

Chapter one

Introduction

1.1 Prelude

Silver is one of the eight precious, or noble, metals; the others are gold and the six platinum-group metals (PGM). World mine production in 2001 was 18,700 metric tons (t) and came from mines in 60 countries; the 10 leading producing countries accounted for 86 percent of the total.

Silver and gold have been known and prized for at least six millennia. The two metals commonly are found together in nature and were almost certainly the first metals known to man. In streambed gravel deposits, from which they were first recovered, the gold invariably contains silver, sometimes enough to form the natural alloy “electrum,” in which the silver content can range from about 18 to 36 weight percent. The separation of silver from gold in these alloys probably was not achieved until about 2000 B.C. or later, but silver had been recovered as native silver and by charcoal reduction from certain silver minerals, such as cerargyrite (AgCl), as early as 4000 B.C.

Like gold, silver is soft, malleable, and ductile; in fact, it is the most ductile of metals. These properties led to its being fashioned into items of personal adornment and decorative items of various kinds. Thus, silver belt buckles, bracelets, brooches, chain necklaces, neck rings, and other items of jewelry were developed early. Later, silver was used for such things as decorative handles for daggers and swords, and eventually, in relatively modern times, eating utensils and various items of tableware [1].

1-2 The Object of Study:

By using x-ray technique one can predict the type of material such as gold and silver in order to detect their karat as non destructive testing.

1-3 The Problem:

The gold and silver which are available in the market is one of the most important metal which are used are jewelry so the people who is going to use them is subject to different types of cheatings. so it is very important to identify their karat before import operation.

1-4 Layout of the Research

This research consist of four chapters. in chapter one introduction ,the aim of study ,the problem and the methodology in addition to research lay out and the previous study

1-5 Literature Review

In 2009,2010 s. Shankar, S. V. and R. Seeta Laxman on recovery of silver from waste x-ray film by alkaline protease from conidiobolus coronatus the waste x-ray/ photographic films contain 1.5 - 2 % (w/w) black metallic silver which is recovered and reused. Around 18-20% of the world's silver needs are supplied by recycling photographic waste. Since silver is linked to gelatin in the emulsion layer, it is possible to break the same and release the silver using proteolytic enzymes. Alkaline protease from *Conidiobolus coronatus* was investigated for enzymatic hydrolysis of gelatin from waste X-ray films. At the end of the treatment, gelatin layer was completely removed leaving the polyester film clean and silver was recovered in the hydrolysate, both of which can be reused. Various parameters such as pH, temperature, enzyme concentration, time etc on silver removal from the film were studied. Gelatin hydrolysis was monitored by measuring increase in turbidity in the hydrolysate, which was accompanied by release of protein and hydroxyproline. Gelatin layer was stripped completely within 6 min with 1.35 U ml⁻¹ of protease at 40°C, pH 10. Rate of gelatin hydrolysis increased with increased in protease concentration. The enzyme could be effectively reused

for four cycles of gelatin hydrolysis. Silver in hydolysate was around 3.87 % (w/w) based on total weight of sludge.

in 2010 chiojdeanu, daniela cristea stan on gold and silver coating characterization using an x-ray fluorescence based method – the case of archaeological artifacts xrf studies were performed for some ancient Au or Ag coated artifacts in order to evaluate the gilding/silvering layer thickness and to identify different techniques used during their manufacture – from simple mechanical application of a thin malleable gold foil to the use of (mercury) amalgamation. These results can be used for authentication of archaeological objects and for various historical studies for validation of various hypotheses on the habits, commercial and cultural exchanges of old populations.

XRF proved to be a useful tool for characterization of contemporaneous and modern monetary fakes, as well as for other coatings (nickel, copper, stainless steel) and thin layer structures (electronics, solid state physics) investigation.

In 2010 K. V. Radha & C. Arun Recycling of exposed photographic X-ray films and recovery of silver using Bromelain The Bromelain enzyme was extracted by using the juice extracted from pineapple apex. Concentration of total protein in crude homogenate was estimated at 0.959 mg/ml and after purification the concentration of total protein

was found to be 0.872mg/ml. Maximum operating ph and temperature for Bromelain was found to be 6.5 and 55°C respectively. Effect of time on silver recovery shows that at 35 min essentially all silver grains on X-ray film was completely stripped out from the polymeric material. It is confirmed by analyzing the X-ray film before and after treatment using SEM. The cleared X-ray film was collected and dried. The collected film can be reused for manufacturing of X-ray film and also used for production of fabrics, packaging films, recording tapes, and soft-drink bottles. All the above results show that this process is cheaper, pollution free and efficient. By this process 98% of silver can be recovered from X-ray film and the silver can be reused for silver solder, jewels, silver plating of utensils, electrical components and

film manufacture. The purity of silver obtained was found to be 99.9%. Thus this process is an eco friendly process.

In 2013 Vaishali Choudhary on Recovery of Silver from used X-ray films by *Aspergillus versicolor* protease Reuse or recycle of natural mineral resources remains most feasible option to slow down the exhaustion caused due to their depletion. This study indicates that the alkaline protease of *Aspergillus versicolor* PF/F/107 had the potential of being applied for reusing of silver from used x-ray films in an eco-friendly manner.

Chapter Two

X-ray Fluorescence Analysis

2.1 Introduction

This chapter is concerned with the physics of XRF, Also concentrates and the XRF spectrometer and the techniques used to determine concentration of elements.

2.2 X-rays properties

X-rays are form of electromagnetic radiation. They occur in the region of the electromagnetic Spectrum between 0.01nm & 10 nm so is bounded on the short wavelength side by Gamma rays and on the long wave length side by Ultra-Violet radiation.

X-ray radiation has both a wave and a corpuscular (particle –like)character, X-rays were discovered in 1895 by Wilhelm Conrad Rontgen, whore ceived the first Nobel Prize in Physics in 1901.the properties of these X-rays were investigated, and by 1912 the principles of diffraction physics and reciprocal space were developed by Rontgen, on Laue, E wald and Summered .

The Name of X-rays is suggested by Roentgen because their nature was unknown at that time, unlike ordinary light, X-rays are invisible, they travel instraight lines and affects .they are much more penetrating than light and could easily pass through the human body, wood, metal etc.

Exponentially absorbed in matter with the exponent proportional to the mass of the absorbing material and they are not affected by the magnetic field.

X-rays emitted by sudden stoppage of the fast moving electrons. It can also be scattered with and without losing part of their energy (coherent or Raleigh-scatter and incoherent or Compton - scatter).When an electron from the inner shell of an atom is lost due to some sort of excitation, it is replaced with an electron from the outer shell; the difference in energy is emitted as an X-ray

photon which has a wavelength that is characteristic for the element (there could be several of characteristic wavelengths per element). Analysis of the X-ray emission spectrum produces qualitative results about elemental composition of the specimen.

Comparison of spectrum of the specimen with spectra of standards of known composition produces quantitative results (after some mathematical corrections for absorption, fluorescence and atomic number)[6].

When X-ray beam passes through matter, some photons will be absorbed inside the material or scattered away from the original path. Most modern stand alone X-ray spectrometers use X-ray excitation sources rather than electron excitation. All conventional X-ray spectrometers comprise three parts: the primary source unit, the spectrometer itself and the measuring electronics. An X-ray detector is a transducer for converting X-ray photon energy into easily measurable and countable voltage pulses. All detector types work through a process in which interaction between the entering X-ray photon and the active detector a number of electrons[7].

(2-3) Production of x-ray

There are two known types of x rays: characteristic radiation and bremsstrahlung. Both types of x rays are important in medical physics, since both are used extensively in diagnostic imaging and in external beam radiotherapy. Characteristic x-rays are produced by electronic transitions in atoms triggered by vacancies in inner electronic shells of the absorber atom. Bremsstrahlung, on the other hand, is produced by Coulomb interactions between an energetic light charge particle and the nucleus of the absorber atom. When very fast electrons strike atoms they are decelerated. Thus it can emit electromagnetic radiations according to Maxwell's electromagnetic theory. The kinetic energy of the stopped electron is converted to photon energy.

An X-ray tube consists of two electrodes, one negative, and glow cathode, which upon being heated emits electrons, and one positive anode.

The electrodes are capsulated in a vacuum. By applying an acceleration potential (20-200 kV), the electrons are accelerated towards the anode. The electrons gain kinetic energy which is the product of their charge and the potential difference.

When the electron reaches the anode it imparts the main part of its energy to the atoms of the anode by ionizations and excitations [8] .

This energy will finally appear as heat energy. If an electron passes close to an atomic nucleus, it will change its direction of motion, i.e., exhibits an acceleration. At each such acceleration there is a small probability that the electron loses energy in the form of a photon, these photons are called bremsstrahlung photons and constitute the main part of the X-ray being used in X-ray diagnostic imaging.

Bremsstrahlung is generated when an electron with high energy changes its direction of motion in the neighborhood of an atomic nucleus and thereby loses energy.

The bremsstrahlung photon can obtain an arbitrary energy between zero and the whole kinetic energy of the electron (T).

The relative amount of bremsstrahlung emitted increases with increasing electron kinetic.

$$hf = T = \frac{1}{2}mv^2 \quad (2.1)$$

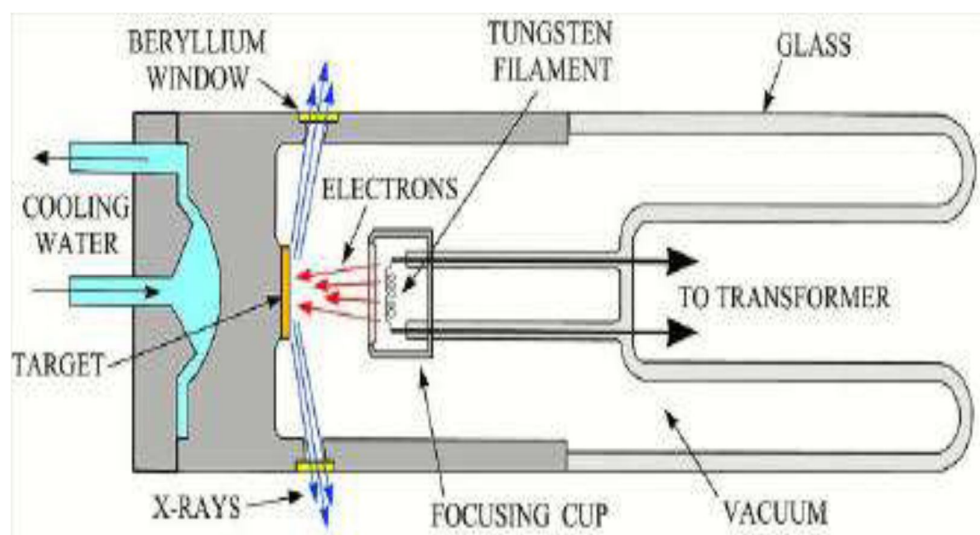
Where:

h : stand for blank const, f : is the photon frequency , m is mass, e : is the electron charge and v : is the accelerating potential of the battery Energy and within creasing atomic number, Z , of the anode material. Since the major part of the energy of the electrons is converted into heat in the anode (About 1% will appear as X-rays), the anode material should have high melting point and good heat conduction ability. To get a high relative amount of X-ray energy, the Anode material should be of high atomic number. Tungsten is the

dominating anode Material and is in modern X-ray tubes often mixed with rhenium ($ZW=74$; $Z Re=75$).

Modern X-ray imaging requires a small focal spot and high X-ray Fluence rates (number of photons per unit area and unit time). To meet these requirements, technical solutions with a line shaped focal spot and rotating anode have been introduced.

X-rays are produced when electrically charged particle with a sufficient kinetic energy is rapidly decelerated. X-rays are generated in a cathode ray tube contains a source of electrons and two metal electrodes.



Fig(2.1) shows X-Ray production

Free electrons are produced by heating filament called the cathode to a high temperature by the passage of an electric current. Then, negatively charged particles are accelerated to high energy by applying a voltage of several tens of kilovolts between the filament and the target or a node. If the electrons have sufficient energy, x-rays are produced at the point of impact and emitted in all directions but only the x-rays making a certain angle is allowed to pass through the window. Most of the kinetic energy of electrons is converted to heat.

A target (composed of a metallic element and must be pure: **Cr, Fe, Co, Cu, Mo, Ag, etc**).The tube is cooled by water and housed in a shielding aluminum tower.

In an x-ray tube, the interactions are between the electrons and the target.

Since energy must be conserved, the energy loss from the interaction results in the release of x-ray photons. The energy (wavelength) will be equal to the energy loss.

This process generates a broad band of continuous radiation.

Electrons traveling from the filament (cathode) to the target (anode) convert a small percentage (1%) of their kinetic energy into x-ray photons by the formation of Bremsstrahlung and characteristic radiation, filament lamp, is of the spontaneous type.[9]

In bremsstrahlung interactions, the primary source of x-ray photons from an x-ray tube, are produced by the sudden stopping, breaking or slowing of high-speed electrons at the target. When the electrons from the filament strike the tungsten target, x-ray photons are created if they either hit a target nucleus directly (rare) or their path takes them close to the nucleus. If a high speed electron hits the nucleus of a target atom, all its kinetic energy is transformed into a single x-ray photon. (Total absorption has occurred). Thus, the energy of the resultant photon is numerically equal to the energy of the electron. Bremsstrahlung interactions generate x-ray photons with a continuous spectrum of energy.

2-4 Bremsstrahlung Radiation

In bremsstrahlung interactions, the primary source of x-ray photons from an x-ray tube, are produced by the sudden stopping, breaking or slowing of high-speed electrons at the target. When the electrons from the filament strike the tungsten target, x-ray photons are created if they either hit a target nucleus directly (rare) or their path takes them close to the nucleus. If a high speed

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(Total absorption has occurred). Thus, the energy of the resultant photon is numerically equal to the energy of the electron. Bremsstrahlung interactions generate x-ray photons with a continuous spectrum of energy [10].

2-5 Characteristic Radiation

This radiation occurs when an electron from the filament displaces an tungsten atom is quickly attracted into the void in the deficient inner-shell.

When the displaced electron is replaced by the outer-shell electron, a photon is emitted with an energy equivalent to the difference in the two orbital binding energies.

$$hf = E_2 - E_1 \quad (2.2)$$

Characteristic radiation from the K-shell occurs only above 70 kv with a tungsten target and occurs as discrete increments compared with bremsstrahlung radiation.

Characteristic radiation has a higher intensity, is preferred but is only a minor source of radiation from an x-ray tube [11].

2-6 Physics of x-ray Fluorescence

The name florescence was derived from the mineral fluorite (calcium difluoride). Fluorescence occurs when an orbital electron of a molecule, atom or nanostructure relaxes to its ground state by emitting a photon of light after being excited to a higher quantum state by some type of energy. The atom emits X-ray Fluorescence in the region 0.2–20 Å.

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation .in most cases; the emitted light has a longer wave length, and therefore lower energy than the absorbed radiation.

When the absorbed electromagnetic radiation is intense, it is possible for one electron to absorb two photons; these two absorption photons can lead to

emission of radiation having a shorter wave length than the absorbed radiation. The emitted radiation may also be of the same wave-length as the absorbed radiation, termed (resonance fluorescence).

The fluorescence quantum yield gives the efficiency of the fluorescence process; it defined as the ratio of the number of photons emitted to the number of photon absorbed. Fluorescence has any practical applications, including mineralogy, geology, chemical sensors, cosmic ray detection, and practical analysis [12].

The process of emissions of characteristic x-rays is called "X-ray Fluorescence" or XRF. Analysis using x-ray fluorescence is called "X-ray Fluorescence Spectroscopy." The main principle of X-Ray Fluorescence Spectroscopy (XRF) is based on the fact, that atoms, when irradiated with X-Rays, radiate secondary X Rays – the Fluorescence radiation. X-rays need energy to pass through the material to be analyzed and to reach the detector or photographic plate.

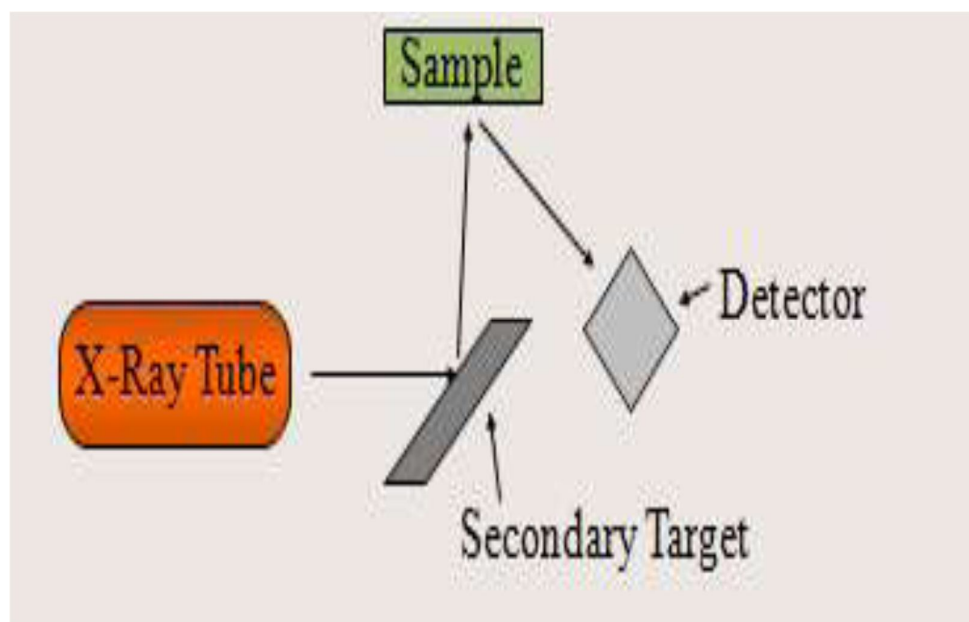


Fig (2.2) the X-ray fluorescence detector

On this basis XRF-analysis is possible because:

- 1) The wavelength and energy of the Fluorescence radiation is specific for each element.
- 2) The concentration of each element can be calculate using the intensity of the Fluorescence radiation.

The optimum energy for X-ray beams depend on interaction cross section and on the nature (density) of material.

XRF analysis is a powerful analytical tool for the spectroscopic determination of almost all the elements present in a sample. XRF radiation is induced when photons of sufficiently high energy, emitted from an X-ray source, impinge on a material.

High-energy photons induce ionization of inner shell electrons by the photoelectric effect and thus electron vacancies in inner shells (K, L, M ...) are created.

The creation of a vacancy in a particular shell results in a cascade of electron transitions, all correlated with the emission of photons with a well defined energy corresponding to the difference in energy between the atomic shells involved.

The family of characteristic X-rays from each element including all transitions allows the identification of the element.

According to the Bohr model of an atom the electrons surrounding the

Nucleus are confined to different orbits, constituting so called electron shells at discrete energy levels, labeled K, L, M,...etc, and also further subdivided. The electrons in the K-shell are closest to the nucleus, and also the most tightly bound.

When an atom absorbs an incident photon which has an energy that exceeds an electron binding energy, it may result in the emission of a so called photoelectron from the current shell of the atom. This photoelectric absorption process leaves a vacancy in the electron shell. It will immediately be filled by another electron, usually coming from an outer shell and thus less

tightly bound, with a subsequent rearrangement of shell electrons. As energy will be liberated when a vacancy is filled, it may be emitted as electromagnetic radiation (a photon) or be transferred to an electron with less binding energy (Auger electron) which is ejected from the atom.

The probability of having photons emitted is represented by the fluorescence yield.

It can be found tabulated among spectroscopic data. The emitted photons will have an energy representing the difference between the discrete energy levels of the shells involved. These emitted X-ray energies are characteristic of the involved element, enabling identification. Another element will have a different set of possible characteristic X-rays. If the vacancy is created in the K-shell, the emitted energies associated are denoted $K\alpha$ and $K\beta$. When characteristic X-rays like these are captured by a detector and the energies identified, it will reveal the presence of the element. The number of detected photons, or counts, is proportional to the concentration of the element in the measurement volume. [13]

2-7 X-ray Fluoresce and Instrument

There are some main benefits in favor for analysis of elements with a higher atomic number such as heavy metals, making them appropriate candidates for investigation.

The probability for a photoelectric process to occur is higher than for low atomic numbers, there is a higher fluorescent yield and the higher emitted energy is better at penetrating the surrounding tissue.

The XRF method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample, it is the 14 method of choice for field applications and industrial production for control of materials.

X-ray Fluorescence (XRF) device which used; is from Oxford instruments productions, this device named as X-strata-920, it works by exposing a

sample to be measured to a beam of primary X-rays. The atoms of the sample absorb energy from the x-rays, become temporarily excited and then emit secondary x-rays.

Each element emits x-ray at a unique energy. By measuring the intensity and characteristic energy of the emitted X-rays; an XRF analyzer can provide qualitative and quantitative analysis regarding the thickness and composition of the material being tested[14].

2-8 The XRF spectrometer

Spectrometer systems are generally divided into two main groups Energy dispersive system (EDXRF) and wavelength dispersive systems (WDXRF). The difference between the two systems is found in the detection systems. 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 the different directions [15].

2-9 XRF analysis

Qualitative analysis followed by Quantitative analysis. Qualitative Analysis determines which elements are present and their net intensities from the measured spectra.

2-10 interaction x-ray with matter

Electrons traveling from the filament (cathode) to the target (anode) convert a small percentage (1%) of their kinetic energy into x-ray photons by the

formation of bremsstrahlung and characteristic radiation. Bremsstrahlung radiation Bremsstrahlung interactions, the primary source of x-ray photons from an x-ray tube, are produced by the sudden stopping, breaking or slowing of high-speed electrons at the target.

When the electrons from the filament strike the tungsten target, x-ray photons are created if they either hit a target nucleus directly (rare) or their path takes them close to the nucleus. If a high-speed electron hits the nucleus of a target atom, all its kinetic energy is transformed into a single x-ray photon. (Total absorption has occurred). Thus, the energy of the resultant photon (keV) is numerically equal to the energy of the electron. This in turn is equal to the kilo voltage applied across the x-ray tube at the instant of its passage. This happens rarely.

Most high-speed electrons have near or wide misses with the nuclei. In these interactions, a negatively charged high-speed electron is attracted toward the positively charged nucleus and loses some of its velocity. This deceleration causes the electron to lose some kinetic energy, which is given off in the form of a photon. The closer the high-speed electron approaches the nuclei, the greater is the electrostatic attraction on the electron, the braking effect, and the greater the energy of the resulting Bremsstrahlung photon.

Bremsstrahlung interactions generate x-ray photons with a continuous spectrum of energy. The energy of an x-ray beam may be described by identifying the peak operating voltage in (kVp). A dental x-ray machine operating at a peak voltage of 70,000 volts (70 kVp) for example, applies a fluctuating voltage of as much as 70 kVp across the tube. This tube therefore produces x-ray photons with energies ranging to a maximum of 70,000 keV (70 keV). The reasons for this continuous spectrum are as follows:

1. The continuously varying voltage difference between the target and the filament, which is characteristic of half wave rectification, causes the electrons striking the target to have varying levels of kinetic energy.

2. Most electrons participate in many interactions before all their kinetic energy is expended.

As a consequence, an electron carries differing amounts of energy at the time of each interaction with a tungsten atom that results in the generation of an x-ray photon.

3. The bombarding electrons pass at varying distances around tungsten nuclei and are thus deflected to varying extents. As a result, they give up varying amounts of energy in the form of Bremsstrahlung photons.

4. Depth of generation of photons in the target [16].

Chapter three

Micro- Energy Diffraction x-ray Fluorescence (EDXRF)

3.1 Introduction

The analysis of gold karat alloys is a central function in manufacturing and distributing jewelry as well as brokering and refining related gold karat scrap. In particular, gold karat alloys containing large quantities of Au, Ag, and Pd, as well as base metals Cu, Ni, and Zn need to be accurately monitored and controlled. XRF is commonly used for elemental analysis of precious metals for such screening and production control purposes. Advances in spectral processing and quantitative fundamental parameter algorithms have expanded the usefulness of the proportional counter-based Micro-EDXRF spectrometer. This work presents a description of: basic XRF theory, a low cost proportional counter-based Micro-EDXRF spectrometer, analytical technique, and analysis data of gold karat alloys. Data is presented comparing fire assay versus Micro-EDXRF [6].

3-2 XRF Theory and Principles

Stokes Law defines fluorescence as a process in which an atom or molecule absorbs a photon of one energy and subsequently emits another photon of lower energy.

The specific fluorescence process on which XRF analysis is based is called the Photoelectric Effect. An orbital electron, usually of the K, L, or M shell is ejected from the atom after initial absorption of an incident photon of sufficient energy, leaving a 'vacancy' behind.

The vacancy is filled by another orbital electron from within the atom which 'jumps' down from a higher energy orbital. The difference in energy between the two involved orbitals is emitted as an X-Ray photon of electromagnetic radiation that is characteristic to that particular atom, Figure (3.1).

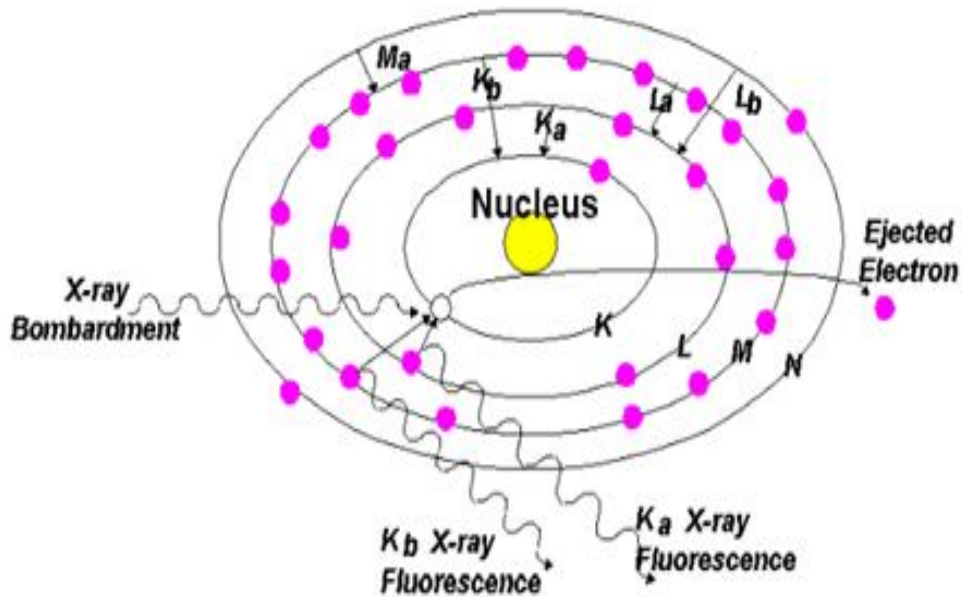


Fig (3.1) X-ray fluorescence: the photoelectric effect

Thus each element will fluoresce its own unique characteristic secondary X-Rays, or usually, a family of X-Ray lines when exposed to sufficiently energetic X-Ray radiation.

The intensity of the characteristic secondary X-Rays produced in the sample are related to the analyte concentration, the sample matrix, and excitation and detection conditions.

An example of a 14K yellow gold karat alloy X-Ray spectrum is shown in Figure 2, below. Note in this X-Ray Fluorescence spectrum, the number of photons, or intensity, is plotted on the Y-axis and the energy, in KeV units, of the photon is plotted on the X-axis.

This plot results in each element being represented by a peak, or group of peaks, which may or may not be totally resolved from one another.

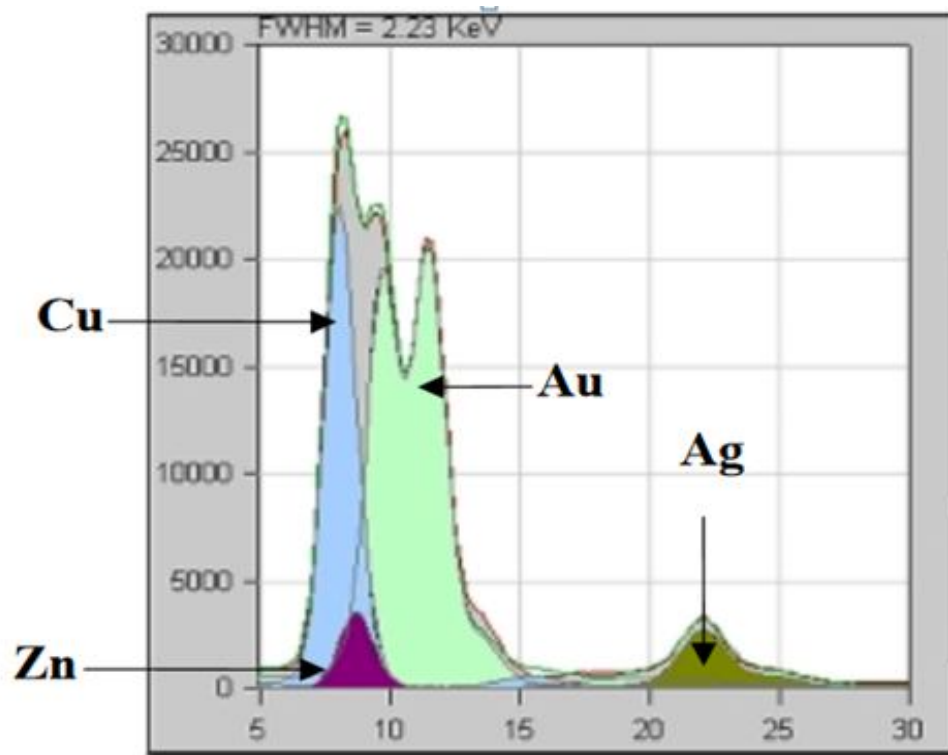


Fig (3.2) shows the spectra of data for different elements

Worth mentioning here, is the Gaussian statistical law that governs the precision, or repeatability, of XRF measurements. Precision should not be confused with accuracy, as they are two different parameters of the quality of the analysis. Accuracy pertains to the closeness to ‘true value’ and precision to repeatability.

The statistical index that quantifies repeatability is the ‘standard deviation’. When ‘N’ number of X-Rays are counted, or collected, during a measurement, then the uncertainty, or standard deviation, of the measured quantity ‘N’ is simply the square root of ‘N’. For example, if 100 Au X-Rays are collected during a measurement, then the standard deviation is 10 Au X-Rays. Thus, this measurement would have a 10% relative standard deviation. To improve the precision it would be necessary to collect more counts, which is usually done by increasing the measurement time, or further optimizing the other measurement conditions. See Table 1, below. Note that ultimately, it is not just the total number of counts, N, that matters, but also the peak-to-

background ratio of the analyte X-Ray intensities since the precision of the background intensities are propagated into the overall precision as well.

3-3 The Micro-EDXRF Spectrometer

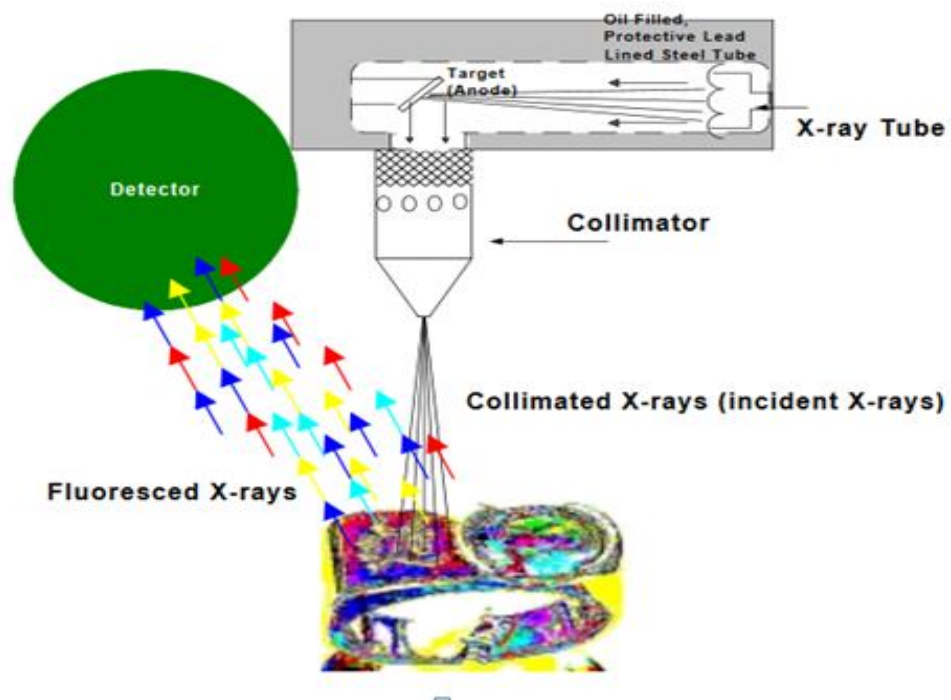
The basic ‘kernel’ of the Micro-EDXRF spectrometer is shown in Figure 3. A pin-hole fixture (“collimator”) typically 0.3mm in diameter, is used to collimate X-Rays from a 50KV micro focus X-Ray tube source onto the sample, which is placed below on a high precision motorized programmable 12”x 12”x 6” XYZ stage.

The stage serves to ‘raster’ the sample back and forth under the X-Ray beam to enhance uniform sampling, change measurement locations, or move a new sample into measurement position. Samples are observed on CCTV with an overlaid crosshair reticle that facilitates accurate and repeatable positioning of the primary X-Ray beam on the sample measurement site within 10 μ m.

The fluoresced X-Rays are captured with a 2” diameter cylindrical Xe-filled sealed gas proportional counter, also mounted above the sample. The X-Rays captured by the detector generate electric pulses in the gas that are amplified and sent to the computer to be processed by a multi-channel pulse height analyzer. The resulting X-Ray spectrum (Figure 3. 2) is treated with spectral processing algorithms and then interpreted quantitatively by an advanced comprehensive fundamental parameter algorithm. Results are displayed directly on the PC’s CRT, printed, or archived for statistical treatment.

In addition to quantitative bulk elemental analysis, the Micro EDXRF spectrometer, or ‘small spot XRF’, has the unique added dimension of analyzing the distribution of elements within a material. That is, it can ‘map’ the elemental uniformity of the sample by analyzing multiple areas with a small spot, or by scan-averaging large areas. Material uniformity is also important in understanding a manufacturing process in addition to just knowing the overall bulk material composition. For example, an entire casting tree can be analyzed at various points to ensure uniformity of Au distribution

from top to bottom in addition to overall bulk Au content. Figure (3.4) a Micro-EDXRF spectrometer.



Fig(3.3) shows Micro EDXRF optics



Fig(3.4) Micro-EDXRF spectrometer

3-4 Analytical Technique

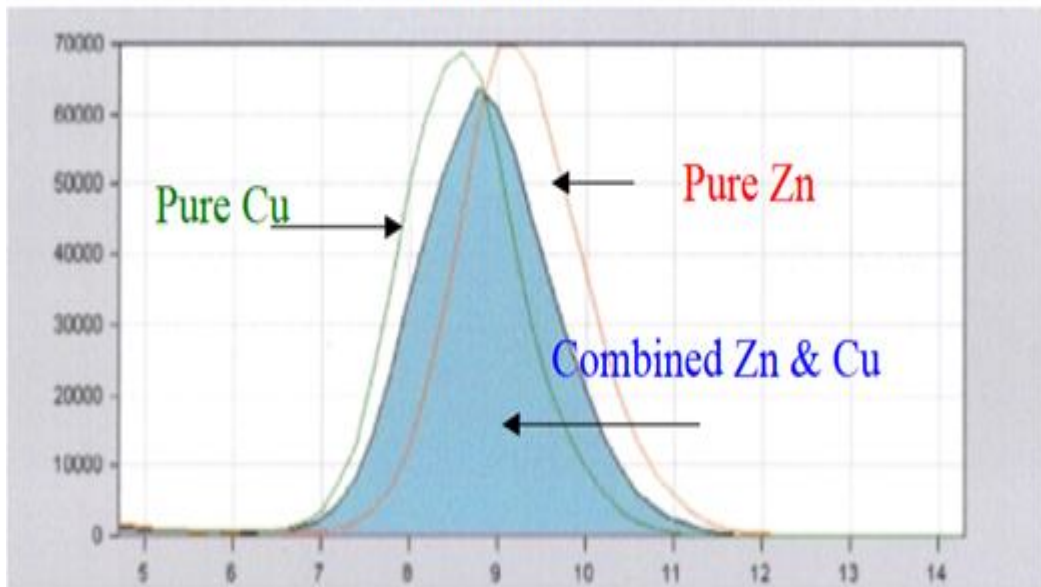
Spectral Processing With A Proportional Counter EDXRF:

Figure 2 shows the X-Ray spectrum of a yellow 14 Karat gold alloy containing Au, Ag, Zn, and Cu. Notice that the proportional counter spectrum is actually almost one continuous complex curve function wherein the constituent elemental peaks are sometimes not resolved one from another. It is necessary, then to further process the gross spectrum and deconvolute the overlapping signals from each element present. The resulting resolved element spectral peaks are also overlaid onto the gross spectrum in Figure 2. It is these separate net calculated peak intensities that are passed over to the fundamental parameter algorithm for quantification of elemental concentration. Any error in extraction of true peak intensities will cause subsequent error in the calculated elemental concentrations.

As mentioned above, the major challenge and limitation of the proportional counter is that the resulting spectrum typically involves the overlap of individual analyte peaks that must be resolved for accurate quantitative analysis. A simple example is shown in Figure of how the deconvolution of overlapping Cu and Zn spectra, two elements typically found in gold karat materials, using a linear fit approach is achieved.

In this technique, the individual spectrum of each pure element is measured and represented by a separate curve that can be described by a corresponding equation. The Zn-Cu sample's combined overlapped multi-element spectrum is also 'fit' to an equation after subtraction of background, and is the linear combination of the weighted individual pure element spectra, in this example Cu and Zn. Figure (3. 6).

Zn and Cu Spectra



Fig(3-5) show Zn-Cu separation

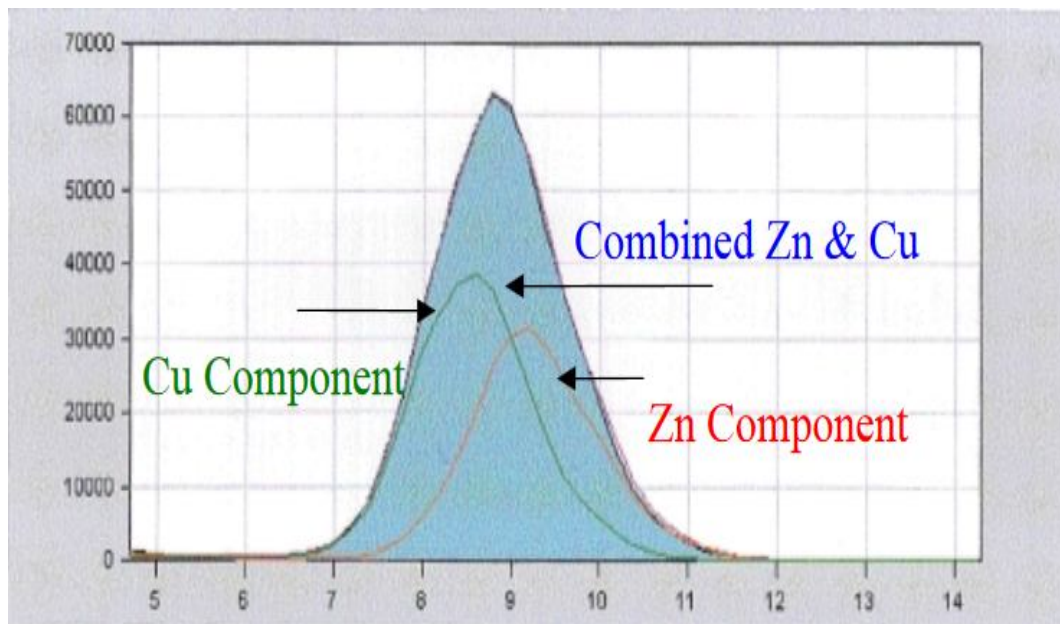
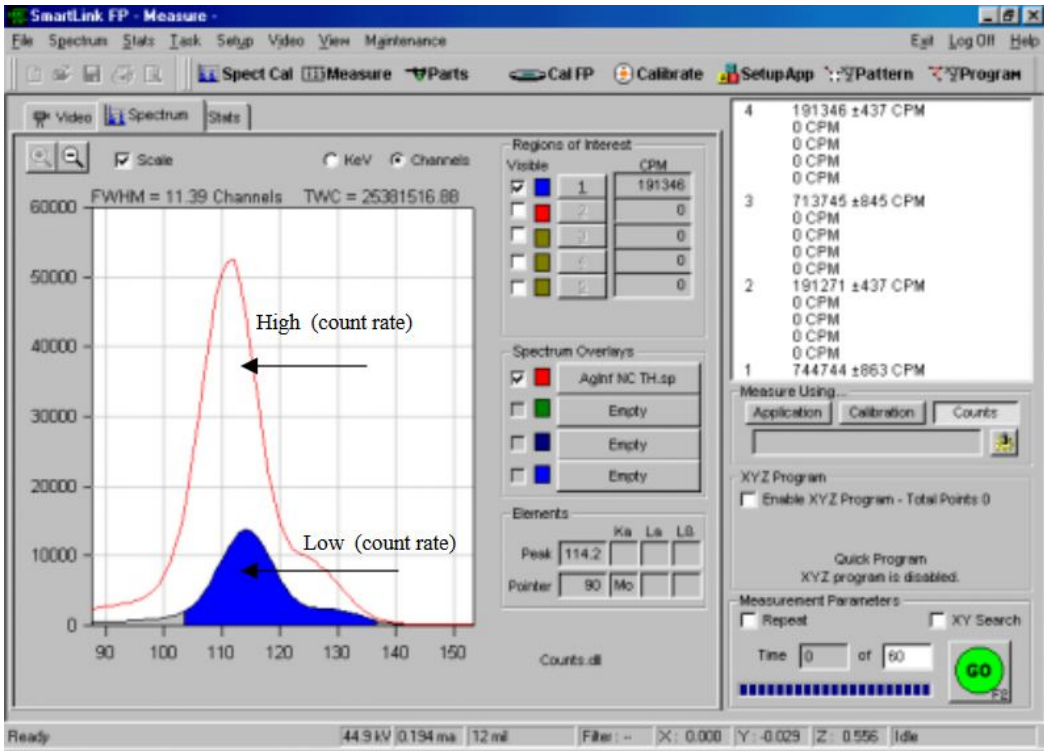


Fig (3- 6): Zn-Cu Spectrum: Linear Fit.

Thus, the complex gross spectrum can be effectively deconvoluted by solving for an appropriate linear fit of the combined individual analyte spectra of Zn and Cu. One must select, in advance, which elements to attempt to fit to the sample spectra when using this linear fit method. Additionally, background

models can be applied to the spectrum to remove background counts from the analyte intensity.

The linear fit model is effective only when the proportional counter's normal drift characteristics can be effectively accounted for. A major drift characteristic of this type of detector is count-rate-induced peak shift. That is, the location and shape of the peaks can change as the number, or rate, of the X-Rays processed increases or decreases, as is shown in Figure 7. To account for this, a complex peak shift algorithm is applied to all the spectra of the calibration standards and samples so that each spectrum is correctly processed to obtain true net intensity.



Fig(3- 7) Peak shift of pure silver spectrum at high and low intensities

This processing overcomes the proportional counter's typical resolution limitations and allows for analysis of more complex sample analyte combinations. The linear fit, peak shift, and background removal models expand and define the analytical capacity of the proportional counter well beyond what its intrinsic characteristics would normally allow.

In this application alone, overlapping elements Au-Cu-Ni-Zn, Ru-Rh-Pd-Ag, and even Pt-Au or Pt-Ir can be successfully separated and used.

3-5 Quantitative Analyses Using Fundamental Parameter

Fundamental Parameters, known as FP, is an atomic physics algorithm which theoretically describes the interaction between the X-Ray spectrometer and the sample analytics. It is the engine that basically interprets the processed X-Ray spectra into elemental composition and takes into consideration the physical parameters of the spectrometer, generation of primary X-Rays from the X-Ray tube, secondary fluorescent X-Ray production in the sample, inter-element matrix effects, and in some cases, detection of X-Rays. It has become more advanced and more popular in XRF instruments over the last 10-15 years and is now fairly commonplace, especially in high-end XRF spectrometers.

The incorporation of a complete and comprehensive FP program into a 'low-end' proportional counter-based Micro-EDXRF spectrometer is unique. This considerably simplifies operation and enhances the analytical range of the instrument to address more complicated sample matrixes with the use of fewer calibration reference materials. In fact, it is not necessary to use specific 'type-standards' at all for instrument calibration when using FP for screening applications, however, it is recommended for the high accuracy needed in the quantitative analysis of precious metals. Hence the analysis of complex matrixes of gold karat alloys, or other precious metals, theoretically involving up to 25 elements at once, can be achieved with relative speed and ease. It should be noted that, spectral processing techniques notwithstanding, the proportional counter is practically limited to less than 25 elements at one time. Gold karat alloys and scraps matrixes usually involve between 2-10 elements simultaneously which is favorable for this technique. Figure 8 shows an example of an FP calibration. Earlier classical empirical calibration curve models required large suites of standards to fully and accurately analyze the

sample. The number of standards required can be generally expressed as: $(N+2)^2$, where N is the number of elements to be analyzed and accounted for in the sample. Thus Analysis of Au, Ag, Cu, Zn, Ni would require 49 standards to completely develop a calibration that fully characterizes this sample matrix. Usually, this approach would be accurate for routine testing of a finite set of known materials and when copious amounts of reference standards are available.

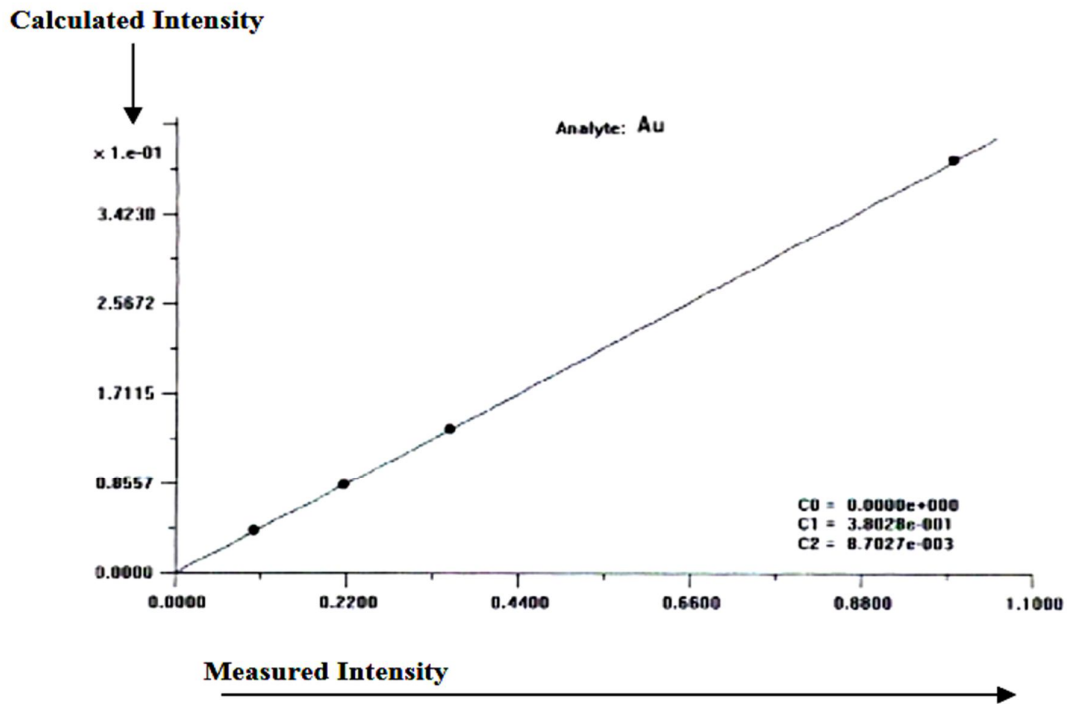


Fig (3-8): Example of Au FP Calibration Curve

The range of accuracy possible with this Micro-XRF technology, the relatively low product cost / maintenance, the ease of operation, the speed of analysis, and overall flexibility match up well to the analysis requirements and needs of jewelry production casting, karat screening of finished jewelry, and gold karat metal recovery operations. This has been made possible by advances in the comprehensive quantitative analysis FP engine, spectral processing techniques, hardware refinements, and methods development that have been infused into this basic Micro-EDXRF spectrometer [17].

Chapter Four

Practical work

4.1 Experimental method

After receipt silver species from silver smiths in a Sudanese standard and metrology organization so as to determine silver karat and sealing their pieces; we chose several specimens from both jewelry.

Jewelry samples were put in specialize envelopes in which their data recorded, also we made silver bullions ready to tolerate x-ray testing, small chunks were taken from the whole pieces by a cutter machine (Electric mini drill), they put in same envelopes and sent to x-ray laboratory to start testing.

Before x-ray start working, temperature and air moisture were registered by a digital thermo-hygrometer device, then we turned the device on and selected the application which can define the ratio of three elements, gold, silver and copper from the total ratio 1000 stocks.

Calibration operation started to make sure that results or reading values are exactly correct. Calibration were done in two steps, the first step is an internal calibration in which a pure specimen of silver and copper submitted to small-spot x-ray for 240 second, it's reading became as a standard reference. The second step is an intermediate check, here the measured standard which define karat was calibrated (usually we check a pure specimen of 90 silver karat which contain 900 stocks of silver ratio), calibration time for this intermediate check was 60 second. After calibration operation, X-ray producer device worked at first so as to give enough time to generate x-ray. Silver samples were putted on XRF device; and then we choose a flat smooth surface of the specimen to illuminate x-ray on it, the radiation direction was dropped by using a class two focus laser which use here as a direction controller, XRF radiation is induced when photons of sufficiently high energy, emitted from an x-ray source, impinge on a material. The

characteristic x-rays from each element including all transitions allows the identification of the element. Results displayed within seconds. The figure below shows the device used to find the karat of silver in Sudan stander metrology organization (Khartoum).



Fig (4-1) x-strata-920 XRF device

Table (4.1) : Results of Silver Rings Investigation.

Specimen type	Ag ratio	Cu ratio	Zn ratio	Silver karat type
Imported silver /Ring	923.9 ppt	59.9 ppt	7.2 ppt	925 silver karat
Imported silver /Ring	924.7 ppt	51.7 ppt	23.7ppt	925 silver karat
Imported silver /Ring	834.0ppt	148.0ppt	18.0ppt	800 silver karat
Imported silver /Ring	937.2ppt	43.6ppt	19.2ppt	925 silver karat
Imported silver /Ring	744.7ppt	201.2ppt	54.1ppt	600 silver karat
Imported silver /Ring	916.7ppt	57.6ppt	25.8ppt	900 silver karat
Imported silver /Ring	931.2ppt	36.1ppt	32.8ppt	925 silver karat
Imported silver /Ring	946.5ppt	46.3ppt	6.8ppt	925 silver karat
Imported silver /Ring	690.5ppt	255.6ppt	53.9ppt	600 silver karat
Imported silver /Ring	916.8ppt	58.5ppt	24.7ppt	900 silver karat
Imported silver /Ring	930.0ppt	31.3ppt	38.7ppt	925 silver karat
Imported silver /Ring	611.1ppt	355.7ppt	3.2ppt	600 silver karat
Imported silver/concatenate	947.8ppt	43.7ppt	8.5ppt	925 silver karat
Imported silver/pendant	928.8ppt	49.7ppt	21.7ppt	925 silver karat
Imported silver/pendant	971.1ppt	12.5ppt	16.4ppt	925 silver karat
Imported silver/throat	928.3ppt	49.1ppt	22.6ppt	925 silver karat

4.2 Conclusion

In this research the karat of silver has been investigated using micro –EDXRF and it revealed high accuracy in determination of the karat elements.

Reference

- 1- Mineral Commodity Profiles, W.C. Butter man and H.E. Hilliard,
S. Shankar, S. V. more, R. Seeta Laxman*, Division of Biochemical Sciences,
- 2- Recovery of Silver From Waste x-ray Film by Alkaline Protease from
Conidiobolus Coronatus, Kathmandu University Journal of Science,
Engineering and Technology vol. 6, no. i, march, 2010, pp 60-69.
- 3- Catalina Chiojdeanu, Daniela Cristea stan, Gold and Silver Coating
Characterization Using an X-ray Fluorescence Based Method – the case of
Archaeological Artifacts, p.o.box mg-6, ro-077125 . Bucharest-magurele,
Romania, bconst@nipne.ro received july 15, 2010.
- 4- K. V. Radha & C. Arun, Recycling of Exposed Photographic X-ray Films
and Recovery of Silver Using Bromelain, A. C. College of Technology, Anna
University, Chennai, India
- 5-Vaishali Choudhary, Recovery of Silver from used X-ray films by
Aspergillus versicolor protease, Volume 2, Issue 1 June 2013, Journal of
Academia and Industrial Research (JAIR)
- 6- <http://www.adhesiveandglue.com/destructivetesting>
- 7- Elizabeth M.Slyter, Henry S.Slyter, Light and Electron Microscopy
- 8- Cartz louis, Nondestructive Testing, 1995, asm international, isbn
9780871705174
- 9- C. leroy and P. Rancoita, Principles of Radiation Interaction in Matter and
Detection, 2nd edition, 2009, isbn 978-981-4470-89-6
- 10- C. Leroy and P. Rancoita, Principles of Radiation
- 11- <http://missionscience.nasa.gov/ems>

- 12- Production of X-rays and Interactions of X-rays with Matter, Goaz and Pharoah, Pages 11-20. Neill Serman
- 13- Clark, George I, Applied X-rays, 2nd edition, 1932, McGraw Hill Company 23
- 14- Goaz and Pharoah, Production of X-rays and Interactions of X-rays with Matter, Pages 11-20. Neill Serman
- 15- Charles Hellier, Handbook of Nondestructive Evaluation, McGraw-Hill, 2003, isbn 0-07-028121-1
- 16- Interaction in Matter and Detection, 2nd edition, 2009[17] X-strata-920 Brochure, Oxford instrument
- 17- Don Kloos, Analysis of Gold karat Alloys Using Proportional Counter Based MICRO- EDXRF, International Precious Metal Institute 24th International Precious Metal Conference, June 2000

Appendix



Fig (4-2) standard sample of silver

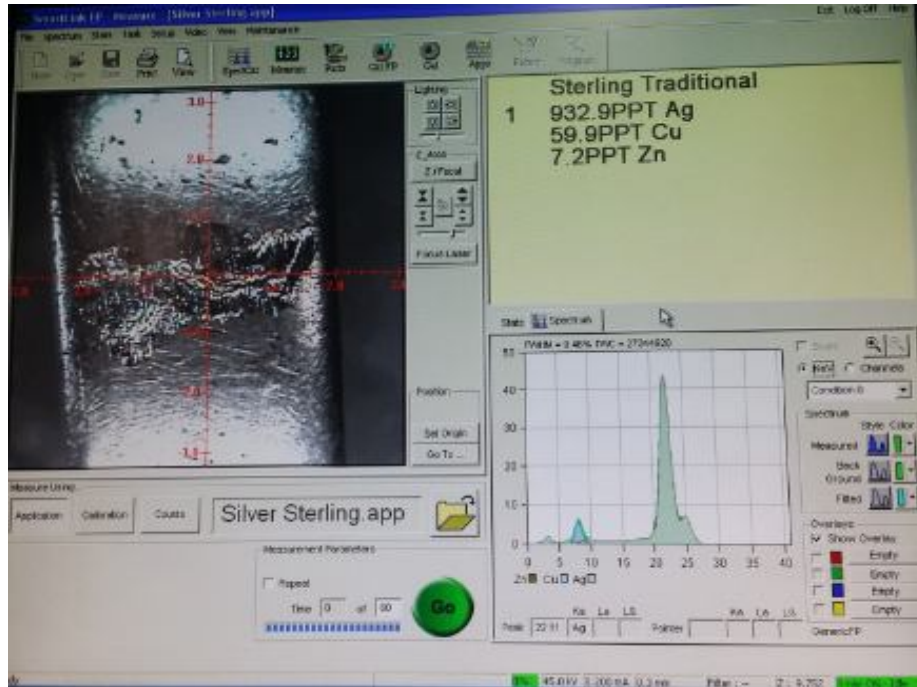


Fig (4-3) shift of silver sample spectrum at high and low intensities



(A)



(B)



(D)



(E)

Fig (4-4) samples of silver rings (A,B,D,E)



Fig (4-5) thermo hygro & clock

