Sudan University of Science and Technology

College of Graduate Studies

The Effect of Temperature on Determining the Traces elements of River and Purified Water using X-Ray Fluorescence Techniques

أثر تغير درجة الحرارة على تحديد العناصر المكونة لمياه النهر والمياه النقية بإستخدام تقنية فلورة الأشعة السينية

A thesis Submitted in Partial Fulfillment for the Requirement of a Master Degree (M. Sc) in solid state Physics

By

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الاية

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قَال تعالى : ﴿ قَالَ الَّذِي عِنْدَهُ عِلْمٌ مِنَ الْكِتَابِ أَنَا آتِيكَ بِهِ قَبْلَ أَنْ يَرْتَدَّ إِلَيْكَ طَرْفُكَ فَلَمَّا رَآهُ مُسْتَقِرًّا عِنْدَهُ قَالَ هَذَا مِنْ فَضْلِ رَبِّي لِيَبْلُوَنِي أَأَشْكُرُ أَمْ أَكْفُرُ وَمَنْ شَكَرَ فَإِنَّمَا يَشْكُرُ لِنَفْسِهِ وَمَنْ كَفَرَ فَإِنَّ رَبِّي غَنِيٌّ كَرِيمٌ ﴾

صدق الله العظيم

Dedication

To my dearest mother who always supported and encouraged me

To my brother Al Makki "even after this so long time, the sun never says to the earth that you owe me"

Acknowledgement

I thank Allah who made all these possible.

I would like to thank **Dr. Ali sulaiman Mohamed** for his continuous helpful support and supervision of this dissertation. His willingness to give his time so generously has been very much appreciated.

I also wish to thank my beloved family who gave life it is real meaning and covered me with the support.

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Abstract

The X-ray fluorescence technique is used to determine different types of materials in its different states solid, liquid, powder, gas and other form.

It was used to determine most kinds of material in the method it is fast, accurate and nondestructive and usually requires only a minimum of sample preparation.

The precision and reproducibility of XRF analysis is very high, very accurate, results are possible when good standard specimens are available.

In this thesis one of most important application of X-ray Fluorescence techniques (XRF) with the helium system for liquid analysis was used to determine traces elements which exist as composition of any samples of water. Due to importance of water for life two different sources of water were presented to determine the trace elements which dissolved on each sample with varying the temperature (8^0C , 32^0C and 90^0C) the river water and purified water. The applied procedure allows determination of various elements in broad concentration range of analyzed elements as function of temperature variation. The techniques reveals accurate results as a function of temperature it was found that some elements disappear under certain temperature while some element appear.

المستخلص

تُستخدم تقنية فلورة الأشعة السينية لتحديد أنواع مختلفة من المواد في حالاتها المختلفة الصلبة والسائلة والمسحوق والغاز وأشكال أخرى.

تم استخدامه لتحديد معظم أنواع المواد بطريقة سريعة ودقيقة وغير مدمرة وعادة ما تتطلب فقط الحد الأدنى من إعداد العينة.

دقة واستنساخ تحليل XRF عالية جدًا ودقيقة للغاية ، وتكون النتائج ممكنة عندما تتوفر عينات قياسية جيدة.

في هذه الأطروحة ، تم استخدام أحد أهم تطبيقات تقنيات فلورةالأشعة السينية (XRF) نظام الهليوم لتحليل السائل لتحديد العناصر الأثرية الموجودة كتكوين لأي عينات من الماء.

نظرًا لأهمية الماء للحياة تم تقديم مصدرين مختلفين للمياه لتحديد العناصر النزرة التي تذوب في كل عينة بدرجات حرارة متفاوتة 80) درجة مئوية ، 320 درجة مئوية ، 900 درجة مئوية (مياه النهر والمياه النقية. يسمح الإجراء المطبق بتحديد العناصر المختلفة في نطاق تركيز واسع للعناصر التي تم تحليلها كدالة لتغير درجة الحرارة.

تكشف التقنيات عن نتائج دقيقة كدالة لدرجة الحرارة فقد وجد أن بعض العناصر تختفي تحت درجة حرارة معينة بينما يظهر بعض العناصر.

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Abbreviations

(XRF)	X-rayFluorescence
(EDXRF)	energy dispersive systems
(WDXRF)	wavelength dispersive systems (WDXRF)

Introduction

1.1 Background

Water is a fundamental human need. Each person on earth requires at least 20 to 50 liters of clean safe water a day for drinking, cooking, and simply keeping themselves clean. Water pollution

XRF is used to determine different types of materials in its different states solid, liquid, powder, gas and other form. Water pollution is a global issue and world community is facing worst results of polluted water. Major sources of water pollution are discharge of domestic and agriculture wastes, population growth, excessive use of pesticides and fertilizers and urbanization. Bacterial, viral and parasitic diseases are spreading through polluted water and affecting human health. It is recommended that there should be proper waste disposal system and waste should be treated before entering in to river. Educational and awareness programs should be organized to control the pollution. Mortality rate due to cancer is higher in rural areas than urban areas because urban inhabitants use treated water for drinking while

Water is a fundamental human need. Each person on Earth requires at least 20 to 50 liters of clean, safe water a day for drinking, cooking, and simply keeping themselves clean. Water pollution happens when undesirable materials enter in to water, variations the excellence of water [1] and injurious to environment and human strength [2]. Water is a significant natural supply used for drinking and other evolving purposes in our lives [3]. Safe drinking water is compulsory for human health all terminated the world. Animation a universal solvent, water is a major basis of pollution. According to world health organization (WHO) 80% ailments are water borne. Ingestion water in various countries organizes not meet WHO principles [4]. 3.1% deaths occur due to the unsanitary and deprived quality of water [5].Assessing water quality enables the natural characteristics of the water to be documented and the extent of the pollution to be determined; however, today monitoring is a more holistic process relating to health and other socio-economic issues. Ensuring poor people's access to safe drinking-water and adequate sanitation and encouraging personal, domestic and

community hygiene will improve the quality of life of millions of individuals. An important share of the total burden of disease worldwide—around 10%—could be prevented by improvements related to drinking-water, sanitation, and hygiene and water resource management. Water is a life giver - even a life creator. It lies at the basis of our understanding of how life works. It also lies at the basis of how we understand our own personal lives. Of the four (or five) basic building blocks of life, water is the only one with a visible cycle, which we call the hydrologic cycle. Fire has no cycle that we can see, neither do earth nor air. And we don't understand spirit enough to know if it does or not. Water is a constant reminder that life repeats. Waste from the industries like, sugar, textile, electroplating, pesticides, pulp and paper are polluting the water [9]. Many waterborne infectious diseases are linked with fecal pollution of water sources and results in fecal-oral route of infection [11].

Water has been used since antiquity as a symbol by which to express devotion and purity. Some cultures, like the ancient Greeks, went as far as to worship gods who were thought to live in and command the waters. Whole cities have been built by considering the location and availability of pure drinking water. The place of gathering was around the wells, which is perhaps the following trend in building fountains in the middle of piazzas.

Traditional and modern medicine has been makings use of the psychological and physiological diverse properties of water, in all forms of hydrotherapy (composite Greek word: hydro, of water and therapy. We all know of the simple, yet effective, calming qualities of a warm bath or the invigorating qualities of a cold shower. For centuries, numerous healing springs located all around the world have been recognized for their benefits.

Science clearly states that a human being can survive three weeks without food, but where water is concerned most people can't go on 3-4 days without it! Dehydration sets in, and even if the person continues to breathe, they will go into shock and become vegetative. In other words, water is the primary

necessity. Without it, a living being simply cannot survive. Yet, it is a horrific fact that there are billions of people around the world who do not have access to clean drinking water. Water is an Water is an important natural resource used for drinking and other developmental purposes in our lives [6]. Water pollution occurs when unwanted materials enter in to water, changes the quality of water [7] and harmful to environment and human health [8].10% of the population depends on food and vegetables that are grown in contaminated water [10].Our drinking water today, far from being pure, contains some two hundred deadly commercial chemicals. Add to that bacteria, viruses, inorganic minerals (making the water hard) and you have a chemical cocktail that is unsuitable (if not deadly) for human consumption. John Archer in his book 'the water youdrink, how safe is it?' refers to an estimate of 60,000 tonesof fifty different chemicals being deliberately added annually to Australia's water. Some of fifty different chemicals being deliberately added annually to Australia's water. Some of these are chlorine: studies1 indicate that chlorine is involved in heart disease, hardening of the arteries (arteriosclerosis), anemia, high blood pressure, allergies and cancers2 of the bladder, stomach, liver and rectum. Further, chlorine can destroy protein in the body and cause adverse effects on the skin and hair. The US council of environmental quality states thatcancer risk among people drinking chlorinated water is 93% higher than among those whose water does not contain chlorine". Chlorine binds and reacts with many other chemicals, forming carcinogens like Trihallomethanes3 (THMs), with chloroform being the most common one. Furthermore, recent real life evidence in the tap water of Sydney shows that certain viruses and parasites, like giardia and cryptosporidium, are being resistant to chlorine and can survive the long journey from the sewage treatment to your tap. That y from the sewage treatment to your tap. That makes chlorination aneven more pointless and dangerous practice.

risk of disease due to improper sanitation, hygiene and water supply [12].In contaminated water, a large number of bacteria are also found which is harmful for human health [13].Contaminated water has large negative effects in those women who are exposed to chemicals during pregnancy; it leads to the increased rate of low birth weight as a result fetal health is affected [14].

These are some of the most basic requirements for human health, and all countries have a responsibility to ensure that everyone can access them.

Sadly, clean water is still inaccessible for many and will remain that way until governments are willing to take a stand. Here are five reasons why everyone needs access to clean drinking water and safely managed sanitation, right at home.

Water is life. The sooner those in power understand this, the sooner this law of water being available to everyone can be implemented. Water is the number one source of nutrition. The human body is made of 60% water, and this is a clear enough indication of the importance of water. Humans need to be adequately hydrated for their physiological systems to function

Fatal medical conditions like cholera, typhoid, and hepatitis A all occur because of the consumption and or the presence of contaminated water. Clean water is essential not only to remain safe from disease but also to maintain good health.

Clean, fresh and safe drinking water also helps in getting the body rid of all kinds of toxins, whether they are created due to bodily reactions, obtained from outside sources or ones that occur because of the consumption of contaminated water.

When it comes to the production of food, clean water is an essential ingredient. If the crops and grains are given contaminated water, the bacteria and disease will spread to those who consume the fresh produce. Therefore, water that is used for agriculture must also come from safe and clean resources.

1. 2 The problem statement

Clean water is not just needed for drinking but for sanitation purposes as well. If clothes are washed, or the body is washed with contaminated water, this too will result in the rise of diseases. Same is the case for cooking, cleaning and other similar tasks that are an integral part of our lives. Clean water is necessary for good health.

1.3 General Objective

- To give some basic information about Energy Dispersive X-ray Fluorescence.

1.4 Specific Objective

- 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 .

1.5 The Methodology

Uses of XRF techniques to determine trace element on selected samples of water

1.6 previous studies

1.6.1 B. Kot, R. Baranowski, A. Rybak(Analysis of Mine Waters Using X-ray

Fluorescence Spectrometry)

They conclude that In this paper investigations on the application of XRF method with the helium system for liquid analysis and for the determination of the composition of saline mine water have been presented.   The   applied procedure allows determination of various elements in broad concentration range   of   analyzed   elements (g/dm3- mg/dm3).[16]

  1.6.2Samuel Akoto Bamford,Darius Wegrzynek,Ernesto Chinea-Cano,Andrzej Markowicz**.** Application of X-ray fluorescence techniques for the determination of hazardous and essential trace elements in environmental and biological materials .

They conclude that The utilization of X-ray fluorescence technique for the determination of trace element concentrations in environmental and biological samples is presented. The analytical methods used include energy dispersive X-ray fluorescence with polarizing secondary targets, total reflection X-ray fluorescence, direct *in-situ* X-ray fluorescence, and micro-beam X-ray fluorescence spectrometry. These methods were applied to analysis of different samples including soil, water, plant material and airborne particulate matter collected on polycarbonate filters. The performance and achieved detection limits of elements for different techniques, established by measuring appropriate reference standards, are presented. Also described is the utilization of microbeam X-ray fluorescence technique for studying element distribution in heterogeneous samples and investigating the 2D- and 3D-morphology of minute samples by means of computerized X-ray absorption and X-ray fluorescence tomography. The different X-ray techniques have their unique advantages. The micro-beam X-ray fluorescence set-up has an advantage of producing very well collimated primary X-ray beam (about 15 µm in diameter), in front of which the analyzed sample can be precisely positioned, providing local information about the sample composition. The energy dispersive X-ray fluorescence with secondary targets offers rapid analysis of broad range of elements (Na–U) combined with a simple sample preparation method. Total reflection X-ray fluorescence technique, characterized by the lowest detection limits of elements, has its leading edge in analysis of liquid samples, and dealing with particle size effects in air particulates collected on filter papers. *In-situ* X-ray fluorescence spectrometers are truly portable and enable on the spot, in field analysis. It is shown that the combination of several XRF methods allows for a better characterization of a variety of materials, e.g. solids, liquids, and minute heterogeneous samples.[17]

1.7 The thesis layout

This thesis is constructed as the follow: in chapter one we give a concise introduction. The pervious study of reaction of X-ray with matter is reviewed in chapter two. Chapter three Principle of XRF Techniques. Material and method, discussion, conclusion and recommendation are presented in chapter four.

Principles of X-rays

2.1 Introduction

X-rays can be seen as electromagnetic waves with their associated wavelengths, or as beams of photons with associated energies. Both views are correct, but one or the other is easier to understand depending on the phenomena to be explained.

Other electromagnetic waves include light, radio waves and y-rays. Figure (2.1) shows that X-rays have wavelengths and energies between y-rays and ultra violet light.

The wavelengths of X-rays are in the range from 0.01 to 10 nm, which corresponds to energies in the range from 0.125 to 125 keV. The wavelength of X-rays is inversely proportional to its energy, according to E*λ=hc. E is the energy in keV and λ the wavelength in nm. The term hc is the product of Planck's constant and the velocity of light and has, using keV and nm as units, a constant value of 1.23985.
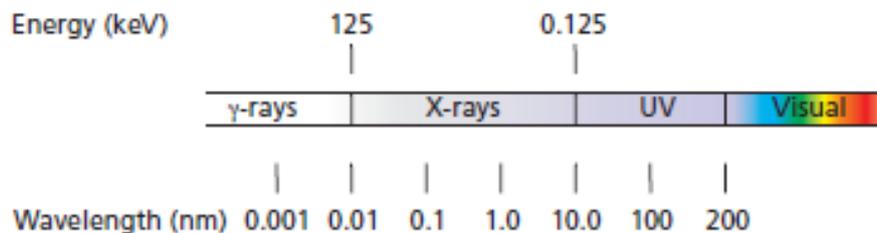
Figure (2.1) X-rays and other electromagnetic radiation

2.2 Interaction of X-rays with matter

There are three main interactions when X-rays contact matter: Fluorescence, Compton scatter and Rayleigh scatter (see figure 2.2). If a beam of X-ray photons is directed towards a slab of material a fraction will be transmitted through, a fraction is absorbed (producing fluorescent radiation) and a fraction is scattered back. Scattering can occur with a loss of energy and without a loss of energy. The first is known as Compton scatter and the second Rayleigh scatter. The fluorescence and the scatter depend on the thickness (d), density (p) and composition of the material, and on the energy of the X-rays. The next sections will describe the production of fluorescent radiation and scatter.
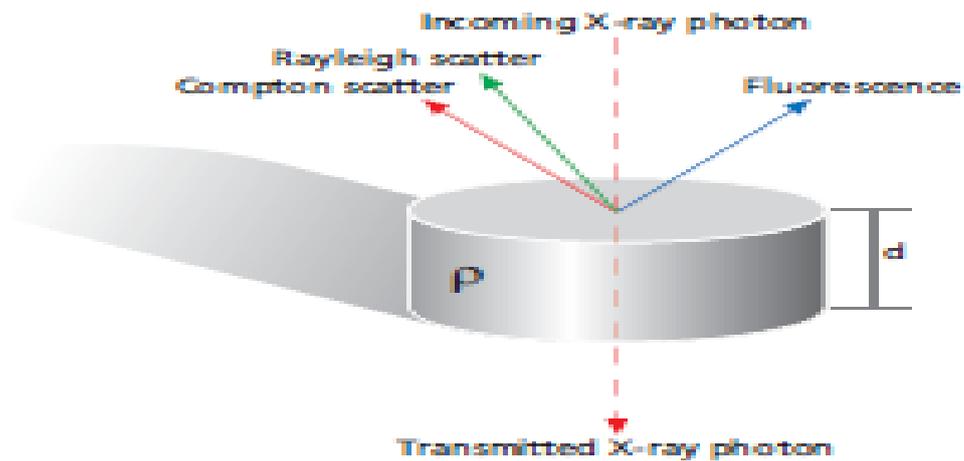
Figure (2.2) three main interactions of X-rays with matter

2.3 Production of characteristic fluorescent radiation

The classical model of an atom is a nucleus with positively charged protons and non-charged neutrons, surrounded by electrons grouped in shells or orbitals. The innermost shell is called the K-shell, followed by L-shells, M-shells etc. as one moves outwards. The L-shell has 3 sub-shells called L_I, L_{II} and L_{III}. The M-shell 8 and the M-shell 18. The energy of an electron depends on the shell it occupies, and on the element to which it belongs. When irradiating an atom, particles such as X-ray photons and electrons with sufficient energy can expel an electron from the atom (figure 2.3).
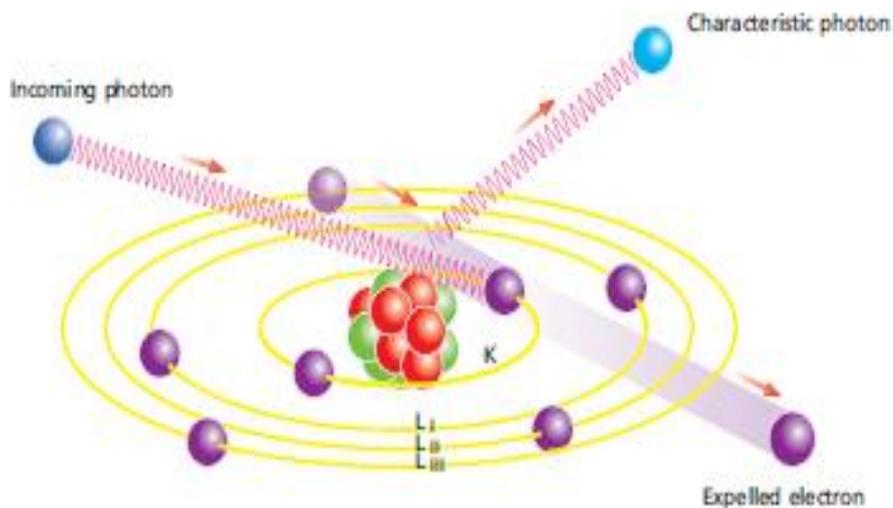
Figure (2.3) Production of characteristic radiation

This produces a 'hole' in a shell, in the example (figure 2.3) a hole in the K-shell, putting the atom in an unstable excited state with a higher energy. The 'hole' in the shell is also called the initial vacancy. The atom wants to restore the original configuration, and this is done by transferring an electron from an outer shell such as the L-shell to the hole in the K-shell. An L-shell electron has a higher energy than a K-shell electron, and when an L-shell electron is transferred to the K-shell, the energy surplus can be emitted as an X-ray photon. In a spectrum, this is seen as a line.

The energy of the emitted X-rays depends on the difference in energy between the shell with the initial hole and the energy of the electron that fills the hole (in the example, the difference between the energy of the K and the L shell). Each atom has its specific energy levels, so the emitted radiation is characteristic of that atom.

An atom emits more than a single energy (or line) because different holes can be produced and different electrons can fill these. The collection of emitted lines is characteristic of the element and can be considered a fingerprint of the element.

To expel an electron from an atom, the X-rays must have a higher energy level than the binding energy of the electron. If an electron is expelled, the incoming radiation is absorbed, and the higher the absorption the higher the fluorescence.

If, on the other hand, the energy is too high, many photons will 'pass' the atom and only a few electrons will be removed. Figure (2.4) shows that high energies are hardly absorbed and produce low fluorescence. If the energy of the incident photons is lower and comes closer to the binding energy of the K-shell electrons, more and more of the radiation is absorbed. The highest yield is reached when the energy of the photon is just above the binding energy of the electron to be expelled. If the energy becomes lower than the binding energy, a jump or edge can be seen: the energy is too low to expel electrons from the corresponding shell, but is too high to expel electrons from the lower energetic shells. The figures show the K-edge corresponding to the K-shell, and three L-edge corresponding with the L_I-L_{II}-and L_{III}-shells.
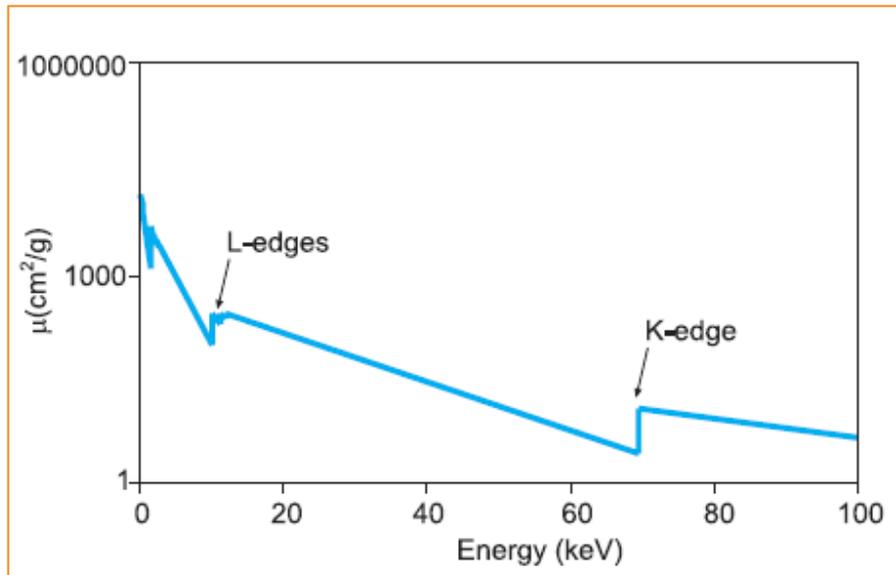
Figure (2.4) shows absorption versus energy

Not all initial vacancies created by the incoming radiation produce fluorescent photons. Emission of an Auger electron is another process that can take place. The fluorescent yield is the ratio of the emitted fluorescent photons and the number of initial vacancies. Figure (2.5) shows the fluorescence yield for K- and L-lines as function of the atomic number Z. The figure clearly shows that the yield is low for the very light elements, explaining why it is so difficult to measure these elements.
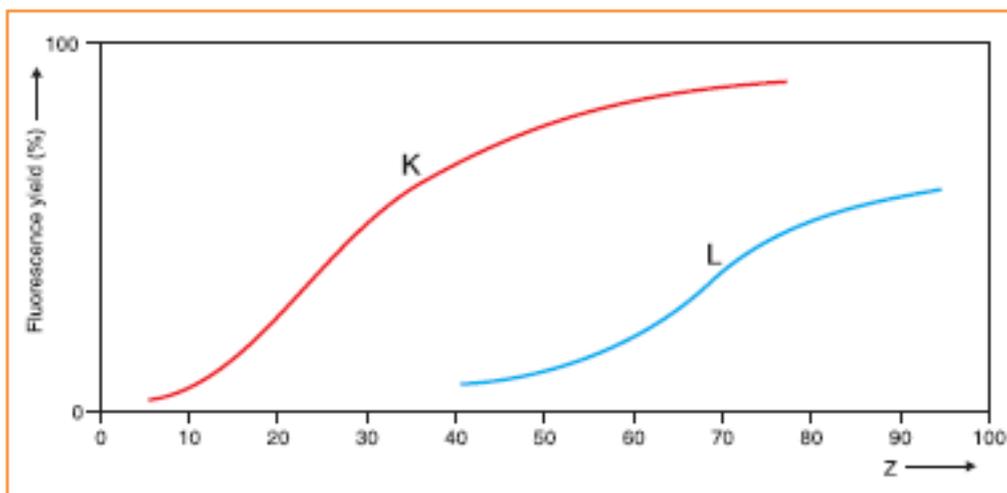
Figure (2.5) Fluorescence yield for K and L electrons

There are several ways to indicate different lines. The Siegbahn and IUPAC notations are the two most often found in the literature. The Siegbahn notation indicates a line by the symbol of an element followed by the name of the shell where the initial hole is plus a Greek letter $(\alpha, \beta, y \ etc)$ indicating the relative

intensity of the line. For example, Fe K α is the strongest iron line due to an expelled K electron. The Siegbahn notation however does indicate which shell the electron comes from that fills the hole. In the IUPAC notation, a line is indicated by the element and the shell where the initial hole was, followed by the shell where the electron comes from that fills this hole. For example, Cr KL_{III} is chromium radiation due to a hole produced in the K-shell filled by an electron in the L_{III}- shell.

Generally, K-lines are more intense than L-lines, which are more intense than M-lines, and so on. Quantum mechanics teaches that not all transitions are possible, for instances a transition from the L_I-to the K-shell. Figure(2.6) gives an overview of the most important lines with their transitions in Siegbahn notation [1].
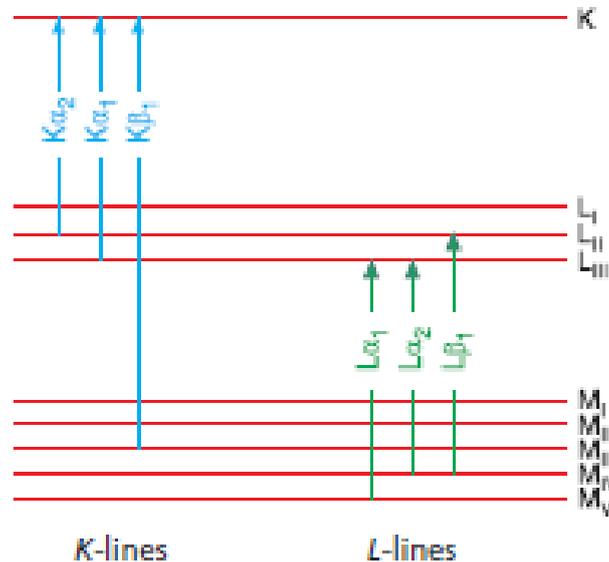
Figure (2.6) Major lines and their transitions

2.4 Absorption and enhancement effects

To reach the atoms inside the sample, the X-rays have to pass through the layer above it, and this layer will absorb a part of the incoming radiation. The characteristic radiation produced also has to pass through this layer to leave the sample, and again part of the radiation will be absorbed.
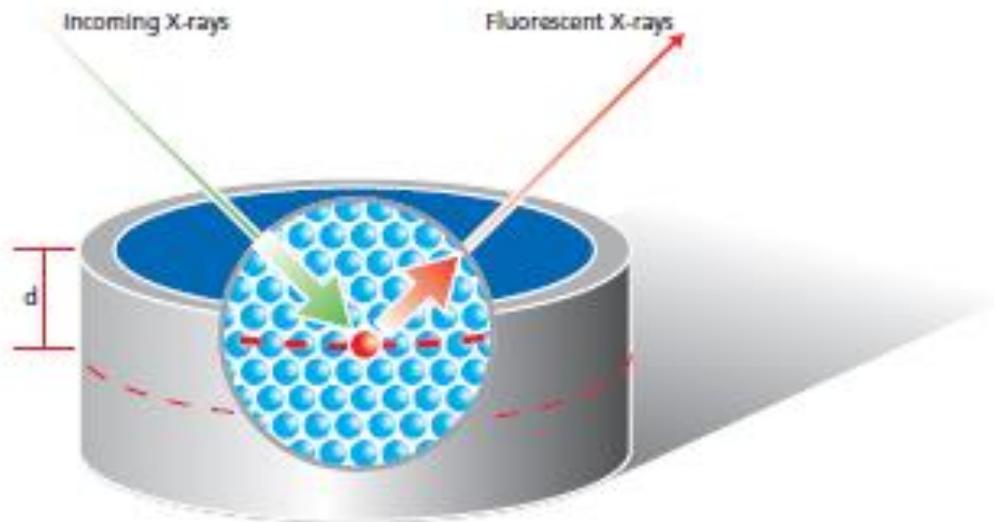
Figure (2.7) Absorption of incoming and fluorescent X-rays

The magnitude of the absorption depends on the energy of the radiation, the path length of the atoms that have to be passed, and the density of the sample.

The absorption increases as the path length, density and atomic number of the elements in the layer increase, and as the energy of the radiation decreases. The absorption can be so high that elements deep in the sample are not reached by the incoming radiation or the characteristic radiation can no longer leave the sample. The means that only elements close to the surface will be measured. The incoming radiation is made up of X-rays, and the characteristic radiation emitted by the atoms in the sample itself is also X-rays. These fluorescent X-rays are sometimes able to expel; electrons from other elements in the sample. This, as with the X-rays coming from the source, results in fluorescent radiation. The characteristic radiation produced directly by the X-rays coming from the source is called primary fluorescence, while that produced in the sample by primary fluorescence of other atoms is called secondary fluorescence[2].

2.5 Absorption and analysis depths

As the sample gets thicker and thicker, more and more radiation is absorbed.

Eventually radiation produced in the deeper layers of the sample is no longer able to leave the sample. When this limit is reached depends on the material and on the energy of the radiation.

Table (2.1) gives the approximate analysis depth in various materials for three lines with different energies. Mg Kα has energy of 1.25 keV, Cr K α 5.41 keV and Sn Kα 25.19 keV.

Table (2.1) Analysis depth in mm (unless indicated otherwise) for three different lines and various materials.

Material	Mg Kα	Cr Kα	Sn Kα
Lead	0.7	4.5	55
Iron	1	35	290
SiO$_2$	8	110	0.9 cm
Li$_2$B$_4$O$_7$	13	900	4.6 cm
H$_2$O	16	1000	5.3 cm

When a sample is measured, only the atoms within the analysis depth are analyzed.

If samples and standards with various thicknesses are analyzed, the thickness has to be taken into account.

2.6 Rayleigh and Compton scatter

A part of the incoming X-rays is scattered (reflected) by the sample instead of producing characteristic radiation. Scatter happens when a photon hits an electron and bounces away. The photon loses a fraction of its energy, which is taken in by the electron as shown in figure (2.8) it can be compared with one billiard ball colliding with another. After the collision, the first ball loses a part of its energy to the ball that was hit. The fraction that is lost depends on the angle at which the electron (ball) was hit. This type of scatter is called Compton or incoherent scatter.
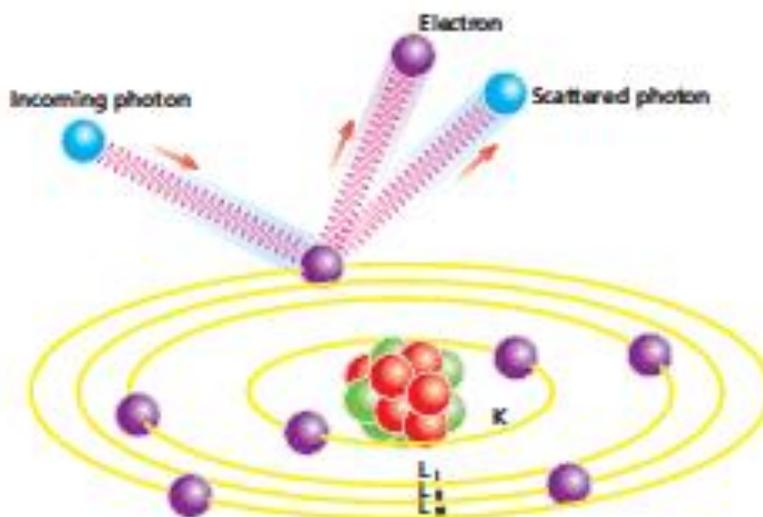
Figure (2.8) shows Compton scattering for electron

Another phenomenon is Rayleigh scatter. This happens when photons collide with strongly bound electrons. The electrons stay in their shell but start oscillating at the frequency of the incoming radiation. Due to this oscillation, the electrons emit radiation at the same frequency (energy) as the incoming radiation. This gives the impression that the incoming radiation is reflected (scattered) by the atom. This type of scatter is called Rayleigh or coherent scatter.

Samples with light elements give rise to high Compton scatter and low Rayleigh scatter because they have many loosely bound electrons. When the elements get heavier the scatter reduces. For the heavy elements, the Compton scatter disappears completely, and only Rayleigh scatter remains. Figure (2.9) shows the Compton and Rayleigh scatter for lead (a heavy element) and for Perspex (light elements). The spread of energy in the Compton scatter is larger than for Rayleigh scatter; in a spectrum this can be observed by the Compton peak being wider than the Rayleigh peak.
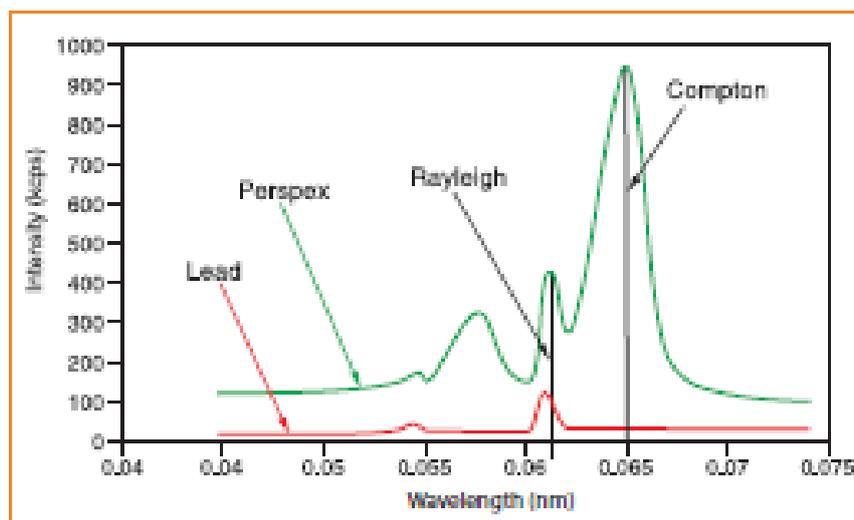
Figure (2.9) Compton and Rayleigh scatter for light and heavy elements

EDXRF spectrometers can be divided into spectrometers with 2D and 3D optics. Both types have a source and an energy dispersive detector, but the difference is found in the X-ray optical path. For 2D spectrometers the X-ray path is in one plane, so in 2 dimensions. For the 3D spectrometers, the path is not limited to one plane but involves 3 dimensions[6].

2.7 Polarization

X-rays are electromagnetic waves with electric and magnetic components E and B. This discussion is limited to the electrical component E but also holds for the magnetic component B.The amplitude of the electromagnetic waves

corresponds to the intensity of the X-rays. Electromagnetic waves are transversal waves, which means that the electrical component is perpendicular to the propagation direction.

This is similar to waves in water. If a stone is thrown into water, the waves are vertical but the propagation direction is horizontal.

X-rays are said to be linear polarized if the electrical components are all in one plane as shown in figure (2.10) if the electrical component has no preferred direction then the waves are called non-polarized.
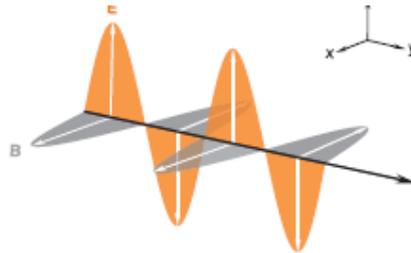
Figure (2.10) X-rays polarized in vertical direction

An electrical component E pointing in any direction can always be resolved into two perpendicular directions. Figure(2.11)shows how a component is resolved into a vertical and a horizontal direction.
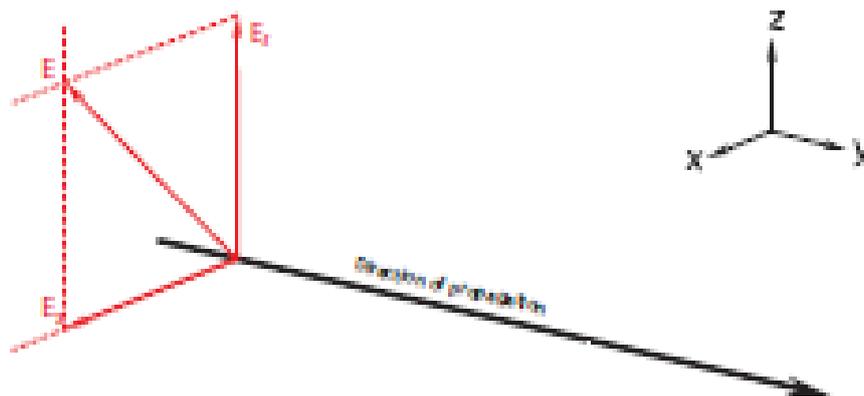
Figure (2.11) Electrical component resolved in horizontal and vertical components

If non-polarized X-rays are reflected (scattered) by a specimen through 90°, the reflected X-rays will be polarized in one direction. Figure (2.12) shows that the vertical electrical component is not reflected because this would point in the

new propagation direction. What remains after one reflection is the horizontal component alone, and the scattered X-rays polarized horizontally.

Figure (2.12) (bottom) shows what happens if the X-rays are scattered again but perpendicular to the previous direction. In the second reflection the horizontal component is not reflected because it would point in the new propagation direction. Nothing is left from the incoming radiation after two perpendicular reflections. This feature is used in EDXRF spectrometers to eliminate the background profile from a spectrum[9].
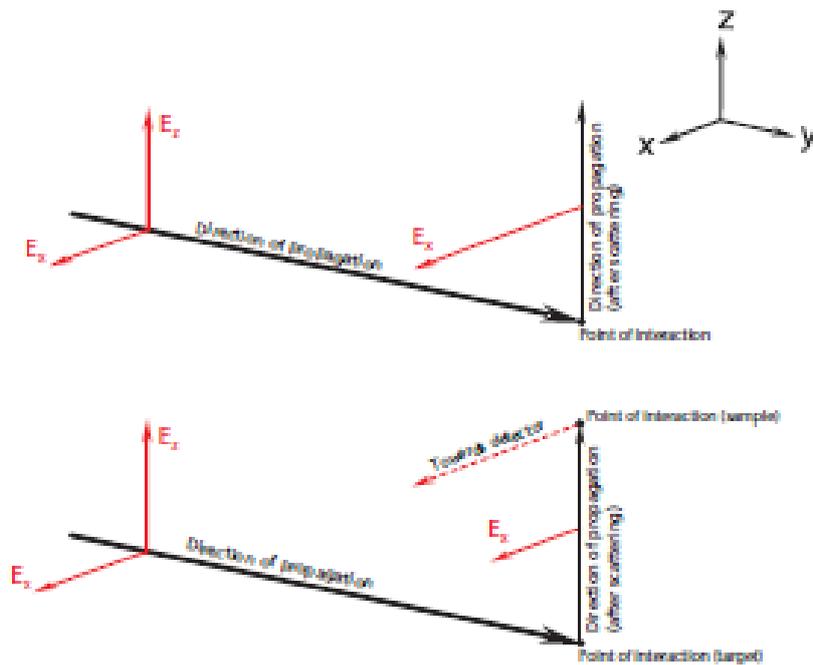
Figure (2.12) Polarization after 1 and 2 scattering events

Chapter three

Principle of XRF Techniques

3.1 Introduction

XRF is an analytical method to determine the chemical composition of all kinds of materials. The materials can be in solid, liquid, powder, filtered or other form. XRF can also sometimes be used to determine the thickness and composition of layers and coatings.

The method is fast, accurate and non-destructive, and usually requires only a minimum of sample preparation. Applications are very broad and include the metal, cement, oil, polymer, plastic and food industries, along with mining, mineralogy and geology, and environmental analysis of water and waste materials. XRF is also a very useful analysis technique for research and pharmacy.

Spectrometer systems can be divided into two main groups: energy dispersive systems (EDXRF) and wavelength dispersive systems (WDXRF), explained in more detail later. The elements that can be analyzed and their detection levels mainly depend on the spectrometer system used. The elemental range for EDXRF goes from sodium to uranium (Na to U). for WDXRF it is even wider, from beryllium to uranium (Be to U). The concentration range goes from (sub) ppm levels to 100%. Generally speaking, the elements with high atomic numbers have better detection limits than the lighter elements.

The precision and reproducibility of XRF analysis is very high. Very accurate results are possible when good standard specimens are available, but also in applications where no specific standards can be found.

The measurement time depends on the number of elements to be determined and the required accuracy, and varies between seconds and 30 minutes. The analysis time after the measurement is only a few seconds.

Figure (3.1) shows a typical spectrum of a soil sample measured with EDXRF-the peaks are clearly visible. The positions of the peaks determine the elements present in the sample, while the heights of the peaks determine the concentrations[8].
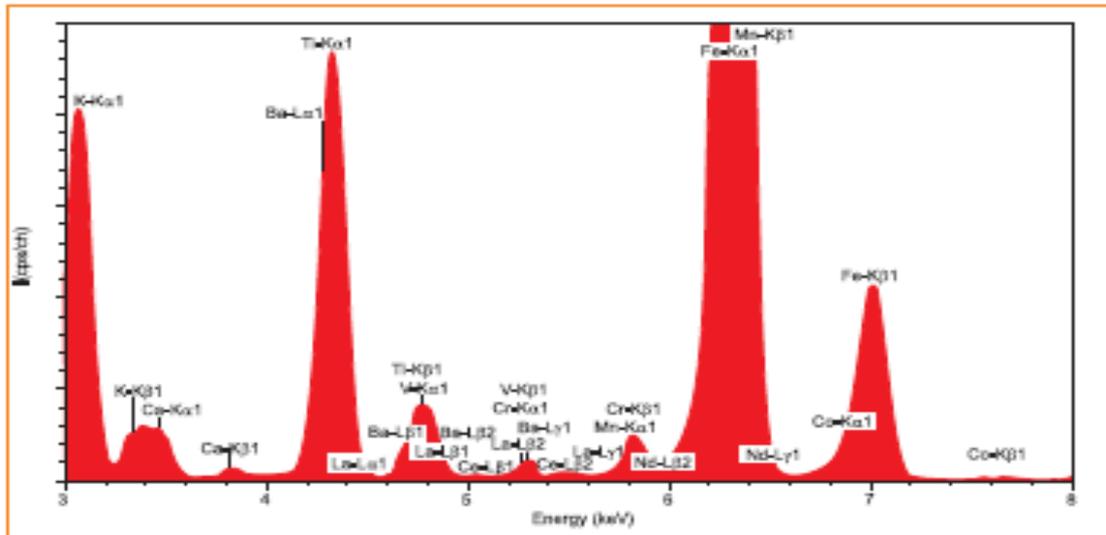
Figure (3.1) typical spectrum of a soil sample measured with an EDXRF spectrometer

3.2 Basics of XRF

In XRF, X-rays produced by a source irradiate the sample. In most cases, the source is an X-ray tube but alternatively it could be a synchrotron or a radioactive material. The elements present in the sample will emit fluorescent X-ray radiation with discrete energies (equivalent to colors in optical light) that are characteristic for these elements. A different energy is equivalent to a different color. By measuring the energies (determining the colors) of the radiation emitted by the sample it is possible to determine which elements are present. This step is called qualitative analysis. By measuring the intensities of the emitted energies (colors) it is possible to determine how much of each element is present in the sample. This step is called quantitative analysis.

3.3 The XRF spectrometer

The basic concept for all spectrometers is a source, a sample and a detection system. The source irradiates a sample, and a detector measures the radiation coming from the sample.
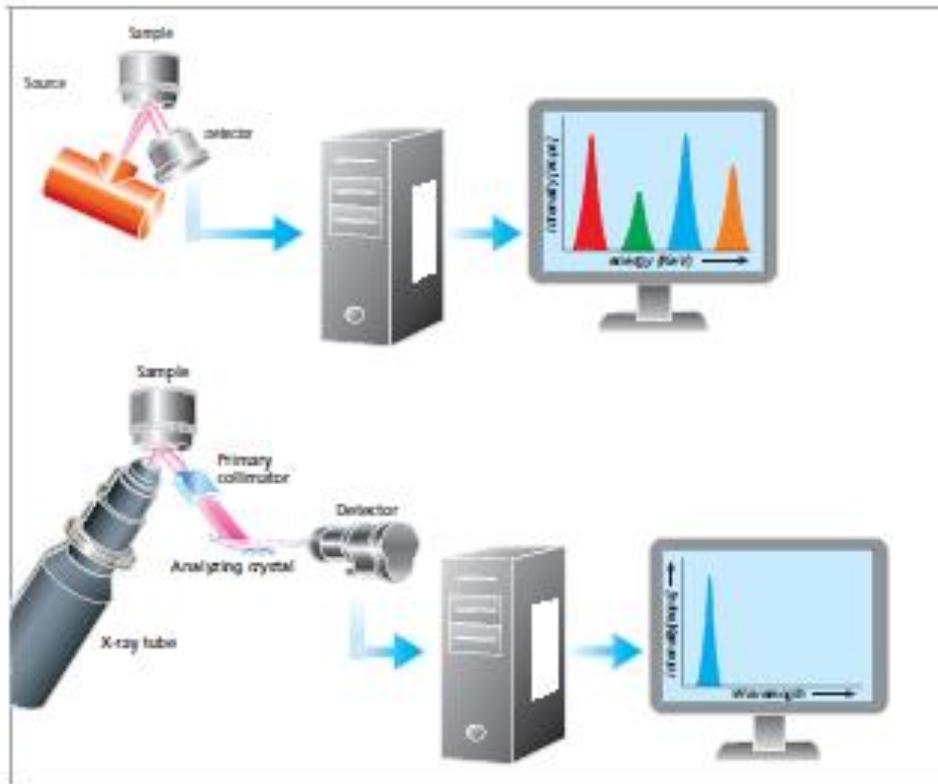
Figure (3.2) Basic designs of EDXRF and WDXRF spectrometers

In most cases the source is an X-ray tube, and this booklet will only discuss such spectrometers (alternative types use a radioactive source or synchrotron).

Spectrometer systems are generally divided into two main groups: energy dispersive systems (EDXRF) and wavelength dispersive systems (WDXRF).

The difference between the two systems is found in the detection system.

EDXRF spectrometers have a detector that is able to measure the different energies of the characteristic radiation coming directly from the sample. The detector can separate the radiation from the sample into the radiation from the elements in the sample. This separation is called dispersion.

WDXRF spectrometers use an analyzing crystal to disperse the different energies. All radiation coming from the sample falls on the crystal. The crystal diffracts the different energies in different directions, similar to a prism that disperses different colors in different directions. The next sections explain the differences between the spectrometer types in more detail, followed by a description of all the individual spectrometer components.

3.4 Small spot instruments

In most XRF applications the size of the samples is around one centimeter giving the average composition of the samples. For some application the local composition at different spots on the sample is required like spots on a chip wafers or on magnetic disks. For other applications, only a very small sample is available like a sliver of paint. Typical required spot diameters are between 50 mm and a few millimeters[3].

An option is to use pinholes between tube and sample and/or between sample and detector but the sensitivity is very low. In most cases, lenses are used for small spot analysis.

Figure (2.3) shows three possible optical paths using lenses, each having its advantages and disadvantages. The first optical path has the advantage that only the spot of interest is irradiated, the sensitivity is relatively high and alignment is not difficult. A disadvantage is that for optimal excitation a point source is required.

The second option has a good sensitivity, is not difficult to align, but the sample is irradiated outside the spot of interest.

The last option has the best spatial performance but has a low sensitivity and is very difficult to align.
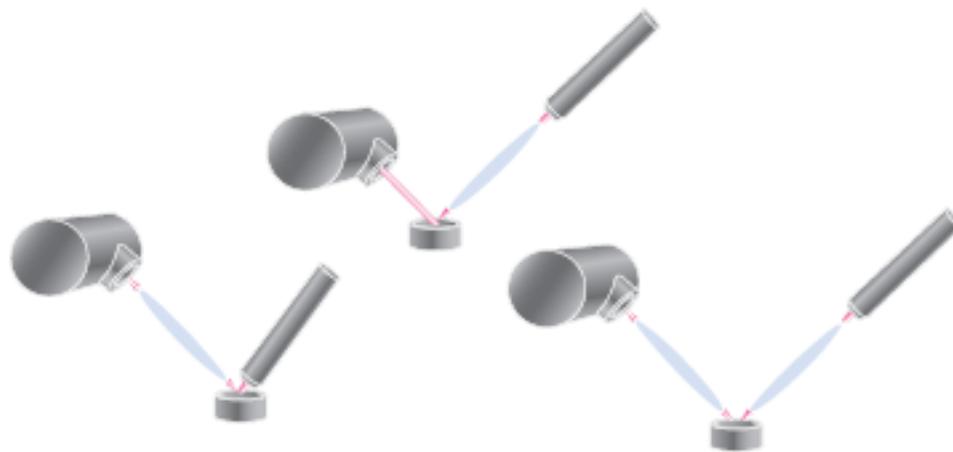
Figure (2.3) possible optical paths using lenses

3.5 EDXRF spectrometers with 2D optics

The simplest configuration is shown in figure (2.4) (left). The tube irradiates the sample directly, and the fluorescence coming from the sample is measured with an energy dispersive detector. An alternative is to place a secondary target between the tube and the sample as shown in figure 18 (right). The tube

irradiates the secondary target and this target will emit its characteristic radiation. The advantage of a secondary target is that emits (almost) monochromatic radiation but its disadvantage is that energy is lost. Using different secondary targets can achieve optimum excitation for all elements.

The detector is able to measure the energies of the incoming radiation directly. Besides the fluorescence, scattered tube radiation will reach the detector, which results in a background profile and background and noise. Due to this background, it is difficult to detect low peaks and as a result to determine low concentrations. The X-ray path is in one plane, so is 2-dimensional, and the X-ray optics are called 2D optics[2].

Figure (3.5) shows a typical spectrum of a soil sample measured with an EDXRF spectrometer with 2D optics. The next section discusses a spectrum of the same sample but measured with 3D optics, showing that the background with 3D optics is significantly lower.
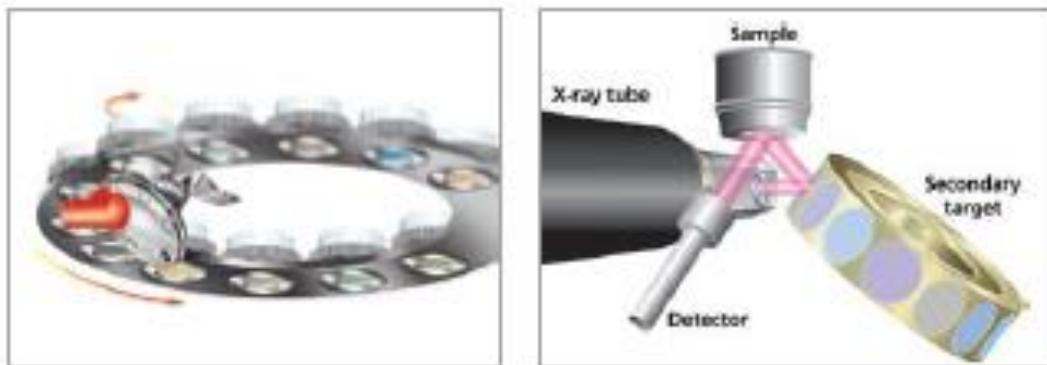
Figure (3.4) energy dispersive spectrometers with 2D optics and direct excitation (left) and polarized optics (3D) with indirect excitation (right)
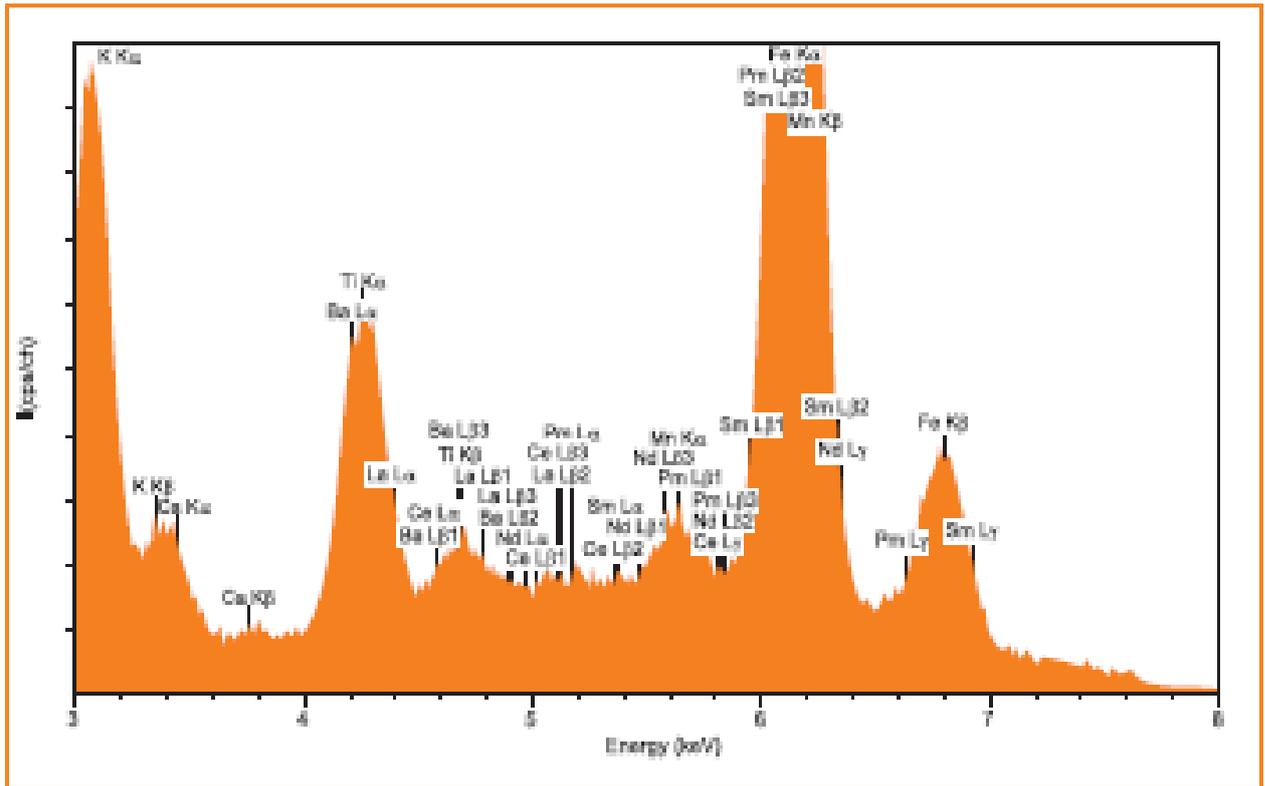
Figure (3.5) typical spectrum of a soil sample measured with EDXRF
spectrometer having 2D optics and direct excitation

3.6 EDXRF spectrometers with 3D optics

Figure (3.6) shows an EDXRF spectrometer using 3D optics. The X-ray path is
not in one plane but in two perpendicular planes, and the optics for this type of
spectrometers are called 3D optics. The tube irradiates a secondary target which
emits its characteristic X-rays and scatters a part of the incoming X-rays.

The radiation coming from the target is used to irradiate the sample, so for the
sample the target behaves like a source. The sample emits its characteristic
radiation, which is measured by an energy dispersive detector.
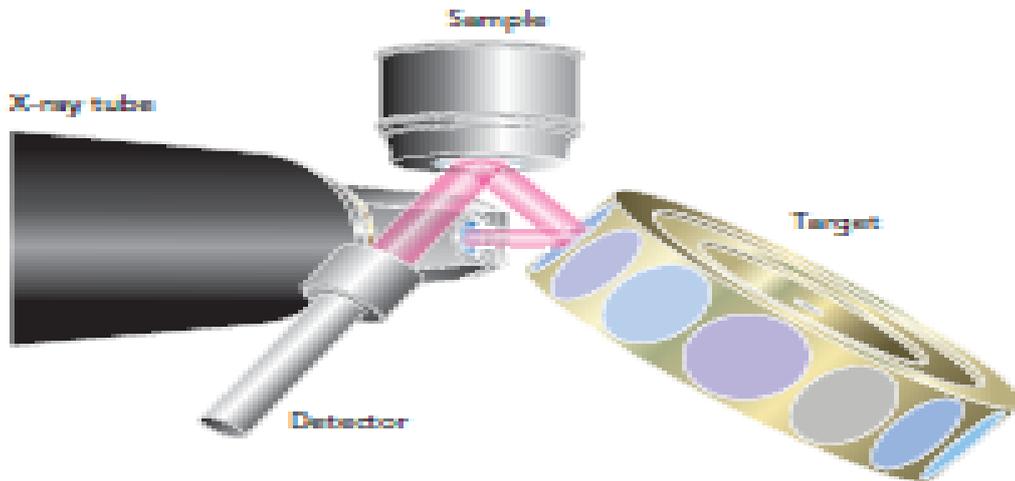
Figure (3.6) energy dispersive spectrometer with 3D optics and indirect excitation

The advantage of this geometry is that scattered tube radiation cannot reach the detector because of polarization. To reach the detector, The tube radiation must scatter in 2 perpendicular directions, but the X-rays vanish after two perpendicular reflections. As a consequence, the radiation coming from the tube will not reach the detector. This will result in a very low background to the spectrum and makes it possible to detect very weak peaks, and hence to determine very low concentrations[13].

The characteristic radiation of the target is partly scattered by the sample and reaches the detector. This radiation is scattered in only one direction and so it will not vanish. Figure (2.7) shows a typical spectrum of a soil sample measured with an EDXRF spectrometer with 3D optics. The background to a spectrum measured with 3D optics is significantly lower than the same spectrum measured with 2D optics.
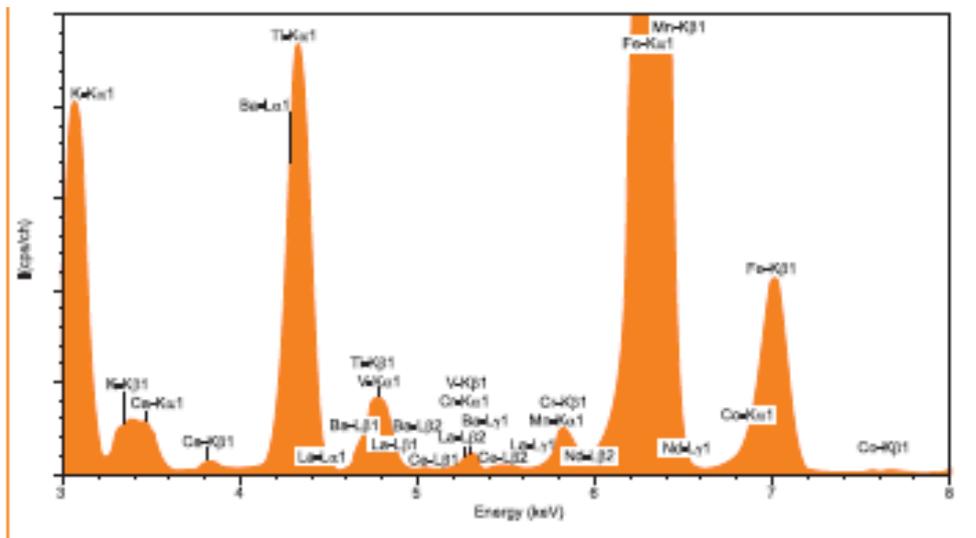
Figure (3.7) typical spectrum of a soil sample measured with an EDXRF spectrometer having 3D optics and indirect excitation

3.7 WDXRF spectrometers

The first part of a WDXRF spectrometer is equivalent to an EDXRF spectrometer with 2D optics and without a secondary target. The tube irradiates a sample and the radiation coming from the sample is detected. The detection system is however different from EDXRF spectrometers[4].

For WDXRF, detection system is a set of collimators, a diffraction crystal and a detector. The X-rays coming from the sample fall on the crystal, and the crystal diffracts (reflects) the X-rays with different wavelengths (energies) in different directions. (This is equivalent to a prism that separates white light into all the directions. (This is equivalent to a prism that separates white light into all the different colors). By placing the detector at a certain angle, the intensity of X-rays with a certain wavelength can be measured. It is also possible to mount the detector on a goniometer and move it through an angular range to measure the intensities of many different wavelengths. Spectrometers that use a moving detector on a goniometer are called sequential spectrometers because they measure the intensities of the different wavelengths one after another[14].

Figure (3.8) Construction of wavelength dispersive spectrometer with 2D optics and direct excitation

Chapter Four

Materials and method

4.1Apparatus and equipment:

Flask, sample cup XRF device thermometers cooler, heater, and tow sample of water (river water and purified water)

4.2 Method:

Samples of water which is being tested by using XRF is prepared river water and purified water.

0.25 liter of water at room temperature putted on sample cup then XRF is putted over the liquid inside the container for 6 to10 seconds. The previous steps were repeated three times in order to calculate the average value of readings and stander deviation (this reading done by the device itself or auto read). A previous step was repeated for different temperature of (8°C, 32° and 97°C) for two different sample, river water, purified water the results shown in the tables (4.1 to 4.6). In order to find element exist in this samples and to investigate the effect of temperature on mechanism of detecting the elements in the samples. The results were drawn by Exel

4.3 Results:

Table (4.1) river water at 8˚C

Elements	100%	STD
W	43.35	3.508
Cu	0.50	0.345
V	0.28	0.199
Fe	38.01	0.307
Cr	0.29	0.112
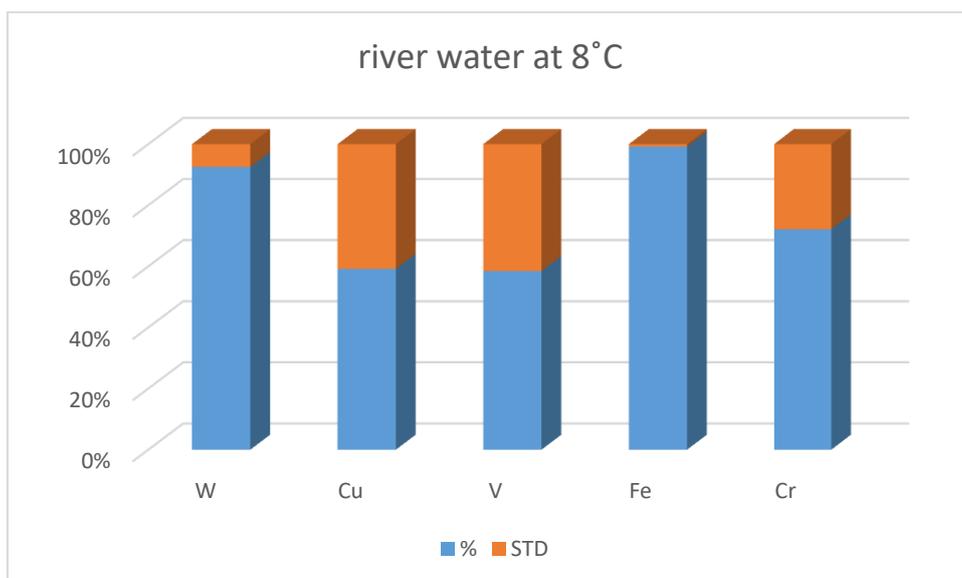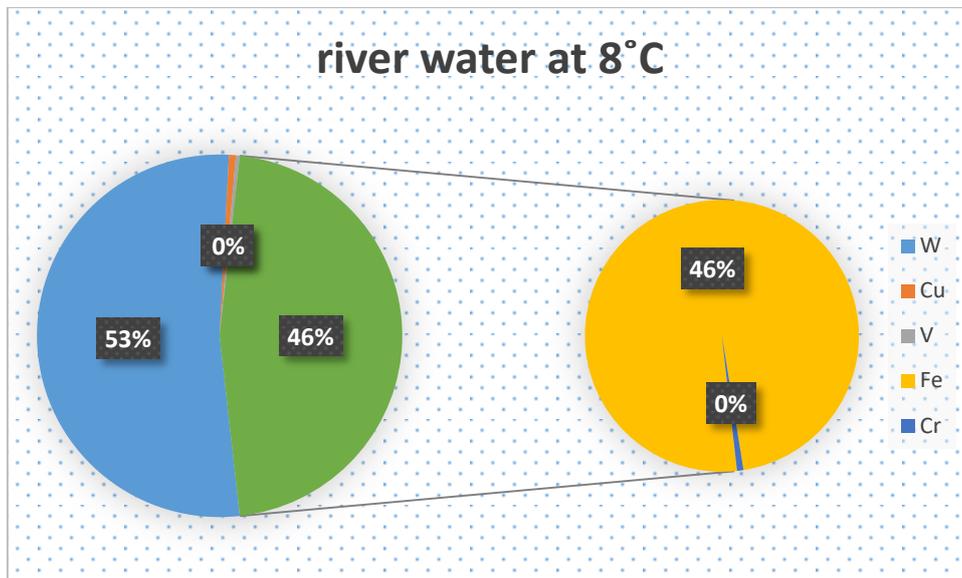
Figure (4.1) traces elements on river water at 8^0C

Table (4.2) river water at 32˚C

Elements	%	STD
W	42.28	2.820
V	0.56	0.219
Cr	0.34	0.169
Mn	0.05	0.092
Fe	37.26	0.193
Cu	0.35	0.318
Ni	0.12	0.212
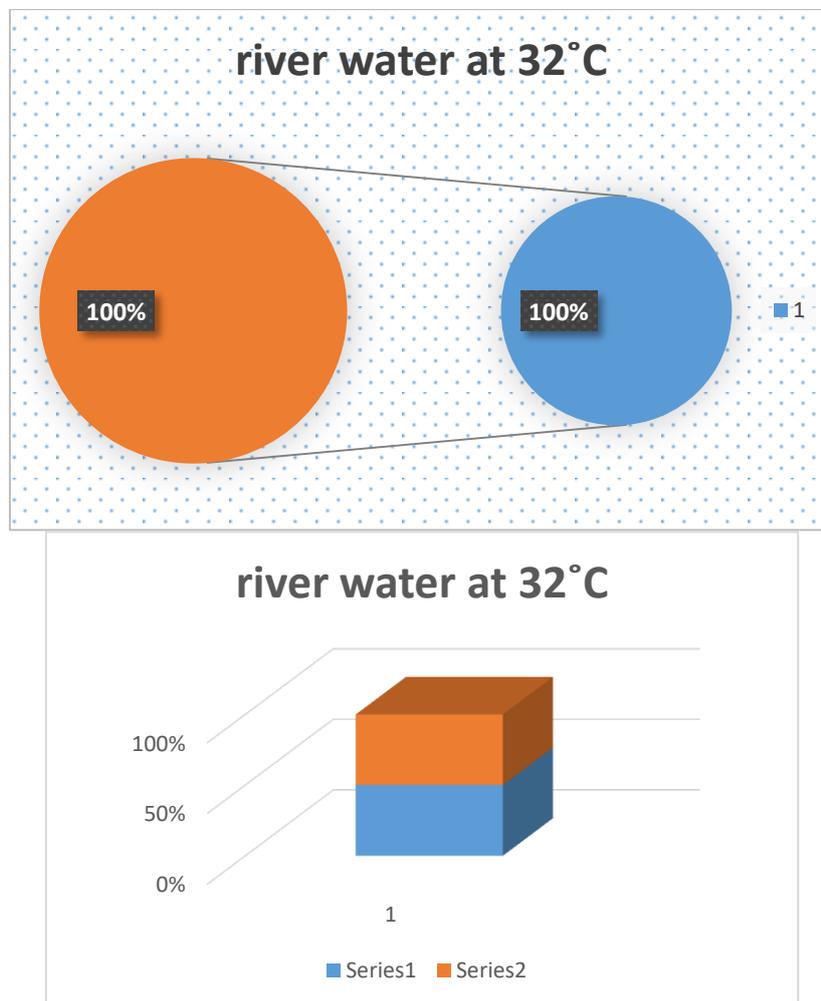
Figure (4.2) traces elements on river water at 32^0C

Table (4.30) river water at 97˚C

Elements	%	STD
Pb	0.00	0.000
Zn	0.00	0.002
Cr	0.02	0.005
Fe	0.27	0.190
Ni	0.01	0.001
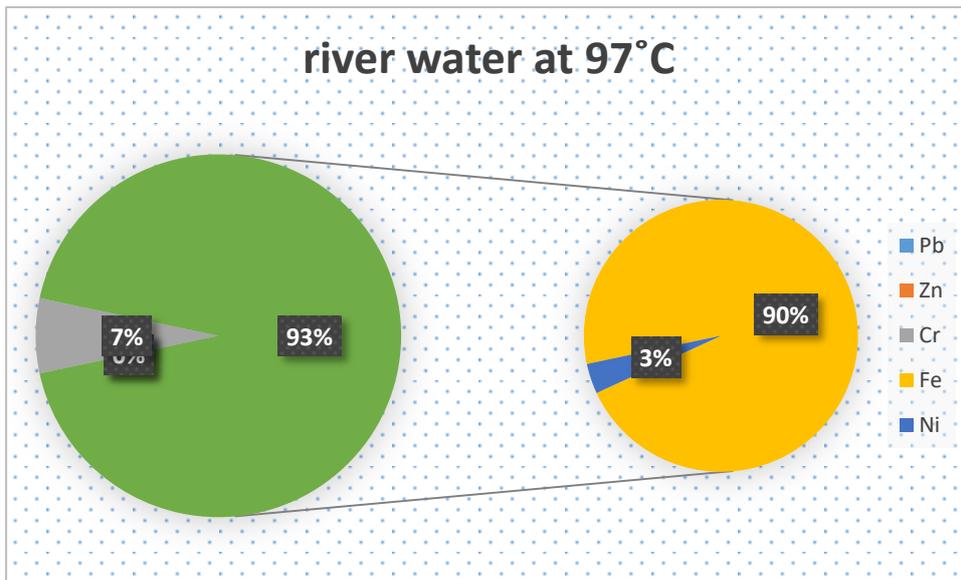
Figure (4.3) traces elements on river water at 97^{0}C
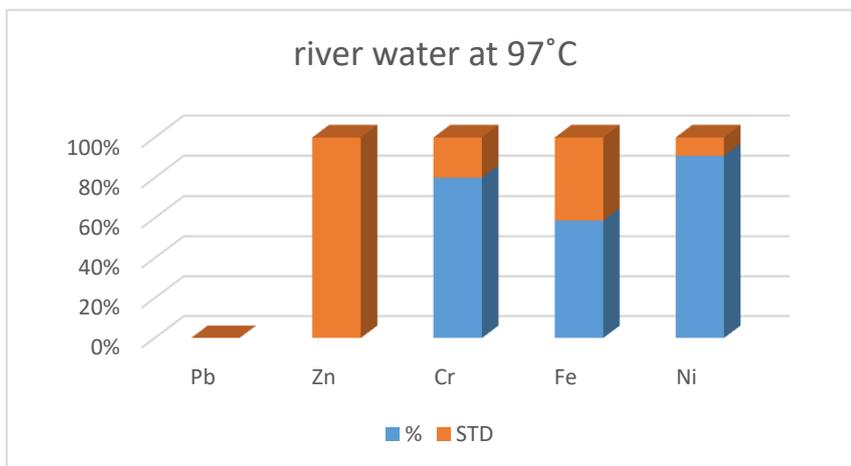
Table (4.4) purified water at 8˚C

Elements	%	STD
W	43.04	1.172
V	0.64	0.251
Cr	0.26	0.227
Fe	37.53	0.599
Cu	0.50	0.289
Mn	0.01	0.1010
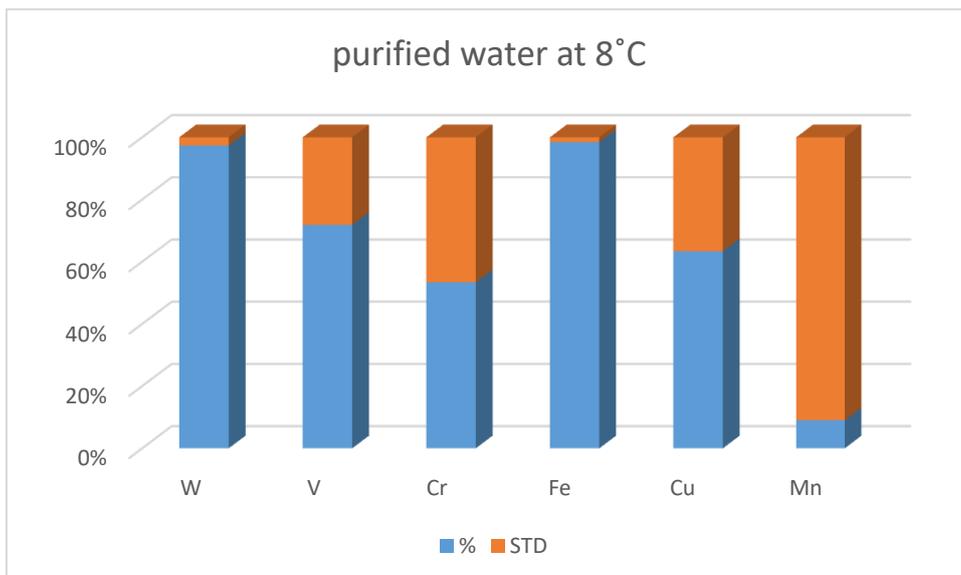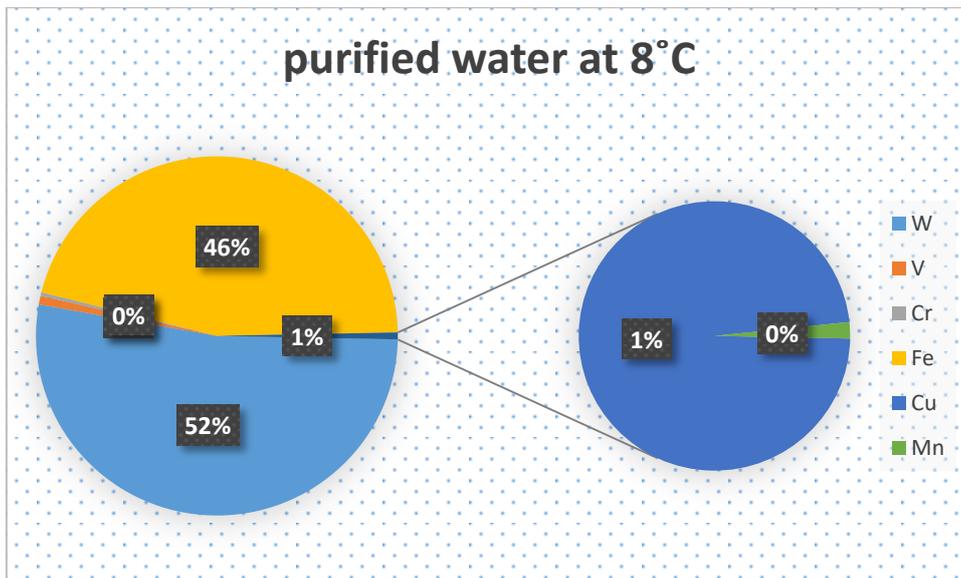
Figure (4.4) traces elements on purified water at 8^0C

Table(4.5) purified water at 32˚C

Elements	%	STD
W	43.03	2.953
Cu	0.65	0.137
Cr	0.29	0.064
Fe	37.62	0.628
V	0.42	0.254
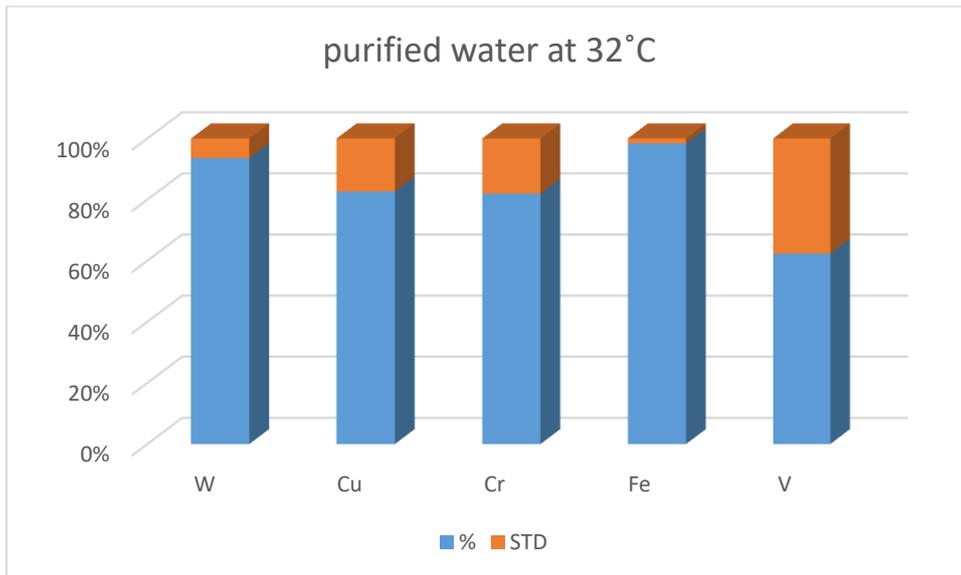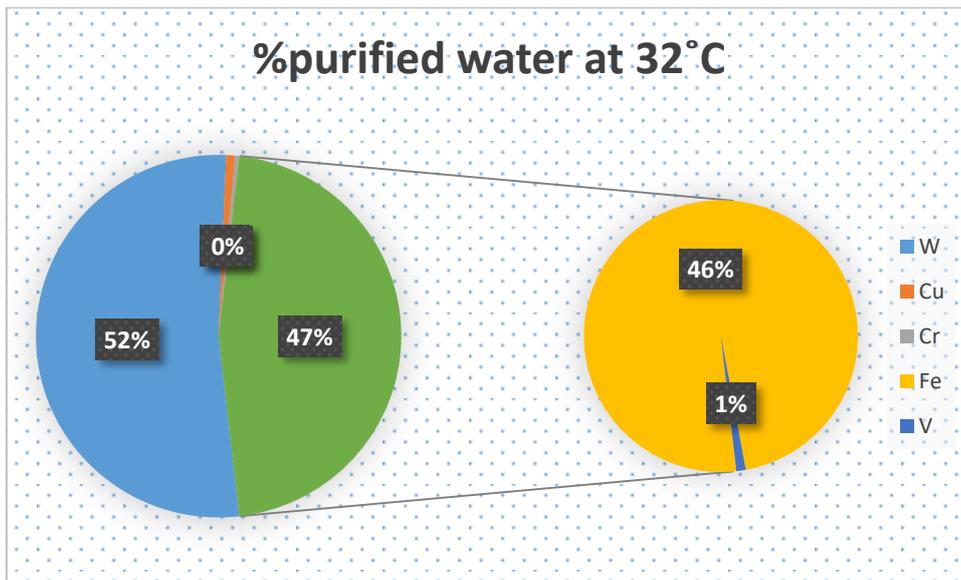
Figure (4.5) traces elements on purified water at 32^0C

Table (4.6) purified at 97˚C

Elements	%	STD
W	41.27	2.430
Cu	0.81	0.127
Cr	0.40	0.151
Fe	37.82	0.328
V	0.52	0.33
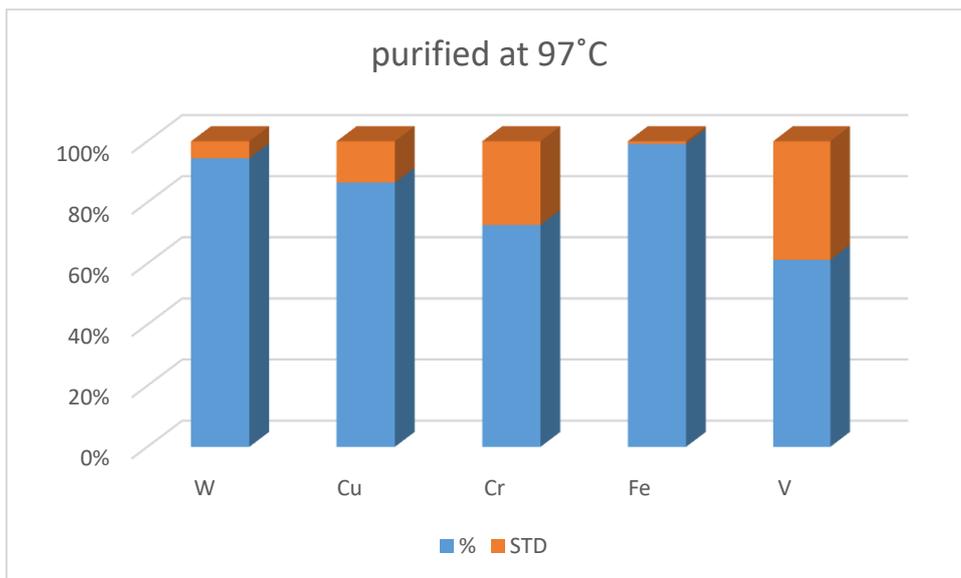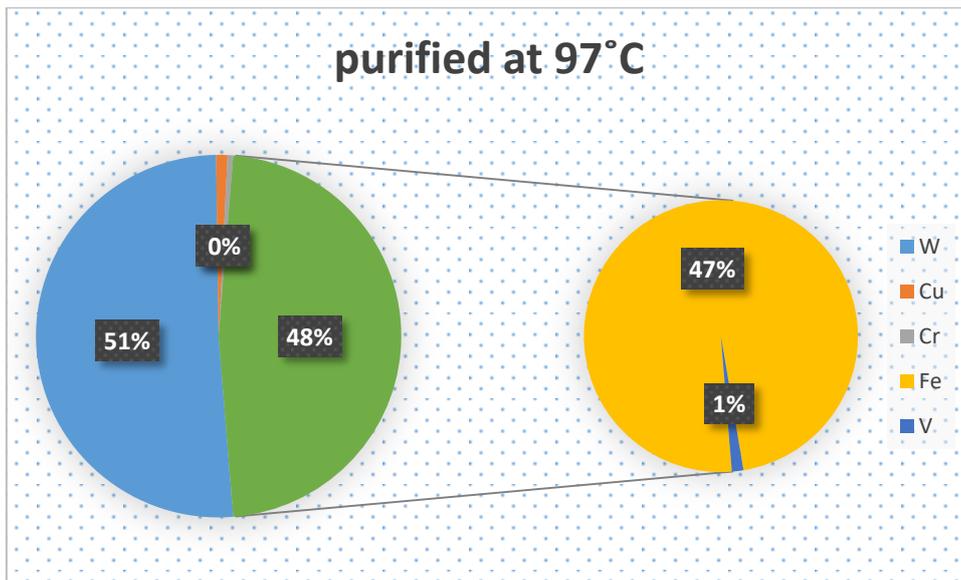
Figure (4.6) traces elements on purified water at 97[0]C

4.3 Discussion:

The following are the water samples analyzed using XRF . from the figures was obtained, that ultimate temperature used to detect elements which exist in the tow different samples is 32°C. below this temperature there are some element disappear and the same thing happened for temperature above this temperature .

The percentage of iron in the tow samples remains constant for different temperature and this percentage slightly for 8°C.

The element W which is available at all temperature for the tow samples was disappeared at 97°C for river water.

4.4 Conclusion:

This study demonstrates the utility of the X-ray fluorescence method to obtain fast and accurate elemental analysis of water samples the extraction of which could be detrimental to the environment and present serious health hazards to the population of Khartoum .the work has analyzed two different water samples which represent a variety of economically important in our live (river and purified water. The samples and that is both affordable and readily accessible is XRF. This technique can also provide a rapid evaluation of the economic potential of a health of the community impacted by the element extraction process.

4.5 Recommendation:

Researchers should be encouraged and fully supported by the government of the republic of Sudan. These goals can be met by ensuring that more research centers are created and encouraged by robust funding sources and that industry is incentivized to partner with researchers to preserve the environment of the future.

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