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Use of X-Ray in Non Destructive Testing to determine gold karat

إستخدام الأشعة السينية في الكشف غير الاتلافي لتحديد قيراط الذهب

A thesis submitted for partial fulfillment for the Academic
Requirements of Master degree in General physics

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الآية

قال تعالى :

﴿ وَمَن يَعمَلْ سُوءًا أو يَظلِمْ نَفْسَهُ ثُمَّ
يَسْتَغْفِرِ اللهَ يَجِدِ اللهَ غَفُورًا رَّحِيمًا ﴾

سورة النساء
الآية 110

Dedication

To
✎ The Queen of my life: my mother
Fawzia Fadl-allah
Dear father **Albagir Aljaily**
Brothers: **Moied, Razan**
Family, Friends

By the grace of Allah then your believe on me
I progress on my study, complete my Master thesis
Thanks a lot

Acknowledgement

✎ I would like to express my appreciation and respect to Dr-Ahmed Elhasan Elfaki. He strives to help me succeed.

My humble thanks are due to all the staff in a Sudanese Standard and Metrology Organization (SSMO); from them I saw unlimited patience, unsparing guidance, and unfailing trust.

Abstract

The fire assay technique is the oldest and most reliable method used to determine gold karat, because of the destruction of gold into pieces and the long time which spent at analyzing; a well powerful for nondestructive analytical analyzer had took it place, it is x-ray fluorescence spectroscopy (XRF) that we used to analysis gold specimens. It is fast and accuracy technique, XRF can provide qualitative and quantitative analysis regarding the thickness of the tested material by measuring the intensity and characteristic energy of the emitted x-rays.

The present work explained the analyzing of eleven specimens of gold bullions and jewelry at XRF laboratory in Sudanese standard and metrology organization (SSMO). As a result of x-ray fluorescence analysis; only three alloys were observed in XRF spectrum of all gold samples, gold metal, silver and copper metal with different ratios which calculated by stocks instead of gram, a pure gold piece 24 karat includes 1000 stocks of gold, also three different gold karats were determined jewelry testing: 21 gold karat which contain about 875 stock of gold, 18 gold karat has 750 stock of gold, 14 gold karat has 580 stock. Alloys values were recorded for all specimens.

ملخص البحث

تقنية التحليل الناري من أقدم الطرق المستخدمة لتحليل الذهب ومعرفة عيار وكمية الذهب في العينة وهو ما يعرف بقيراط الذهب ، ونسبة لأن تلك التقنية تستغرق زمن طويل في عملية التحليل و تؤدي إلى إتلاف المعدن - بالرغم من دقة نتائجها- تحول الاتجاه في الآونةِ الأخيرة إلى إستخدام طرق التحليل الغير إتلافي للمواد وأبرزها في التعامل مع المعادن تقنية الفلورة بالأشعة السينية التي تعتمد في طريقة التحليل على قياس طاقة وشدة طيف فوتونات الأشعة السينية المنبعثة بعد اصطدامها بعينة المعدن .

في البحث الحاضر أُخذت ١١ عينة من الذهب في شكل سبائك ومشغولات ومن ثم حُللت بواسطة جهاز الأشعة السينية المتفلورة في معمل الأشعة السينية التابع للهيئة السودانية للمواصفات والمقاييس . لُوحظت شدة التداخل الطيفي للذهب مع العناصر المضافة (النحاس والفضة) و حُسبت نسب المعادن بالأسهم بدلاً عن الجرام حيث أن قطعة الذهب النقي ٢٤ قيراط تحوي ١٠٠٠ سهم من الذهب و صفر سهم من المضاف .أظهرت النتائج نسبة تركيز الذهب في عينات السبائك وحُددت ثلاثة أنواع مختلفة لعيارات الذهب في كشف المشغولات : قيراط ٢١ به ٨٧٥سهم من الذهب و١٢٥ سهم للعناصرِ مضافه، قيراط ١٨يحوي ٧٥٠سهم من الذهب، قيراط ١٤ يحوي ٥٨٠ سهم من الذهب .سُجلت نسبة المضاف من الفضة والنحاس لكل العينات .

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List of Symbols:

symbol	The meaning
A	Internal calibration disk (pure samples of Ag and Cu)
B	21 gold karat standard (pure sample)
C	Copper reading spectrum from standard disk
D	x-strata920 instrument with its appendix computer
E	Some samples of gold bullion chunks
F	Gold bullion chunks from x-strata920 camera, ready for dropping x-ray
G	Electric mini drill, use for furnishing jewelry samples before radiation, clamping container 3.2 mm
H	Thermo-hygrometer, to determine temperature and moisture degree
I	A bracelet picture, taken by xrf camera and x-ray focusing point
J	Samples of pure bullion bars
K	Samples of out-broad jewelry

Chapter One
Introduction

Chapter One

Introduction

1.1 Overview:

Material tests had known for a long time. Some are carried out to the specimen's failure, in order to understand structural performance or material behavior under different loads, this type of testing are called destructive physical analysis tests. They have many forms (stress tests bend, strike, hardness and crash tests).

Recently the other type of testing which is Non destructive testing (NDT) classified as an invasive technique, it plays an important role in assuring that structural and mechanical component perform their function in a safe, reliable and the cost-effective manner, with several ways which explicit in the first chapter.

This research present one of the major non destructive testing methods by using x-ray fluorescence which is a proven technique for material analysis in a broad range of industries and applications. The principle work of XRF is to get the incorporated element under investigation to fluoresce, where both the activating and the emitted light quantum, or photon, is in the X-ray energy spectrum. It is a well established and powerful tool for nondestructive elemental analysis of virtually any material. It is widely used for environmental, industrial, pharmaceutical, forensic, and scientific research applications to measure the concentration of elemental constituents.

As a consequence much thought and extensive research had been devoted to develop this method for analyzing the most precious mineral; gold, compare with being metal; it has a beautiful shine color, it attracted human specially women of all cultures and civilizations.

Precious metals, especially gold, silver, platinum; have been known to take on greater symbolic meaning and cultural significance by various groups throughout history. Looking beyond industrial and ornamental uses, these metals can take on unique traits, giving them purpose beyond their traditional uses.

Gold is the most popular as an investment; it has traded continuously throughout the world based on the intra-day spot price, derived from over the counter gold trading markets around the world (code “XAU”), according to the world gold council.

Gold is highly valued for many reasons but its physical properties are essential to the functioning of modern society. It is very soft [2.5 - 3.0 on the hardness scale] and is the most malleable and ductile of metals. This means it can be beaten into very thin sheets and drawn out into very thin wires. Gold does not readily form compounds and does not oxidize or tarnish. Only a mixture of hydrochloric acid and nitric acid, some cyanide solutions and mercury will dissolve gold under surface temperatures and pressures. All metals conduct heat and electricity; gold is no exception. In fact it is a better conductor than most metals. Silver is a better electrical conductor but gold is the metal of choice in mission-critical situations due to its ability to also resist corrosion. [1]

Because gold is so soft it is often alloyed with other metals in order to improve its durability, commonly it mixed with copper, platinum or silver. Gold alloys are rated using the 24 point karat system. 24 karat gold is pure (100% Au). In this humble research I had tested ten specimens of gold in two forms, bullions and jewelry; by oxford x-ray fluorescence instrument which called X-Strata920. The next pages explain fluorescence technique to test gold metal.

1.2 Research significance:

Since its first appearance; gold has been a symbol of wealth and power, it plays on dollar’s demise. Gold has fascinated most cultures around the world and the desire for it has led to the destruction of some cultures and the growth in status of others. The consumption of gold produced in the world is about 50% in jewelry, 40% in investments, and 10% in industry.

Gold has many uses, in electronics, as it conducts electricity and is ductile; gold is used for wiring in computers - from digital radios to microwaves, from telephone systems to rocket launchers! Gold is very useful for wiring that is difficult to repair, such as under water and in outer space, because it does not corrode or wear out quickly. Also as money gold has been used as coins since early times, but very few coins are made from gold today. More than half the world’s gold is stored by governments and banks. In medicine gold is used to replace or repair teeth and in the treatment of arthritis and other diseases. Lasers in industry and medicine use gold-coated reflectors to focus light energy. As gold is malleable and durable, it is often used to coat metal or glass objects. Small sheets of ‘gold leaf’ are often used for decorative letters, gilding book edges and picture frames, and to coat religious statues. [2]

Although pure gold (24 carat) is rarely used as it is too soft, gold is often mixed (alloyed) with other metals such as copper, silver or nickel for jewelry (18 carat gold means 18 parts gold and 6 parts other metals).

Pursuant to an exaggeration importance of gold as a metal; we used in the present papers to explain the quantity, kind of metal alloys by the most suitable technique to analyzing this costly mineral, it is x-ray fluorescence technique; which is a well powerful tool for nondestructive elemental analysis of virtually any element, its fast and accurate, treat with metal gently, easily differentiating between various gold karats.

1.3 Methodology:

X-Ray Fluorescence technique represented in oxford device X-strata920; was applied to test gold jewelry and gold bullion bars samples. Instrument calibration was occurred in two ways; internal calibration in which a pure specimen of specific alloy submitted to small-spot x-ray for 240 second. And intermediate check were done, here the measured standard which define karat was calibrated. Calibration time for an intermediate check was 60 second.

After calibration operation, gold samples had putted on XRF device; the radiation direction was dropped in a smooth flat part of a specimen by using a class two focus laser. Results displayed within seconds.

1.4 Layout of the research:

The present study shows use of x-ray fluorescence to calculate the identity of gold karat, metals ratio in ten samples of gold specimen clearly.

The first chapter explains research significance, methodology which employee. Chapter two shows material testing methods and their application in general. In the third chapter electromagnetic radiation and its spectrum, interaction of x-ray with matter are illustrated.

In chapter four; x-ray properties, generation, physics of fluorescence technique, and gold karat concept idea are brought up. In this work the last chapter records the results of experimental work and discussion.

Chapter Two
Material testing

Chapter Two

Material Testing

2.1 Testing in general:

Tests that show material property, quality, type, defect; had known beforehand. Generally it has two types; one of them is Destructive testing (DT) which may destroy the metal when it tested. The other type is Non Destructive Testing which permits testing the components without affecting their usefulness.

A general definition of non destructive testing (NDT) is an examination, test, or evaluation performed on any type of test object without changing or altering that object in any way, in order to determine object characteristics such as size; dimension; configuration; or an internal structure, including alloy content, hardness, grain size, etc.

Nondestructive testing or Non-destructive testing (NDT) is a wide group of analysis techniques used in science and industry to evaluate the properties of a material, component or system without causing damage. The terms Nondestructive examination (NDE), Nondestructive inspection (NDI), and Nondestructive evaluation are also commonly used to describe this technology. Because NDT does not permanently alter the article being inspected, it is a highly-valuable technique that can save both money and time in product evaluation, troubleshooting, and research.

Although NDT cannot guarantee that failures will not occur, it plays a significant role in minimizing the possibilities of failures. Other variables, such as inadequate design and improper application of the object, may contribute to failure even when NDT is appropriately applied. [3]

2.2 Destructive Tests:

To eliminate most of the risk in our environments, one of the ways in which we accomplish this is by testing thing. This principle applies to industries, too, in their quest to: assure safety, extend the useful life of their products and equipment and to maximize profits.

Destructive testing is defined as those tests that are made to a material through the use of tools or machines, which produce an irreversible alteration of their chemical composition or dimensional geometry.

Destructive tests (DT) carried out to the specimen failure, they performed on the piece to identify characteristics such as toughness, strength, ductility and hardness .some examples of destructive test is tensile test, hardness test, impact test and bend test.[4]

Advantages of destructive testing:

- Allows a roughly identify the mechanical properties of the adhesive joint (fracture strength, elongation, modulus of elasticity …)
- The mechanical properties can defined according to different types of stresses, efforts such as tension, compression, shear, peel, dynamic forces of impact.
- The costs of its equipment are cheaper compare with the equipment used in non destructive testing.

Although this technique has some benefits; it has more disadvantages, such as: when we used DT we cannot identifies internal defectology (bubbles, pores, wrong thickness …) of the real specimen, preventing repairs before being put in use on during their lifetime, not directly identifies the status of the adhesion area in the bonded joint. [5]

2.3 The Common NDT Methods:

NDT is divided into various methods, each based on a particular scientific principle. These methods may be further subdivided into various techniques. The various methods and techniques, due to their particular natures, may lend themselves especially well to certain applications and be of little or no value at all in other applications. Therefore choosing the right method and technique is an important part of the performance of NDT.

- Visual inspection (VT) :

  It used reflected light from test object that is imaged with the human eye or other light-sensing device.

- Ultrasonic testing (UT):

  High frequency sound pulses from a transducer propagate through test material. Ultrasonic testing has high-sensitivity results quickly; thickness information, depth (until 10 meters), and type of flaw can be obtained from one side to the component.

- Liquid penetrant testing (LT):

  A liquid containing visible or fluorescent dye is applied to the surface and enters discontinuities by capillary action.

- Radiographic testing (RT) :

  Radiographic film is exposed when radiation passes through the test object. Usually we use x-rays or gamma rays as a source of radiation.

- Magnetic particle testing (MT) :

  Magnetic particle testing has many advantages; relatively easy and materials are inexpensive and extremely sensitive. And some limitations like using only for surface defect; and for ferromagnetic material only.

- Eddy-current testing (ECT) :

  Localized electrical fields are induced into a conductive test specimen by electromagnetic induction. [4]

2.4 NDT Applications:

NDT has many applications all of them digested in an industrial field, engineering fields, nuclear reactors, pipes generally (petroleum pipes, airplanes, building).

NDT methods may rely upon use of electromagnetic radiation, sound, and inherent properties of materials to examine samples. This includes some kinds of microscopy to examine external surfaces in detail, although sample preparation techniques for metallographic, optical microscopy and electron microscopy are generally destructive as the surfaces must be made smooth through polishing or the sample must be electron transparent in thickness.

The inside of a sample can be examined with penetrating electromagnetic radiation, such as X-rays or 3D X-rays for volumetric inspection. Sound waves are utilized in the case of ultrasonic testing. Contrast between a defect and the bulk of the sample may be enhanced for visual examination by the unaided eye by using liquids to penetrate fatigue cracks. One method (liquid penetrant testing) involves using dyes, fluorescent or non-fluorescing, in fluids for non-magnetic materials, usually metals.

Another commonly used method for magnetic materials involves using a liquid suspension of fine iron particles applied to a part while it is in an externally applied magnetic field (magnetic-particle testing). Thermoelectric effect (or use of the Seebeck effect) uses thermal properties of an alloy to quickly and easily characterize many alloys. The chemical test, or chemical spot test method, utilizes application of sensitive chemicals that can indicate the presence of individual alloying elements. [4]

Chapter Three

Electromagnetic radiation

Chapter Three

Electromagnetic Radiation

3.1 Preface:

About 1890 the greatest English physicist James Clerk Maxwell found the experimental laws of electricity and Magnetism, Maxwell equations show the Electromagnetic waves properties which are produced whenever charge particles are accelerated. [6]. Since the mid-20th century, it has been understood that Maxwell equations are not exact laws of the universe, but are a classical approximation to the more accurate and fundamental theory of quantum electrodynamics.

Electrons moving with some frequency produce electromagnetic radiation, or radiant energy. This energy is associated with an electromagnetic field. Radiant energy of any frequency travels in a vacuum at $3 * 10^8$ meters per second, or 186,000 miles per second, this constant is known as the speed of light and is given the symbol c. Radiant energy can be thought of as a wave with a wavelength and frequency. The speed of a wave = frequency * wavelength.

As light passes from one medium to another it is refracted, or bent.

Light travels at different speeds in materials such as in water or glass. The ratio of these speeds is the index of refraction of the material n.

n = speed of light in a vacuum/speed of light in a material

Electromagnetic radiation is a phenomenon takes the form of self-propagating waves in a vacuum or in matter; it consists of electric and magnetic field components which oscillate in phase perpendicular to each other or to the direction of energy propagation. [7]

An explanation of electromagnetic radiation also requires the quantum model, which treats radiant energy as consisting of small packets of energy called photons.

The electromagnetic spectrum can be divided into types of radiant energy based on the wavelength or frequency of the radiation: radio waves, microwaves, infrared radiation, visible light, ultraviolet light, x–rays, and gamma rays. [6]

3.2 Electromagnetic Radiation Spectrum:

Electromagnetic radiation is reflected or absorbed mainly by several gases in the Earth’s atmosphere, among the most important being water vapor, carbon dioxide, and ozone.

Electromagnetic waves differ from mechanical waves in that they do not require a medium to propagate; they formed by the vibrations of electric and magnetic fields. These fields are perpendicular to one another in the direction the wave is traveling.

EM waves have some physical properties when interacted with matter (reflection, absorption, diffraction, scatter, refraction). They cover a wide range of frequencies or wave length and classified into:

- **Radio frequency waves:**

Radio waves have the longest wave length in the electromagnetic spectrum, ranging from a few kilometers down to 0.3m, and the frequency range is from a few Hz up to 10^9 Hz. These waves are used in television and radio broadcasting system; they are generated by electronic devices, mainly oscillating circuit, also used in nuclear techniques such as nuclear magnetic resonance imaging.

- **Micro waves:**

These waves have wave length range from 0.3m down to 10^{-3} m and from 10^9Hz up to $3 * 10^{11}$Hz as a frequency. They are used in radar and other communication systems, as well in the analysis of very fine details of atomic and molecular structure.

- **Infrared waves:**

Infrared region is subdivided into three areas, far infrared (its wave length from 10^{-3} m to 3 x 10^{-5} m), middle infrared (its range from 3 x 10^{-5} m to 3 x 10^{-6} m), and near infrared extending to about 7.8 x 10^{-7} m. Infrared waves produced by molecules and hot bodies whose atoms have been excited by thermal energy. Infrared spectrum has many applications in industry, medicine, astronomy field. A typical television remote control uses infrared energy at wave length around 940 nanometers. Infrared heat lamps emit both visible and infrared energy at wave length between 500nm to 3000nm. They can be used to heat the place or keep food warm.

- **Visible light spectrum:**

All electromagnetic radiation is light, but we can only see a small portion of this radiation called visible light, other portions of the EM spectrum have wave length too large or too small and energetic for the biological limitations of our perception.

Light is so important in optics, deal with vision phenomena, which is the result of the signal transmitted to the brain by the retina of eye. The wave lengths of light separate into the colors of the rainbow, each color has a different wave length and frequencies.

Table 1: the wave length and frequency of each color in the light

color	**Wave length/ m**	**Frequency/ Hz**
Violet	$3.9 – 4.5 * 10^{-7}$	$7.6 – 6.5 * 10^{14}$
Blue	$4.5 – 4.9 * 10^{-7}$	$6.5 – 6.1 * 10^{14}$

Green	4.9 – 5.7 * 10^{-7}	6.1 – 5.2 * 10^{14}
Yellow	5.7 – 5.9 * 10^{-7}	5.2 – 5.0 * 10^{14}
orange	5.9 – 6.2 * 10^{-7}	5.0 – 4.8 * 10^{14}
Red	6.2– 7.8 * 10^{-7}	4.8– 3.8 * 10^{14}

- **Ultra violet spectrum:**

This region covers from 3.8 * 10^{-7} m down to about 6 * 10^{-10} m, with frequency from 8 * 10^{14}Hz to 6 * 10^{14}Hz. These waves are produced by excited atoms and molecules as well as in electric discharge. The sun is very powerful source of the chemical effect of the ultraviolet radiation which is commonly subdivided into UV-A, UV-B, and UV-C. The last kind UV-C rays are the most harmful and are almost completely absorbed by the atmosphere. UV-B rays cause sunburn and also cause skin cancer. Ultraviolet rays are used usually in medical applications.

- **X-rays:**

X-rays have very small wave lengths, between 0.01 and 10nm, they are radiated by accelerated charged particles or bombarding matter with the inner electronic shells of atoms. X-rays can be detected by properly designed radiation counters.

- **Gamma rays:**

They have a shortest wave length, high frequency and high energy; include wave length less than 0.01nm. Gamma rays are produced by nuclear [8]

3.3 Atomic structure:

Atoms are made up from three basic particles, protons, neutrons and electrons. The nuclei of atoms contain protons and neutrons. Both of these particles have a mass about the same as a hydrogen atom. Neutrons have no charge. Electrons which are moving around the nucleus have a negative charge, they arranged in layers or shells at different distances from the nucleus. The mass of the electron is so small that it can be ignored when working out the total mass of the atom. The positions, masses and charges of these three sub-atomic particles are shown in the next table.

Table 2: properties of the three sub-atomic particles

particle	**Position**	**Mass (relative to a proton)**	**Charge**
proton	Nucleus	1	+1
Neutron	Nucleus	1	0
electron	Shells	1/1840	-1

Different atoms have different numbers of protons, neutrons and electrons. Atomic number equals number of protons and mass number is the number of the nucleus contents (protons and neutrons). The atoms of the same element with different masses are called isotopes; all the isotopes of one element have the same number of protons. Therefore, they have the same atomic number but different mass numbers. [9]

The typical length scale of nuclear physics is 1 fm (femtometer, Fermi) = 10^{-15} m. Nuclear radii can be measured with electron beams of about 10^8eV, proton radii with 10^9 ev.

The term “atomic spectroscopy” concern about interaction of light with matter, it use to describe those experiments which determine the decay products of excited states. In this way, one can study the properties of the excited states as well as the interactions between the constituents. “States” can be different nuclides (proton or neutron) or in hadrons physics different mesons or baryons. The energies required to produce excited states are similar to those for scattering experiments.

Atomic masses (actually, ionic masses) can be determined with high precision using mass spectrometers. Because the electron mass is know very precisely this allows to determine the mass of the concerned nucleus.

Energy can be emitted or absorbed matter only in small discrete units called quanta. Photons are particles which transmit light; in quantum mechanics each photon has different characteristic quantum of energy. The photon energy can be related to frequency or wavelength by the relation:

$$E = hc/\lambda = hf$$

Where

E = energy of a photon (joules)

h = is a proportionality constant = $6.63 * 10^{-34}$ joule sec

f = frequency (Hertz)

c = speed of the radiant energy = $3 * 10^{8}$ meters/sec in a vacuum

λ = wavelength (meters).

From these equation, the higher frequency or the shorter wavelength, are the higher energy of the photon. [10]

3.4 Radiation Interaction with matter:

The classical theory of electromagnetism deals with electric and magnetic fields and their interaction with each other and with charges and currents. The interaction of photons with matter involves several distinct processes. X-rays and gamma rays are both high-energy photons. In the energy range 1–100 kev, these photons are usually called X-rays and above 100 kev they are usually called gamma rays. The x-ray photons are either absorbed or scattered out of the beam. In scattering, photons are ejected out of the primary beam as a result of interactions with the orbital electrons of absorber atoms.

The main interactions of x-ray specifically with matter are:

- **Rayleigh or coherent scattering:**

When a photon interacts with atom, it may or may not impart some energy to it. The photon may be deflected with no energy transfer. This process is called Rayleigh scattering and is most probable for very low-energy photons.

- **Compton Effect:**

The Compton Effect is usually the predominant type of interaction for medium energy photons (0.3 to 3 Mev). Compton scattering is the elastic collision between a photon and an electron. In this process the photon interacts with an atomic electron sufficiently to eject it from orbit, the photon retains a portion of its original energy and continues moving in a new direction. Thus, the Compton Effect has an absorption component and scattering component. The amount of energy lost by the photon can be related to the angle at which the scattered photon travels relative to the original direction of travel.

The scattered photon will interact again, but since its energy has decreased, it becomes more probable that it will enter into a photoelectric or Rayleigh interaction. The free electron produced by the Compton process may be quite energetic and behave like a beta particle of similar energy, producing secondary ionization and excitation before coming to rest.

- **Photoelectric Effect:**

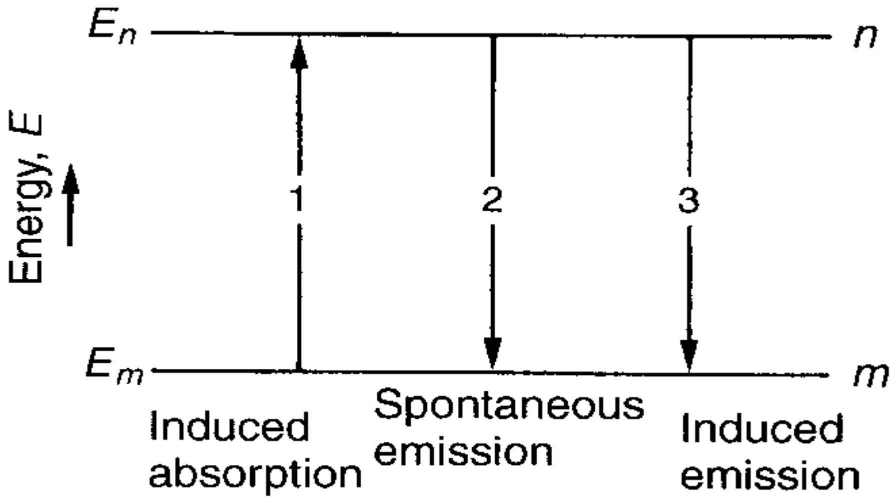
The most probable fate of a photon having energy slightly higher than the binding energy of atomic electrons is photoelectric absorption. In this process, the photon transfers all of its energy to the electron and its own existence terminates. The electron will escape its orbit with a kinetic energy equal to the difference between the photon energy and its own binding energy. Photoelectric absorption is most important for photons below 0.1 Mev if the absorbing medium is water or biological tissue. However, in high Z (atomic mass number) materials such as lead, this process is relatively important for photons up to about 1 Mev.

As with ionization produced by any process, secondary radiation are initiated, in this case, by the photoelectron which may have sufficient energy to produce additional ionization and excitation of orbital electrons.

- **Pair Production:**

Photons with energy greater than 1.024 Mev, under the influence of the electromagnetic field of a nucleus, may be converted into electron and positron. At least 1.024 Mev of photons energy are required for pair production, because the energy equivalent of the rest mass of the electron and positron is 0.51 Mev each. Pair production is not very probable, however, until the photon energy exceeds about 5 Mev. The available kinetic energy to be shared by the electron and the positron is the photon energy minus 1.02 Mev, or that energy needed to create the pair. The probability of pair production increases with Z of the absorber and with the photon energy. [11]

3.5 Absorption and Emission:



Every change in orbital by the electron corresponds to the absorption or emission of a quantum of radiation, as a resulting of increasing or decreasing energy.

A transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecules is called absorption. Atoms or molecules that are excited to high energy levels can decay to lower levels by emitting radiation (emission or luminescence). The figure above show the three physic processes of interactions. The states m and n of an atom or molecules which are stationary states; m refers to the lower energy level, and state n is a higher energy level. The three processes may occur when such a two-state system is subjected to radiation of frequency ν, or wave number ṽ, corresponding to the energy separation ΔE where

$$\Delta E = En - Em = h\nu = hc\tilde{\nu}$$

These processes are:

- **Induced Absorption:**

In which the molecular (or atom) M absorbs a quantum of radiation and is excited from m to n:

$$M + hc\tilde{\nu} \rightarrow \acute{M}$$

- **Spontaneous emission:**

Scattering or emission is the interaction between radiation and matter which causes the photon to change direction. Here Ḿ from n state spontaneously emits a quantum of radiation:

$$\acute{\mathrm{M}} \rightarrow M + hc\tilde{\mathrm{v}}$$

Almost all the emission that we encounter, such as that from tungsten filament lamp, is of the spontaneous type.

- **Induced or stimulated emission:**

This is a different type of emission process in which Ḿ stimulated and go from n to m, this process produce two photons, It happens when the electron already in the excited state (upper energy level). It represented as:

$$\acute{\mathrm{M}} + hc\tilde{\mathrm{v}} \rightarrow M + 2hc\tilde{\mathrm{v}}$$

A new photon which created in this manner has the same phase, frequency, direction of travel as the photon of the incident wave. Stimulated emission often uses in laser production. [12]

Chapter Four

X-ray fluorescence

Chapter Four

X-ray fluorescence

4.1 X-rays properties:

X-rays are form of electromagnetic radiation. They occur in the region of the electromagnetic Spectrum between 0.01nm & 10nm 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 Röntgen, who received the first Nobel Prize in Physics in 1901. By 1912 the principles of diffraction physics and reciprocal space were developed by Rontgen,Von Laue, Ewald and Sommerfed.

Named as x-rays by Roentgen because their nature was unknown at that time, unlike ordinary light, x-rays are invisible, they travel in straight 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.

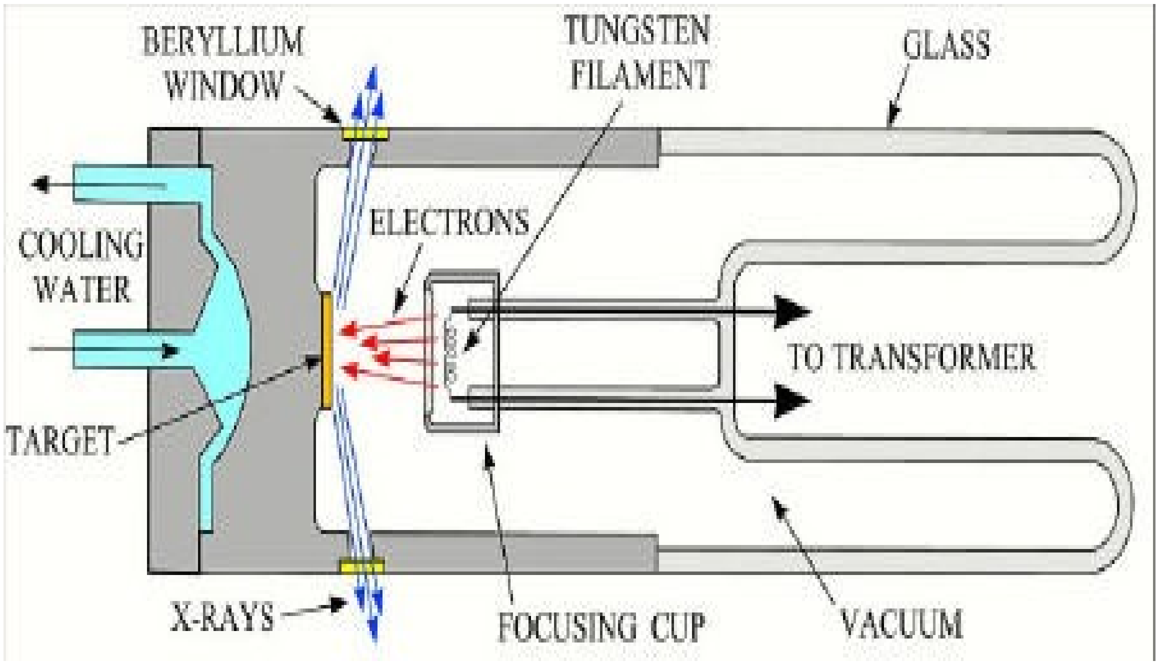
X-rays emitted by sudden stoppage of the fast moving electrons. It can also be scattered with and without losing part of their energy (coherent or Raleigh-scatter and incoherent or Compton - scatter).When an electron from the inner shell of an atom is lost due to some sort of excitation, it is replaced 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). [13]

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 material produces a number of electrons. [14]

4.2 Generation of x-ray:

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



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. [14]

- **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 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.

- **Characteristic Radiation:**

This radiation occurs when an electron from the filament displaces an electron from an inner-shell of the tungsten target atom, thereby ionizing the atom. When this happens, another electron in an outer-shell of the 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. 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]

4.3 Physics of x-ray Fluorescence:

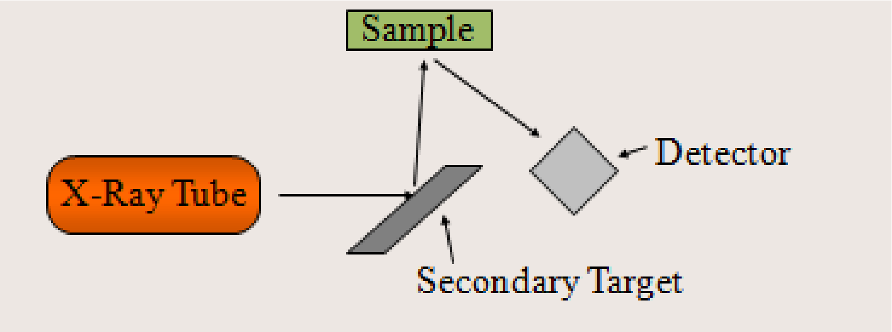
The name florescence was derived from the mineral fluorite (calcium difluoride). Fluorescence occurs when an orbital electron of a molecule, atom or nanostructure relaxes to its ground state by emitting a photon of light after being excited to a higher quantum state by some type of energy. The atom emits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

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. [15]

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.



On this basis XRF-analysis is possible because:

- The wavelength and energy of the Fluorescence radiation is specific for each element.
- The concentration of each element can be calculated 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.

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 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. 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. [16]

4.4 X-ray Fluorescence instrument:

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. 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 method of choice for field applications and industrial production for control of materials.

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.

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 off the emitted x-rays; an XRF analyzer can provide qualitative and quantitative analysis regarding the thickness and composition of the material being tested.

X-strata-920 is a non destructive analyzer present rapid analysis of solids. It generally used for jewelry and alloys analysis in which it present precious metal alloy assay, karat analysis and material identification. This device contains Powerful Smart-link software with pre-loaded calibration parameters for easy setup. The next picture shows x-strata-920 with its annex computer.

X-strata-920 XRF device

The device analyze up to three layers, top layer Au (gold coating thickness), second layer Ag (silver coating thickness), the third layer Cu (copper coating thickness). It may analysis more layers such as palladium, platinum, nickel; if we have the identity standard disc of the required measurement. [17]

4.5 Gold karat:

Gold is a chemical element with symbol Au and atomic number 79 makes it one of the higher atomic number elements that occur by nature effect. The metal therefore occurs often in free elemental (native) form, as nuggets or grains, in rocks, veins and in alluvial deposits. It's the most malleable of all metals. The melting point of gold is ~ 1064°Cand it boils to a vapor at 2856°C. Gold is a very dense material. It has a specific gravity or density of 19.3. This means 1cm3 weighs 19.3 grams while 1cm3 of water only weighs 1 gram. [1]
The largest gold nugget ever found was the 'Welcome Stranger', found in 1869 just under the soil at the base of a tree! It weighed 70 kg and on today's value would be worth over 1 million dollars.

Because of the softness of pure gold; it is usually alloyed with base metals for use in jewelry, altering its hardness and ductility, melting point, color and other properties. Alloys with lower carat rating, contain high percentages of other metals (copper, silver, zinc, lead…etc). Gold colors depend on alloys ratio in the specific chunk. Yellow, red, pink and white are the basic gold colors. [18]

Gold in Sudan are found in schist rocks shape in the east and southern areas, and as a sedimentary shape near the expanding of the Nile River. Gold weight is measured in karat. The number of karats in a piece of gold indicates the percentages of pure gold in the piece. Pure gold is designed as 24 k; it is seen only in bullion bars, 24 karat gold equals 1000 gram or 1000 stocks of pure gold in jeweler's idiom; if gold ratio is less than 1000 stocks that mean the gold is not pure. Gold is an extremely soft metal which loses particles if used or handled a lot, so other metals have to be added to strengthen it before it can be made into jewelry or coins, usually we need to add silver or copper to harden and toughen it. Gold jewelry alloyed with copper has a slightly redder tint. The famous and canonical types of gold karats in Sudanese standard and metrology organization are:

- 24 karat gold covers a highest ratio of gold; it's valued at around 999. 9 gram from the total quantity 1000 stocks.

- 21 karat gold contains 875 stocks or grams of Au, the remaining stocks are copper, silver or zinc or other minerals. Most high quality gold jewelry is made of 21 karat gold.
- 18 karat gold contains about 750 stocks; it has a different color than 21 karat because gold ratio is less. Most rose gold and pink gold is also18 karat.
- 14 karat gold contains about 583 stocks or grams and the remaining stocks are another metal.
- 9 karat gold has a lowest percentage of gold reach to less than 400 grams in a kilo gram; this is a cheapest type of gold jewelry. If the other metal in the alloy is copper, it will look a dull bronze color and if it is silver it will look white gold color. [19]

The purity of gold could be estimated by using a touchstone but the only effective way of determining the purity of silver was by assaying.

Whatever their purity, much gold and silver had to be refined before use or re-use as they were often significantly debased.

The process known as cupellation was used to separate precious metals from base ones, while silver was separated from gold by parting. In cupellation the metal to be refined was melted with an excess of lead which was oxidized, forming litharge (lead oxide) which dissolved any base metals present, separating them from the silver or gold.

Small scale cupellation or fire assaying (testing the purity of a sample of precious metal) was carried out on small shallow dishes or discs known as tests.

The general method of assaying gold bullion is by cupellation and parting. First, a preliminary analysis to determine the approximate composition of the bullion is required. Then sample portions are weighed, and wrapped in a predetermined amount of lead foil, lead is used as a collector, the lead oxidizes and is absorbed into the cupel in a high temperature leaving a precious metal bead. The bead is then dissolved in aqua regia (HCl: HNO3 solution in volume ratio of 3:1) for analysis by a chemical way. Fire assay method guarantee high accuracy in karat calculation, but due to the long time in measuring; we prefer to use x-ray analysis. The next chapter explains an experimental detail of testing gold. [20]

Chapter Five

Practical work

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Practical work

5.1 Experimental method:

After receipt gold species from goldsmiths in a Sudanese standard and metrology organization so as to determine gold karat and sealing their pieces; we chose several specimens from both jewelry and bullions. Jewelry samples were put in specialize envelopes in which their data recorded, also we made gold 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 21 gold karat which contain 875 stocks of gold 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. gold 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.

5.2 The results:

[1] Jewelry testing:

specimen type	**Au ratio**	**Ag ratio**	**Cu ratio**	**Gold karat type**
Imported gold/bracelet	893.6	5.0	101.4	21 gold karat
Imported gold/pink/ ring	877.0	21.2	101.8	21 gold karat
Imported gold/ ring	851.8	16.2	132.0	18 gold karat
Local gold/necklace	584.3	126.2	289.5	14 gold karat
Local gold/necklace	886.0	4.7	109.3	21 gold karat
Local gold/bracelet	822.1	33.6	144.4	18 gold karat

[2] Gold Bullions testing:

specimen type	**Au ratio**	**Ag ratio**	**Cu ratio**

Local gold/pure	999.9	0.0	0.0
Local gold	885.5	111.0	3.5
Local gold	912.8	82.9	4.3
Local gold	900.0	97.8	2.2
Local gold	873.4	121.3	5.4

5.3 Conclusion:

XRF can be successfully utilized for analyzing materials which contain gold, particularly jewelry. Jewelry testing results explained gold, silver and copper ratio which were found in six pieces with different ratios. Imported gold always characterized by an accurate industrialization and homogeneity shape because they have high instrument capability.

It is being noted that the karats which known are 14 gold karat (58.4% of Au), 18 gold karat (contain 85.1% of Au), 21 gold karat specimens (contain 89.3%, 87.7% and 88.6% of Au). Copper and silver ratio specifies gold color, yellow and pink gold, red gold, and white gold. In jewelry results we noticed that copper ratio is higher than silver ratio in different jewelry karats, because of the cheap prize which copper possess, and its color (near to gold); jewelers generally used plenty of it in jewelry.

Gold bullion results showed elements ratio in five chunks, one of them is pure gold bullion didn't contain alloys, the other bullions had high gold ratios. Goldsmiths concern about gold quantity in the bullion to re-create it by adding alloys until gold ratio reach to the closer karat of jewelry.

5.4 Discussion:

X-ray fluorescence method saves wasting time, it shows testing results in 60 seconds only and allows to analysis around a hundred samples alternately.

XRF proved to be a simple, fast, non-destructive and reliable method for the analysis of alloys. It should be put in mind that XRF is unable to see deep inside a metallic sample due to absorption and it doesn’t characterize element isotopes from each other, it will give one analytical result.

5.5 Recommendation:

Application selection in x-strata920 device depends on the kinds of standard reference disks also accuracy of the results depends greatly on the reliability of the standards test.

In this experiment we used two standard references which include two pure samples of alloys; silver and copper. If there is another alloy in the testing sample, as example: platinum, nickel, zinc….etc; the computer will not define it, its value will join to gold ratio spontaneously and increase it, this will affect on karat kind accuracy.

To solve this problem we must possess at least the most adhesion alloys reference disks which are usually neglected, although its high cost (one alloy disk worth about 500 dollars); so as to comply accuracy results in calculating gold karat value.

References:

[1] Neville F.Mott, H.Jones, The Theory of the Properties of Metals and Alloys, 1958

[2] Danielle Leiner, The cultural significance of precious metal, 2012

[3] Cartz Louis, Nondestructive testing, 1995, ASM International.

[4] Charles Hellier, Handbook of Non destructive Evaluation, McGraw-Hill, 2003

[5] http://www.adhesiveandglue.com/destructivetesting

[6] Marcelo Alonso, Edward J. finn, physics, 2003

[7] David J Griffiths, Introduction to Electrodynamics, third edition, 1999

[8] http://missionscience.nasa.gov/ems

[9] Graham Hill, Chemistry Count, 1986

[10] Kenneth S-Krane, Introductory Nuclear physics, 3th edition

[11] C. Leroy and P. Rancoita, Principles of radiation interaction in matter and detection, 2nd Edition, 2009

[12] Elizabeth M.Slyter, Henry S.Slyter, Light and Electron Microscopy

[13] Clark, George l, Applied x-rays, 2nd Edition, 1932, McGraw Hill company

[14] Goaz and Pharoah, Production of X-rays and Interactions of X-rays with Matter, Pages 11-20. Neill Serman

[15] Reinhold Klockenkamper, Total Reflection X-ray fluorescence analysis.

[16] Lakowicz Joseph R, Principle of Fluorescence spectroscopy, 1999, 2nd Edition

[17] X-strata-920 Brochure, Oxford Instrument

[18] Inlide, D.R,Ed, Handbook of chemistry and physics, 2005

[19] Sudanese standard and metrology organization library

[20] Bayley,J, 1995. Precious Metal Refining, in historical Metallurgy society. Datasheets: http://hist-met.org/hmsdatasheet02.pdf (accessed january13, 2010)

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Appendix

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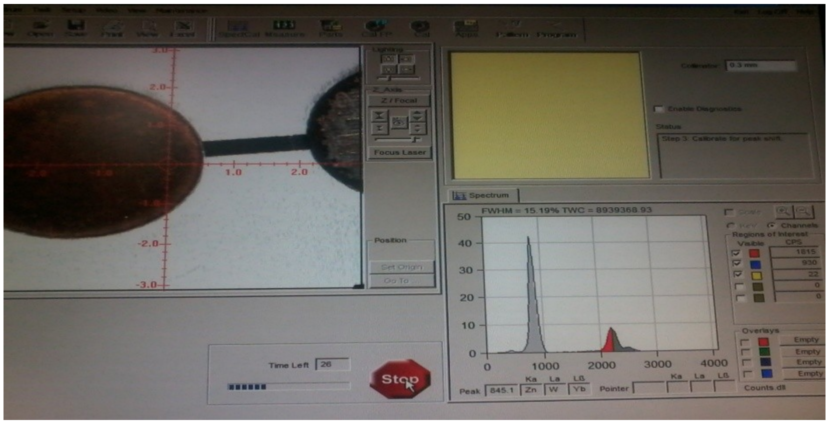

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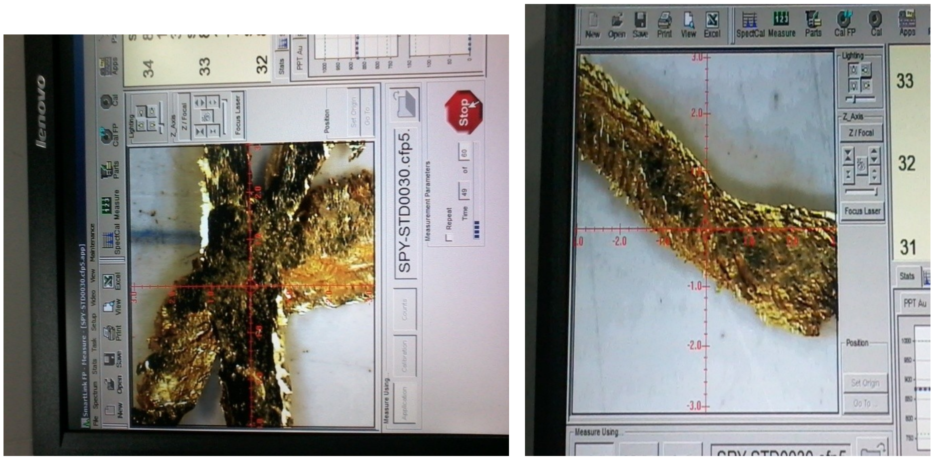
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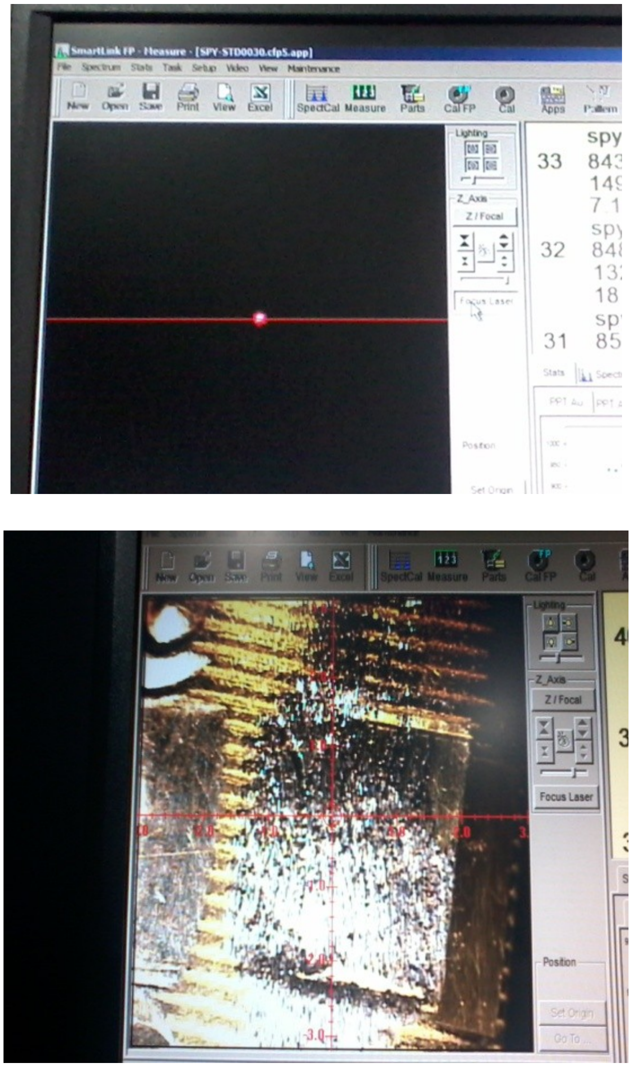
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