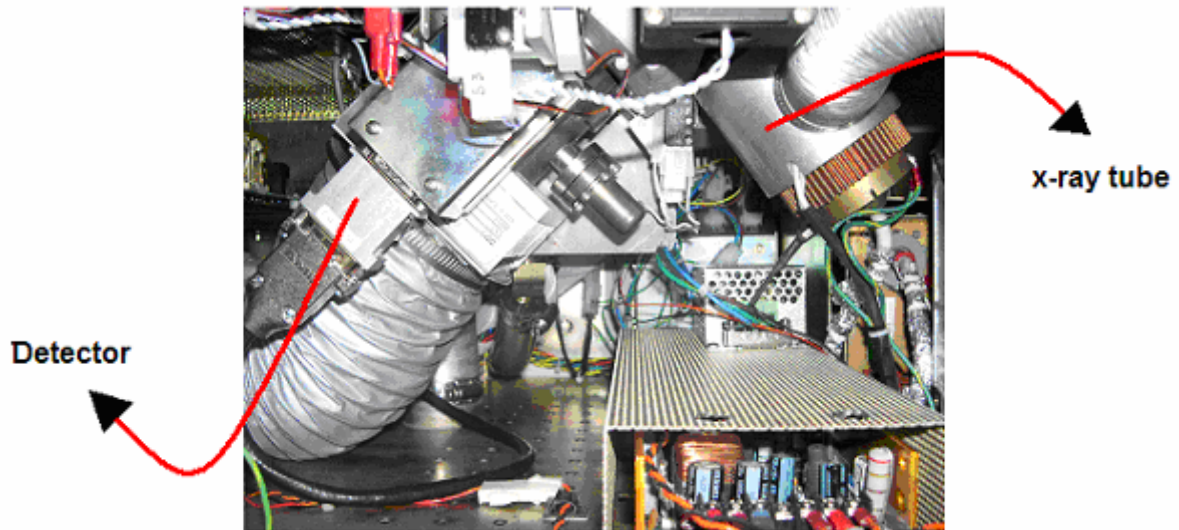

Figure 17.-

Internal ARL QUANT 'X EDXRF view (principal components)

The ARL QUANT'X EDXRF utilizes an exclusive Peltier cooled Si(Li) detector and unique Digital Pulse Processing (DPP) technology for high-performance, multi-element analysis of environmental and industrial applications, such as air particulates, soil contamination, toxic elements in plastic, and forensic science.

Another critical component are the x-ray tube filters. Their function is to absorb/transmit some energies of source x-rays more than other in order to reduce the counts in the region of interest while producing a peak that is well suited to exciting the elements of interest.

Secondary targets are an alternative to filters. A secondary target material is excited by the primary x-rays from the x-ray tube, and then emits secondary x-rays that are characteristic of the elemental composition of the target.

Where applicable secondary targets yield lower background and better excitation than filter but require approximate 100 times more primary x-ray intensity.

One specialized form of secondary targets is polarizing targets. Polarizing XRF takes advantage of the principle that when x-rays are scattered off a surface they are partially polarized. The target and sample are place on orthogonal axis' to further minimize the scatter and hence the background at the detector.

Two other important components are the collimator and the goniometer.

All of the above mentioned will be discussed in detail in the following parts of the text.

4.3.2.1 The X-ray Tube

4.3.2.1.1 General information about X-ray Tubes

Since x-rays are high energy electromagnetic waves, a high-energy event is needed to produce them. In principle, almost any high energy particle can be used for the excitation of characteristic x-ray radiation.

Generally x-rays are produced by a change in momentum of a charged particle, typically an electron. This can be achieved in a number of ways:

1) driving electrons down a high voltage drop in a vacuum tube into a metal target which essentially stops their linear velocity.
   The way in which the x-ray tube of our ARL QUANT 'X produce x-rays, is applied to a metal cathode that produces free electrons. The x-rays are produced by accelerating electrons to a high velocity with a high voltage field and causing them collide the metal target of the tube (anode). The x-ray tube may be of the high-power (2-5 kW) or low-power (≤ 100 W) type.

2) In a vacuum, accelerating electrons or protons with high voltage and suddenly changing their path using magnets.

3) Changing the direction of electrons in a conductor under high voltage, x-rays are produced by high voltage transformers.

4) Decelerating electrons in a video display or TV, colour TV's and video generate x-rays.

5) high-energy events such as nuclear explosions and cosmic events produce high intensity x-rays and cosmic rays (lower wavelength than x-rays).
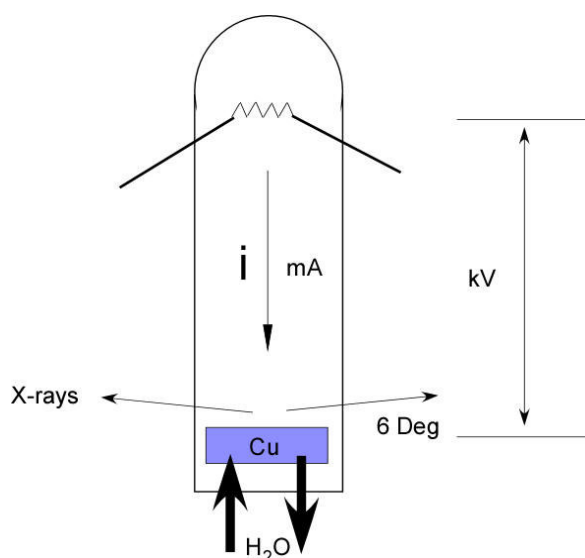
The components of a tube generator are a filament which serves as a source of electrons and which generates a tube current, i, flowing from the cathode (filament) to the anode, a high voltage drop, V, between the filament and an anode composed of a metal such as copper. A high vacuum to allow for free transport of electrons (electrons are quickly absorbed even by gas atoms). X-ray transparent windows, usually made of beryllium (a toxic metal). A cooling system to dissipate the large amounts of heat which are generated when electrons collide with the anode.

Figure 18.- shows the cross-section of an x-ray tube.

The main limitation to the flux or intensity of x-rays that can be generated by a tube source is the heat generated in the process. More than enough heat is generated to melt the anode and destroy the tube. High flux generators use a rotating anode which dissipates the local heating of the anode over a cylinder of target metal and can operate at much higher power than a fixed anode generator.
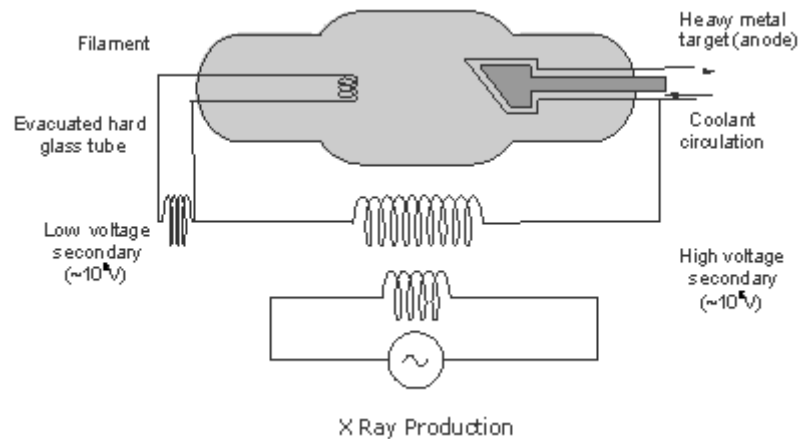

Figure 19.- The apparatus for production of x-rays.

Thermo-ionic emission occurs from a filament heated by a low voltage (~100 volts). The filament is contained in an evacuated hard glass tube. At the opposite end of the same tube is a hollow target made of heavy metal. There is a coolant circulating in the target. Applied between the filament and the target is an accelerating voltage (~104volts). This is drawn from the high voltage secondary of a transformer. The heating voltage is drawn from a low voltage secondary wound on the same transformer.

There are four basic requirements of an x-ray source:

a) Sufficient photon output over the required wavelength range
b) High stability (generally better than 0.1 %).
c) Ability to work at reasonably high potentials (i.e., to around 60 to 100 kV).
d) Freedom from too many interfering characteristic x-ray lines.

X-ray tubes can be used for excitation in any of three modes:

1) direct excitation by the unfiltered primary beam in the usual way so that both continuum and target-line x-rays irradiate the specimen

2) direct excitation by the primary beam filtered so that substantially monochromatic target-line x-rays irradiate the specimen

3) excitation of a secondary target having its strongest line at wavelength just shorter than that of the analyte absorption edge; the secondary x-rays in turn irradiate the specimen.

As with any vacuum tube, there is a cathode to emit electrons into the vacuum and an anode to collect the electrons, thus establishing a flow of electrical current through the tube. A high voltage power source is connected across cathode and anode, e.g. 30-150 kilovolts (kV), such that the voltage can be quickly switched on, then off, for precise amounts of time, e.g. 0.001 to 1.0 second, and the current flow, often in the 1.0 to 1000 milliampere range, once started, can be controlled.

Electrons focused on the tungsten anode from the cathode, collide with and accelerate other electrons, ions and nuclei within the anode material and about 1% of the energy generated is emitted/radiated, perpendicular to the path of the electron current, as x-ray photons.
The x-ray photon-generating effect is generally called the Bremsstrahlung effect, a contraction of the German brems for braking, and strahlung for radiation (see also 2.3.1)
Over time, tungsten will be deposited from the anode onto the interior glass surface of the tube. This will slowly degrade the quality of the x-ray beam.
Eventually, the tungsten deposit will become sufficient enough to act as a conductive bridge, and at high enough settings, arcing will occur.
The arc will jump from the cathode to the tungsten deposit, and then to the anode. This arcing will cause an effect called "crazing" on the interior glass of the x-ray window. As time goes on, the tube will become unstable even at lower potentials, and must be replaced.

The range of photonic energies emitted by the system can be adjusted by changing the applied voltage, and installing aluminium filters of varying thicknesses. For example: aluminium filters are installed in the path of the x-ray beam to remove "soft" (non-penetrating) radiation. The number of emitted x-ray photons, or dose, are adjusted by controlling the current flow.

Simply put, the high voltage controls x-ray penetration, the current affects contrast, and the time affects brightness.

4.3.2.1.2 X-ray Tube Working Principle in the ARL QUANT 'X EDXRF

The tungsten filament is heated by a pulse width modulated AC current from the Voltage/Current Control board. The heated filament cathode emits electrons which are attracted to the anode by a positive potential. During transit they gain energy from the electric field which exists between the anode and cathode.
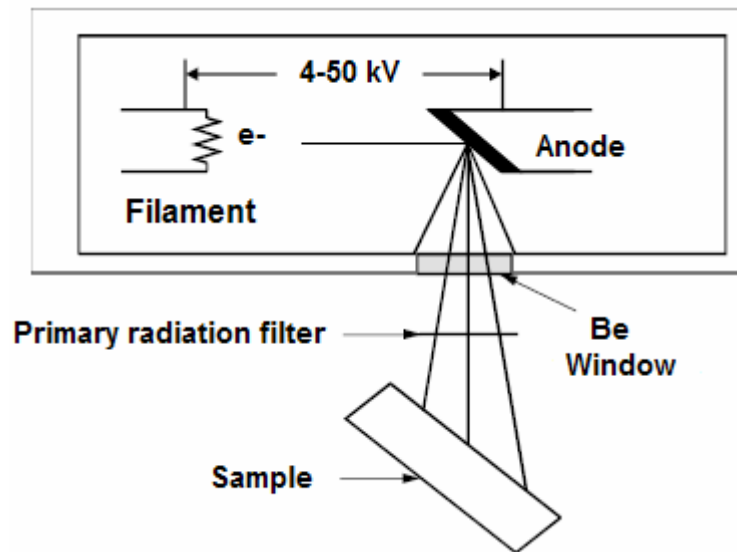

Figure 20

When the electrons strike the anode, they lose this energy by producing both x-rays and heat.
A focusing electrode causes the electrons to impact the anode in a spot about 1mm2.
The magnitude of the electron current is controlled by the Voltage/Current Control board, and is limited to 1.98 mA.
The anode, also called the target, consists of a thin disk of rhodium or other material plated on a copper block. The anode is typically cut such that the angle between the face of the target and the normal to the exit window is 20° . The window is made of thin beryllium foil, which allows x-rays to escape and at the same time holds a high vacuum.

Use of the x-ray tube in quantitative analysis requires attention to the following three considerations:

1)   It is important to measure the spectrum from the x-ray tube to make sure that the correct target material is used. This can be done by observing the scattered spectrum. The characteristic K and L lines of the target should be present.

2)   Slight changes occur in the position and dimension of the filament and other internal dimensions as the tube warms up to its equilibrium temperature. These changes may affect the intensity distribution of the primary beam. It is thus important to wait half an hour at operating voltage and current before making precise quantitative measurements.

3)   The output flux of the x-ray tube at constant kV and mA decreases approximately 3% for each 1000 hours of operation due to pitting and sublimation of target material on the inside of the tube window.
To obtain accurate results, this effect should be calibrated out.

4.3.2.2 Peltier Cooled X-ray Detector (PCD)

The function of the x-ray detector is to convert the energies of the x-ray photons into voltage pulses which can then be counted, giving in turn a measurement of the total x-ray flux.
Detector used in modern x-ray spectrometers are almost invariably "proportional" detectors, and these have the property that the energy of the incident x-ray photon determines the size of the voltage pluses produced by the detector. Where this is the case, it is possible to employ a means of selecting only a narrow range of voltage pulses, and this may be useful in discriminating against unwanted radiation.

The Peltier Cooled x-ray detector provides the means for sensing fluoresced x-ray photons and thus it converts the x-rays emitted and scattered by the sample into electrical pulses which are amplified by the preamp before transmission to the board.

The detector assembly consists of a Si(Li) detector crystal which is the x-ray sensing device, the thermoelectric Peltier cooler to cool the Si(Li) detector to its operating temperature, the charge-sensitive pre-amplifier, the beryllium window and an optional ion pump for PCD detectors with the Helium flow option.

The Si(Li) crystal and Peltier cooler are under high vacuum inside the housing. The beryllium window acts as an x-ray transparent, vacuum tight seal.
The ion pump is used to help maintain a good vacuum in the presence of the Helium.
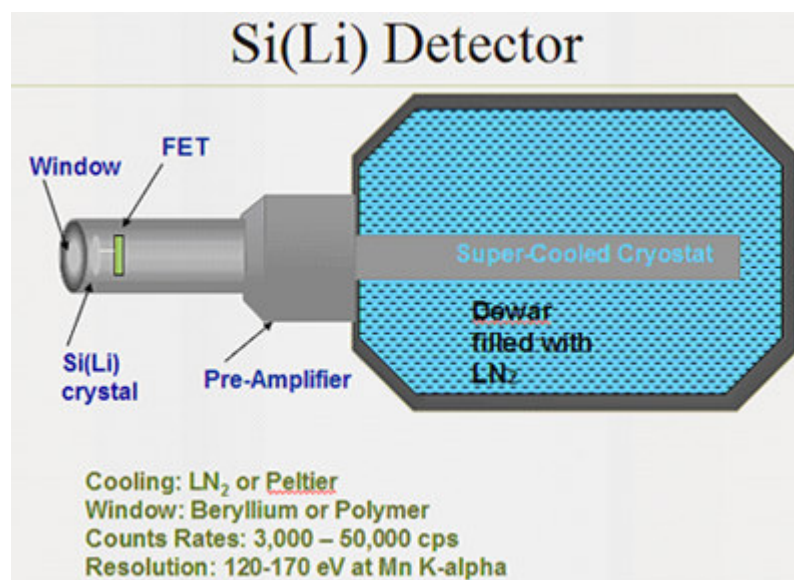
Figure 21

4.3.2.3 Filters

The filters are used to modify the characteristics of the primary x-ray beam emitted from the x-ray tube and are selected based on the elements being analyzed.

Filters are positioned between the sample and detector to filter out unwanted x-ray peaks.
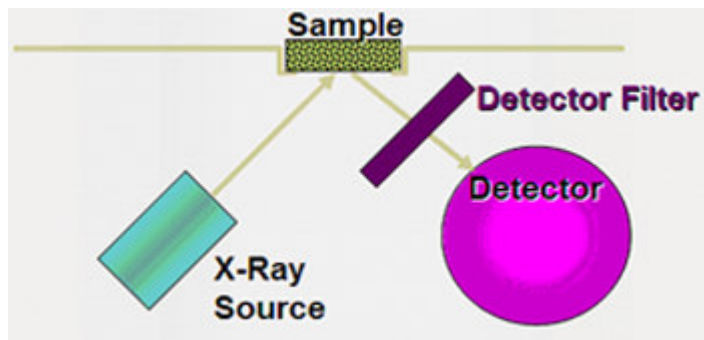
Figure 22

There are also source filters which perform one of two functions:

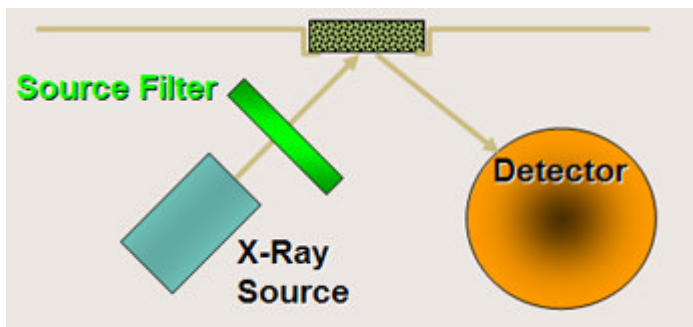–   Background Reduction
–   Improved Fluorescence

Figure 23

The filter wheel assembly is an eight position turret driven by a step motor. An optical sensor is used to detect the rotational position. Each position on the wheel may hold one transmission filter.

Filters: Automated 8 position filter selection.
Al, cellulose, 2 Cu and 3 Pd filters are provided and one of the eight positions is kept for measurements without filter.

4.3.2.4 Collimator

In x-ray and gamma ray imaging, a collimator is a device that filters a stream of photons so that only those travelling parallel to a specified direction are allowed through. The illustration below shows a lead collimator used in x-ray machines.

Without a collimator (top picture) rays from all directions will be recorded; for example, a ray that has passed through the top of the specimen (to the right of the diagram) but happens to be travelling in a downwards direction may be recorded at the bottom of the plate. This will not produce a readable image.

Without a collimator
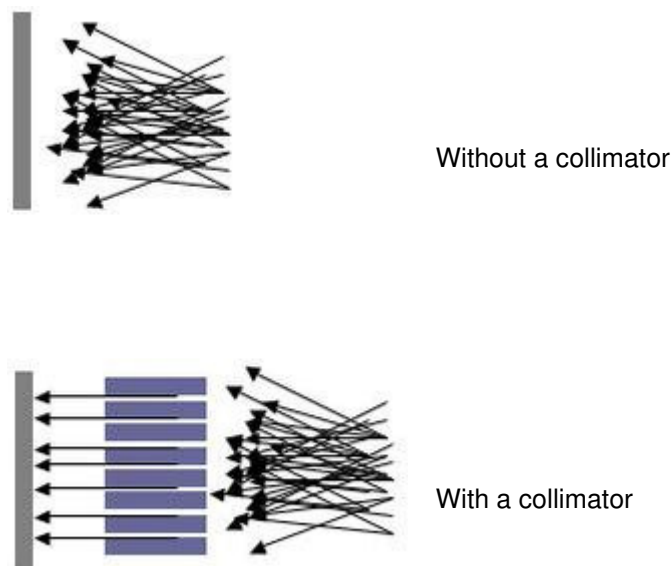
With a collimator

Figure 24

Collimators are used in x-ray and gamma-ray imaging because it is not yet possible to focus such short wavelengths into an image with lenses as at optical or near-optical wavelengths.

In the bottom of the illustration, a collimator has been added. This is a sheet of lead or other material opaque to the incoming radiation with many tiny holes bored through it. Only rays travelling nearly parallel to the holes will pass through them - any others will be absorbed by hitting the plate surface or the side of a hole. This ensures that rays are recorded in their proper place on the plate, producing a clear image. Although collimators improve the resolution, they also reduce the intensity of the signal. Most lead collimators let less than 1% of incident photons through. For this reason, attempts have been made to replace collimators with electronic analysis.

4.3.2.5 Goniometer

A goniometer is an instrument that either measures angles or allows an object to be rotated to a precise angular position.

The whole goniometer assembly is composed of the base, the goniometer itself and the head. The goniometer is mounted on the base, which can be shifted horizontally in a direction perpendicular to the x-ray beam. The lower section of the goniometer is firmly mounted on the base and thus can only move together with the base. The upper section of the goniometer can be rotated with respect to the lower section.

The goniometer head (there are different types) can be taken off from the goniometer. The head provides additional flexibility for aligning a sample, which is mounted on the very top of the head. The top of the head can be translated horizontally.
Furthermore, the top can also be moved up-and-down.

The most critical thing about the goniometer is that its rotation axis must intercept perfectly with the x-ray beam and this is probably the only thing that requires frequent check.
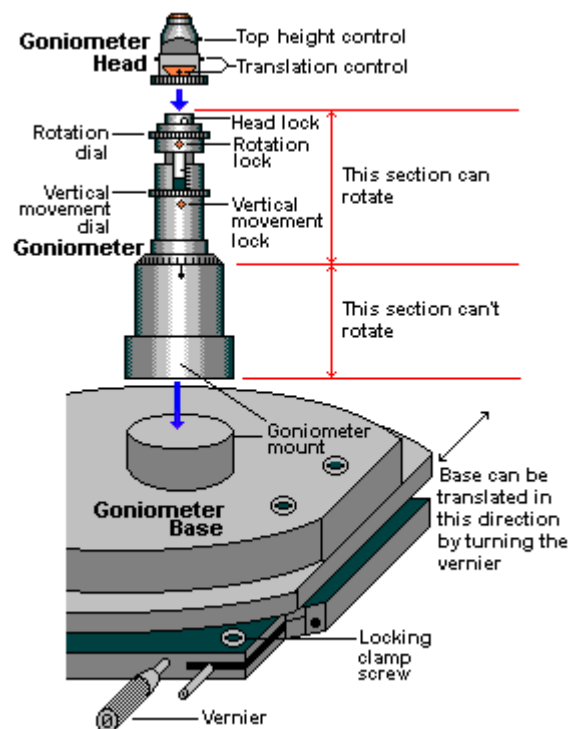
Figure 25

5. Experiments

5.1 Sample Preparation

5.1.1 Introduction

Good sample preparation is by far the most important step in any analytical technique. Whatever samples you're working with –loose or pressed powders, fused beads, solid samples or liquids– .How well the sample is prepared and presented will affect the ability to yield accurate data from the instrument. X-ray fluorescence is not immune to this crucial step, despite the ability to correct for standard counting errors, instrument variation errors, operatoration errors, and matrix effects. Choosing the right sample preparation technique will depend on the goals of accuracy and precision the analyst needs or wishes to attain.

The importance of sample preparation is especially relevant today as XRF analysis plays a growing role in the daily activities of producers around the world. Fortunately, XRF analysis usually doesn't require extensive sample preparation work, and methods are normally inexpensive, easy to learn and easy to use. So even when the need for sample preparation is taken into account, XRF spectrometry is still easier and quicker than almost all other chemical analysis techniques.

5.1.2 XRF Samples

Specimen preparation is crucial to the relationship between spectral line intensity and the element concentration. Factors such as surface roughness, particle shape, particle size, homogeneity, particle distribution, and mineralization can affect this relationship.

The key to selecting the appropriate sample preparation technique are reproducibility, accuracy, simplicity, cost, and time required for sample preparation.

Samples must be in a form that are similar to available standards in terms of matrix, density and particle size.

1) Solids: generally solids must be polished as surface roughness may give erratic results.

2) Powders and pellets: powdered samples are often pressed into pellets, suspensions may also be analysed

3) Fusions: fusions with potassium pyrophosphate ($K_2P_2O_7$) or a tetraborate ($Na_2B_4O_7$ or $Li_2B_4O_7$) present a homogenised sample which can often be analysed directly.

4) Liquids and solutions: a x-ray transparent cover and sample cup must be provided to be able to measure liquid samples.

5.1.2.1 Powders Samples

The analysis of powder samples is important across a whole range of industries, with some being among the most common materials to undergo XRF analysis. Among the countless powders sent for XRF analysis are raw materials for cement production, metals and plastics, soils, and geological materials.

Grinding is an effective way of eliminating large and/or inconsistent grain sizes to produce homogeneous samples from loose powders. Grinding can minimise scatter affects due to particle size. Additionally, grinding insures that the measurement is more representative of the entire sample, vs. the surface of the sample.

Pressing (hydraulically or manually) compacts more of the sample into the analysis area, and ensures uniform density and better reproducibility.

The powders can also be pressed into pellets, either hydraulically or manually. With pressing, compacts more of the sample into the analysis area and ensures uniform density and better reproducibility.

5.1.2.1.1 Loose Powders

The simplest approach to analyzing a loose powder sample is to simply fill a sample cup approximately ¾ full and analyze it without any additional preparation, or simply tapping the cup on a clean surface to pack it to a more consistent density. This method is satisfactory in same cases where the reproducibility requirements are not very strict. The greatest advantage with this method is that it is easy. Spinning the sample during the measurement may improve the consistency of the measurement by averaging over a larger area.
There are many shortcomings with this technique; the bulk density may not be consistent, grain size variation cause the readings to vary and finer grains can be forced to the surface during tap packing. Because of these problems this method works best with homogenous material that has been dried and ground to a uniform grain size.

5.1.2.1.2 Beads

Fusing powdered samples into beads is now widely seen as an excellent way of overcoming problems of particle size variation as well as surface and mineralogy effects. The powdered sample is mixed with a flux, heated in a crucible to between 900-1300 °C, then cast in a dish to produce a homogeneous glass-like bead.

5.1.2.2 Solid Samples

Among the samples that can be analyzed as solids are metals and plastics, as well as ores, slags and geological materials. Here, the samples are usually in the form of solid discs, drillings, filings, small pieces and shavings.

Some advices concerning solid samples:

1) Orient surface patterns in same manner so as minimise scatter affects.
2) Polishing surfaces will also minimise scatter affects.
3) Flat samples are optimal for quantitative results.

5.1.2.3 Liquid Samples

5.1.2.3.1 General Liquid Sample Preparation

Liquid samples can be the easiest or most difficult samples to work with depending on the composition and stability. A sample cup is filled about ¾ full and then presented to the analyzer. The problems with liquid samples are that they evaporate, stratify, and precipitate. The liquid may attack or be absorbed by the window film, wick up and out of the cup.

Because of these issues liquid samples should be freshly prepared, preferably immediately prior to analysis, although some liquids are stable for a day or more. Solutions should be well mixed prior to pipetting them into a sample cup. The sample should be taken from the center of the container since some components may concentrate on the walls.

Issues associated with use of liquid samples:

1) Evaporation

All liquids have some vapour pressure at standard pressure and temperature. Some low vapor materials such as water or mineral oil may be stable for a day or more, while gasoline and other volatile liquids may only be stable for a few seconds. Highly volatile samples should be prepared and analyzed one at a time and the time from pouring to starting the analysis should be consistent within a few seconds.

A cover or cap may be placed over the cup to reduce evaporation, but the film will bulge causing poor reproducibility. Single end cups and caps for double-ended cups can be punctured with a pin, and some have a snap off device that leaves a hole. Window film covers can also be punctured to relieve pressure. Most cup manufactures also make baffled cups that are designed to minimize evaporation and in theory the sample.

2) Stratification

Liquids stratify when they either contain two or more immiscible liquids like oil and water, or if they contain several molecules that have different density such as a crude oil. Various organo-metalics are also higher in density and tend to settle out over a long period of time. Most liquids need only be well mixed prior to pipetting it into a cup, and they will be stable during analysis. Others will stratify during analysis and must be analyzed quickly.
Immiscible liquids are a special challenge. Sometimes it is possible to produce a meta-stable emulsion. Others times it may be necessary to analyze the two components separately. Lastly solidification techniques can be attempted.

3) Precipitation

As with stratification, liquid samples that precipitate may be well mixed and analyzed one at a time if the particles stay suspended long enough. Normally the supernatant liquid is pipetted off the top and measured separately from the precipitate, which should be dried, weighed, and measured as a powder. Solidification techniques have also been used successfully with rapidly precipitating samples.

4) Wicking

Wicking happens when the liquid is hydrophilic with respect to the window film. The liquid is drawn along the film, out, up, and over the bottom retaining ring. This can also happen even with a hydrophobic liquid because of gravity, when the liquid level is above the height of the bottom retaining ring. One cup vender attacks this problem by having a taller bottom ring, while others use collars that slide up the outside of the cup holding the window film above the sample height. Another technique that works in a pinch is to use tape around the outside of the cup to hold the window film up.

5.1.2.3.2   Alternative Liquid Sample Preparation Methods

Since many liquid samples are inherently unstable there are a number of alternative methods for stabilizing the samples. There are also a number of pre-concentration techniques that are available that have been used with some success.

1) Liquid Sample Solidification

Solidification is one useful method when the sample contains immiscible liquids such as oil and water, or that it precipitates rapidly. Several materials including, cellulose, carbon, gelatin, and alumina, have been used successfully as solidifying agents. Lower atomic number solidification agents are preferred when analyzing low Z elements. The ideal mixing ratio must be determined experimentally.

2) Thin Film Preparations

Another popular method to attempt, is to deposit a sample on a thin sample support and then measure it either wet or after drying. By reducing the sample thickness it is possible to reduce the background while keeping the elemental net intensities high, thus improving the detection limits. Drying the sample helps even more since much of the background due to backscatter is due to the hydrogen and other low atomic elements in the base matrix.

Common support materials include filter paper and IR cards. A few, typically 5-50 microliters of sample can be pipetted onto the support, and allowed to soak in and distribute.

The method has also been done using an atomizer to spray the sample. It can be presented wet provided the moisture content and distribution is consistent from sample to sample or else it can be dried. The primary problem with these techniques is that they are often not reproducible enough for routine laboratory work.

3) Sample Concentration

There are several concentration/thin films techniques that have been used for XRF analysis. The simplest involves filling up a sample cup and drying it. This works best when the matrix is a highly volatile solvent.

If the elements of interest are particulates in suspension then a filter can be used to filter a large volume of fluid. Then the filter can be analyzed wet or dried. One instrument vender uses this method to analyze trace metals such as iron in nuclear reactor coolant.

Another method involves the use of ion exchange filters or resins. A large amount of fluid can be moved through an ion exchange medium removing the ions of interest. The medium can be measured to determine concentrations of the elements of interests. Filters can be analyzed wet or dry. It is important to select an ion exchange medium that does not interfere with the XRF analysis

5.1.2   Sample Cups

There are a wide variety of sample cups available with many features. To best compare them it will be compared each feature, and showed when it is beneficial.

1) Diameter

Cups come in a variety of diameters from 20 mm to 40 mm. For the most part it comes down to individual user preference or the size of the hole provided by the manufacturer but there are some important criteria for selecting the diameter. Ideally the inner cup diameter should be larger than the spot size on the sample.
The penetration depth of the x-rays for the elements of interest is also important.
For characteristic x-rays above 10 keV, penetration depths of more than 1 cm are possible.
With a 20 mm cup the x-rays may hit the cup wall. Larger diameter cups, 40 mm, are recommended for higher atomic number elements in transparent matrices to achieve the best performance. Alternatively the cup position must be tightly controlled.
The third criterion is reproducibility of the film. The larger the diameter the greater the range of film heights at the center and the higher the probability that some cups come out wrinkled. For ease of assembly and best reproducibility 32 mm or smaller cups are often preferred.
A 6.3 mm cup is offered by Spex that is useful when only a limited volume of sample is available.

2) Height

Height selection is also a function of penetration depth. It is important to know the angle of the x-ray source when making this determination. If it is at a 45 degree angle there is generally no benefit to having a cup that is taller than it is wide. If the source points straight upward then a deeper cup is beneficial when analyzing high energy x-rays from a x-ray transparent sample.

3) Single Vs Double Open Ended

The obvious benefit to single open-ended cup is that it saves the step of putting a cover on the cup, and they are usually less expensive. The problem with them is that the amount of air that gets trapped varies causing the window film to bulge different amounts each time. Even after venting the film will remain stretched to a degree. A single open-ended cup will usually have poorer reproducibility. This is exacerbated by the fact the fact that a bubble can form over the pin hole causing the cup to pressurize and the film to bulge enough to affect the results.
In many cases this error is minor relative to the benefits, so they are popular for analyzing high concentration elements in solution.
Double open-ended cups offer many other benefits. They offer a variety of choices for covering the sample. Even if a film cover is used, the pressure is distributed over both films causing less bulging. They are highly recommended for powdered samples since it allows the sample to be manually pressed. They are recommended when the highest degree of precision is required.

4) Collar Vs no Collar

Collars are intended to prevent wicking of the sample along the film and out of the cup. They are recommended for all liquid applications. Tape can be used instead of a collar. The Somar cup design uses a tall bottom retaining ring designed to eliminate the need for a collar and it works provided that the sample level is not above the top of the ring.

5) Cup Covers

There is a lot of variation in cup covers. It is common to use no cover at all for pressed powders, and some brave technicians will not cover solutions or powders.

Window film is a common cover but it is labor intensive to install and causes both the top and bottom films to bulge slightly affecting reproducibility. It is recommended to put a pinhole it to equalize pressure. If the top film gets wet it is possible for a bubble to form across it holding in additional pressure. Cups with and without this bubble will read slightly different in some difficult applications.

A solid snap on cover is easier to install, but it flexes the bottom window as much as the single open ended cup and is prone to having problems with bubbles over the vent hole if it is allow to get wet. The solid covers area few cents more expense than a simple ring.

Solid vented covers are an excellent choice. They are easy to install, do not pressurize the cup and only cost a few cents more than a simple ring and the same as a solid cap. The holes should be large enough that even when wetted, bubbles do not form over the surface.

A variety of baffled cap designs are offered. Each is designed to slow the evaporation process while preventing the cup from becoming pressurized. Some are designed with the intent of causing the sample to reflux. These designs are slightly more expensive than a solid vented cap. Many operators have failed to find any benefit versus a solid vented cap, while others swear by them. They may be worth experimenting with when analyzing highly volatile samples.

6) Inverted Cups

Cups are offered that allow the samples to be inverted. One vender, Somar, designed the cover so that it slightly depresses the Teflon window film covering the sample. The cup is filled to the top and the Teflon film placed over it leaving no air bubbles. The cups can then be inverted for use in instruments with downward facing optics. The problem with this design is that the film height changes from cup to cup, but many instruments with downward facing optics have movable sample stages that can be used to position the sample reproducibly enough for quantitative analysis. Other innovative designs have also been produced for this purpose.

5.2. Analytical Standards

5.2.1 Introduction

Standards are materials containing a known concentration of an analyte. They provide a reference to determine unknown concentrations or to calibrate analytical instruments.

The accuracy of an analytical measurement is how close a result comes to the true value. Determining the accuracy of a measurement usually requires calibration of the analytical method with a known standard. This is often done with standards of several concentrations to make a calibration or working curve.

- Standards (such as certified reference materials) are required for Quantitative Analysis.
- Standard concentrations should be known to a better degree of precision and accuracy than is required for the analysis.
- Standards should be of the same matrix as samples to be analyzed.

5.2.2 Primary Standards

A primary standard is a reagent that is extremely pure, stable, has no waters of hydration, and has a high molecular weight.

5.2.3 Secondary Standards

A secondary standard is a standard that is prepared in the laboratory for a specific analysis. It is usually standardized against a primary standard.

5.3 Chamber Atmosphere

Sample and hardware chambers of the instrument may be filled with air, but because air absorbs low energy x-rays from elements particularly below Ca, Z=20, and Argon sometimes interferes with measurements purges are often used.

The two most common purge methods are:

Vacuum - For use with solids or pressed pellets

Helium - For use with liquids or powdered materials

5.4 Analysis of Samples

5.4.1 Analysis of a Powdered Sample

A powdered sample from the people of the SIS-project was delivered to the department for later analysis. SIS stands for Sick Installation Syndrome and the aim of that project is to determine the cause of problems in central heating systems.

The request was to perform a qualitative analysis to determine which components are present in the sample, followed by a quantitative analysis to know in which amounts the several components are present.

The way the sample was provided did not require any sample preparation.

5.4.1.1 Qualitative Analysis

A first qualitative analysis was run to detect all the elements in the matrix.
Several elements were identified:

Fe, Al, Cu, Mo, Mg, P, Si, Ni, Zn.

⇨ **Overlap spectrum obtained:**
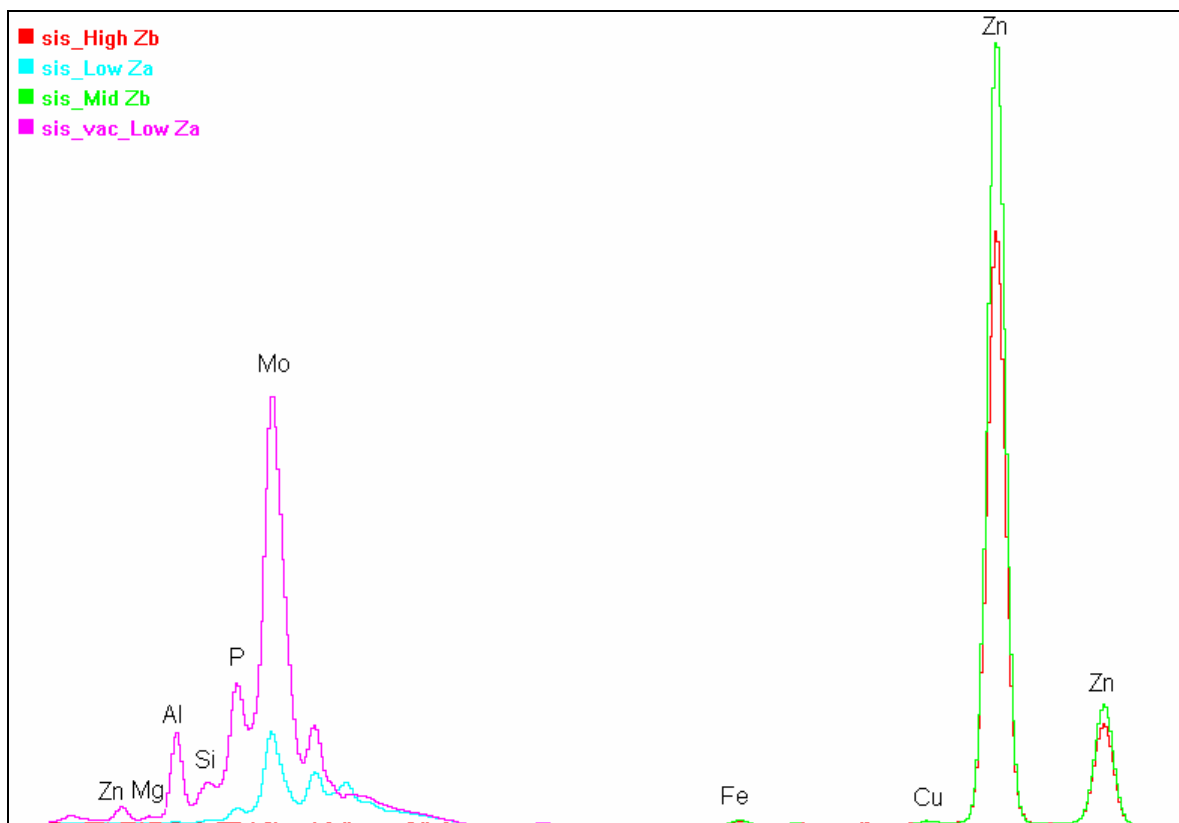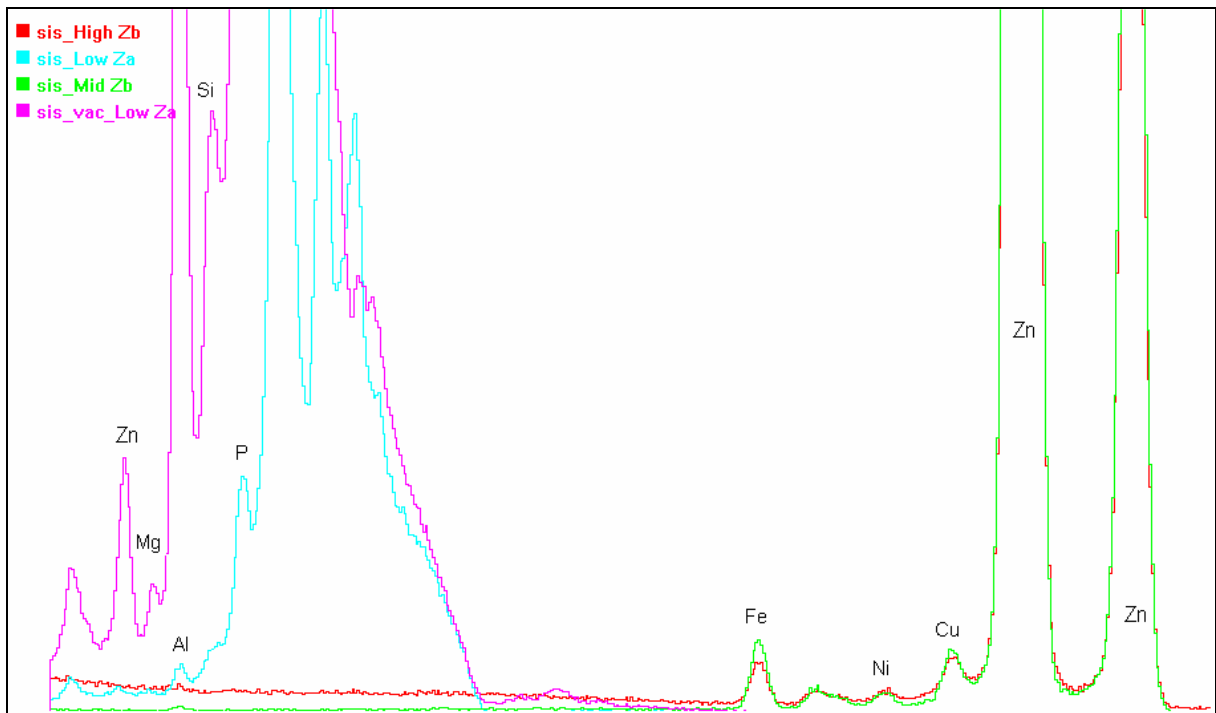
5.4.1.2 Quantitative Analysis

As EDXRF is a reference method, standards are required for quantitative results.

Standards are analysed, intensities obtained, and a calibration plot is generated (intensities vs. concentration).
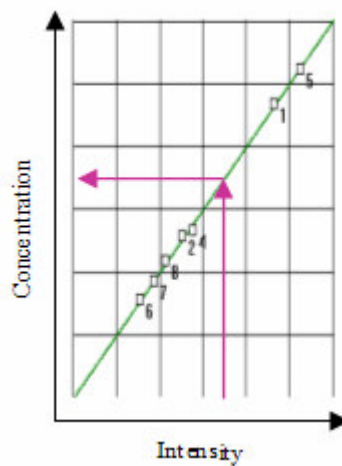
The instrument compares the spectral intensities of unknown samples to those of known standards.

So, the first step was to get the reference lines that are used in the deconvolution of the unknown spectra. The last step consists in the acquisition of some standards or pure elements to get the concentrations of the samples. In some cases, it was necessary to work with helium atmosphere because otherwise elements of low intensities (Al, Mg, Si, P …) would not have been detected by the system.

The software allows the quantification with a very good precision.

The time for an acquisition depends a lot from the limit of detection expected:
50 seconds is a basic time but for few ppm, it might require more seconds.

1) Preparation of Standards

As said before, during the qualitative analysis, 9 elements were identified:
Fe, Al, Cu, Mo, Mg, P, Si, Ni, Zn

To prepare the standards, mixtures of these elements (compounds) were made by considering their atomic number (well separated in the periodic table) because in that way, it is more easy to identify the peaks.

Table 1 represented below, shows the atomic number of each identified element and the corresponding compound that was used for the standards.

Element	Atomic Number	Compounds used for the Standards
Mg	12	MgO
Al	13	Al_2O_3
Si	14	Si
P	15	$(NH_4)_2HPO_4$
Fe	26	Fe
Ni	28	NiO
Cu	29	CuO
Zn	30	ZnO
Mo	42	MoO_3

Table 1

Table 2 below, shows the standards prepared with the molar percentage of each element

Standard 1	Mg 100	Standard 4	Cu 100
	Mg 75 P 25		Cu 75 Mo 25
	Mg 50 P 50		Cu 50 Mo 50
Mg + P	Mg 25 P 75	Cu + Mo	Cu 25 Mo 75
	P 100		Mo 100
Standard 2	Al 100	Standard 5	Zn 100
	Al 75 Fe 25		Zn 75 Si 25
	Al 50 Al 50		Zn 50 Si 50
Al + Fe	Al 25 Fe 75	Zn + Si	Zn 25 Si 75
	Fe 100		Si 100
Standard 3	Si 100		
	Si 75 Ni 25		
	Si 50 Ni 50		
Si + Ni	Si 25 Ni 75		
	Ni 100		

Table 2

Example calculation for standard 1:   Mg + P

Atomic Weight of compounents used:

AW MgO = 40,31 g/mol
AW $(NH_4)_2HPO_4$ = 132 g/mol
Real weight (g) in the cup

Mg 100

100 % Mg $\rightarrow$ 1,0810 g MgO

Mg 75 P 25

75 % MgO + 25 % (NH₄)₂HPO₄
(% molar)

$$0,75 \text{mols MgO} \cdot \frac{40,31 \text{ g MgO}}{1 \text{ mol MgO}} = 30,23 \text{ g MgO} \rightarrow \text{ reduct: } 1/10 = 3,023 \text{ g MgO}$$

$$0,25 \text{mols } (NH_4)_2 HPO_4 \cdot \frac{132 \text{ g } (NH_4)_2 HPO_4}{1 \text{ mol } (NH_4)_2 HPO_4} = 33 \text{ g } (NH_4)_2 HPO_4 \rightarrow$$

$$\rightarrow \text{ reduct: } 1/10 = 3,3 \text{g } (NH_4)_2HPO_4$$

Mg 50 P 50

50 % MgO + 50 % (NH₄)₂HPO₄
(% molar)

$$0,50 \text{ mols MgO} \cdot \frac{40,31 \text{ g MgO}}{1 \text{ mol MgO}} = 20,155 \text{ g MgO} \rightarrow \text{ reduct: } 1/40 = 0,5038 \text{ g MgO} \rightarrow$$

$$\rightarrow 0,5113 \text{ g MgO}$$

$$0,50 \text{mols } (NH_4)_2 HPO_4 \cdot \frac{132 \text{ g } (NH_4)_2 HPO_4}{1 \text{ mol } (NH_4)_2 HPO_4} = 66 \text{ g } (NH_4)_2 HPO_4 \rightarrow$$

$$\rightarrow \text{ reduct: } 1/40 = 1,65 \text{ g } (NH_4)_2HPO_4 \rightarrow 1,6637 \text{ g } (NH_4)_2HPO_4$$

Mg 25 P 75

25 % MgO + 75 % (NH₄)₂HPO₄
(% molar)

$$0,25 \text{ mols MgO} \cdot \frac{40,31 \text{ g MgO}}{1 \text{ mol MgO}} = 10,0775 \text{ g MgO} \rightarrow \text{ reduct: } 1/30 = 0,3359 \text{ g MgO} \rightarrow$$

$$\rightarrow 0,3378 \text{ g MgO}$$

$$0,75 \text{mols } (NH_4)_2 HPO_4 \cdot \frac{132 \text{ g } (NH_4)_2 HPO_4}{1 \text{ mol } (NH_4)_2 HPO_4} = 99 \text{ g } (NH_4)_2 HPO_4 \rightarrow$$

$$\rightarrow \text{ reduct: } 1/30 = 3,3 \text{ g } (NH_4)_2HPO_4 \rightarrow 3,3017 \text{ g } (NH_4)_2HPO_4$$

P 100

100 % (NH$_4$)$_2$HPO$_4$ → 5,82 g (NH$_4$)$_2$HPO$_4$

The rest of the standards were calculated in a similar way.

Once the standards were prepared and the reference lines were acquired, the final step was performing the quantitative analysis for the SIS sample.

Reports obtained:

EDXRF Analysis Report 1

Sample List: 2006/02/16 09:46   **Analyzed:** 02/16/06 09:53:11
Analysis Technique: Intensity Correction   **Last Calibrated:** 02/15/06 17:09:10
                                                      Software version: 4.1 Build 9

Conditions

Mid Za

Voltage	12 kV		Current	Auto
Livetime	50 seconds		Counts Limit	0
Filter	Pd Thin		Atmosphere	Air
Maximum Energy	20 keV		Count Rate	Medium
Warmup time	0 seconds			

Low Za

Voltage	4 kV		Current	Auto
Livetime	50 seconds		Counts Limit	0
Filter	No Filter		Atmosphere	Helium
Maximum Energy	10 keV		Count Rate	Medium
Warmup time	0 seconds			

Results

Element	Concentration	Std. Dev.	Peak (cps/mA)	Background (cps/mA)
SIS				
Fe	0.845 %	0.013	98	5
Al2O3	10.506 %	0.058	662	153

EDXRF Analysis Report 2

52

Sample List: 2006/02/16 10:05
Analysis Technique: Intensity Correction

Analyzed: 02/16/06 10:09:34
Last Calibrated: 02/15/06 15:46:02
Software version: 4.1 Build 9

Conditions

Mid Zb

Voltage	15 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Filter	Pd Medium	Atmosphere	Air
Maximum Energy	20 keV	Count Rate	Medium
Warmup time	0 seconds		

Mid Zc

Voltage	35 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Filter	Pd Thick	Atmosphere	Air
Maximum Energy	40 keV	Count Rate	Medium
Warmup time	0 seconds		

Results

Element	Concentration	Std. Dev.	Peak (cps/mA)	Background (cps/mA)
SIS				
CuO	0.429 %	0.015	49	23
MoO3	0.1499 %	0.0095	1064	851

EDXRF Analysis Report 3

Sample List: 2006/02/16 10:14
Analysis Technique: Intensity Correction

Analyzed: 02/16/06 10:18:00
Last Calibrated: 02/15/06 16:15:15
Software version: 4.1 Build 9

Conditions

Low Za

Voltage	4 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Filter	No Filter	Atmosphere	Helium
Maximum Energy	10 keV	Count Rate	Medium
Warmup time	0 seconds		

Results

Element	Concentration	Peak (cps/mA)	Background (cps/mA)
SIS			
MgO	0.00 %	0	112
(NH4)2 HPO4	4.712 %	890	743

EDXRF Analysis Report 4

Sample List: 2006/02/16 11:23
Analysis Technique: Intensity Correction

Analyzed: 02/16/06 11:31:00
Last Calibrated: 02/16/06 11:22:31
Software version: 4.1 Build 9

Conditions

Low Za

Voltage	4 kV		Current	Auto
Livetime	50 seconds		Counts Limit	0
Filter	No Filter		Atmosphere	Helium
Maximum Energy	10 keV		Count Rate	Medium
Warmup time	0 seconds			

Mid Za

Voltage	14 kV		Current	Auto
Livetime	50 seconds		Counts Limit	0
Filter	Pd Thin		Atmosphere	Air
Maximum Energy	20 keV		Count Rate	Medium
Warmup time	0 seconds			

Results

Element	Concentration	Std. Dev.	Peak (cps/mA)	Background (cps/mA)
SIS				
Si	0.3643 %	0.0090	161	419
NiO	0.1164 %	0.0080	60	39

EDXRF Analysis Report 5

Sample List: 2006/02/16 11:32
Analysis Technique: Intensity Correction

Analyzed: 02/16/06 11:39:17
Last Calibrated: 02/15/06 16:42:45
Software version: 4.1 Build 9

Conditions

Low Za

Voltage	4 kV		Current	Auto
Livetime	50 seconds		Counts Limit	0
Filter	No Filter		Atmosphere	Helium
Maximum Energy	10 keV		Count Rate	Medium
Warmup time	0 seconds			

Mid Zb

Voltage	17 kV		Current	Auto
Livetime	50 seconds		Counts Limit	0
Filter	Pd Medium		Atmosphere	Air
Maximum Energy	20 keV		Count Rate	Medium
Warmup time	0 seconds			

Results

Element	Concentration	Std. Dev.	Peak (cps/mA)	Background (cps/mA)
SIS				
Si	2.200 %	0.052	170	416
ZnO	81.46 %	0.16	32940	-23

5.4.1.3 Conclusion

Table 3 shows a resume of the identified elements and their concentration, which was performed with the Intensity Correction analysis technique.

The concentration result of Mg = 0,000 % is maybe due to some problems during measurements such as errors with the standards or during their preparation, because when performed qualitative analysis of the SIS sample, Mg was actually identified.

Identified elements in the SIS sample	Concentration (%)
Mg	0,000
Ni	0,116
Mo	0,149
Cu	0,429
Fe	0,845
Si	1,282
P	4,712
Al	10,506
Zn	81,460
TOTAL (%)	**99,499**

Table 3

5.4.2 Analysis of a Liquid Sample

The purpose of this experimental part is to determine the lowest concentration of several metals in water which can be detected by ARL QUANT'X using different nitrates dissolved in water.

5.4.2.1 Sample Preparation

Nitrates were chosen because generally they have good solubility to dissolve in water.

⇨ The following table shows the nitrates which were used and its corresponding solubility in cold water:

Compound	Solubility in cold water (g/100 c.c)
$Fe\ (NO_3)_2 \cdot 9\ H_2O$	Soluble
$Zn\ (NO_3)_2 \cdot 6\ H_2O$	184,3
$Cd\ (NO_3)_2 \cdot 4\ H_2O$	215
$Pb\ (NO_3)_2$	37,65

Table 4

⇨ Calculated molarity of each compound according to its solubility in cold water:

Compound: $Fe\ (NO_3)_2 \cdot 9\ H_2O$
Solubility $\approx$ 10,1 g / 10 mL

$$10,1\ g\ Fe\left(NO_3\right)_2 \cdot 9H_2O \cdot \frac{1\ mol}{404\ g} = \frac{0,025\ mols}{10\ mL} \cdot \frac{1000\ mL}{1\ L} = 2,5\ M$$

Compound: $Zn\ (NO_3)_2 \cdot 6\ H_2O$
Solubility $\approx$ 18 g / 10 mL

$$18g\ Zn\left(NO_3\right)_2 \cdot 6H_2O \cdot \frac{1\ mol}{297,47\ g} = \frac{0,0605\ mols}{10\ mL} \cdot \frac{1000\ mL}{1\ L} = 6,05\ M$$

Compound: $Cd(NO_3)_2 \cdot 4\,H_2O$
Solubility ≈ 20 g / 10 mL

$$20g\ Cd\ (NO_3)_2 \cdot 4H_2O \cdot \frac{1\ mol}{308,49\ g} = \frac{0,064\ mols}{10\ mL} \cdot \frac{1000\ mL}{1\ L} = 6,4\ M$$

Compound: $Pb(NO_3)_2$
Solubility ≈ 35 g / 100 mL

$$35g\ Pb\ (NO_3)_2 \cdot \frac{1\ mol}{331,21\ g} = \frac{0,1057\ mols}{100\ mL} \cdot \frac{1000\ mL}{1\ L} = \mathbf{1,057\ M}$$

Among the compounds used, the lowest concentration (**1,057 M**) is considered in order to prepare 50 mL of stock solution well dissolved.

Preparation of 50 mL stock solution 1,057 M

$$50\ mL \cdot \frac{1\ L}{1000\ mL} \cdot \frac{1,057\ mols}{L} \cdot \frac{308,49\ g\ Cd(NO_3)_2 \cdot 4\ H_2O}{1\ mol} = 16,3\ g\ Cd\ (NO_3)_2 \cdot 4\ H_2O \rightarrow$$

$$\rightarrow \text{real weight} = 16,3\ g\ Cd\ (NO_3)_2 \cdot 4\ H_2O$$

$$50\ mL \cdot \frac{1\ L}{1000\ mL} \cdot \frac{35\ g\ Pb(NO_3)_2}{1\ L} = 1,75\ g\ Pb\ (NO_3)_2 \rightarrow \text{real weight} = 1,8\ g\ Pb\ (NO_3)_2$$

$$50\ mL \cdot \frac{1\ L}{1000\ mL} \cdot \frac{1,057\ mols}{L} \cdot \frac{297,47\ g\ Zn(NO_3)_2 \cdot 6\ H_2O}{1\ mol} = 5,721\ g\ Zn\ (NO_3)_2 \cdot 6\ H_2O \rightarrow$$

$$\rightarrow \text{real weight} = 15,7\ g\ Zn\ (NO_3)_2 \cdot 6\ H_2O$$

$$50\ mL \cdot \frac{1\ L}{1000\ mL} \cdot \frac{1,057\ mols}{L} \cdot \frac{404\ g\ Fe(NO_3)_3 \cdot 9\ H_2O}{1\ mol} = 21,35\ g\ Fe\ (NO_3)_3 \cdot 9\ H_2O \rightarrow$$

$$\rightarrow \text{real weight} = 21,3\ g\ Fe\ (NO_3)_3 \cdot 9\ H_2O$$

Stock solution = grams of each nitrate at 1,057 M + H_2O until 50 mL

Dissolutions prepared from Stock Solution 1,057 M

Solution	Preparation	Concentration
"A"	50 mL stock solution 1,057 M + 50 mL H_2O	0,5285 M
"B"	10 mL of solution "A" + 90 mL H_2O	0,05285 M
"C"	10 mL of solution "B" + 90 mL H_2O	$5,285 \times 10^{-3}$ M
"D"	1 mL of solution "B" + 99 mL H_2O	$5,285 \times 10^{-4}$ M
"E"	10 mL of solution "D" + 90 mL H_2O	$5,285 \times 10^{-5}$ M

5.4.2.2 Qualitative Analysis

The analysis were performed with these conditions, according to the Excitation Guide (see appendix) :

Component:	**Fe**		
Condition Name:	Mid Za	Filter Material	Thin Pd
Voltage	20 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Atmosphere	Air	Maximum Energy	20 keV
Count Rate	Medium	Warmup time	0 seconds

Component:	**Zn**		
Condition Name:	Mid Zb	Filter Material	Med Pd
Voltage	20 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Atmosphere	Air	Maximum Energy	20 keV
Count Rate	Medium	Warmup time	0 seconds

Component:	**Pb**		
Condition Name:	Mid Zc	Filter Material	Thik Pd
Voltage	40 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Atmosphere	Air	Maximum Energy	40 keV
Count Rate	Medium	Warmup time	0 seconds

Component:	**Cd**		
Condition Name:	High Za	Filter Material	Thin Cu
Voltage	40 kV	Current	Auto
Livetime	50 seconds	Counts Limit	0
Atmosphere	Air	Maximum Energy	40 keV
Count Rate	Medium	Warmup time	0 seconds

The following table 5 shows the results that were performed with the ARL QUANT'X spectrometer using qualitative analysis technique.

Every solution was analysed with the same conditions for each compound, as mentioned before.

Solution	ppm compound	✓ = detected	X = not detected
"Stock Solution"	59.033,45 ppm Fe 69.106,66 ppm Zn 11.8817,37 ppm Cd 219.010,4 ppm Pb	✓ ✓ ✓ ✓	
"A"	29.516,73 ppm Fe 34.553,33 ppm Zn 59.408,69 ppm Cd 109.505,20 ppm Pb	✓ ✓ ✓ ✓	
"B"	2.951,67 ppm Fe 3.455,33 ppm Zn 5.940,87 ppm Cd 10.950,52 ppm Pb	✓ ✓ ✓ ✓	
"C"	295,11 ppm Fe 345,53 ppm Zn 594,09 ppm Cd 1095,05 ppm Pb	✓ ✓ ✓ ✓	
"D"	29,52 ppm Fe 34,55 ppm Zn 59,41 ppm Cd 109,51 ppm Pb	✓ ✓ 	 X X
"E"	2,95 ppm Fe 3,45 ppm Zn 5,94 ppm Cd 10,95 ppm Pb		X X X X

Table 5

Shows the concentration (ppm) of each element in different dissolutions:

✓ = detected → you can see a peak when performing qualitative analysis
X = not detected → you cannot see a peak when performing qualitative analysis

⇨ **Calculation example of ppm compound in "Stock Solution":**

$$1,057 \ \frac{mols \ Stock \ Solution}{L} \cdot \frac{55,85 \ g \ Fe}{1 \ mol \ Fe} \cdot \frac{1000 \ mg}{1 \ g} = 50933,45 \ ppm \ Fe$$

$$1,057 \ \frac{mols \ Stock \ Solution}{L} \cdot \frac{65,38 \ g \ Zn}{1 \ mol \ Zn} \cdot \frac{1000 \ mg}{1 \ g} = 69106,66 \ ppm \ Zn$$

$$1,057 \ \frac{mols \ Stock \ Solution}{L} \cdot \frac{112,41 \ g \ Cd}{1 \ mol \ Cd} \cdot \frac{1000 \ mg}{1 \ g} = 11817,37 \ ppm \ Cd$$

$$1,057 \ \frac{mols \ Stock \ Solution}{L} \cdot \frac{207,2 \ g \ Pb}{1 \ mol \ Pb} \cdot \frac{1000 \ mg}{1 \ g} = 219010,4 \ ppm \ Pb$$

The rest of the solutions appearing in table 5, were calculated in the same way.

⇨ **Resulting spectra with all the compounds detected: solution "C"**
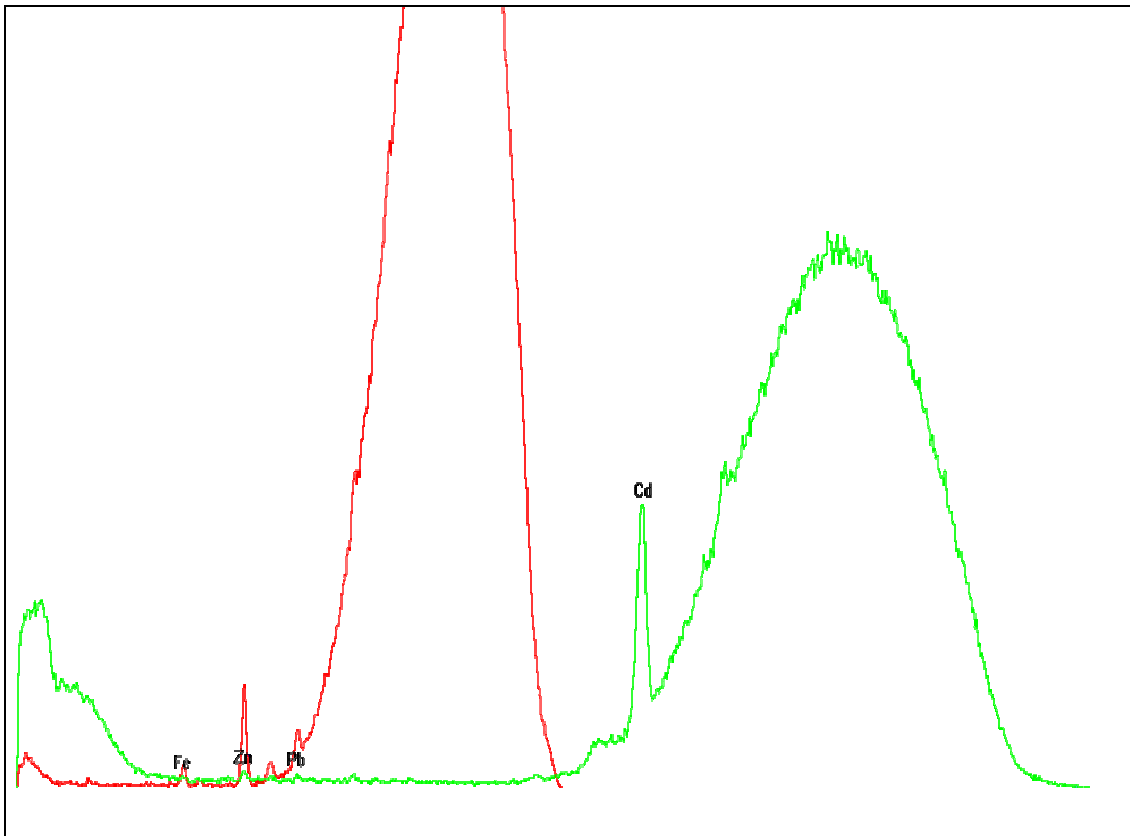
⇨ **Resulting spectra of no-detected compounds: solution "E"**
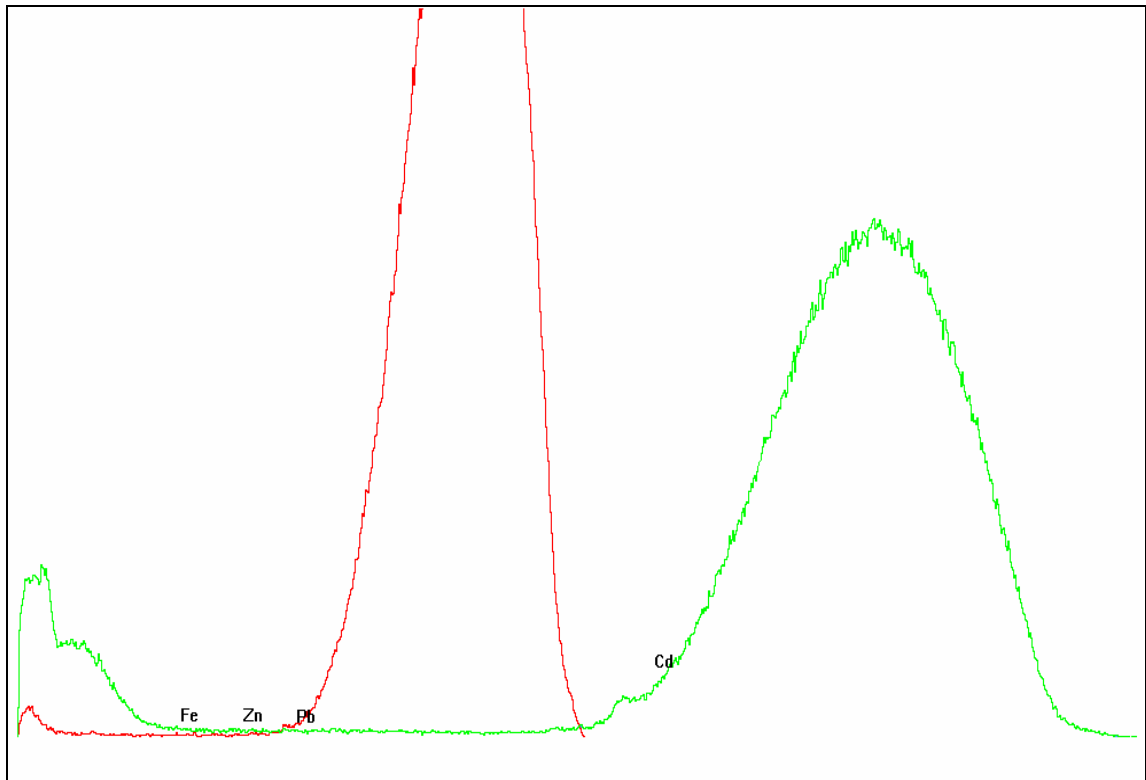
5.4.2.3 Conclusion

In solution "A", "B" and "C" we can clearly see the peaks of each compound. Contrasting with the solution "E" where you cannot see any peak.

Regarding the qualitative results and spectras obtained, one can say that when concentration is approximately higher than 100 ppm, peaks appears clearly.
As you can see in solution "D" and "E", the range approximately between 10 – 100 ppm is the critical zone, which means that within this rang there is the limit of detection.

Generally, when concentration is lower than 10 ppm you cannot see any peaks appearing.

5.4.3   Analysis with Oil Samples

5.4.3.1 Qualitative Analysis

A first qualitative analysis was performed in order to detect all the elements present in a sunflower oil sample.

- **Conditions used :**

Condition name	Low Za
Filter	No filter
Voltage	4 kV
Atmosphere	Air
Analyzed element	P
Count Rate	Medium
Live Time	100 sec

The spectrum obtained from the sunflower oil with the conditions mentioned above, was not so good (peaks did not appear), because it was not possible to perform the qualitative analysis with the optimal conditions for the analyzed element: phosphorus (element of low intensity) and also because this sunflower oil, in theory contained a very little amount of phosphorus. The results would have been much better if we were able to work with a helium atmosphere.

⇨ **Spectrum obtained of the sunflower oil :**
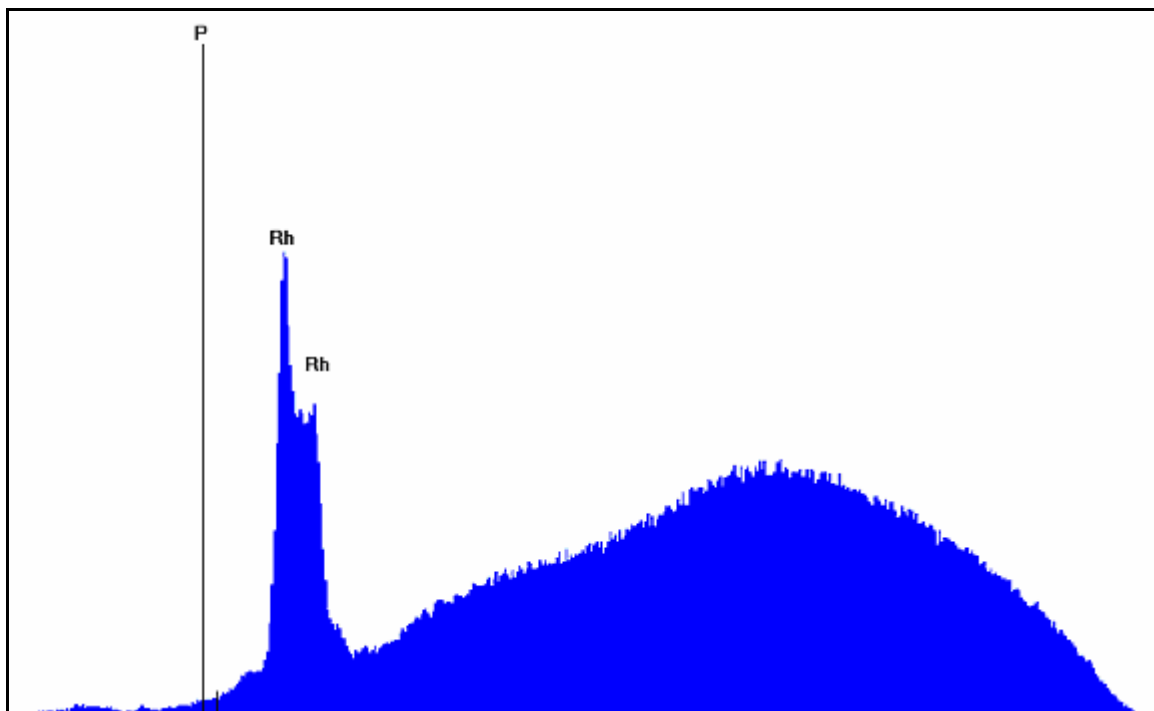
A second qualitative analysis was also performed to measure the bolecht sample (lecithin).
The set conditions were the same as the ones mentioned before, but the results obtained were a little bit better than the sunflower oil, because the bolecht sample analysed had a higher concentration of P.
Just like the sunflower oil, the analysis result of the bolecht sample would have been better if had been possible to work under helium atmosphere.

⇨ **Spectrum obtained of the bolecht sample (lecithin) :**
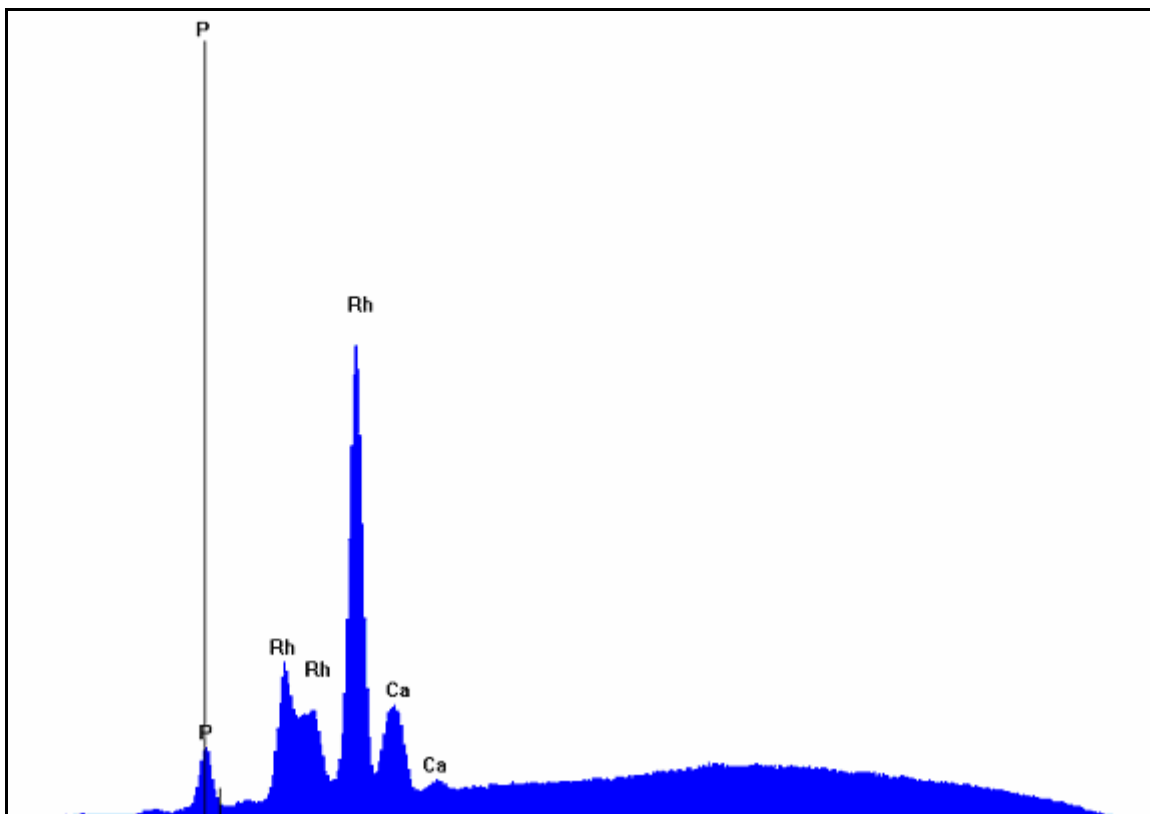
Another part of this analysis was to determine the detection limit for P by adding bolecht to sunflower oil, starting with the addition of 0,46 % (w/w) bolecht (lecithin) to sunflower oil.

- Theoretic measurement: 0,46 % (w/w) lecithin → 0,46 g lecithin + 99,54 g sunflower oil
  Real measurement: 0,45 % (w/w) lecithin → 0,4628 g lecithin + 102,074 g sunflower oil

  Detection of P → spectra obtained with no P peak
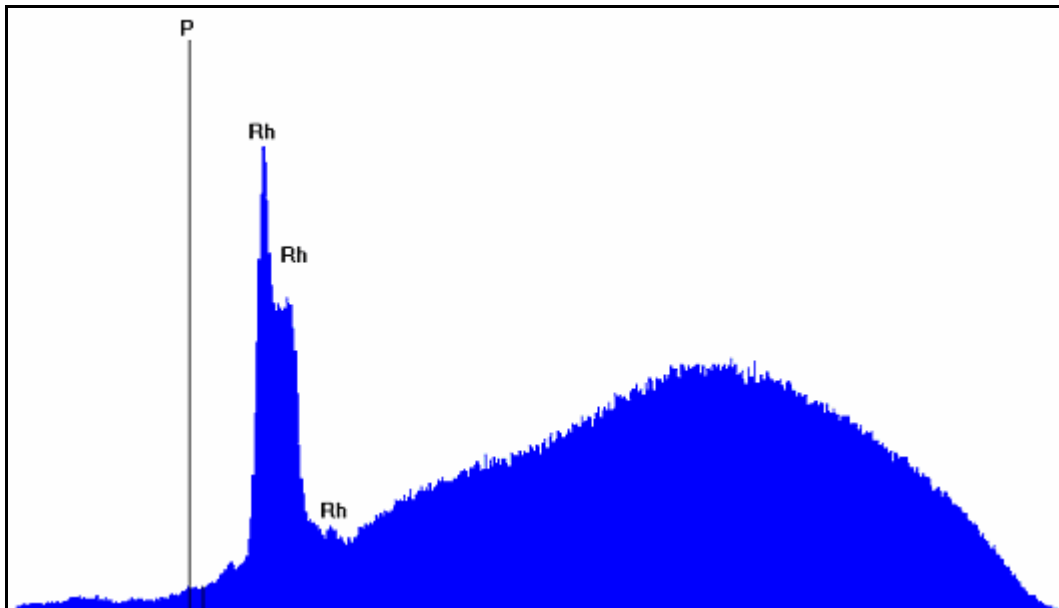
- Theoretic measurement: 1,00 % (w/w) lecithin → 1 g lecithin + 99 g sunflower oil
  Real measurement: 1,18 % (w/w) lecithin → 1,1853 g lecithin + 98,8614 g sunflower oil

  Detection of P → spectra obtained with an apparently very small P peak
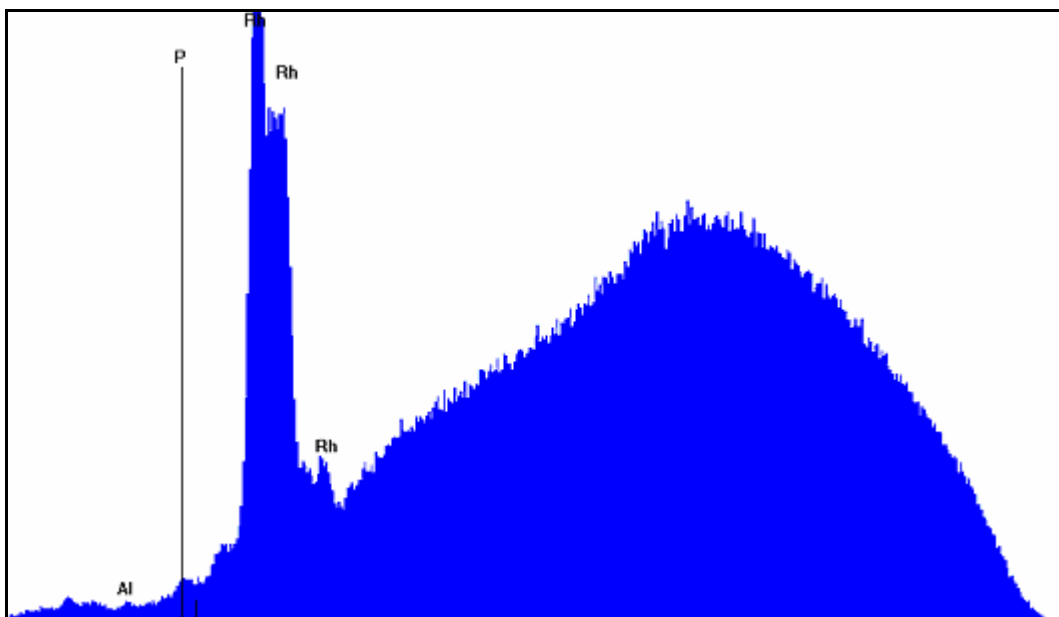
- Theoretic measurement: 2,00 % (w/w) lecithin → 2 g lecithin + 98 g sunflower oil
  Real measurement: 2,394 % (w/w) lecithin → 2,395 g lecithin + 97,613 g sunflower oil

  Detection of P → spectra obtained with a clearly P peak
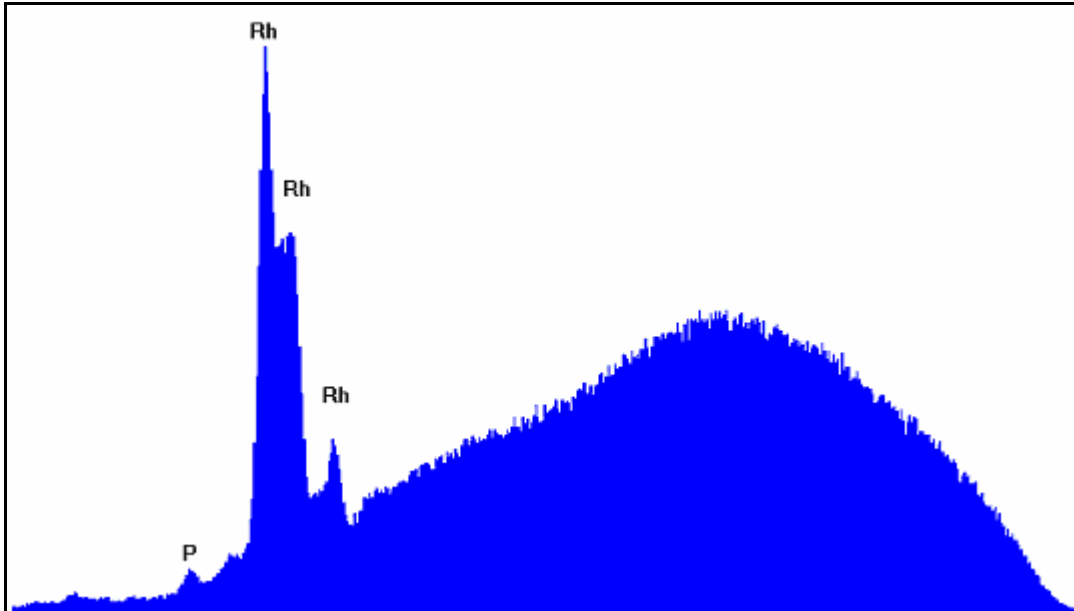
- Theoretic measurement: 5,00 % (w/w) lecithin → 5 g lecithin + 95 g sunflower oil
  Real measurement: 4,95 % (w/w) lecithin → 5,2 g lecithin + 99,86 g sunflower oil

  Detection of P → spectra obtained with a very clear P peak
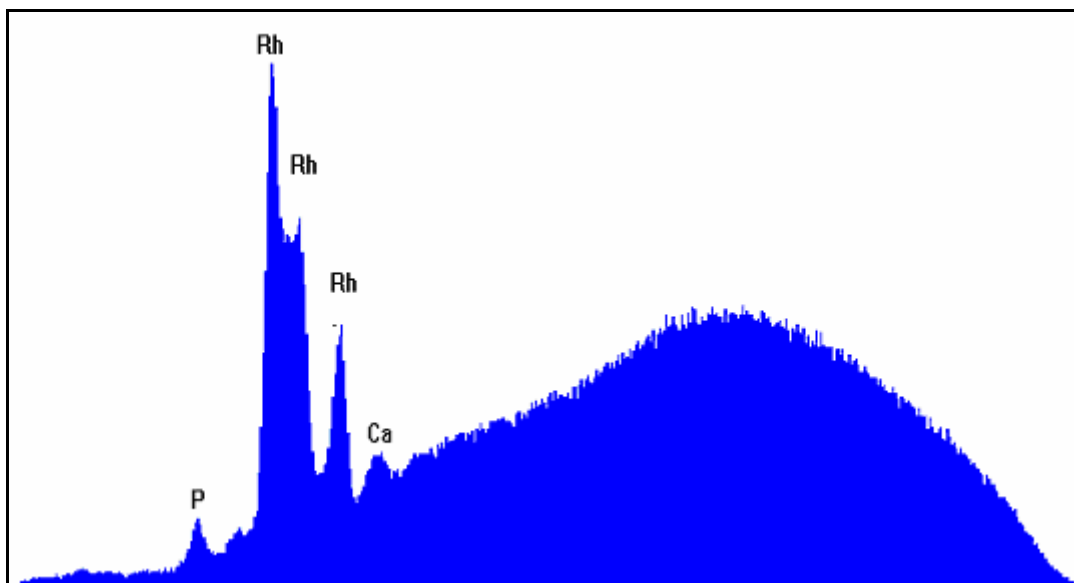
5.4.3.2 Quantitative Analysis

The last part of this analysis was to set up a calibration line for P in oil and measure a palm oil sample in order to determine quantitatively how much P is present in this palm oil sample.

The table 6 represented below, shows the standards that should have been used to perform the calibration line, but unfortunately and because of some technical problems of the QUANT'X ARL, it was not possible to make a calibration line, and consequently the quantitative analysis of the palm oil sample could not be finished.

Standard	Total (%)	H	C	N	O	P
Units		% ▼	% ▼	% ▼	% ▼	ppm ▼
Zero Intercept						☑
Results Condition						Low Za
Include		☑	☑	☑	☑	
Reference						
A	100.000	11.23	77.85	0.0002817	10.92	6.23
B	100.000	11.23	77.85	0.0001073	10.92	2.373
C	100.000	11.23	77.84	0.001177	10.92	26.03
D	100.000	11.23	77.85	0.0005694	10.92	12.59
lecitin	100.000	11.22	77.71	0.02378	10.99	525.8
sunflower oil	100.000	11.23	77.85	0	10.92	0

Calibration Standards

Table 6

5.4.3.3 Conclusion

As showed in the results obtained, in concentrations lower than 1 % (w/w) of bolecht (lecithin) is hardly impossible to detect phosphorus.
In contrast, when concentrations are higher than 2 % (w/w) of bolecht, phosphorus is detected clearly.
As is said before, all of these results would have been much better if the analysis could have been performed under conditions of helium atmosphere which was not possible for some technical problems with the QUANT'X ARL apparatus.

6.   General Conclusion

Looking at the experiments performed, unknown elements from the SIS sample (powder) were well identified using the qualitative technique, afterwards the concentration of each identified compound was analysed using the quantitative technique, and their concentration was obtained quite accurately since the total concentration was nearly equal to 100%.

Concerning the experiment using different nitrates of heavy metals dissolved in water, with the purpose of determining the lowest concentration possible detected by the ARL QUANT'X, I can say that when the concentration is approximately higher than 100 ppm, one can identify elements with no problem.
In contrast, when the concentration is lower than 10 ppm, it is impossible to identify elements because then spectrum-peaks do not appear.
The critical zone is in the region of 10-100 ppm, where the detection limit is found.

In relation to the last analysis performed with oil samples, it can be said that the detection of phosphorus is hardly impossible when the concentration of bolecht (lecithin) is lower than 10 ppm. On the other hand, when concentrations are higher than 15 ppm of bolecht, phosphorus is detected clearly.

As a general conclusion, I can say that EDXRF is an easy, efficient and suitable technique to analyse both powder and liquid samples.

7. References

- Principles and practice of X-ray spectrometric analysis / Bertin, Eugene P. - New York, 1970
- An introduction to X-ray spectrometry / Jenkins, Ron. - London, 1976
- Energy dispersive X-ray spectrometry / Heinrich, Kurt F.J. - Washington, D.C., 1981
- Energy dispersive X-ray fluorescence analysis / Dziunikowski, Bohdan. - Amsterdam, 1989
- X-ray fluorescence spectrometry / Jenkins, Ron. - New York, 1999

- www.answers.com
- www.amptek.com
- www.britannica.com
- www.csep10.phys.utk.edu
- www.eng.uc.edu
- www.en.wikipedia.org
- www.fate.clu-in.org
- www.hyperphysics.phy-astr.gsu.edu/Hbase/
- www.imagine.gsfc.nasa.gov
- www.isotopes.lbl.gov
- www.iupac.org
- www.learnxrf.com
- www.omniinstruments.com
- www.plus2physics.com
- www.rigakumsc.com
- www.scienceofspectroscopy.info
- www.spectroscopynow.com
- www.thermo.com
- www.wcaslab.com
- www.xrfcorp.com

8.   Appendix: Excitation Guide