Sudan University of Science and Technology
College of Graduate Studies

Elemental Analysis of Scalp Hair Samples from Workers in the Industrial Area of Omdurman by using Spectroscopic Techniques

تحليل العناصر لعينات شعر فروة الرأس لعمال منطقة أم درمان الصناعية باستخدام تقنيات الأطياف

A Thesis Submitted in Fulfillment of the Requirement for
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by

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بسم الله الرحمن الرحيم

قَالَ تَعَالَىٰ:

﴿فَتَعَٰلَى ٱللَّهُ ٱلۡمَلِكُ ٱلۡحَقُّۗ وَلَا تَعۡجَلۡ بِٱلۡقُرۡءَانِ مِن قَبۡلِ أَن يُقۡضَىٰٓ إِلَيۡكَ وَحۡيُهُۥۖ
وَقُل رَّبِّ زِدۡنِي عِلۡمٗا ١١٤﴾

صدق الله العظيم

سورة طه: ١١٤

DEDICATION

I dedicate this work

to the soul of my late father,

to my beloved mother,

to my brothers and sisters,

to colleagues in the dependent,

and to all those who offered me advice and help.

Mariam

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ABSTRACT

In this study, scalp hair samples were collected from workers working in workshops and perfume factories in Omdurman area where there is an expectation of exposure to environmental pollution. The hairs content determination was performed using X-ray fluorescence (XRF), Laser-Induced Breakdown Spectroscopy (LIBS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICPE) to assess elements (Mn, Cu, Zn, Hg, Pb, Sr and Fe) due to the adoption of hair tissue scalp as a biological indicator of toxic elements in the human body. An alternative approach of hair sample treatment was implemented by grinding in liquid nitrogen at temperature of 77^{o}K to form a dry weight samples in fine powder mode. In a comprehensive assessment the results have been compared with the results of International Atomic Energy Agency (IAEA) as a reference value. Data obtained by using three ways: (XRF), (LIBS) and (ICPE) to make sure the values extracted from this study for contributions to the analysis of pollution factors resulting from work in industrial areas. The percentage of manganese Mn contamination was high in each of the samples (No:11, No:18 and No:C9), as the sample No:11 average concentration 15.499 ppm, the sample No:18 average concentration 13.31 ppm and the sample No: C9 average concentration 12.47 ppm, while the reference value equals 9.6 ppm. The pollution by copper Cu was top on the sample No: 12 with an average value of 56.43 ppm, while the reference value is 17.6 ppm. The zinc Zn component was highest in the sample No:18 with an average value 370.3 ppm, while the reference value equals167 ppm. The pollution by mercury Hg was top on the sample No: 12 with an average value of 39.36 ppm. The largest proportion was enough strontium Sr component of pollution category No:18 with an average 7.364 ppm, while the reference value equals 4.97 ppm. The pollution by iron Fe was top on the sample No: B24 has an average value of 205.14 ppm, while the reference value equals 123ppm.

The study concluded that most of the samples were suffering from pollution from industrial areas selected elements in a clear disparity. The study shows that the concentrations are nearly similar in all techniques, which results from the burning technique which get rid of light elements. The highest concentrations for (Mn, Cu, Zn, Hg and Fe) are found in XRF, while the highest concentration for Pb and Sr are in LIBS. This study recommended expanding the study to include more other groups working in the workshops of other ages for more accurate information processing. The study also recommends examining the impact of the work time on increasing pollution.

المستخلص

في هذه الدراسة تم جمع عينات شعر فروة الرأس من العمال الذين يعملون في ورش الصناعة ومصانع العطور فى منطقة أم درمان لتوقع التعرض للتلوث البيئي. تم إجراء تحديد محتوى الشعر باستخدام توهج الاشعة السينية (XRF) ومطيافية أنهيار البلازما بالليزر (LIBS) و مطيافية الانبعاث الذرى للبلازما المقترنة بالحث (ICPE) لتقييم عناصر (المنجنيز ، النحاس، الزنك، الزئبق، الرصاص، الاسترنشيوم والحديد) باعتماد نسيج شعر فروة الرأس كمؤشر أحيائى للعناصر السامة في جسم الإنسان . و تم تطبيق نهج بديل لعلاج عينة الشعر بطحنها في النيتروجين السائل عند درجة حرارة 77 درجة كلفن لتشكيل عينات الوزن الجاف في شكل مسحوق ناعم.في تقييم شامل لْلنتائج تمت مقارنتها مع نتائج الوكالة الدولية للطاقة الذرية كقيمة مرجعية .البيانات أستخدمت ثلاثة طرق (XRF) و(LIBS) و(ICP) للتأكد من القيم المستخرجة من هذه الدراسة للمساهمات في تحليل عوامل التلوث الناتجة من العمل في المناطق الصناعية . وكانت نسبة التلوث بعنصر المنجنيز عالية لكل من العينات (No:11 وNo:18 وNo:C9) حيث بلغت متوسط 15.499 ppm للعينة No:11 و 13.31 ppm للعينة No:18 و 12.47 ppm للعينة No:C9، بينما القيمة المرجعية تساوى 9.6 ppm. نسبة التلوث بواسطة النحاس كانت أعلي عند العينة No: 12 بقيمة متوسطة 56.43 ppm، بينما القيمة المرجعية هي 17.6 ppm . عنصر الزنك كانت أعلي قيمة عند العينة N:18 بنسبة متوسطة 370.3 ppm بينما القيمة المرجعية تساوي 167ppm.كانت نسبة التلوث بواسطة عنصر الزئبق أعلي عند العينة No: 12 بقيمة متوسطة 39.36 ppm . فى عنصر الأسترنشيوم كانت أكبر نسبة تلوث من نصيب الفئة No:18 حيث بلغت متوسط 7.364 ppm، بينما القيمة المرجعية هي 4.97 ppm. كانت نسبة التلوث بواسطة الحديد أعلي عند العينة No:B24 بقيمة متوسطة 205.14 ppm، بينما القيمة المرجعية تساوى 123 ppm . أوضحت الدراسة تقارب نسب التركيز المتحصل عليها فى كل التقنيات وذلك بفضل تقنية الحرق التى تتخلص من العناصر الخفيفة. وقد سجلت تقنية (XRF) أعلى تركيز لعناصر (المنجنيز ، النحاس، الزنك، الزئبق والحديد)، بينما سجلت تقنية (LIBS) أعلى تركيز لعناصر الرصاص والاسترنشيوم .خلصت الدراسة أن معظم العينات كانت تعاني من التلوث الناتج من العمل في المناطق الصناعية بالعناصر المحددة في الدراسة بتفاوت واضح. أوصت هذه الدراسة بتوسيع الدراسة بحيث تشمل عدد أكبر وفئات أخري تعمل في الورش بأعمار أخري لزيادة دقة المعلومات المعالجة .كما توصي الدراسة بدراسة أثر الفترة الزمنية للعمل في زيادة التلوث.

CHAPTER ONE

INTRODUCTION

CHAPTER ONE

INTRODUCTION

1.1 Contamination detection Techniques:

Hair is extra product of human tissue that reflects elements of metabolism in the body and become a subject of interest to environmental and biomedical sciences. Thus, element concentrations in hair are reflection of the levels in other tissues. Moreover, the elements in hair can be absorbed from the environment over historical time, which reflects the impact of accumulation of the trace elements in the body (Abdulrahman et al., 2012). The levels of elements in human hair are important implications that serve as a useful biochemical index for assessing elements the burden in human body. Hence, trace element concentrations in scalp hair are affected by various factors such as environmental exposure, foods, gender and geographical location. The determination of impact of substances in blood and urine, hair and other specimens in people relative to exposure to environmental contamination is known as human bio-monitoring. Human bio-monitoring is defined as the approach to measure the chemical substances or their metabolites in biological tissues and to identify the relation between element exposure to contamination sources and disease (Abdelrazig et al., 2013).

The bio-monitoring of hair assessment has the advantage of detecting element variation representing the long-term historical exposure trend and recent exposure of the individuals when compared to urine and blood engaged to observe the current element status of the human body. Also, many trace elements accumulate in hair at concentrations at least ten times higher than in blood serum or urine. Hair is widely accepted for many advantages to evaluate the relation between essential elements in body burden and disease. In addition to its potential as a biomarker, the analysis of hair samples has several advantages. The primary component of hair is the protein keratin, which makes it stable and robust (Gellein et al., 2008).

Therefore, scalp hair is one of the easier samples to be collected at low cost, which facilitates the storage and transport processes that offer several advantages for analysis including matrix stability in the human body (Abdelrazig et al., 2013). Moreover, the elements concentrations are at higher levels in hair, so that accurate results of analysis can be obtained (Dean et al., 2001). The main disadvantage of hair samples as a bio-indicator is the difficulty in differentiating between external and internal exposure. So that, pollutants from exogenous sources, such as aerosol, water and detergents, can also adhere to the hair. The scalp hair analysis, investigation has improved the analytical considerations and limitations of heavy metals in a variety of environmental health, which is related to the broad spectrum of pollution, occupational exposure and the geographical distribution of contaminated regions (Gellein et al., 2008) (Amarteyet al., 2011). Additionally, hair grows; structure included trace elements that are separated from the metabolic activity of the body, which is influenced by numerous internal and external factors. However, the trace element content of hair is used as an indicator for screening population groups as well as individuals exposed to environmental contaminants and in internal chemical variations in human body balances.

The former most frequently techniques used for analyzing scalp hair included atomic absorption spectrometry (AAS), neutron activation analysis (NAA), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and to a lesser extent X-ray fluorescence (XRF), isotopic dilution mass spectrometry (IDMS), graphite furnace atomic absorption spectrometry (GFAAS) and proton-induced X-ray emission (PIXE)(Linn Johansson, 2011) .Since the mid-90s inductively coupled plasma mass spectroscopy (ICP-MS) has been used by the majority of commercial clinical laboratories. ICP-MS has the advantage of detecting trace element levels at lower levels than its precursor ICP-AES, which is beneficial when analyzing toxic metals that are found at levels as low as a part per billion (ppb)). However, this causes concern as reference values are hard to establish with data derived from less sensitive instruments before the availability of ICP-MS. Moreover, many factors can affect hair composition, including age, gender, and geographical area, dietary and environmental factors. Such factors can influence the levels of trace elements that assessment of reference values for study populations or subgroups based on control (healthy) and disease group cases (Linn Johansson, 2011).

1.2 Problem statement:

The two types of works (workshops, perfume) make the worker subjected to heavy elements and by observations a number of workers hairs was noticed to be changed during their work specially, if the worker spent long period in such type of work. Perfume workers also have been subjected to this problem. These play a motivation to study the effect of these two types of works on the human hair.

1.3 Objectives:

The general purpose of this work is identified to determine the heavy elements and its concentrations in scalp hair of workers in two sites in the industrial area of Omdurman city using XRF, ICPE and LIBS techniques.

The specific objectives of this work were:

- To determine the ratios of the existence of the heavy elements in workers human hair from their work sites (Workshops and Perfume Factory) in Omdurman industrial area.
- To compare between the existence and ratios of the heavy elements in the worker hairs of the two types of works.
- Identifications of the toxic heavy elements in all samples.

- To study the correlation between the heavy metal's levels in human scalp hair with each other’s.

1.4 Methodology:

The experimental part of the research uses the X-ray fluorescence, laser induced breakdown spectroscopy, and inductively coupled plasma spectroscopic techniques to identify the heavy elements existing in human hair for the workers who work in workshops and perfume factory in Omdurman industrial area. It also uses the statistical concepts to compare between the obtained results of the elements existing in worker's human hairs in the two types of work (workshops, and perfume factory) in Omdurman industrial area.

1.5 Outline of the thesis:

The first chapter is a general introduction that contains problem statement, objectives and the methodology of the study. Chapter two is the theoretical part of this research introducing the theory and basic concepts related to the topic of the study together with the historical background and literature review. The materials (human hair samples, method of preparation) heavy metals measurements techniques, and the method used to complete the study are presented in chapter three. Chapter four contains the results and analysis of the obtained results. Finally, discussion, conclusion and recommendations for future work are presented in chapter five.

CHAPTER TWO

THEORY AND BASIC CONCEPTS

CHAPTER TWO

THEORY AND BASIC CONCEPTS

2.1 Introduction:

Metal poisoning is not only expensive but also difficult to diagnose, particularly in developing countries where resources are limited. The use of human hair as an excellent tool to assess changes in our bodies has received a great deal of attention for a few decades and become successful in different applications, including criminal investigations such as detection of doping relevant substances or drugs and their metabolites. Complementary information concerning monitoring of exposure to a broad spectrum of pollutants can be provided by means of hair analysis. Determination of toxic substances in human media results from general interest to evaluate the degree of impact mainly of work place (occupational exposure), criminal activity or environmental conditions on health status of individuals as well as population groups. Trace metal analysis on hair material presents several advantages when compared with other body tissue or fluids, while it was found that hair level of some elements, toxic in particular, is strongly correlated with many disorders. Hair analysis is useful, especially in reflecting the long-term history of individual exposure. We are able to trace back changes in hair composition in time. Hair study is a noninvasive method of investigation. Moreover, it can deliver valuable information about our state of health, the application of certain drugs and diagnosis of some diseases (Szynkowska M. I., et al., 2009). There are 35 metals, the presence of which is of concern because of occupational or residential exposure. Twenty-three are so-called toxic elements or “heavy metals”: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc. These elements occur naturally in the environment, and additionally are emitted from anthropogenic sources. Heavy metals may enter the human organism body through food, water, air, or absorption through the skin. Exposure can be from agriculture and from manufacturing, pharmaceutical, industrial, or occupational exposure. Industrial exposure accounts for a common route of exposure for adults. Trace element analysis of biological samples can be useful for diagnostics of diseases caused by accumulation of some elements in the organism (Z. Grolmusová et al., 2009). The most used analytical techniques for the trace of the heavy elements in human hairs that are works in a rich environment with these elements such as perfumes workers are X-ray fluorescence (XRF), Laser induced breakdown spectroscopy (LIBS), and Inductive couple plasma (ICP) spectroscopic techniques. Each of this technique has its merits and demerits. During the initial stage of the use of X-ray spectroscopy for chemical analysis, the samples being analyzed were modified (or even destroyed) when electron excitation was applied, leading to changes in the X-ray intensities. For that the X-ray excitation method was adopted as a nondestructive analysis method. The beginning of modern X-ray spectroscopy was successfully first business travel spectrometer rays in 1948 which were a result of the expansion in the scope of Friedman and Birks' work. Trace elements have many definitions like potentially toxic elements, trace metals, heavy metals, micronutrients, and minor elements. The definitions depending on the field of study (Alloway, 2009).

The term "potentially toxic elements" is meant, to illustrate toxicity to humans and plants, not all elements are toxic at all concentrations. In fact, some elements (like iron) are necessary for life in small amounts. (Alloway, 2007) (Linn Johansson, 2011). Laser induced breakdown spectroscopy (LIBS) is a promising analytical method which has many advantages: simplicity, no sample preparation, rapid analysis, ability to sample gases, liquids and solids equally well. LIBS have manifold utilizations e.g. detection of versatile hazardous materials (Z. Grolmusová, 2009). Comparing to XRF technique the LIBS technique is considered new since it’s depended on the laser and the laser invented late than the X-ray.

While inductively coupled plasma spectroscopy (ICPS) is one of the most powerful methods for qualitative and quantitative trace element. The technique was introduced into atomic emission spectrometry by Greenfield in 1964. ICP-AES is today one of the most widely used techniques for trace metal and semimetal determination in a huge variety of different samples (N. Ulrich, 2003).

However, definitions of trace elements change between disciplines. For example, chemists define trace elements, or transition metals, as those elements which fall in the center of the periodic table (between Group IIA and IIIA) and exhibit partial d-orbital filling. Other chemical definitions are based on density (greater than 5gcm^{-3}), atomic weight (greater than that of sodium), and metallic properties health or the environment. This definition is not based on abundance in the environment, or density or metallic properties Geologists define trace elements as any element in rocks other than the most abundant eight elements found in the Earth’s crust. Soil fertility experts define trace elements as those elements that are essential to plant growth in small amounts, but toxic to plants at higher concentrations. Toxicologists consider trace elements as those elements distributed into the environment by industrial processes that are detrimental to human, but solely on the adverse effects of the element in the environment. Interest in trace elements has increased because of the widespread trace element contamination caused by industrial processing. The manufacture of many goods requires the use of trace elements such as iron (Fe), aluminum (Al), copper (Cu), lead (Pb), cadmium (Cd), nickel (Ni), mercury (Hg), arsenic (As), and selenium (Se), so these elements have become common in industrial wastes and in some cases end up in the environment. The Resource Conservation and Recovery Act (RCRA), enforced by the United States Environmental Protection Agency (EPA), have set mandatory cleanup guidelines for the following trace elements: silver (Ag), arsenic (As), barium (Ba), cadmium (Cd), chrome (Cr), mercury (Hg), lead

(Pb), and selenium (Se). The scalp is made up of a thick layer of skin that contains a lot of hair follicles in addition to the skin glands and sebaceous glands that produce a fatty layer that gives hair to this gloss. The scalp has a rich network of blood vessels that deliver food and oxygen to hair follicles and surrounding glands. Note that the number of bulbs in the centimeter varies between 80 and 120 bulbs, and each bulb contains one hair or several hairs according to its congenital structure.

2.2 The Hair:

The hair consists of two main parts, the first is a hair follicle and the second is a hair shaft.

Cross Section of the Hair Follicle and its Components: See figure (2.1):

- At the base of the hair bulb, the germinating layer merges into the outer root sheath (which forms the inner wall of the follicle).
- The outer root sheath then forms the germinal matrix (hair root) which surrounds the dermal papilla.
- The germinal matrix grows the inner root sheath (this is the white bit at the end of a hair if it's pulled out).
- The germinal matrix also contains stem cells - these grow the hair shaft through constant cell division which continuously pushes older cells upwards.
- Hair shaft cells are similar at first. But as they move up through the follicle, they begin to change shape, and a protein called keratin develops inside the cells، three different types of hair cell then form. And hair cells are mostly made from keratin (up to 95%). See figure. (2.2).

- A sebaceous gland lies within each follicle. This produces an oily substance called sebum from a duct that opens up into the hair follicle about halfway down from the skin surface.
- The follicle also has a bulge directly below the sebaceous gland in the outer root sheath at the attachment point of the arrector pili muscle. The bulge produces stem cells that regenerate the follicle during the ext. hair growth cycle.

Hair structure diagram (hair shaft):

The shaft is a prominent part of the hair, it has three layers:

- The cuticle (outer layer) is made from 6 to 11 layers of overlapping semi-transparent keratin scales (which make the hair waterproof and allow it to be stretched). Thick hair consists of more layers overlapping layers of soft hair.
- The cortex (middle layer) made from tiny fibers of keratin running parallel to each other along the length of the hair shaft. It gives flexibility and tensile (stretching) strength to hair and contains melanin granules, which give hair its color.

The medulla (inner layer) is a honeycomb keratin structure with air spaces inside. The hair is a full member growing about 12 mm (1 cm) a month and the rate of growth in women faster than men, each hair grows at a time different from the adjacent hair so the hair varies in stages and does not grow all the same speed and does not fall at the same time. Hair development is broken into three developmental stages, called the anagen (growth), catagen (growth and change), and telogen (dormant) stages.

Fig. (2.1): Cross Section of the Hair Follicle and its Components.

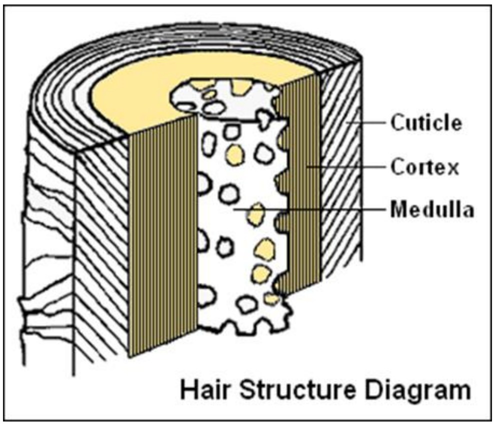


Fig. (2.2): Hair Structure Diagram.

Additionally, hair grows; structure included trace elements that are separated from the metabolic activity of the body, which is influenced by numerous internal and external factors. However, the trace element content of hair being used as an indicator for screening population groups as well as individuals exposed to environmental contaminants and in internal chemical variations in human body balances (Szynkowska, 2009) In general, hair is a record of metabolic processes in the organism for a long period of time with a lower metabolic activity of protein tissue. Scalp Hairs characterization, properties and element concentrations are the mirror of individual peculiarities of a human being such as sex, age, diet, cosmetics and pharmacological effects (Vazina et al., 1998). Hair is a site of excretion for essential, non-essential and potentially toxic elements. The hair element's contents and amount are incorporated with growing that proportional to the level of the element in other body tissues (Piotr Trojanowskil,2010) Therefore, elements cadmium, lead and mercury are toxic heavy metals can be exposed to the hairs via a continuous daily process in the place of work, water, food and in the air (Goyer 1996) (Margarita et al.,2014) (Amarty et al 2011).Trace elements have a wide range of roles of the living system of the human body, with some elements of toxic effects, if inhaled at sufficiently high levels for long enough times a(Flavialaur et al.,2011).

2.3 Trace Elements in Scalp Hair:

Scalp hair a unique potential to reveal retrospective information about the nutritional status and exposure of subjects (Sela et al., 2007). Trace element in hair is accurate and precise analysis for external contaminations. Hair has also been reported to be a valuable indicator of environmental pollution. Trace elements are incorporated into hair during the growth process and reflect the composition of trace elements in blood plasma at the time of formation (Benner and Levin, 2005). At the same time, hair is easily collected and does not require any special storage or preservation. Also, many trace elements accumulate in hair at concentrations at least ten times higher than in blood serum or urine (Shamberger, 2002). The scalp hair analysis, investigation has improved the analytical considerations and limitations of heavy metals in a variety of environmental health, which is related to the broad spectrum of pollution, occupational exposure and the geographical distribution of contaminated regions (Dean et al., 2001).

2.3.1 Role of elements in living systems:

Trace elements are multifunctional components in living systems, and play a wide range of roles in the human body. In the human body, 23 elements have known physiological functions, of which 11 are considered trace elements due to their quantity in biological systems. Most of the elements are metals, and a trace element can be bound to a part of the enzyme molecule as a metal ion. When the metal ion is bound firmly the enzyme is known as a metallo-enzyme or metallo-protein, and when the metal ion is replaced with certain other metal ions and bound loosely, the enzyme is a metal ion activated enzyme (Fraga, 2005).

The metal ion in these enzyme systems participates in catalytic processes and stabilizes the proteins structure. In addition, it induces the binding of the substrate to the protein. The metal ions, moreover, are important in transport processes, membrane permeability, and oxidation and reduction reactions. They are equally important in respiration, muscle contraction, nerve conduction, growth, reproduction and on sub-cellular level (Adair, 2002).

2.3.2 Dose-Response:

Consumption of trace elements in less than the required quantity during a prolonged period of time results in deficiencies, their ingestion in excess can cause toxicity reactions, since very element has a specific dose-response curve, this means that a specific dose of each essential element is needed to obtain an optimum function of the biological process in which an essential element is involved. The effect on the human health is not determined by amount of trace element ingested alone, since species of trace elements have different bio availabilities and therefore the absorption depends of the species present. The differences in bio availabilities are partly due to the use of different absorption and distribution pathways in the body. In addition, the homeostasis of a trace element is a necessary condition to activate and regulate metabolic processes. Homeostasis is achieved a result of excretion (through hair and urine) and replenishment (through exposure or consumption) of a specific organ, which requires the trace element and the achievement of a relatively constant concentration of every individual functional element in the body. Homeostasis of elements might not be reached due to several reasons. In the short-term this might be due to menstruation, exercise, food intake or the time of the day. Over a prolonged period of time, imbalance in homeostatic control may be the effect of aging, occupation, geographical location, gender, dietary habits or body mass. Clinical symptoms when happens may result in diseases (Bernard, 2008).

2.3.3 Disorders associated with elemental deficiencies:

If the intake of an essential trace element is inadequate or elimination is impaired, a nutritional imbalance may occur, resulting in a trace-element-related disorder. This disorder may also result from genetic defects, excessive work-related defects or environmental exposure to trace elements (Adair, 2002). Because certain biological processes require specific trace element, the absence of that trace element may cause impairment, hence adequate intake; absorption and digestion of trace elements are of vital importance.

Additionally, impairment of processes may be caused from antagonism, as other elements of similar physical and chemical properties may replace the desired trace element. Examples of antagonistic elements are: iron and cobalt, copper and manganese, copper and molybdenum, copper and zinc, calcium and potassium and cadmium and zinc. Cadmium is a competitor to zinc and also a by-product of industrial zinc production. It has the ability to disrupt various biological functions, even in low doses, by replacing elements such as zinc. Cd irreversibly accumulates in living systems. It is a contributor to nephropathy because the kidneys are the primary storage tissue of cadmium. As a well-documented fact, lung cancer can be caused by cadmium due to the inhalation of tobacco smoke or from work-related exposure. Zinc, conversely, can protect the body against the harmful consequences caused by cadmium. Other elements can protect against other altering mechanisms caused by toxic elements (Bernard, 2008).

2.3.4 Human Tissues (Scalp Hair):

Trace elements are important for bio-monitoring of chemical exposure, monitoring toxic, essential and non-essential, and the possible identification of diseases caused by an excess or deficiency in these elements (Miekeley, 1998). The frequently used biomarker of nutritional status is hair, because it possesses several advantages over other markers, such as urine, blood and serum.

Firstly, due to the high affinity of metals to the structural components (especially sulphur-based amino acids or proteins) of hair, trace elements accumulate in hair (Paddock, 2006), which yields higher concentrations of the elements in hair than in other biomarkers. The accumulation occurs as elements bind in the keratin structure and also, the follicular protein melanin can bind actions through ionic interactions (Senofonte *et al*, 2000).

Secondly, due to the growth of hair, it reflects endogenous sources for an extended period of time, implying that imbalances in metabolism can be seen from several months back (Forte *et al*, 2005). Exogenous influences such as shampoos, however, bleaching and dyeing of hair can result in elevated levels. In contrast, leaching of elements from hair can occur due to competitive binding, repeat and regular hair washing and hair treatments (Senofonte *et al*, 2000) [58]. In a similar fashion, increment in the levels of chemical contaminants in the hair can cause by an environmental source, such as polluted air (Miekeley, 1998).

2.4 The roles of elements in life:

Although elements in a certain concentration can be hazardous but they are essential for life, below is a brief discussion of the role of elements in life: special attention is given to the Lead (Pb) and Mercury (Hg), and Strontium (Sr), in addition to the essential elements such as Calcium (Ca), etc.

2.4.1 Highly Toxic Heavy Metals:

Hair has a long history of successful use models in detecting chronic exposure to toxic heavy metals in humans and animal because hair concentrates heavy metals several hundred folds above concentrations found in blood. Because high levels in hair may reflect early chronic exposure before other signs and symptoms appear, investigating the origin of exposure when any of the toxic heavy metals are elevated in hair is a very sound argument here. The rise in the accumulation of heavy metals in hair may be due to combinations of exposure to environmental or work-related exposure, such as welding, smoke exposure, painting and printing, the use of heavy metal-containing products, such as hair coloring treatments, paints in art works and inks and increased intestinal uptake, such as chronic digestive problems, malnutrition or antibiotic use. On the other hand, Clinical manifestations vary with the patient health history level and duration of exposure.

To manage high-toxic metal body burden, several requirements need to be considered. These include avoidance of exposure, increased elimination by intravenous or the use of a nutritional program that includes increasing total dietary fiber intake in the 30 - 40 g/day range.

2.4.1.1 Lead (Pb):

One good way of measuring long-term exposure is hair lead levels. Common sources of lead in the environment are lead-pigment paints, occupations involving metal working or printing and industrial emission of airborne particles or water contamination. The earliest sign, especially in children, is, often, interrupted neurological development and followed by chronic anemia from the metabolic interference of lead in hematopoiesis, which results in lowered hemoglobin levels. The human body can tolerate only 1 to 2 mg of lead without suffering toxic effects. Chronic negative calcium balance may prolong the potential toxic effects of lead as lead absorption is higher when calcium intake is not adequate to maintain normal intestinal calcium concentration. Calcium, apparently, competes with lead for absorption in the gut. Any further uptake of lead from ingested sources must to be minimized. Individuals with high levels of lead should increase dietary sources of calcium, such as milk, green vegetables, almonds, etc.) and consider calcium supplementation at 500 mg or more (Fredi and Jone ,2011).

Lead is a highly toxic trace element and in the last few years' human exposure to lead poisoning has both changed in nature and increased in magnitude. Food containing lead is poorly absorbed by the human body and is mainly excreted through feces. The skin and gastrointestinal tract are two parts through which lead may enter the body. Absorbed lead enters the blood and is stored in the bones and soft tissues, including the liver. Direct accumulation of lead in the body is caused by inhalation from motor vehicle exhausts, and indirect accumulation comes from deposition in the soil and plants along high ways and in urban areas. Acute Lead toxicity is manifested in abdominal colicky function of the brain, known as chronic anemia. This toxicity attacks the central nervous system and may be one cause of hyperactivity in children.

2.4.1.2 Mercury (Hg):

Hair mercury reflects accurately the total body mercury content because of the chronic exposure to this toxic metal. Chronic low level or acute toxic environmental or food exposure can result in elevations. A significant source of mercury toxicity is high intake of contaminated fish (e.g., tuna), and fish is also a rich source of selenium, which protects against mercury toxicity**.**

Eating fish from a variety of water sources and avoiding buying it regularly from the same place is quite a good deed, and there is a grog concern is the likely release of mercury from dental amalgams. Also, chronic mercury elevation has been related to a wide variety of symptoms ranging from growth retardation to neurological degeneration. Muscle and joint pain and possibly brain damage are manifestations of acute severe toxicity, and the combination of high mercury with low selenium is a reason for additional concern about mercury toxicity. By competing with the binding of mercury to enzyme sulfur centers where much of the metabolic damage is done, Selenium helps protect against toxic effects of mercury (Phelps *et al,* 2002). A good practice is to assure adequate selenium availability through diet or supplemental intake.

2.4.2 Potential Toxic Elements:

Though present in the environment as airborne particles or in water and foods, these elements have no known function in human physiology (Alloway, 2009). Their detection in hair reflects their levels in soft tissues and bone, depending on total absorbed amounts. There are various reports of toxic effects, especially in the presence of specific disorders, of toxic effects upon the accumulation of these elements. For example, when patients are exposed to high levels in dialysis fluids, aluminum can produce toxic nervous system effects in cases of renal failure. These toxicities, however, are of much lower levels compared to those of the "Highly toxic" elements discussed above.

2.4.2.1 Strontium (Sr):

In all-natural dietary sources of calcium, the stable isotope of the element strontium is commonly found. Like calcium and magnesium, strontium is deposited in bone and mobilized from bone when blood calcium levels fall. Elevated levels in hair may signal negative calcium balance and, can provide a valuable marker for the risk of bone loss.

2.4.3 Essential Elements:

These elements have essential function in human biochemistry because they are nutritionally essential and must be continually supplied by dietary sources to replace daily losses. In terms of the presence of current or recent past health threats, the abnormalities found in the levels of essential elements in hair have varying significance (Adair, 2002).

2.4.3.1 Calcium (Ca):

The most abundant mineral in the body is Calcium, and about 99% of it is deposited in the bones and teeth, while the remainder is in the soft tissue. The National Research Council of USA recommends 800 mg as daily calcium intake High intake of calcium may relieve the symptoms commonly associated with aging some of the disorders associated with calcium deficiency include bone pain backaches, insomnia, brittle teeth with cavities and tumors of the fingers (Shamberger, 2002).

Hair calcium, in contrast to serum or plasma which does not vary except in serious pathologies, displays a broad range of normal values. The ability of hair to accumulate calcium from the fluids of the hair follicle when the calcium is available in the ionized form is reflected in fluctuations of these values. The factors which affect the levels of ionized calcium in blood can cause alterations in hair calcium over long time intervals, and calcium accumulation in hair can reflect the end result of the process of chronic mobilization from bone. Thus, high levels are associated with calcium loss, which may indicate early signs of osteoporosis, especially in females in the age range of 30-50 years.

In younger women, high hair calcium may, by inference, indicate that calcium loss, which has not yet shown, as a sign of bone density decrease. Low hair calcium may indicate increased risk of myocardial infarction with increased associated aortic calcium concentrations (Yukawa *et al*, 1984). There are several practical suggestions for maintenance of health against the implication for rapid advancement of the process of arteriosclerosis, which include a regular aerobic exercise program, quitting smoking, and eating fiber and foods rich in trace elements. Special attention is devoted, on a daily basis, to whole grains and vegetables. Manifestation of cystic fibrosis in children is in loss of calcium-binding ability of hair as calcium levels in the hair of children are generally lower than in adults. There is an altered distribution of calcium, during the active growing years, due to rapid uptake by osteocytes of bone. Low hair calcium in children, thus, reflects calcium distribution, and is not directly related to dietary intake of calcium.

2.4.3.2 Copper (Cu):

Copper is a tracing mineral that is found in all body tissues. In case of low-hair copper, evidence shows that either dietary copper is low or other conditions have diminished tissue copper supply. Copper serves as cofactor in the processes of lipid metabolism, and neurological control. Hair copper elevation has been associated with elevated systolic blood pressure. High copper has been associated with learning disabilities and other mental disorders (Dombovari *et al,* 1999). Heavier exposure of the hair to copper-treated swimming pool water will give higher values. Copper and zinc are related in the way they impact body function, and the combination of high copper and low zinc makes the individual findings take on greater significance. Clinical researches correlate imbalances of copper and zinc with dysfunction in lipid metabolism and neurological control.

2.4.3.3 Iron (Fe):

Iron in hair is unrelated to the major iron pool in the pathways of hemoglobin, which is present in every living cell. The process of intracellular iron becoming incorporated into growing hair is poorly understood, but conditions of iron accumulation, such as hemochromatosis, do not appear to manifest as elevated hair iron. The National Research Council of USA suggests daily Iron intake of 18 mg for women and 10 mg for men. Long term chronic iron deficiency has been associated with low hair iron (Shamberger, 2002).

2.4.3.4 Manganese (Mn):

Several studies have shown that manganese in hair reflects dietary manganese. However, there are differences among the normal manganese contents of hair of various colors, as red and black hair generally has higher manganese than white or gray hair. Standards for setting reference range differences for color are not yet available. Sources of manganese, when manganese is high, may need to be investigated. Contaminated well water, in the rare instance of well water purifier containing manganese, has led to toxic body burdens associated with neurological dysfunction. Extreme conditions that have been associated with low hair manganese are exhibited in the form of neurological disorders, such as epilepsy and Down syndrome. Although hair may not be the most sensitive monitor of nutritional status of manganese, it is advisable to assure adequate dietary manganese (Shamberger, 2002).

2.4.3.5 Zinc (Zn):

Zinc is an essential trace mineral occurring in the body in larger amounts than any other trace element except iron. Elevations of hair zinc have been reported only during the special metabolic needs of pregnancy, where the high values were present with evidence of zinc deficiency. Though is not indicative of systemic elevation, the presence of such a “false” high value in a tissue like hair, is possibly of the system depletion. Zinc deficiency may be caused by inadequate dietary intake or absorption problems deficiency (Forte *et al*, 2005). And an imbalance in zinc and copper metabolism contributes to the risk of coronary heart disease (CHD). Some US diets have zinc-copper ratios in excess of those that produce hypercholesterolemia in rats. In 47 cities in the US, it was found that mortality rate for CHD was correlated with the ratio of zinc to copper in milk. Also, Nutritional zinc deficiency has been associated with low hair zinc levels as this trace element is one of the most widely distributed metals in the body, and metabolic effects of zinc deficiency are numerous.

These metabolic effects include poor growth and healing, impaired inflammatory response and reproductive dysfunction. Increased risk for developing zinc deficiency due to suboptimal dietary patterns have detected in highly trained female runners, in addition to high iron intakes (which restrict zinc absorption) and training-induced alterations in gastrointestinal function. In the presence of low red cell zinc, low hair zinc not only supports the suggestion of zinc deficiency but further gives evidence of the chronic nature of zinc depletion. Diet and supplementation should aggressively replenish body pools of zinc, whereas the upper range of therapeutic use of zinc supplements is 50-100 mg/day. A three-month follow up testing should be done to monitor zinc status and assure that safe ranges are not exceeded at these levels of intake. Awareness of zinc interactions with other minerals, especially copper, is crucial as it might be antagonized by the extra zinc. In children, even mild zinc deficiency can be growth-limiting. Lower body weight, reduced ability to taste, and possibly lower attention span are likely to occur to boys with hair zinc less than 110 ppm. Although zinc is relatively nontoxic, poisoning may result from eating foods that have been stored in galvanized containers. High intakes of zinc interfere with Copper utilization, which may result in incomplete iron metabolism.

2.5 Spectroscopic techniques, basics:

Spectroscopy is the study of interaction of electromagnetic radiation with matter, and accordingly there at least 50 types of spectroscopic techniques classified according to the type of radiation Uv-Vis, X-ray, IR and so on, also it can be classified according to the type of interaction such as absorption spectroscopy, emission spectroscopy etc., and in addition to some special types of spectroscopic technique such as Raman which is based on inelastic scattering, laser induced breakdown spectroscopy and inductive coupled plasma,. Below are the bases of the last-mentioned spectroscopic techniques which will be use in the experimental part of this work:

2.5.1 X- Ray fundamentals:

X-ray spectra-chemical analysis is based on the fact that the elements emit characteristic radiations when subjected to appropriate excitation. The emission of characteristic line spectra can be induced by either the impact of accelerated particles such as electrons, photons, alpha particles and ions; or by the impact of high energy radiations from an X-ray tube or from a suitable radioactive source. Generally, direct electron excitation is used in electron microprobe techniques, while radioisotope sources and proton generators are commonly associated with energy dispersion.

The X-ray tube and X-ray radioactive sources are used to irradiate the sample to generate fluorescence X-ray in the sample for qualitative and quantitative determination of the elements relative to the intensity, which rapidly analysis the element concentration in very precise method of nondestructive measurement. The precision of an X-ray measurement, therefore, can be predicted by the measured intensity of emitting radiation. For example, an accumulated intensity of counting X-ray photons has a standard deviation of 0.1%, and the counts standard deviation is 0.01%. The measurement of intensity of the sample can be accumulated in equal time to detect X-ray photon of precision with relative intensity and accurate standard deviation of counts measured. The sample intensity is modified by matrix element effects and X-ray beam propagating through it, while the generation of characteristic X-rays absorption of the emitted X-rays along their paths and the enhancement effect due to secondary excitation. The analytical performance of the X-ray fluorescence method depends on the development of X-ray correction methods. The derivation of mathematical correction formula produced from studies of modification processes and related X-ray physical phenomena (Beckhoff et al., 2005).

The incident electrons can undergo elastic or inelastic scatter on target nuclei and can be even back scattered in the opposite direction. Second, incident electrons interact with electrons of the target transferring them their energy. The dominant process consists of subsequent collisions with outer most electrons with small energy losses at every collision. Also, sometimes an inner electron is removed from its orbit as a result of a collision so that an atom is ionized. Thus, orbital electron fills the vacancy radiating an X-ray and process gives rise to the characteristic lines in the X-ray emission spectrum. Most of incident electrons go through elastic scatter and few go through inelastic scatter on target nuclei. There are two type of x-ray spectrum the first is the continuous spectrum or braking radiation: issue from atom nuclei, when incident electrons interact with a strong Coulomb field of nuclei decelerated energy losing as x-ray photon with energy equal energy difference incident before and after. The characteristic lines in the X-ray emission spectrum result from move of an inner electron from the orbit as a result of a collision so that an atom is ionized, then another orbital electron fills the vacancy radiating an X-ray emission. The continuous function and characteristic lines super posited together and create the spectrum. Since every line has an exciting threshold equal to a corresponding absorption edge and the intensity of characteristic lines increases with the accelerating voltage, then presentation a line in a spectrum depends on an accelerating voltage does not exceed this threshold. Some X-Ray techniques are discussed below:

a. Photoelectric Absorption:

When a sufficiently energetic X-ray photon interacts with an atom, several phenomena take place. One interaction involves the transfer of the photon energy to one of the electrons of the atom (K, shell electron) is resulting in its ejection from the atom. The distribution of electrons in the ionized atom is then out of equilibrium and within an extremely short time returns to the normal state, by transitions of electrons from outer shells to inner shells. Each such electron transfer, for example from the L shell to the K shell, represents a loss in the potential energy of the atom; this energy reappears as a photon (in this case a Kα photon) whose energy is the difference between the binding energies of the two shells. The K lines are more probable than the L lines which explain the difference in the yield for the K and L type transitions. In practical X-ray spectrometry, we use the K lines to measure elements with low to medium atomic number while we switch over to measure L lines for the heavy elements, or even to the M lines (Ron Jenkins.,2000). See figure (2.3). In practical XRF, the principle lines of K and L series are selected to measure an element although there may be other lines present. The selection of an analysis line depends mainly on the type of sample, the elements present in it, the concentration range of the elements and the excitation conditions. The heavier the element of the target, the more intense the characteristic lines emitted. However, in practice the efficiency of a given target is dependent on the operating conditions (kV and mA).

b. Scattering:

Scattering of primary X-rays by the sample results in two processes: Coherent scattering (without loss of energy) and Compton scattering (with a little loss of energy). As mentioned before, not all the incident X-rays participates in the photoelectric absorption. Some of them do not reach the inner shells and thus they do not give rise to absorption.

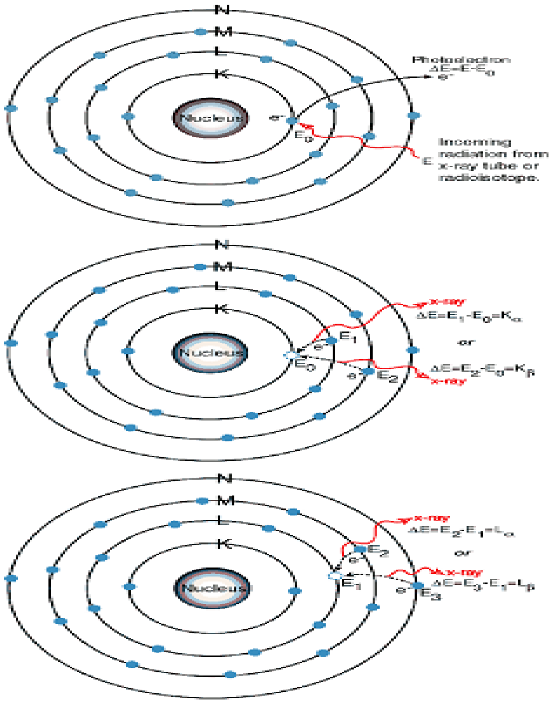


Fig. (2.3): Ionization of the K-shell electron in the atom by photo electron effect and emission of Characteristic

2.6 X-Ray Fluorescence (XRF):

In X-ray fluorescence, distinction is basically made between two types of instruments: The Wavelength Dispersive Spectrometer (WDX) and the Energy Dispersive Spectrometer (EDX). Both WDX and EDX employ an X-ray source for exciting the sample. They essentially differ in the way the X-ray spectra emitted by the sample are detected. In WDX, the fluorescence spectrum is dispersed into discrete wavelengths using a dispersion device (e.g. a crystal) which are then detected using a gas-proportional, or scintillation counter. In EDX, the entire fluorescence spectrum is directly measured, using a solid state detector such as Si (Li) or HPGe, which is then processed using a multichannel analyzer to obtain the information on an energy scale. The energy and the wavelength of a photon are related in the following way:

$$E = h\nu = h\,c/\lambda = 12.4/\lambda \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.5)$$

2.6.1 Spectral Line Interference:

The primary spectrum may not only contain the lines from the target element, but also those from impurities in the target, contaminants like Fe, Cr or Cu from various parts inside the tube. Sometimes, primary beam filters are used to filter out the characteristic lines of the tube if the same element is present in the sample or overlapped by a tube line.

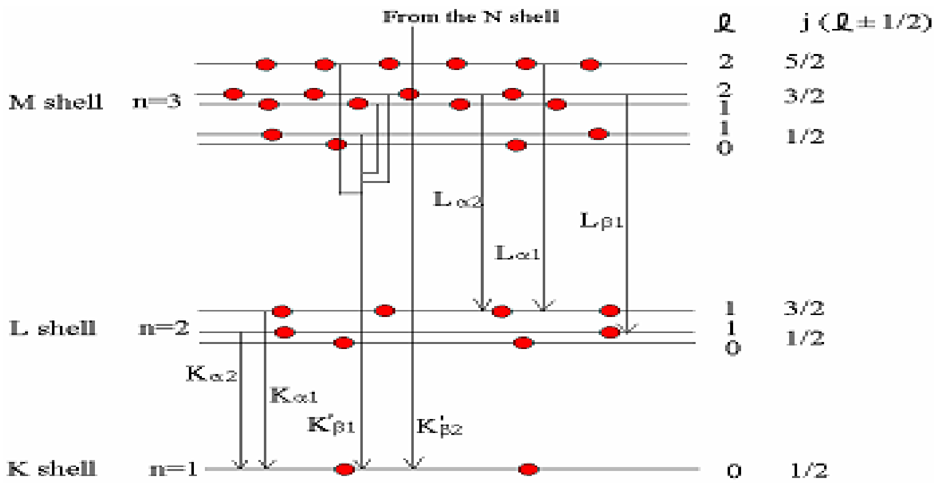


Fig. (2.4): Electron transitions and emitted spectral lines in the atom after the K-shell ionization.

2.7 Errors:

Errors in any measurements are essentially to be understood to avoid it and to get accurate results. Below are examples of some types of errors:

-In XRF the statistical counting errors are depends on the total accumulated counts, in LIBS and ICP the stray light may arise and contribute in the detected or measured quantity and thus get wrong measurements results.

- Instrumental errors, consists of short term and long-term variation, instability and drift in instrumental components, conditions and parameters.

- Operational errors consist of slight non-reproducibility in setting of instrument conditions.

- Specimen errors arise from the specimen itself.

- Errors in the estimation of the calibration curve.

2.8 Source of elemental analysis:

The various operations performed on the sample during its preparation for the stage of final determinations can be a source of many errors crucially affecting the final result of the analysis. The chief sources of error are changes in the composition of the sample under study brought about by a variety of factors. Kinds of error distorting the result of analysis are presented (Sneddon*et al*., 2006). The bias of the final determination result caused by the errors may be due to various processes occurring in the sample and due to the influence of the external environment on the sample. Errors can distort the result of determination of a trace component in a liquid sample. The intensity of the processes and phenomena can vary depending on: the temperature of the sample and its changes, the presence and intensity of solar radiation, and the presence of living organisms in the sample. The contact of analysis present in both gas and liquid mixtures with the walls of vessels, it is the result of adsorption and desorption of analysis on the surface of a solid. These phenomena distorting the sample composition are described collectively as the wall memory effect (Hoenig, 2001).

2.9 Laser Induced Breakdown spectroscopy (LIBS):

Laser-induced breakdown spectroscopy (LIBS) is a laser diagnostic, where a laser beam focused onto a material generates transient high-density plasma as the laser intensity exceeds the breakdown threshold of the material (~1-10 MW/cm^2). The UV and visible emission from the plasma can be spectrally resolved and recorded for qualitative and quantitative analysis of the sample.

2.9.1 LIBS Advantages:

LIBS have many advantages as an analytical technique. There is no need of sample preparation, which avoids further contamination of the material to be analyzed 10-11. The analysis process is fast and can be used for both non-conducting and conducting samples, regardless of their physical states, i.e. aerosols, gases, liquids or solids. A LIBS is also applicable to the analysis of extremely hard materials that are difficult to digest or dissolve, such as ceramics and semi or super-conductors. Its capability for simultaneous multi-element determination, localized microanalysis, and surface analysis are also of great importance and it has been used successfully in hazardous and difficult environmental conditions to study remotely located samples for online and real time information about their spectra. LIBS has been found useful in elemental process monitoring and in field portable analyzers for in situ trace metal analysis of real samples where accuracy and precision are not the main requirement (Rai, 2016).

2.10 Inductive coupled plasma emission (ICPE):

ICP emission spectrometers are analytical instruments used in a broad range of fields. They feature high ppb level detection ability, broad 5-6-digit analysis concentration ranges, and batch analysis of multiple elements. Recent wider usage has resulted in an increased demand for shorter analysis times and improved high-matrix sample detection. Higher accuracy analysis and easier operation are the advantages of the ICPE9000 emission spectrometer. The internal components of the ICPE 9000 are shown in figure (2.5). The Inductive coupled plasma type ICPE 9000 is composed of two parts: the ICP and the optical spectrometer. The ICP torch consists of three concentric quartz glass tubes. The output or "work" coil of the radio frequency (RF) generator surrounds part of this quartz torch. Argon gas is typically used to create the plasma.

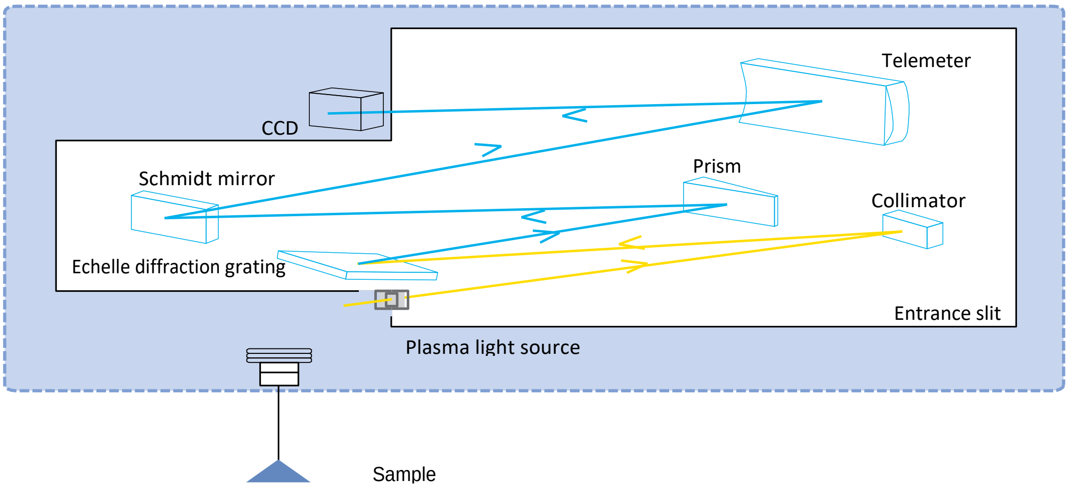


Fig. (2.5): Internal components of the ICPE 9000 spectrometer

2.11 Literature review:

V. Balaram in 2019 his work summarizes the occurrence of the rare each metal in the Earth’s crust, their mineralogy, different types of deposits both on land and oceans from the standpoint of the new data with more examples from the indian subcontinent. In addition to their utility to understand the formation of the major

Earth reservoirs, multi-faceted updates on the applications of REE in agriculture and medicine including new emerging ones are presented. Environmental hazards including human health issues due to REE mining and large-scale dumping of e-waste containing significant concentrations of REE are summarized. New strategies for the future supply of REE including recent developments in the extraction of REE from coal fired ash and recycling from e-waste are presented. Recent developments in individual REE separation technologies in both metallurgical and recycling operations have been highlighted. An outline of the analytical methods for their precise and accurate determinations required in all these studies, such as, X-ray fluorescence spectrometry (XRF), laser induced breakdown spectroscopy (LIBS), instrumental neutron activation analysis (INAA), inductively coupled plasma optical emission spectrometry (ICP-OES),glow discharge mass spectrometry (GD-MS), inductively coupled plasma mass spectrometry (including ICP-MS, ICP-TOF-MS, HR-ICP-MS with laser ablation as well as solution nebulization) and other instrumental techniques, in different types of materials are presented.

Gang Liang et al in 2017 worked in Human hair of different age groups and foodstuff samples were collected in Beijing, China. The concerned metals—Cd, Cr, Pb, As, and Hg—were analyzed, and the metal levels in relation to age, gender, and dietary intake were further assessed. Results showed the highest level of the metals was shown by Pb, with an average concentration of 1.557±0.779 mg/kg, followed by Cr (0.782±0.394), Hg (0.284±0.094), As (0.127±0.078), and Cd (0.071±0.032), following a decreasing order of Pb > Cr > Hg > As > Cd, which were all below the upper limit of normal values in China. The heavy metal concentrations varied greatly among different age groups, and higher concentrations for Cd,Cr, Pb, and As appeared in female hair, whereas higher Hg concentration were found in male hair, suggesting that age and gender were not crucial factors for assessing metal concentrations in human hair. The ingestion of cereals and vegetables were the main route by which heavy metals in the environment create hazardous health effects for local inhabitants, but the estimated metal intakes through food consumption were all lower than the proposed limit of Provisional Tolerable Weekly Intake (PTWI), indicating that heavy metals posed no health risks for the inhabitants. Furthermore, little relationship was found between metal intakes and the corresponding metal levels in hair. Nevertheless, the results of this study can be used to analyze the internal heavy metal burden in the resident population of Beijing area and can also serve as reference for further studies.

In her study, Elif VARHAN ORAL in (2016) analyzed of toxic and essential trace elements, such as Cd, Pb, Cu, and Fe were done in hair samples which we collected from male smokers (10 people) and non-smokers (10 people) who live in Diyarbakır, Turkey and concentrations in hair samples were compared. Hair samples were washed by a standard procedure proposed by the International Atomic Energy Agency. Then the samples were dried for 16 h at 110°C in an oven. Solubilization procedure was carried out by nitric acid-hydrogen peroxide mixture (3:1) in closed vessels in a microwave oven. Trace element analyses were carried out by using inductively coupled plasma-mass spectrometry (ICP-MS) technique. In this study, while concentrations of Cd, Pb, and Fe elements were found to be considerably higher in smokers than non-smokers, similar results were observed in Cu concentrations. The accuracy of the method was evaluated by applying spike method to samples. There was a good agreement between added and found analyte content. Analytical recovery values were determined between 91.2% and 104.6%. The values of R were found to be higher than 0.99.

D. Pozebon et al. (2017), in their work, hair elemental analysis is reviewed their review spans articles published in the last 10 years. They started with a general discussion of history, morphology and possible techniques for elemental analysis, where inductively coupled plasma-mass spectrometry (ICP-MS) was clearly highlighted since this technique was leading quantitative ultra-trace elemental analysis. Emphasis over sampling, quality assurance, washing procedures and sample decomposition was given with detailed protocols compiled in tables as well as the utility of hair to identify human gender, age, diseases, healthy conditions, nutrition status and contamination sites. Isotope ratio information, chemical speciation analysis and analytic pre-concentration are also considered for hair. Finally, the potential of laser ablation ICP-MS (LA-ICP-MS) to provide spatial resolution and time-track the monitoring of elements in hair strands instead of conventional bulk analysis was spotlighted as a real future trend in the field. Their work was important basis for one who wants to study the subject concerning heavy elements in human hairs.

Philip Otieno Abuor in 2011 collected Hair samples (N = 240) which were obtained with assistance of barbers and hair dressers located in Nairobi, Mombasa and Kisumu. Concentrations of Lead, Cadmium, Copper, Manganese, Zinc and Mercury were determined in scalp hair of male and female of children and adults of ages (5-14, 15-20, 21-40, >40 years). Concentrations of the elements in the samples investigated were determined by using Atomic Absorption Spectrophotometer (AAS), applying both flame and flameless techniques in determination of the stated elements. As a control, samples were taken from non-industrialized agricultural rural areas in North Rift, Msambweni and Western Kenya. The generated data was analyzed using Statistical Analysis Software System (SAS) focusing on Analysis of Variance by One-Way (ANOVA), Correlation Analysis, Bar Charts and Line Graphs, Significance tests and Confidence Intervals set at 95 % level of confidence. One-Way ANOVA revealed a significant effect of urban and age on heavy metal concentration (p value of0.0001 and0.002 respectively at $p < 0.05$). Linear Correlation between paired metals indicated strong positive correlations. The results revealed that the hair samples of Kenyan urban inhabitants had significantly higher concentrations of all metals Pb, Cd, Cu, Mn, Zn and Hg than those from the rural counterpart sat 95% confidence level. The concentration of the studied metals was in the increasing order of Hg <Cd < Pb <Cu <Mn <Zn. It was found out that age and geographical location had great influence on metal hair concentration among the Kenyan inhabitants. Comparing the obtained results in this study with the literature data, Kenyan Scalp hair heavy metal concentration emerged the highest among the other regions of the world, particularly with respect to Cd (1.59 mg/kg) and Mn (27. l9 mg/kg). Also, with exception of Nigeria, Libya and Pakistan, Kenya had higher hair Pb (13.52 mg/kg) concentration than the selected countries of the World.

X-Ray Fluorescence Spectrometry (XRF) was used for the first time to measure the material which irradiated As and Hg for Penang by Khalid Saleh et al in 2015 to determined level of arsenic and mercury level in scalp hair from a selected population. This study will be a reference for future studies to compare the ratios of As and Hg in the human hair for people in Penang. Hair samples from 50 individuals in Penang were analyzed for As and Hg concentration. This level of As and Hg in Penang is close to the worldwide range when compared with another countries. The results for both elements investigated do not differ considerably from reported values for other regions of the world (Khalid et al.,2013).

In their Katarzyna Chojnacka work et al., in (2012) hair mineral analysis of 110 individuals was carried out to determine environmental exposure based on the distance from a subject’s residence to a pollutant source. The subjects were asked to fill in a questionnaire concerning their place of living in the city of Wroclaw (lower Silesia, Poland), which was divided in 12 sectors. The content of minerals in hair was determined by ICP-OES and ICP-MS technique in a laboratory certified by the Polish Centre for Accreditation and ILAC-MRA (No. AB 696). The results were elaborated statistically. Each person served as the experimental unit. Post-hoc comparisons were made by Tukey's test and the Spjotvoll/Stolin test. Results were considered significantly different when p<0.1. The differences in the content of as were statistically significant between IV-V regions (p=0.0182), IV-VII (p=0.0720), and IV-XII (p=0.0586). In the case of Cd, statistically significant differences were found between II and XII regions (p=0.0377). Hair has been found to be a valuable indicator of environmental pollution in Wrocław. The highest content of Al was found in sector VII, As – IV, Cd – II, Hg – VIII, Ni – V, and Pb – IX. The explanation could be the vicinity to a heat and power generating plant and a non-ferrous metals plant or other industrial units, as well as interactions between elements in a human organism. Additionally, statistical-ly significant differences between Ni content (p=0.0591) in hair of males and females were found. These results showed that hair mineral content reflected exposure to elements from the environment.

In 1999, Dombovari *et al* studied the cross-sectional and longitudinal distribution of Zn, K, Ca, Fe and Cl in single hair strands of hemodialysis patients with Micro-Proton Induced X-Ray Emission (Micro-PIXE) (Dombovári et al., 1999).

In 2005 in Vienna, Stadlbauer et al analyzed forensic hair from root to tip, analysis in order to obtain the time-resolved monitoring of heavy metal in toxicities in single hair .The samples was evaluated to study the ratio of the concentrations in the outer and inner parts of the hair by using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA–ICP–MS).The results suggest accumulation of metal from the bloodstream during growth of the hair rather than elements secreted by the sweat and/or sebaceous glands which become deposited on the surface of the hair. The difference between heavy-metal concentrations in the outer and inner parts of the hair must be seen in terms of the difference structure and functionality of the cuticle and the cortex (Stadlbauer et al., 2005).

In 2007, Sela et al studied determination of Zn, Fe, Cu, Cr, Pb and U in single strands of human hair by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA- ICP-SFMS). They also compared results obtained by LA-ICP-SFMS with those measured by ICP-QMS in digested hair samples and found that these agreed well (Sela et al., 2007).

In 2008, Kristin Gellein et al in Poland were analyzed trace element in single strands of human hair from five healthy and occupationally unexposed subjects were cut into 1-cm long segments starting from the scalp. Analysis was done by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Profile of trace elements Ag, As, Au, Cd, Cu, Hg, Fe, Pb, Se, Sr, U and Zn was achieved in single strands. The results investigated for analyzing trace element along single strands of human hair can yield information about essential and toxic elements, and for some elements, can be correlated with seasonal changes in diet and exposure. The information obtained from the trace element profiles of human hair in this study substantiates the potential of hair as a biomarker (Gellein et al., 2008).

Y.Muramatsu and R.M. Parr in 1988 were analyzed Autopsy samples of hair, liver and kidney cortex from 30 Swedish subjects (Caucasian). Some trace elements were analyzed by Neutron Activation Analysis (NAA). The observed concentrations of most of the elements were very variable for each tissue. In particular, Co values for hair showed more than a 5000-fold difference. Comparison of the measured and certified values of Fe, Zn, Cu and Ni in the certified reference material (IAEA-85), and the observation was a highly significant positive correlation between Hg in the hair and kidney cortex of autopsy.

Hair grows approximately 1.0 cm a month, and trace element composition in hair reflects blood levels at the time the hair was generated. Blood and urine analysis on the other hand, reflects the trace element status only at the time the sample was obtained. Important information in several past or forensic cases has been obtained from hair analyses. Shamberger in 2003, in study calcium, magnesium, and other elements in the red blood cells and hair of normal and patients with premenstrual syndrome. He compared the levels of 18 red cell elements and 22 hair elements in 46 female patients (median age: 36.2 yr) diagnosed with PMS (premenstrual syndrome) to 50 normal (median age: 37.7 yr). The significantly lower blood cell calcium level found in these studies may provide additional evidence that PMS may be related to a calcium-deficiency state or a metabolic defect involving calcium (Shamberger, 2003).

The samples of hairs can be collected frequently and stored for an unrestricted time used for repeated analyses without damage, which uses occupational potential exposure and environmental conduction's investigation flows up. In 2004, Scalp hair analysis as a tool in assessing human exposure to heavy Metals by Pereiraa et al., in Portugal using AAS. It shows that the heavy metal's exposure As, Cd, Cr, Cu, Mn and Zn have been assessed in hair of two different communities at the South and North of the mine area related to about potential exposure pathways to these elements, which were found, no significant differences were found in the average concentration of these elements between villages (Pereiraa et al., 2004).

The trace elements of hair analysis have become important matter in the fields of medical, biological, forensic, and environmental sciences, which provides one of the most accurate records of the health and trace metal status of the human body. The Multi-element of hair measured by Nnorom of human in towns in Southeastern Nigeria were analyzed for their contents of the trace metals, Pb, Cd, Zn, Ni, Cu, and Cr by atomic absorption spectrometry (AAS). The result of samples was collected in 2005 indicates that occupational exposure of Pb levels is considered dangerous. However, the data show the high magnitude of trace elements are arising from environmental factors probably largely due to high gasoline lead and other elements (Nnorom, 2005).

Muhammad Junaid et al., in 2017 wrote a report on the potential health risk of heavy metals from the leather industries in Pakistan based on multiple biological matrices of the exposed workers and indoor dust samples. The adverse impacts of heavy metals on the oxidative enzyme and their risks to workers' health were also explored. Our results indicated that the level of Cr in indoor industrial dust was more than twice, compared to the background household dust. Blood, urine and hair samples of exposed workers showed significantly high concentrations of heavy metals, compared to those in the control group. Superoxide dismutase (SOD) level in the blood samples expressed significant positive correlation with Cr and Ni. Total hazard quotients (HQs)/hazard index (HI) were >1, and Cr (VI) exhibited higher cancer risks than that of Cd in the exposed workers. In addition, the PCA-MLR analysis confirmed that the industrial sections; cutting, shivering/crusting, and stitching were the principal contributors of heavy metals in the biological entities of the workers. Their results highlighted the occupationally exposed groups would likely to experience the potential health risks due to excessive exposure to the heavy metals from the leather industries.

In 2012, X-Ray Fluorescence Energy Dispersive technique (ED- XRF) used to analysis the elements Cr, Mn, Ni, Cu, Zn and Mo in scalp hair by Peter O. Onuwa in Benue State, Nigeria. Analysis of scalp hair samples of a group of both genders was carried out of among various occupational distributions to ascertain their heavy metal burden. The result of the analysis shows that the mean concentrations of Cr, Cu, and Mo were higher in the females that of Mn, Ni and Zn were more in the males. The relationships between ages, body mass, height, and heavy metal concentrations were also investigated and Statistical analysis of the results indicates that there was no correlation between the bodies Mass Zn showed the highest deviation among other elements in the individual samples for both genders which reflect the individual variation in the concentration of Zn (Peter et al., 2012).

In 2006 Master thesis of Science in environmental study of Philip Otieno Abuor determined of heavy metals in Scalp Hair of selected Kenyan Urban and Rural population. The metals toxicity cannot be broken down to non-toxic forms by the biological system and once the ecosystem is contaminated by them, they remain as a potential hazard to human health. The elements higher concentrations of the donor due to the geographical location in urban centers and in different age groups indicating individual metabolic activity, industrial activity and occupational were obtained. Therefore, the comparison the of Kenyan head hair metal concentration are obtained with the literature data of the available data from various regions of the World reveal head hair metal concentration particularly to the Nigeria, Libya and Pakistan hair metals levels (Philip,2006).

Selma V. Frazão et al in 2007 in Brazil analyzed human scalp hair analysis in order to obtain further reliable reference value ranges using Neutron activation analysis technique (NAA). Human hair of voluntary donors from São Paulo State of aged from 15 to 60 years were studied and the results obtained indicate that As, Co, Cr, Cs, La, Sb, Sc and Se are present in the hair at a low level and the elements Br, Ca, Fe, K, Na and Zn, at high level. The results are investigated for assessing nutritional status and human health or disease, which is considered hair of normal and healthy individuals generally, contains each trace element within a well-defined concentration range (Selma et al., 2007).

The human hair is used as an excellent tool to assess changes in our bodies a biomarker in assessing exposure to toxic metals has received a great deal of attention for successful in different applications. In 2009, M. I. Szynkowska et al from inhabitants of the rural outskirts of Gdańsk, located in the north of Poland and from the donors who were employed in two factories in southwestern Poland was applied human hair as a biomarker in assessing exposure to toxic metals.

Scalp hair content of different elements including toxic metals (Ba, Cd, Pb, Sr) in hair and characterized as urbanized and highly industrialized areas (exposed groups) are revealed significant differences in concentrations of metals that exposed to toxic heavy elements. Therefore, the factors are connected with sex, age, smoking habits that might partially strongly relate to different level of accumulation of toxic elements in hair (Szynkowska et al.,2006).

Neutron Activation Analysis (NAA) has used to determine the distribution of trace elements in human hair in 1984, in Tokyo (Japan). Yukawa et al were analyzed hair samples from five infants (2-7 years of age) with hair length ranging from 15 to 40 cm used to determine the distribution of trace elements in human hair. The hairs were divided into segments, each of 2.5 cm, starting from the scalp end and trace elements were analyzed in each segment. Concentrations ofI, Mg, Ca and Cu increased from the scalp end to the tip. Concentrations of Cl and Br decreased inversely. Different profiles of the concentrations of Hg, Se, Ca and Mn were seen in each sample. The information obtained from these results substantiates the potential of hair as indication of environmental pollution.

CHAPTER THREE

MATERIAL AND METHODS

CHAPTER THREE

MATERIAL AND METHODS

3.1 Introduction:

This chapter Contains material and methods for the trace element analysis of human scalp hair utilizing X-ray fluorescence (XRF) spectrometer in energy dispersive mode and LIBS (laser induced breakdown spectroscopy) technique at the University of Khartoum, faculty of science, department of Physics-Applied Nuclear Sciences Laboratory, and ICPE 9000 at Forensic Laboratory Khartoum. Steps of the practical analytical process include samples collection, preparation and instrumental analysis.

3.2 The study area:

Data for this study were retrospectively collected from workshops for cars maintenance, iron welding workshop and perfume factory in industrial Area in Omdurman. Omdurman City is the most densely populated city in Sudan, is located at N 15º 644´, E 32 º 471´.

3.3 Sample Collection and Preparation:

Sample collection and storage is the first stage of the analytical process and can have a large impact on the subsequent analytical steps. The samples of the scalp hairs were collected from different ages of Sudanese's workers in two sites of both genders. By using stainless steel scissors hair samples were collected from all places on the scalp hair to increase hair sample consistency and to obtain a sample as representative of tissue. The samples were stored in clean sealed plastic bags (approximately 6 cm x 9 cm) and the labeled bags themselves were stored in a dry cupboard until required for analysis. Generally, scalp hairs are influenced with numerous external contaminations such as exogenous contamination, fats, oils and assorted types of organic and inorganic substances (Selma et al., 2007).

Acetone and distilled water are being a polar aprotic solvent, both of which are especially effective at removing all types of exogenous contamination, from fats and lipids to various other organic or inorganic substances. These hair samples were cleaned by implementing the procedure recommended by the International Atomic Energy Agency (IAEA, 1985), using water-acetone solution of water 50% and acetone 50% were used to wash hair samples three times to remove external impurity (Chen *et al*., 1999), (Mikasa et al.1988) and then dry in an oven (Szynkowska et al.,2009). Traditionally, the method of preparing the sample for XRF measurement in simple pellet press solid sample with geometrical dimensions for the X-ray absorption and transmission via homogeneous shape. The new approach of hair samples was prepared in fine mode powder using liquid nitrogen at low temperature of 77 ^{o}K. The solid hair immersed in liquid nitrogen was crushed into a fine powder with a hand grinder rod and tray of Teflon prepare specially for this work. The samples powder was prepared in pellet form using a pressing machine that compress to a manual pressure up to 15 tons to form the sample on a dry weight basis. The diameter of each pellet was about 2.5 cm and the mass 1.0 gm.

3.4 X- Ray Fluorescence (XRF):

The XRF is an important analytical or spectroscopic technique for the trace of elements, the machine was built on the basis of the X-ray fluorescence, below is a detailed discussion of the XRF instrumentation components such as in figure (3.1):

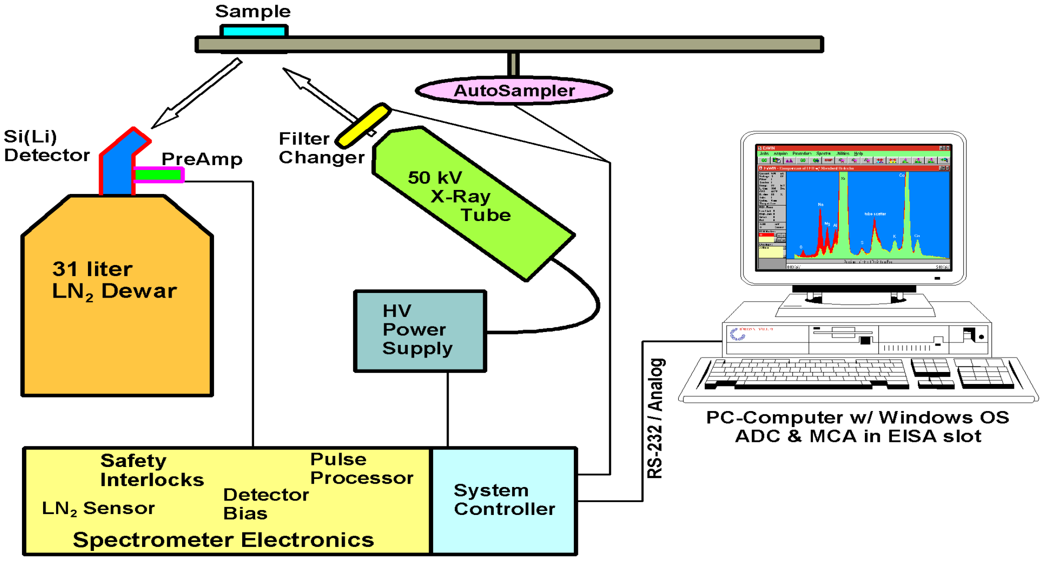


Fig. (3.1): Typical Si (Li) Detector

3.4.1 Electronic Typical Si (Li) Detector:

The system consists of a detector bias supply, preamplifier, and amplifier, an analog –to digital converter, a data storage device and a computer (Ron Jenkins et al., 2000).

3.4.1.1 Detector bias supply:

In order, to collect the charge formed in the detector, a bias voltage must be placed across the detector. The optimum bias voltage is around 1.5 KV. The bias voltage must be stable in order to maintain the same voltage gradients in the detector and thereby the same charges collection characteristic.

3.4.1.2 Preamplifiers:

The information of the absorbed radiation by the detector is a burst of charge (pulse) collected at the detector terminal. The first stage of the preamplifier is most frequently a charge sensitive stage; its function is to integrate the total charge of the pulse and convert it into a voltage signal that retains the proportionality to the energy deposit. In order to minimize the electronic noise, the input stage of the preamplifier, usually a field –effect transistor (FET), is cooled in the same manner as the detector, to optimize the preamplifier performance.

The temperature of this input stage may be kept warmer than the detector by allowing some heat to leak to it from the detector housing which is at room temperature.

3.4.1.3 Amplifiers:

The fundamental function of the main amplifier is to amplify and condition the signals from the preamplifier for the eventual presentation to the multi- channel analyzer (MCA). The prime requirement is that the system retains all-important quantitative characteristics of the signal, while providing an optimum performance in terms of the analytical parameters of specificity, sensitivity and detection limit. The important characteristics of these amplifiers are the linearity, the output pulse shape, the gain stability and the noise level.

3.4.1.4 Rise time and pile –up rejection:

There are two quite different problems that can be reduced by circuitry that rejects certain pulses. The first is related to the slow rise of some pulses due to effects in the detector, and the second is related to pulses that are closely spaced in time that would therefore “pile up” in the amplifier. The rise time of the pulses from a detector will depend on the location of this energy deposition within the detector. The basic operation mode of the function is as follows: from the output of the preamplifier, a separate “fast” signal channel is established that “inspects” the time interval between successive pulses, keyed to the “information” of the effective pulse within the “slow” channels "pulse shaped channel”. A gate signal is provided, denying passage of the signals where effective overlap is “detected”. Appropriate accounting for all pile –up effects must provide sensing both for “leading edge” and “trailing edge” piles up, for optimum performance to discriminate between the two types. This stems from the fact that, as the pulse amplitude is the energy parameter, leading edge pile-up distorts the pulse height on both pulses, hence both pulses must be gated off. Trailing edge pileup, however, distorts only the pulse height of the second pulse, and requires only the gating off of the second pulse.

3.4.1.5 Gain and zero stabilization:

A common method of gain of the amplifier is controlled to keep the count rates in these two channels equal. The gain of the system will be varied by the stabilization system, and therefore the resolution of the spectrum is poorer than in the ideal case. Since the gain changes the observed peaks may deviate significantly from their usual shape.

3.4.1.6 The Multi- Channel Analyzer (MCA):

The purpose of the Multi –Channel Analyzer is to measure the height of each amplifier output pulse and represent this amplitude by an integer number. Fundamentally, the MCA performs a “sorting” function on the variation in pulse amplitude (pulse – height). The pluses are presented from the linear system which ultimately stores and counts the number of pulses that fall within discrete “windows” of pulse amplitudes over a range of pulse amplitudes. The storage and counting of the data take place in the memory of the MCA. In order to transmit the relative quantitative information contained in the pulse amplitude distribution, it must be transformed to a digital form that can be accepted and stored by the MCA memory. This is an analog-digital conversion (ADC) process. Briefly, the incoming pulse charges a capacitor, which is then discharges with a constant current drain, whereby the time for the discharge becomes proportional to the total charge. The number of times a pulse of each height has been detected, where it is accumulated in the analyzer memory to form the spectrum of pulse heights. Subsequently, this information can be displayed as a picture of the analyzed energy spectrum. Each channel in memory can be presented with a particular energy interval, and the display can be presented with the x-axis calibrated in terms of the mean energy of each interval. The y-axis of the display gives the number of photons counted in each energy interval during the entire data accumulation period. They- axis is usually labeled “counts”, an abbreviation for the number of photons counted per energy interval. Consequently, most Multi-Channel Analyzers are equipped with an electronic means of dead time correction, such that observed spectrum represents the true number of photons arriving at the detector during the period of data accumulation.

3.4.1.7 Detector Resolution:

The two quantities of interest of a detector are its efficiency and resolution. The ability of the detector to produce lines or peaks for mono-energetic photons is characterized by the peak width and the detector efficiency. The width is commonly specified as the FWHM in keV, also called resolution, and calculated as the distance in electron volt between left and right sides of the peak at half of its maximum height, or more simply the peak width at half its height. The energy deposited by an absorbed particle goes only in part to the creation of electron-hole pairs, as some energy also goes into other types of excitation processes involving the whole crystal lattice, as well as the generation of heat.

The band gap in single-crystal silicon is 3.76 eV at 77K required to create a free electron- hole pair in silicon is 3.76 eV at 77K. Although the average of number pairs is N=E/e, the division of the photon energy between the different excitation modes causes statistical distribution in the number of pairs. Thus, statistical spread of the amplitude of the pulses is produced by a mono-energetic group of photons, which are completely absorbed in the detector volume. The observed root-mean-square deviation in the pairs is expressed as (F.N), where F is the Fano Factor.

From this expression it follows that this contribution to the observed Peak Width is:

$$FWHM = 2.35\ FVE \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3.1)$$

Where:

(FWHM) = full –width – half – maximum

E= energy KeV.

V= eV/electron – hole pairs.

F= Fano- Factor (dimensionless).

The Fano –Factor must be measured for each detector material.

This factor is an inherent property of the material. The good resolution of semiconductor detectors depends directly on the fact that these values of Fano – Factor are much smaller than the effective resolution of the detector system cannot be separated from the effects of electronic noise. The total resolution from that expression is equal to:

$$FWHM\ (e\ V) = (FWHM) + [2.35\ FvE] \ldots\ldots\ldots\ldots\ (3.2)$$

The relative contribution of the electronic noise increases at lower energies, “and conversely decreasing effect at higher energies”. The detector resolution is conventionally specified at 5.3 KeV as reference energy. The most frequently employed specification is to give full width half maximum (FWHM) at 1000 cps (Beckhoff., 2005).

3.4.1.8 Detection Limits:

Detection limits i.e. the minimum detectable amount, will depend on the sample composition, the energy of radiation, the source- detector distance, the detector efficiency, the background and the available time for measurement. The definition of minimum detection limit in instrumental analysis is frequently based on a statistical criterion, because the values of the detection limit of the element of interest were calculated by extrapolation from much higher concentration.

The detection limit of element is defined here as the concentration of that element which is an equal to 3/B counts in a peak, where B is the number of background pulses in an interval of 2 FWHM around the energy. An important extinction of consideration of statistical counting error and significance of data is found in the area of a very low level or trace analysis, where, the instrumental capability is being strained in determining even qualitatively whether an element is present or not. The detection limit is defined by the equation:

$$D_{Lm} = C_i 3\frac{\sqrt{B}}{P} \text{...... ....} \quad (3.3)$$

Where:

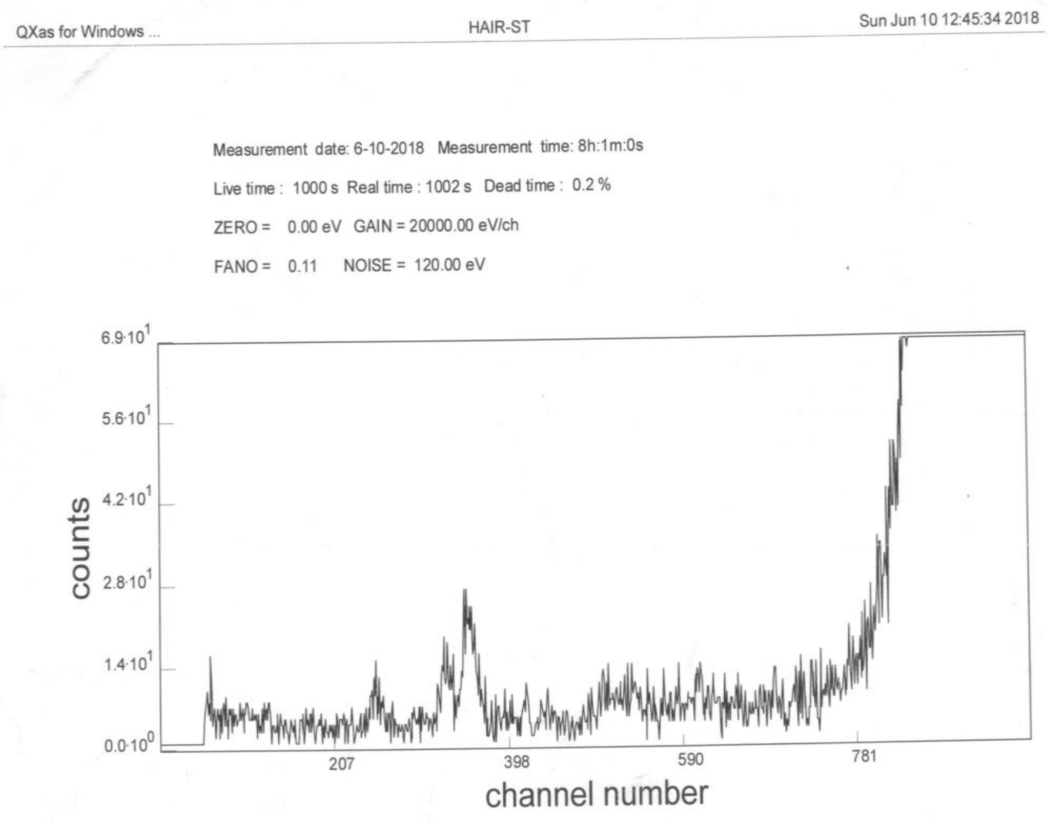
Ci is element concentration.

Pand B is the count rates for the peak and background respectively (Beckhoff.,2005) (Ron Jenkins,2000).

$$\text{The detection limit} = \text{concentration}3\frac{\sqrt{Back\ ground}}{Peak\ area} \text{.........} \quad (3.4)$$

3.4.2.2 Sample Calibration:

A quantitative approach was employed for elements concentration in hairs using a calibration comparative approach to the certified standard sample (Bleise et al., 2000).



QXas for Windows ... HAIR-ST Sun Jun 10 12:45:34 2018

Measurement date: 6-10-2018 Measurement time: 8h:1m:0s

Live time : 1000 s Real time : 1002 s Dead time : 0.2 %

ZERO = 0.00 eV GAIN = 20000.00 eV/ch

FANO = 0.11 NOISE = 120.00 eV

Fig. (3.2): Shows the X-Ray intensities collected from sample as spectrum data from (MCA).

3.5 Laser Induced Breakdown spectroscopy (LIBS):

Laser-induced breakdown spectroscopy (LIBS) is a method of atomic emission spectroscopy (AES) that uses laser-generated plasma as the hot vaporization, atomization, and excitation source (Hammer, S.M., et.al, 2006). Laser-induced breakdown spectroscopy (LIBS) is a laser diagnostic, where a laser beam focused onto a material generates transient high-density plasma as the laser intensity exceeds the breakdown threshold of the material (~1-10 MW/cm^2). The UV and visible emission from the plasma can be spectrally resolved and recorded for qualitative and quantitative analysis of the sample. The LIBS was first used for the determination of elemental composition of materials in the form of gasses, liquids, and solids during 1960 (Ryan, R.M., and Deci, E.L., 2000).

A short duration laser pulse of sufficient energy focused onto the surface of a material sample instantly increases its temperature above the vaporization temperature, regardless of the type of material.

3.5.1 Advantages:

LIBS have many advantages as an analytical technique. There is no need of sample preparation, which avoids further contamination of the material to be analyzed 10-11. The analysis process is fast and can be used for both non-conducting and conducting samples, regardless of their physical states, i.e. aerosols, gases, liquids or solids. LIBS are also applicable to the analysis of extremely hard materials that are difficult to digest or dissolve, such as ceramics and semi or super-conductors. Its capability for simultaneous multi-element determination, localized microanalysis, and surface analysis are also of great importance and it has been used successfully in hazardous and difficult environmental conditions to study remotely located samples for online and real time information about their spectra. LIBS has been found useful in elemental process monitoring and in field portable analyzers for in situ trace metal analysis of real samples where accuracy and precision are not the main requirement (Rai, 2016).

3.5.2 Lasers Used In LIBS:

Generally pulsed lasers are used in the production of plasmas and also in laser-induced breakdown spectroscopy (LIBS). We consider only those properties of lasers relevant to plasma production in gaseous, liquid and solid samples. It is possible to generate short duration laser pulses with wavelengths ranging from the infrared to the ultraviolet, with powers of the order of millions of watts (Mashair,2018).

3.5.2.1 The Q-Switched Nd: YAG laser source:

Nd: YAG lasers are possibly the more widely used lasers either for basic research or for industrial and technological applications. These lasers are also excellent pump sources for laser development, for instance Ti: Sapphire ultrashort pulse lasers are based on CW Nd: YAG pumping. In particular, Nd-YAG lasers have been applied to study laser-induced oxidation in metals as titanium and chromium; semiconductors as silicon (Aygun, G. et al., 2006). (Perezdel Pino, A. et al., 2004) demonstrated that the rutile phase of TiO_2 is obtained by laser oxidation in air of titanium films. Nd:YAG laser pulses have been used to laser-induce a phase transformation from W_3O thin films to WO_3 (Evans R., et al., 2007); laser ablation for micromachining of bulk metals as copper, bronze and aluminum has also been done using Nd:YAG nanosecond pulses (Maisterrena-Epstein R., et al., 2007), (Dumitras, D.C.,2012). The Q- switched Nd: YAG laser is a solid-state type laser emits 1064 nm as the fundamental wavelength, and it emits 532 nm wavelength using frequency doubling technique via nonlinear crystals such as KDP crystals, and it's possible to get 1320 nm wavelength from the Q- switched Nd: YAG source using frequency. The Q-switched Nd: YAG laser source model OW-D1 used to fabricate the oxide thin films was imported from china it’s used mainly for beauty and treatment purposes such as vascular therapy and hair removal, etc. Q-switched Nd:YAG laser used in this work is supported from china and exists in Laser Institute – Sudan University of Science & Technology (Oriental Wison Mechanical & Electronics Co. Ltd., 2017). Figure (3.1) shows the user interface of Q-Nd: YAG laser source OW-D1 source.

3.5.2.2 Specification of Nd: YAG Laser source used in LIBS:

The important features of the Q-switched Nd: YAG (OW-D1 model) used for LIBS are illustrated in table (3.1).

Table (3.1): Specifications of the Q-switched Nd: YAG laser source:

Product Name	ND YAG LASER Age spot removal machine (OW-D1)
Model No.	OW-D1
Theory	Laser
Treatment head	1064nm/ 532 nm/ 1320 nm (Moppet Head)
Spot size	1-8 mm
Frequency	1-6 Hz
Energy	Up to 2000 m J
Indicator	Infrared ray indicator light
Input power	AC 220 V (110 V) / 15 A --- 50 Hz (60 Hz)
Pulse width	10 ns

3.5.2 LIBS Setup:

The experimental setup was implemented by assembling existing components. It is based on a Q-switched Nd: YAG laser, an optical system for focusing the beam and collecting the signal from the sample and a spectrometer. Accompanying the spectrometer and detector is a delay generator which accurately gates the detector's response time, allowing temporal resolution of the spectrum. The setup used for recording the LIBS of human scalp hair is shown in figure (3.3).

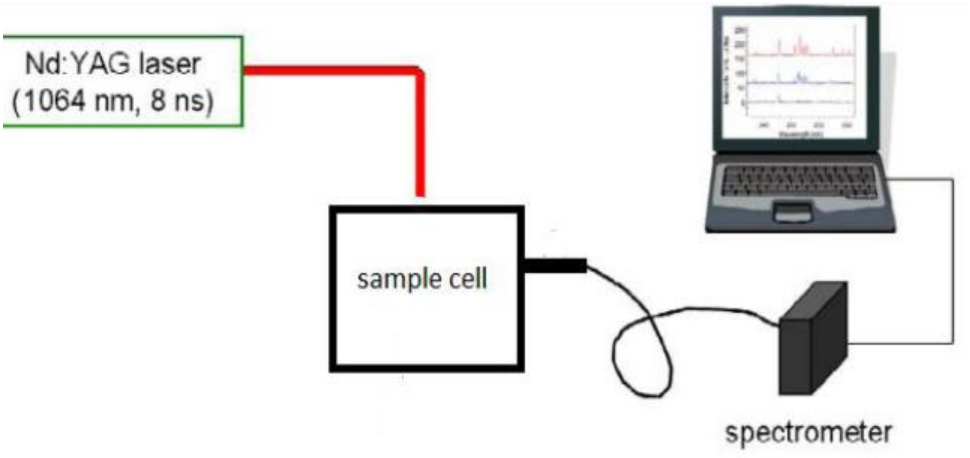


Fig. (3.3): Experimental setup of LIBS

3.6 Inductive coupled plasma emission (ICPE 9000):

This is another spectroscopic technique which benefited from the plasma phenomenon. Generally speaking, ICP emission spectrometers are analytical instruments used in a broad range of fields. They feature high ppb level detection ability, broad 5-6-digit analysis concentration ranges, and batch analysis of multiple elements. Recent wider usage has resulted in an increased demand for shorter analysis times and improved high-matrix sample detection. Figure (3.4) shows a photograph of the ICPE 9000 used in this supplied by Shimadzu.

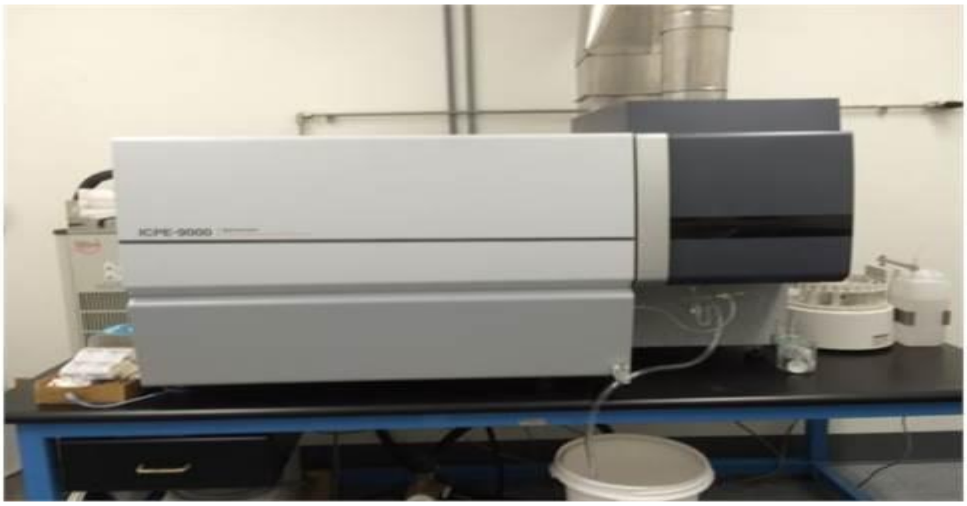


Figure (3.4): A photograph of the ICPE 9000

The internal components of the ICPE 9000; provides higher accuracy analysis and easier operation as an advantage of the ICPE9000 emission spectrometer are shown in figure (2.5) in chapter two.

3.6.1 ICPE Specifications:

The general specifications of the ICPE 9000 are listed below:

Plasma Light Source specification:

Torch unit	Axial observation (axial and radial switching option available)
Plasma torch	Either mini torch (standard accessory) or conventional torch can be used.
Nebulizer	Coaxial type

Radio Frequency Generator specification:

Oscillator Sample	Crystal oscillator
Crystal oscillator	1.6 kW
Output stability	Within 0.3%
Radio frequency circuit element	Transistor element
Ignition method	Fully automatic
Load matching	Automatic matching

3.7 Measurement methods:

The method for carrying out the XRF, LIBS, and ICP results of the human scalp hair of the workers in two sites of Omdurman Industrial area are briefly describe hereunder:

First for XRF: The standard reference sample and the hair samples collected from workers were prepared according to the procedure used for XRF measurement geometry. Samples were analyzed for elements of determination and concentration obtains relative to the data and reference certificate of the standard sample. The experiment was run using radioactive Cd^{109} source X-ray fluorescence spectrometer to utilize the elemental analysis in hairs samples where each of the samples were measured for 1000 sec. The X-ray spectra was collected by Si (Li) detector with energy resolution of 180 eV at Ek_{α} (5.8 KeV) of manganese (Mn) linked to a Canberra 35 plus The Multi-Channel Analyzer (MCA) system that connected to the computer to obtain acquiring data. Fig. (3.2).

For LIBS:

The experimental procedure to record the LIBS spectra of human scalp hair of the samples was done as follows: The setup was arranged as shown in figure (3.3). Then laser energy was adjusted by adjusting the flash lamp voltage in order to obtain sufficient peak power needed to form plasma. Then the spectrometer was connected to the PC through USB cable and the program spectra suit was launched. After that the laser pulse was focused on the surface of the sample cell with Distilled water and the spectrum was recorded and saved as dark spectrum that would be subtracted when getting the sample spectrum. Then the sample was put in the sample cell. The all samples were irradiated with different laser pulse energy of 200 mJ. Using laser power less than 40 mJ gave a spectrum with very few lines indicating insufficient excitation energy to allow for exiting all types of atomic species in the human scalp samples. The sample spectrum was processed by subtracting the dark current. And the result was captured by spectrometer, and the relation between wavelength and Intensity was plot by using origin program. The emitted spectra were analyzed using Atomic spectral database. By referring to the atomic spectra database, the elements in the sample were identified. The same procedure was repeated done for all samples.

Finally, method of measurement using **ICPE 9000:** First 0.1 gram from each sample has been weighted, and then the weighted samples were put in furnace in 700 ^{o}C for 2 hours. Then the samples were dissolved in 5 ml of hydrochloric acid of 0.1 concentrations and then the samples were entered to the ICPE and the results were carried out.

CHAPTER FOUR

RESULTS AND ANALYSIS

CHAPTER FOUR

RESULTS AND ANALYSIS

4.1 Introduction:

A number of 22 hair samples of men in different types of workshops and 20 samples from both genders males and females in perfume factory were collected for the elements Calcium (Ca),Manganese (Mn), Iron (Fe), Copper (Cu), Zinc (Zn),Mercury (Hg) , Lead (Pb) and Strontium (Sr) assessment, the samples covers reference samples for control and comparing the results collected from Khartoum state and the elements were analyzed for them using the three spectroscopic techniques as done with the all other samples. The results of the X-ray intensity of the element's concentration in both standard and samples were obtained after calibration and comparison with standard data using statistical analysis, correlation, t-test value and factor analysis. Also, a number of 16 hair samples from different type's workshops were collected; detection used three method (XRF), (LIBS) and (ICPE) to measure element's concentration and comparison with standard international data.

4.2 XRF Results:

The results for 22 hair sample of men category in the workshops of ages range between 27 to 50 years old in different types of workshops in Omdurman industry area. And the results for 20 samples from both genders, 15 males (22– 56 years) and 5 females (40- 50 years) in perfume factory. Fig (4.1) shows the average element's contents in scalp hair of the workers in the workshops in industry area and indicates the presence of elements Ca, Mn, Fe, Cu, Zn, Hg, Pb and Sr. Also the figure shows the average element's contents in scalp hair of the workers in the Perfume factory and indicates the presence of elements Ca, Fe, Cu, Zn, Hg and Pb.

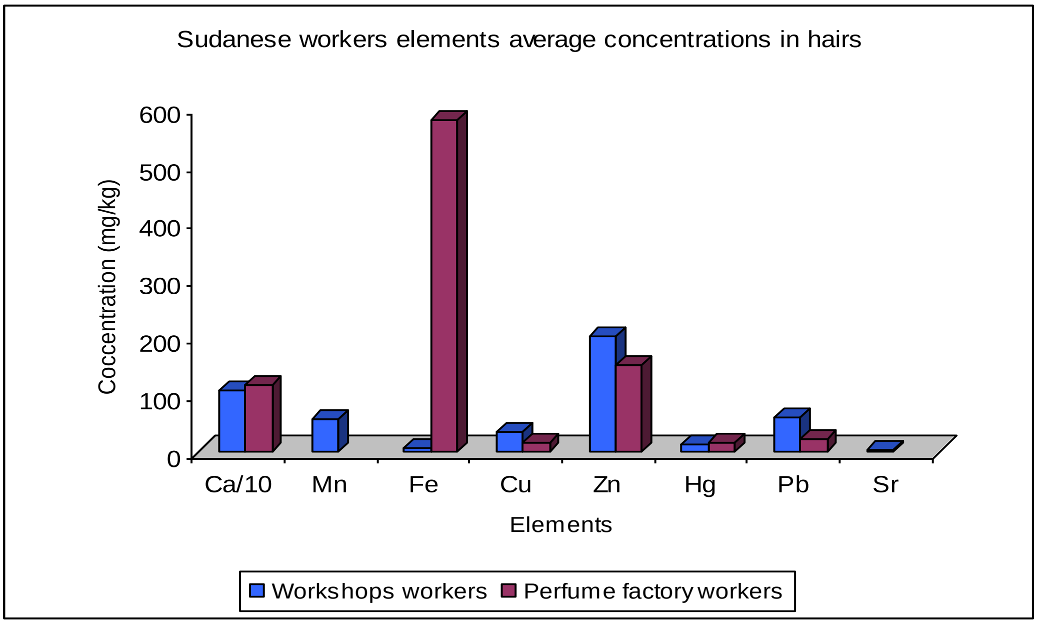


Fig. (4.1): Average elements concentration of Sudanese workers at the two sites.

Statistical treatment of results of data for the elements concentration in hairs in the two sites under study using both correlation analysis, t-test value and factor analysis shows the average elements concentration in hair samples of workshops were subjected to Person Bivariate correlation (r) in table.(4.1) display the elements in hair Cu is correlated with Mn (r= o.70, p < 1) and with Pb (r = o.76, p < 1).

Although, highly significant correlation (p <1) found between the Cu with Zn (r = 0.90) and with Hg (r= 0.90). While Pb correlated with Mn (r= o.69, p <0.7) and with Zn (r = o.5 6, p < 0.7) and significant highly correlation with Cu (r = o.76, p < 1).

The correlations of elements in Perfume Factory groups in table. (4. 2) show that Fe is correlated with Hg (r = o.27, p < 0.4) and with Pb (r = o.42, p <0.7). Although it is correlated with Zn (r = o.53, p <0.7). Table (4.3) compares the factors and t-test of the both groups under investigation. Fig. (4.2) shows elements variation contribution in industry workshops. Elements variation contribution in perfume factory is shown in fig (4.3).

Table (4.4) shows the data of elements concentration in human scalp hairs in other worldwide studies with compared with average results of this work (mg/kg- dry weight basis).

Table (4.1): Correlation of elements in workshops workers hairs

Elements	Ca	Mn	Fe	Cu	Zn	Hg	Pb	Sr
Ca	1.00							
Mn	0.41	1.00						
Fe	0.45	0.81	1.00					
Cu	0.71	0.70	0.70	1.00				
Zn	0.65	0.47	0.50	0.90	1.00			
Hg	0.51	0.52	0.50	0.90	0.90	1.00		
Pb	0.55	0.69	0.80	0.76	0.56	0.63	1.00	
Sr	0.53	0.61	0.53	0.71	0.65	0.54	0.32	1.00

Table (4.2): Correlation of elements in hair workers of perfume factory groups

Elements	Ca	Fe	Cu	Zn	Hg	Pb
Ca	1.00					
Fe	0.77	1.00				
Cu	0.93	0.56	1.00			
Zn	0.86	0.53	0.92	1.00		
Hg	0.68	0.27	0.66	0.77893	1.00	
Pb	0.75	0.42	0.88	0.73	0.34	1.00

Table (4.3): Significant statistical results based on correlations and t-test value for variable contributions elements

	Workshop Workers Hairs				Perfume factory Hairs			
Elements	Factor 1	Factor 2	Facto r 3	t-test	Factor 1	Factor 2	Factor 3	t-test
Ca	0.097	0.066	0.003	6.382	0.213	0.017	0.021	3.979
Mn	0.115	0.215	0.086	4.572	*	*	*	*
Fe	0.119	0.260	0.003	4.789	0.104	0.443	0.297	3.055
Cu	0.175	0.0180	0.005	6.877	0.214	0.001	0.051	4.296
Zn	0.138	0.174	0.015	6.957	0.200	0.047	0.001	3.956
Hg	0.132	0.092	0.078	5.120	0.119	0.461	0.157	2.685
Pb	0.121	0.138	0.227	5.570	0.149	0.032	0.474	3.762
Sr	0.100	0.036	0.583	7.246	*	*	*	*

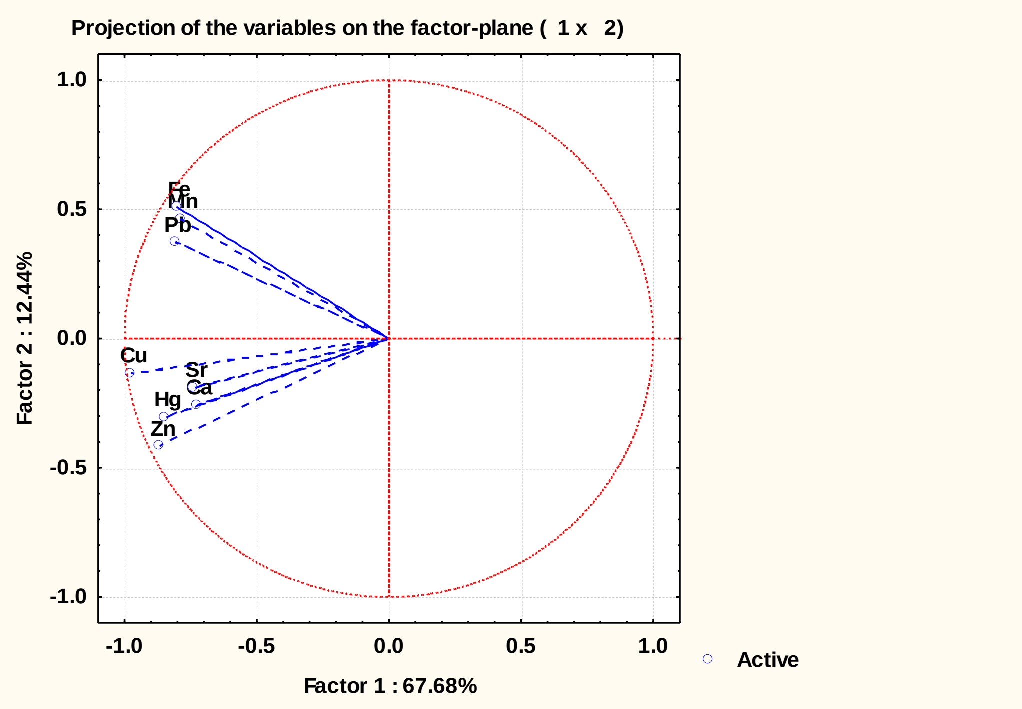


Fig. (4.2): Elements variation contribution in industry workshops

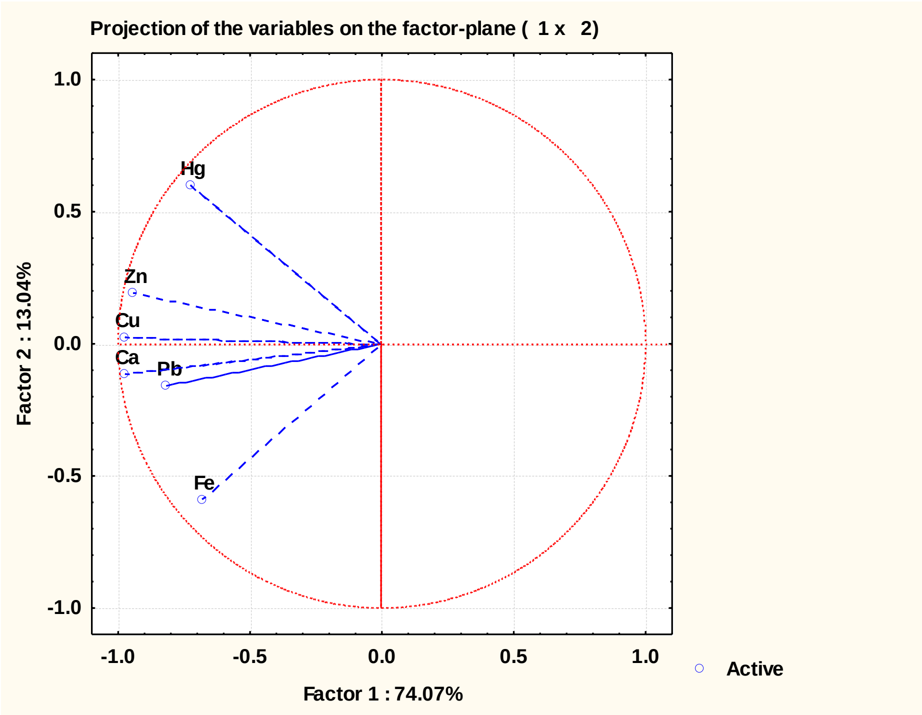


Fig. (4.3): Elements variation contribution in perfume factory

Table (4.4): literatures of elements concentration in human scalp hairs in other worldwide studies with compared with average results of this work (mg/kg- dry weight basis)

Countries (Worldwide Studies)	Ca mg/kg	Mn mg/kg	Fe mg/kg	Cu mg/kg	Zn mg/kg	Hg mg/kg	Pb mg/kg	Sr mg/kg
Present study (samples 42)	1098.7	56.61	593.25	25.22	177.29	14.1	42.41	3.41
I.A.E.A (dry weight) 2000	1120	9.6	123	17.6	167	0.573		
USA, Women Shamberger, 2003				19.8	116.8	0.48	0.97	4.79
Brazil Cameiro et al. 2002 M. I. Szynkowska,2009		0.37		23.5	190	1.28	5.91	5.1
India Samanta et al, 2004		15.48		14.76	152.4	0.88	8.03	
France Goulle et al, 2005		0.41		20.3	162	0.66	0.41	
Poland Y. Takagi et al., 1986 M. I. Szynkowska,2009	1139	0.82	22.1	9.41	160	0.28	4.81	7.50
Japan Y. Takagi et al., 1986	700	2.4	15	10.7	114	2.2	3.62	
Italy, Children (3-15 y) Senonfonte et al. 2000		0.35		22.1	150		7.11	
Sweden, M. I. Szynkowska,2009 Y. MURAMATSU,1988			11.7		137	1.23	0.960	1.20
Libya, Shah *et al.*, (2006);		1.73			190.3		24.95	
Egypt, Rashed and Hossam, (2005);				10.6	172		5.95	

4.3 (LIBS) and (ICPE) results:

A number of 16 hair samples from different type’s workshops covers references samples for control were collected detection elements like (Mn), (Fe), (Cu), (Zn), (Hg), (Pb) and (Sr) assessment. The (LIBS) and (ICPE) methods were used to analyze the elements in human hair scalp for the verification of the obtained results using (XRF) technique, (LIBS) and (ICPE) were used to measure the element's concentration and then comparison with standard International data of the obtained results. Fig. (4.4) shows LIBS spectra as a function of wavelengths from the human scalp hairs (16) samples.

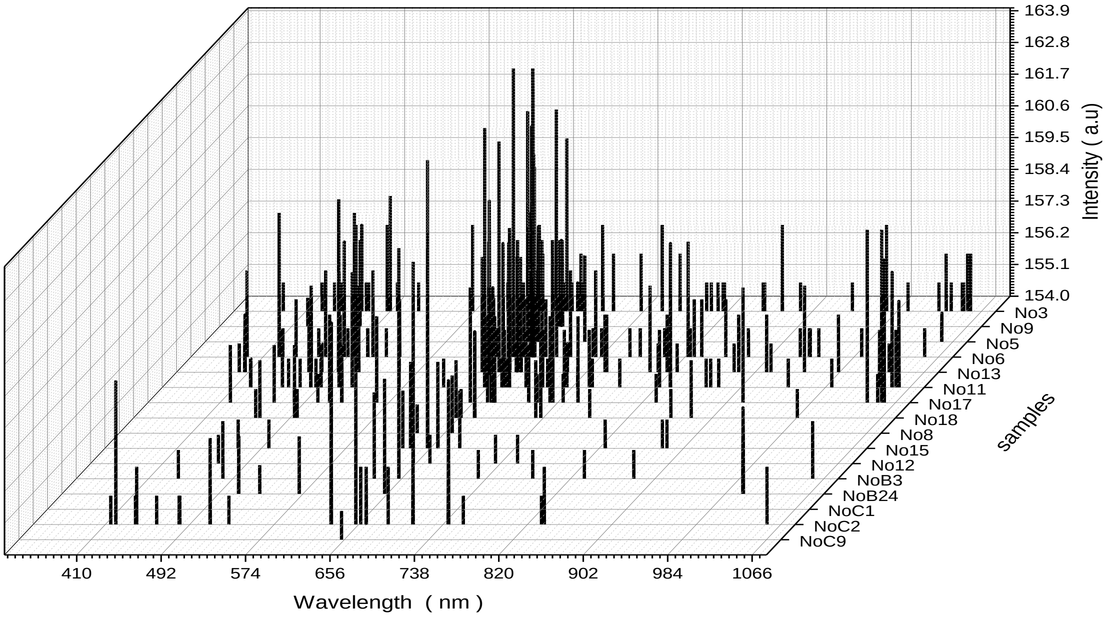


Fig (4.4): LIBS spectra as a function of wavelengths from the human scalp hairs (16) samples

The NIST online software was used for identification of elements and their concentration from LIBS spectrum while the ICPE gives the elements with their concentrations directly.

The ICPE results for the Manganese (Mn) were shown in first column of the table (4.5).

Table (4.5): Manganese (Mn) concentration in human scalp hairs with the three methods (ICPE, LIBS and XRF) used in this work

ICPE(ppm)	LIBS(ppm)	XRF(ppm)	Mn
			Sample N0
9.6	9.6	9.6	**Standard**
4.8	3.308	4.38	**No:3**
10	8.6	8.73	**No:9**
7.9	6.513	4.58	**No:5**
7.2	9.735	8.05	**No:6**
4.9	3.8675	4.23	**No:13**
8.6	13.499	24.4	**No:11**
15	11.53	13.4	**No:17**
14	23.25	11.5	**No:18**
7.7	8.82	6.75	**No:8**
7.5	6.184	6.91	**No:15**
3.4	4.5	3.3	**No:B3**
8.1	8.77	9.3	**No:12**
2.63	3.6085	3.41	**No:B24**
5.3	4.4	0	**No:C1**
4.22	5.43	5.53	**No:C2**
10.33	14.321	12.76	**No:C9**

These results of manganese concentration in human scalp hairs of perfume and workshops workers in Omdurman Industrial area shows slightly differences of the concentration of Mn element of the same sample obtained using the three spectroscopic techniques, these differences may be attributed to the technique sensitivity and the sample preparation for each one. The obtained results of the Mn concentration in different samples of human scalp hairs using the three techniques shown in table (4.5) is plotted in fig. (4.5) for the comparison between the techniques.

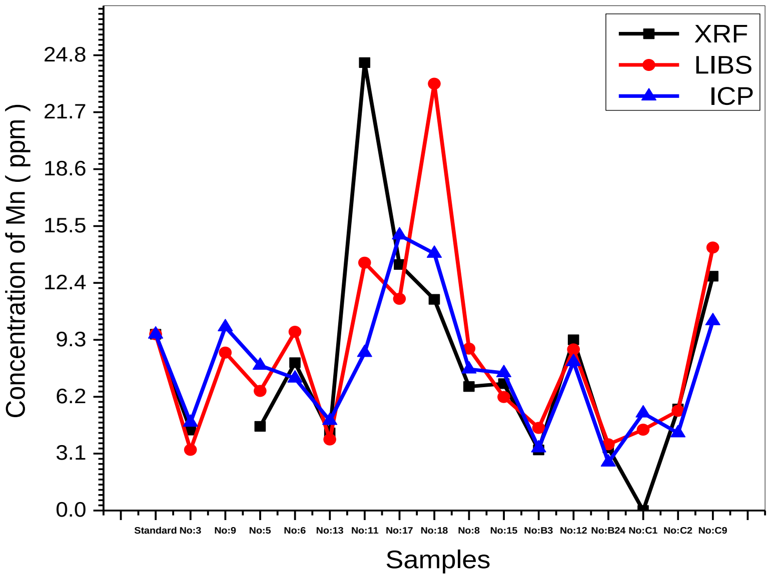


Fig. (4.5): Manganese (Mn) concentration on human scalp hairs different samples for the three measurement methods (XRF, LIBS and ICPE)

Again, the ICPE results of the Cu concentration in human scalp hairs is presented together with that obtained with LIBS and XRF techniques in table (4.6).

Table (4.6): Copper (Cu) concentration in human scalp hairs with the three methods (XRF ICPE, LIBS and XRF) used in this work

ICPE(ppm)	LIBS(ppm)	XRF(ppm)	Cu
			Sample No
17.6	17.6	17.6	**Standard**
16	17.683	18.4	**No:3**
21	24.019	39.1	**No:9**
17	17.78	19.4	**No:5**
26	29.6	33.3	**No:6**
0	10.167	13.9	**No:13**
14	15.351	78.9	**No:11**
20	11.74	65.8	**No:17**
0	51.15	60.6	**No:18**
28	28.16	37.5	**No:8**
36	35.6	36.1	**No:15**
38	35.8	31.4	**No:B3**
58	55.3	56	**No:12**
0	26.2	25.1	**No:B24**
19	14.84	19.0484	**No:C1**
20	19.915	21.9915	**No:C2**
0	0.0977	0.0977	**No:C9**

The same done as in the case of Manganese elements for the comparison the obtained results using the three techniques (ICPE, LIBS, and XRF) shown in table (4.6) is plotted in fig. (4.6) in histogram and in fig.(4.7) in the actual XY results representation.

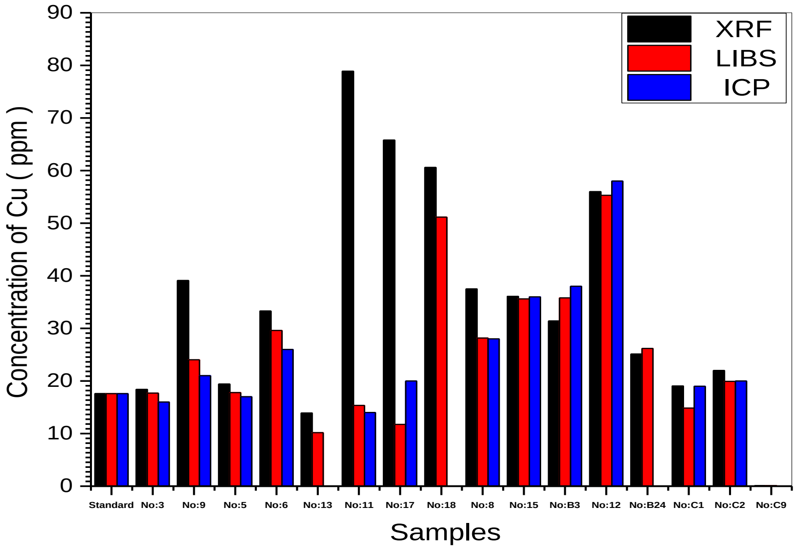


Fig (4.6): Copper (Cu) concentration in different samples of human scalp hairs obtained using (XRF, LIBS and ICPE) techniques

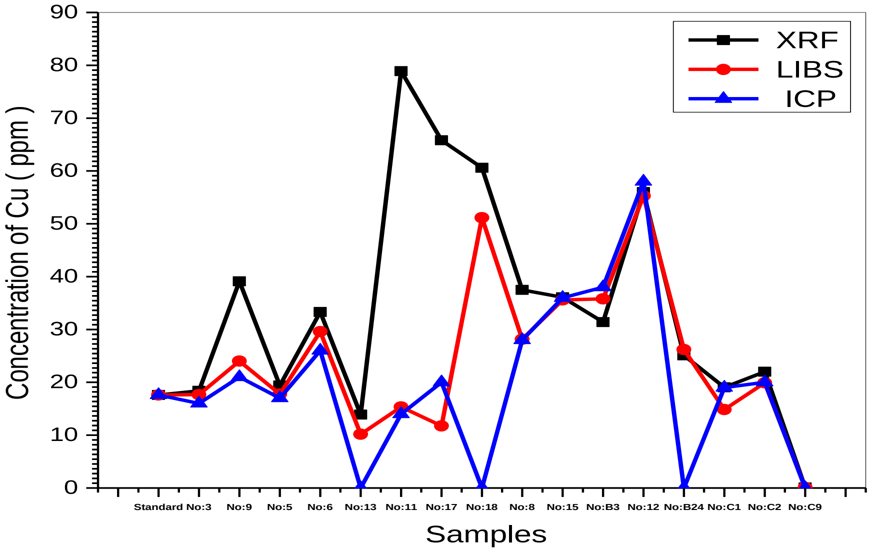


Fig. (4.7) Copper (Cu) concentration in human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

Clearly XRF techniques shows high copper concentration in human scalp hairs of some samples than the ICPE, and LIBS, from this one suggests that this increment in the Cu concentration may due to copper anode in X-ray tube, since the two other techniques give approximately the same results.

Zinc (Zn) is an important element, the concentration of Zinc (Zn) in human scalp hairs of the different samples of worker in perfume and workshops in Omdurman industrial area was detected using the ICPE, LIBS in addition to that obtained with XRF. The result of (Zn) concentration in scalp hairs of the different samples is tabulated in table (4.7).

Table (4.7): Zinc (Zn) concentration in human scalp hairs with the three methods (ICPE, LIBS and XRF) used in this work

ICPE(ppm)	LIBS(ppm)	XRF(ppm)	Zn
			Sample No
167	167	167	**Standard**
150	375.5	261	**No:3**
100	155.4	164	**No:9**
85	170	184	**No:5**
130	125.3	163	**No:6**
90	125	125	**No:13**
120	98.958	351	**No:11**
220	299	380	**No:17**
380	350	381	**No:18**
94	150	177	**No:8**
170	160	168	**No:15**
28	26.9	24.2	**No:B3**
36	34.9	32.4	**No:12**
23.5	24.8	22.9	**No:B24**
49	52	47	**No:C1**
23	24	21	**No:C2**
18	19	16	**No:C9**

Histogram of the Zn concentrations in human scalp hair of the different samples of perfume and workshops worker in Omdurman industrial area is shown in fig. (4.8), and in fig. (4.9).

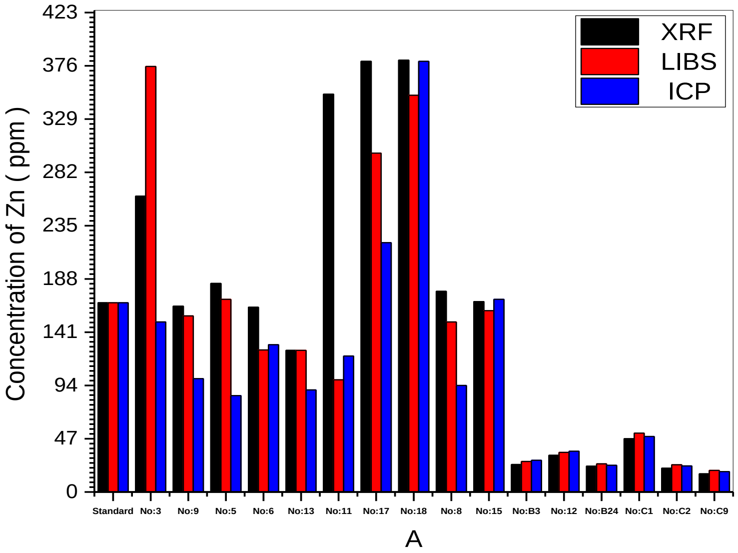


Fig. (4.8) Zinc (Zn) concentration in human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

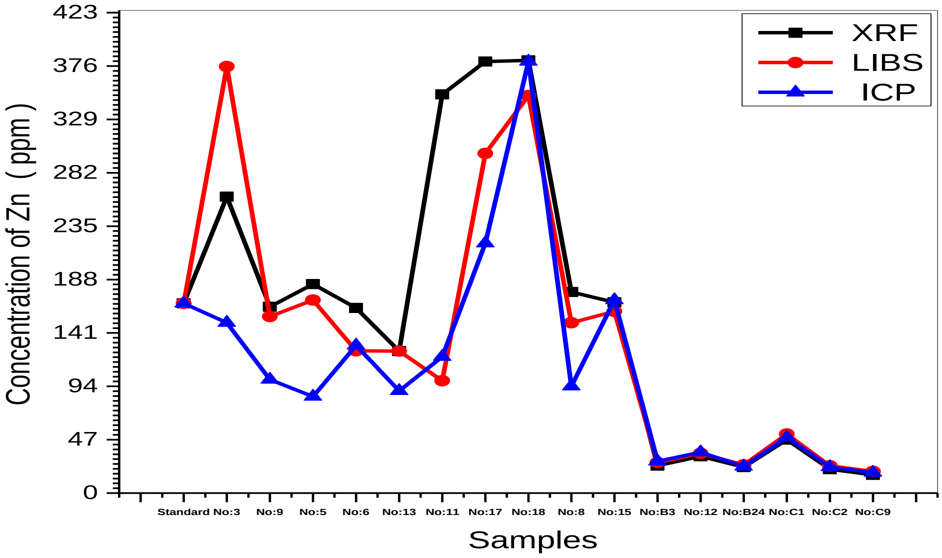


Fig. (4.9): Typical Zinc (Zn) concentration in human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

As shown in fig. (4.9) at least five samples of the human scalp hairs have high concentration when the XRF technique is used. For Mercury (Hg) the same as done with previous elements for deep analysis the ICPE and LIBS in addition to the XRF results of the different human scalp hairs of the perfume and workshops worker in Omdurman industrial area and its results is tabulated in table (4.8).

Table (4.8): Mercury (Hg) concentration in human scalp hairs with the three methods (ICPE, LIBS and XRF) used in this work**:**

ICPE(ppm)	LIBS(ppm)	XRF(ppm)	Hg
			Sample No
0.573	0.573	0.573	**Standard**
11.2	12.502	8.81	**No:3**
13.2	12.625	13.7	**No:9**
10.4	12.37	8.19	**No:5**
9.92	8.82	0	**No:6**
2.145	1.6081	4.7	**No:13**
19.3	17.03	26.7	**No:11**
3.34	2.0038	2.89	**No:17**
4.55	1.5419	2.44	**No:18**
14.3	13.7	10.6	**No:8**
15	17.2	14.8	**No:15**
34.2	33.95	34.56	**No:B3**
35.6	34.49	48	**No:12**
22.32	21.88	14.2	**No:B24**
0	0	0	**No:C1**
0	0	0	**No:C2**
0	0	0	**No:C9**

Fig. (4.10) shows a comparison between the measured Hg concentration in histogram using the three techniques (ICPE, LIBS, and XRF).

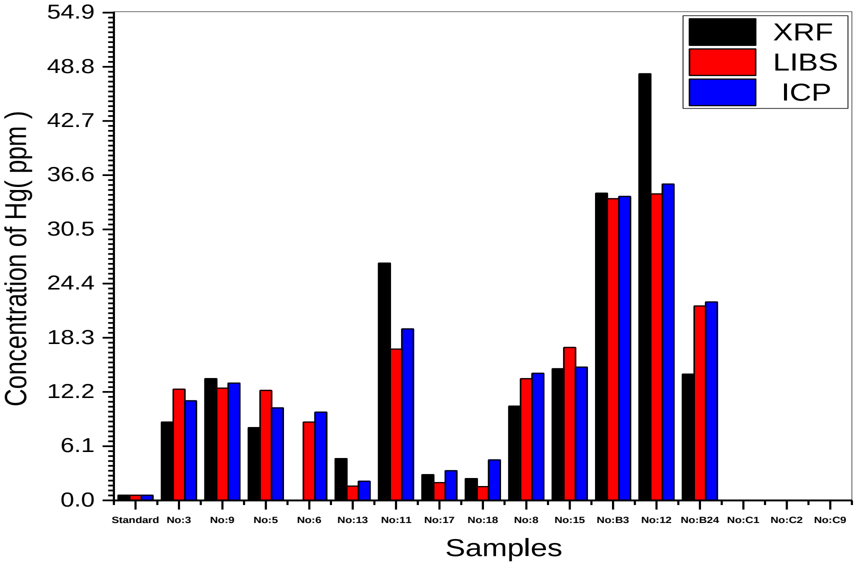


Fig. (4.10) Histogram of Mercury (Hg) concentration of human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

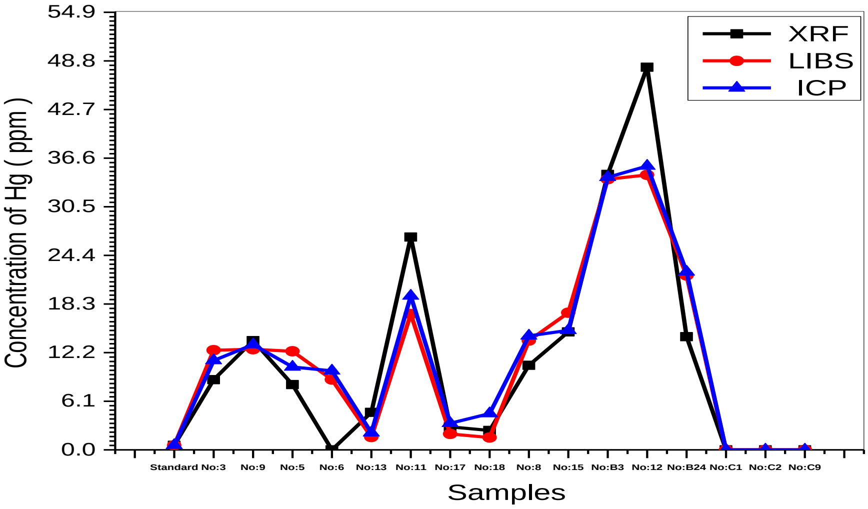


Fig. (4.11): Mercury (Hg) concentration in human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

Fig. (4.11), shows the same results in actual xy obtained results representation.

The Lead (Pb) concentrations in human scalp hairs obtained with (ICPE, LIBS and XRF) techniques are shown table (4.9).

Table (4.9): Lead (Pb) concentration in human scalp hairs using ICPE, LIBS, and XRF techniques

ICPE(ppm)	LIBS(ppm)	XRF(ppm)	Pb
			Sample No
0.97	0.97	0.97	**Standard**
0	36.945	31.8	**No:3**
0	33.455	20	**No:9**
0	36.16	45.1	**No:5**
0	25.8	34.3	**No:6**
0	15.54	22.9	**No:13**
0	173.2	158	**No:11**
0	151.2	114	**No:17**
0	133.5	98.9	**No:18**
46	66.43	51.5	**No:8**
0	118.34	105	**No:15**
0	3.7594	85	**No:B3**
0	3.4213	74.1	**No:12**
0	22	23	**No:B24**
0	11.834	10.5	**No:C1**
0	6.7594	8.5	**No:C2**
0	6.4213	7.41	**No:C9**

The results of Lead (Pb) concentrations in human scalp hairs obtained with (ICPE, LIBS and XRF) techniques shown table (4.9) is plotted in histogram and in actual (x and y) representations in fig. (4.12), and fig. (4.13), respectively.

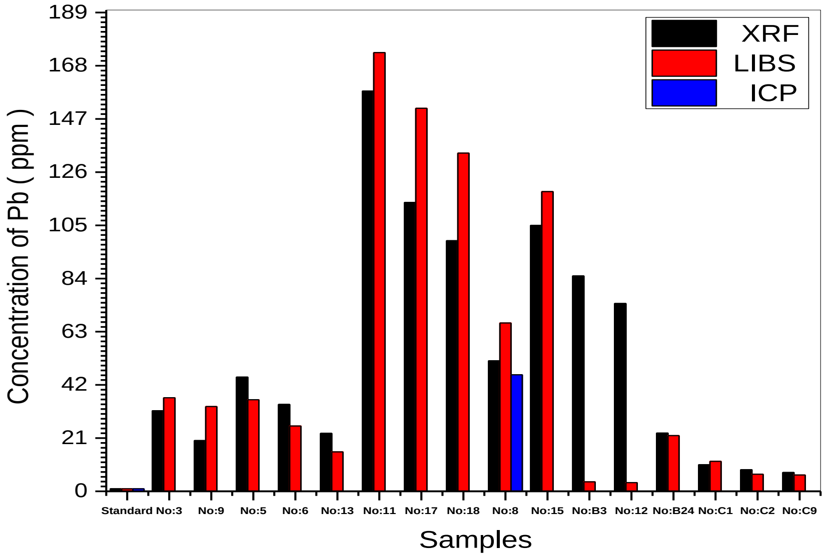


Fig. (4.12) Histogram of Lead (Pb) concentration in histogram of human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

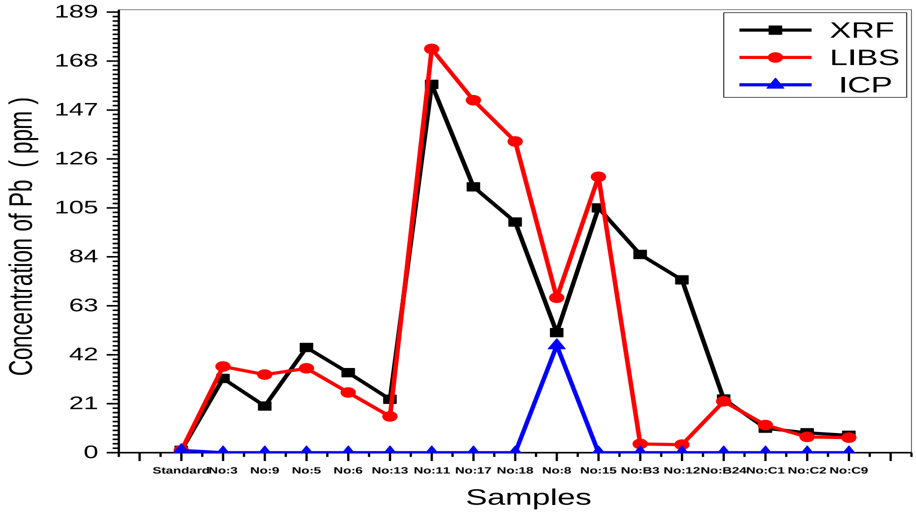


Fig. (4.13) Lead (Pb) concentration in histogram of human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

Fig (4.12) and fig (4.13) showed that the LIBS technique depicts high lead (Pb) concentration of human scalp hairs different samples than the XRF and ICPE techniques. Also, the results showed that the ICPE technique was not measured any lead (Pb) concentration of human scalp hairs except for the sample No. 18 and the reference, from this one can say that the ICPE technique has a limitation in detecting lead element due to the samples preparation. Table (4.10) shows the concentration of the strontium (Sr) element in human scalp hairs of the collected samples as measured using ICPE (shown in the first column of the table), LIBS, and XRF techniques.

Table (4.10): Strontium (Sr) concentration in human scalp hairs of the collected samples measured using (XRF, LIBS and ICPE) techniques

ICPE(ppm)	LIBS(ppm)	XRF(ppm)	Sr
			Sample No
4.97	4.97	4.97	**Standard**
0.89	3.54	2.24	**No:3**
0.79	0	0.01	**No:9**
5	0	4.33	**No:5**
1.8	2.7	4.95	**No:6**
1.3	0	2.28	**No:13**
3.6	5.94	9.36	**No:11**
3.4	12.6567	4.63	**No:17**
4.4	12.2709	5.42	**No:18**
4.2	3.14	5.83	**No:8**
4.3	3.2	2.65	**No:15**
3.5	3.1	3.4	**No:B3**
1.1	0.98	1.23	**No:12**
2.3	2.33	2.54	**No:B24**
2.78	1.99	2.95	**No:C1**
2.22	1.32	1.48	**No:C2**
3.4	2.96	3.3	**No:C9**

For comparison between the concentrations of the strontium elements in human scalp hairs of some workers (perfumes and workshops in Omdurman industrial area) using the three techniques (ICPE, LIBS, and XRF) the results in table (4.10) is plotted in fig. (4.14) and fig. (4.15).

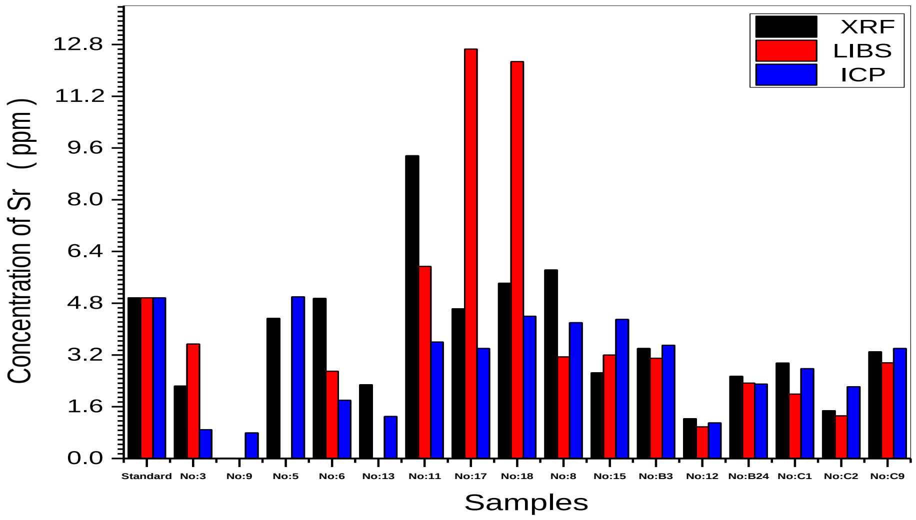


Fig. (4.14) Strontium (Sr) concentration in histogram of human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

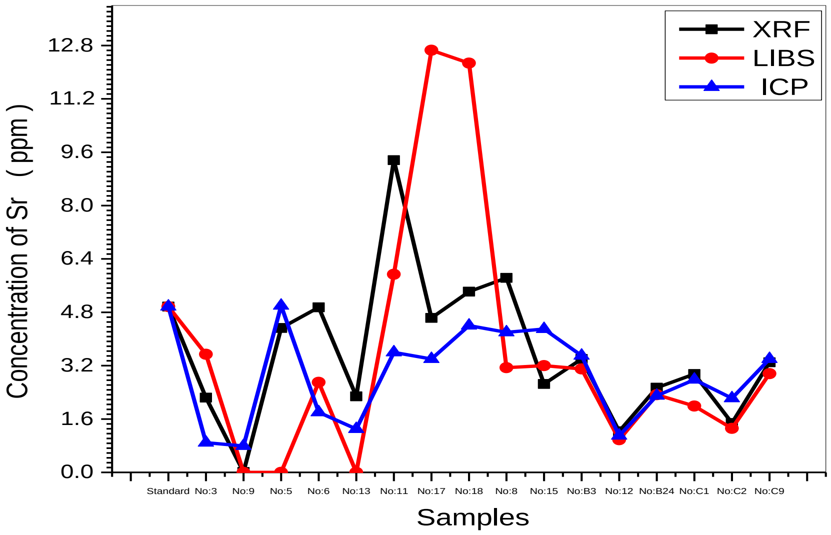


Fig. (4.15) Strontium (Sr) concentration of human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

In table (4.11) Iron (Fe) concentrations associated with human scalp hairs measured using (ICPE, LIBS, and XRF) techniques is presented. The concentration in many samples is exceeded the international minimum level. The minimal concentration was 53.28 ppm by ICPE for sample No: 12 and maximal value was 253.89 ppm by XRF for sample No: B3, as the standard value of Iron (Fe) concentration as reported by International Atomic Energy Agency (IAEA) is 123 ppm. The measured Iron concentration is human scalp hairs of workers in Omdurman industrial area is shown in fig. (4.16) and in fig. (4.17) in histogram and XY representations.

Table (4.11): Iron (Fe) concentration in human scalp hairs of the collected samples measured using (XRF, LIBS and ICPE) techniques:

ICPE(ppm)	LIBS(ppm)	XRF(ppm)	Fe
			Sample No
123	123	123	**Standard**
105.24	183.31	253.89	**No:B3**
53.28	141.46	82.22	**No:12**
154.24	236.79	224.29	**No:B24**
203.9	172.13	190.45	**No:1C**
111.82	112.54	138.13	**No:2C**
131.55	241.39	124.97	**No:9C**

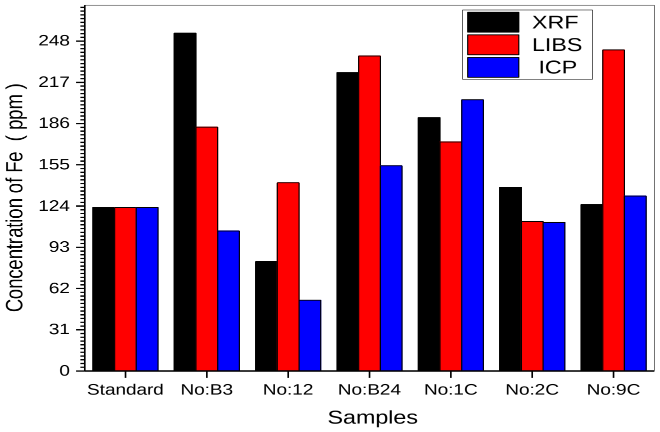


Fig. (4.16): Iron (Fe) concentration in histogram of human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

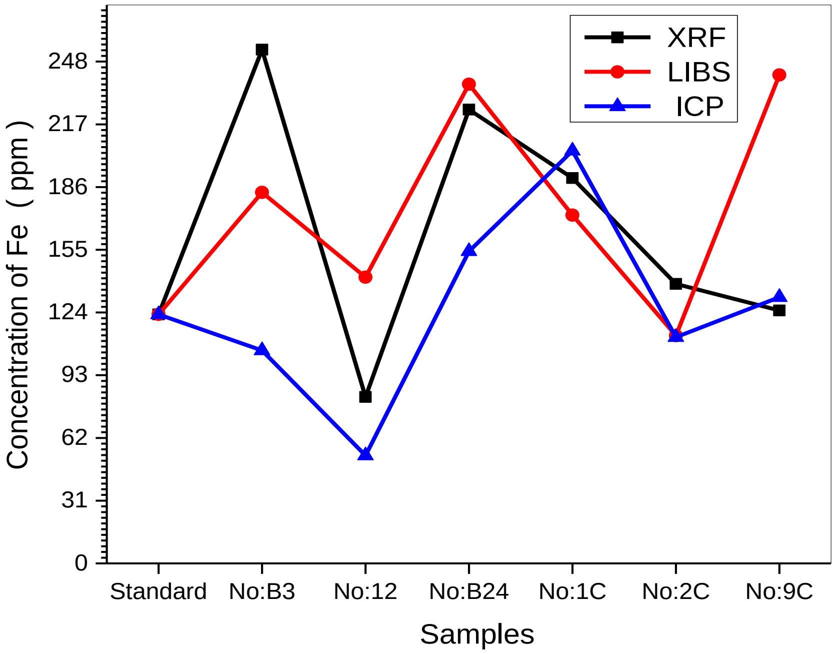


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Fig. (4.17): Iron (Fe) concentration of human scalp hairs different samples obtained using (XRF, LIBS and ICPE) techniques

4.4 Discussion:

The present results are significant in the two major groups of workers, which show the elements Ca, Fe and Sr in the workshop group in optimum values and Mn, Cu, Zn, Pb and Hg are higher levels compared to the International Atomic Energy Agency (IAEA) data and other countries (Takagi et al.,1986).Therefore, the assessment of data indicates the level of Mn is increasing by 5.9 fold, Cu approximately 2 fold, Zn similarly with 1.2 folds; Hg higher by 23 folds and Pb are much higher at 62 fold.

The data on elements concentration of hair workers in perfume factory compared to the international data indicates the elements Ca, Cu and Zn in optimizing value, while Fe is indicating 4.7-fold, Hg of 26-fold higher and Pb shows higher values of 23-fold. However, Mn and Sr were not detected in a perfume factory hairs samples that likely to be impact of environmental contamination in the workshops.

In table (4.1) the elements in workshops hair demonstrate the Cu is correlated with Mn, Pb and is highly correlated with Zn and Hg, while Pb is correlated with Mn, Zn and Hg in group one. The observed correlation between elements Cu, Mn, Zn, Pb and Hg of high levels in the hairs might be explained that are related to external source of contamination. The correlations of elements in table (4.2) shows that Fe is correlated Pb and Hg, which are indicated high level of concentration in hair and possible to be an impact of contamination in the Perfume Factory. Statistical significance was analyzed using analysis of initial Eigen values of total variance and t-tests as appropriate to provide the difference in variation of element concentrations in each site.

Table (4.3) present t-tests were used to analyze the relationship between the elements that possible to be related to sources of contamination, which provides the values of Mn, Pb and Hg in the range of 4.572- 5.570 and values of Cu, Zn 6.877-6.957 in the same range, respectively. Initial Eigen values of the total variance of the workers 67.68% in the workshops group and 74.07% are total variance of the workers in perfume factory. And in this table the results of factor analysis of variance contributions indicate the contents of the element in hairs of high-level Cu and Hg in factor 1 and Mn, Zn in factor 2, while Pb in factor 3 relates to many types of contamination in workshops workers. From this data in table 3, we can see that factors analysis of variance contributions resulted in an optimum level value of elements Ca, Cu and Zn in factor 1 and the high-level elements Fe and Hg in factor 2, while Pb in factor 3. Comparisons between the two figures (4.2) and (4.3) that the projection of variable in fig. (4.2) is revealed the Mn and Pb at the upper section of the graph and Cu, Zn and Hg in the lower section that may be due to different types of impact sources. From the result of the projection of variation in figure (4.3), it is apparent that the elements Fe, Hg and Pb not in the same position in the graph that indicates different levels of values of effect of contamination in hairs workers in a perfume factory.

The data for evaluation of the elements concentration in hairs in the two sites under study using statistical analysis, correlation, and t-test value factor analysis are compared to International Atomic Energy Agency hairs standard (IAEA) and several countries (table (4.4)) that provides a possible suggestion of contamination in the area (Bleise et al., 2000), (Dean et al.,2001), (Rashed et al.,2007) and (shah et al.,2006). The assessments of elements of hairs content in an industrial area in Omdurman in two different sites are indicated by high values Pb and Hg in both sites that possible to be impacted by environmental pollution. It is apparent from this result obtained that Mn, Cu, Zn in hairs of workshops worker and Fe in a perfume factory might be the indoor environmental exposure on both sites. The detection limit of any analytical instrument should be enough to detect the trace amounts of individual elements present in the sample. This detection limit can vary greatly, according to the transitional strength of the elemental line, delay time (time between the firing of the laser pulse and the opening of the USB 2000 spectrometer) and the gate width selected during the measurements, the sample matrix, and collection optic geometry, etc. Experiments were performed to find optimal conditions of temporal delay, incident laser energy to achieve best detection limit prior to the analysis of different human scalp hairs samples under investigation. LIBS spectra of different human scalp hairs samples were recorded over a 400 – 1050 nm wavelength range for qualitative and quantitative analysis in fig (4.4). The laser pulse energy was fixed at 200m J. The distance between the optical fiber and the plasma was 10 mm. The LIBS spectra of the human scalp hairs samples were recorded to identify each element present in human scalp hairs sample. The most sensitive lines (finger print wavelength) for identification of elements for all samples were found between 400–1050 nm region using NIST database and reference show fig (4.4). The finger print wavelength (as specified in (Table (4.5) to table (4.11)) for each element of interest was selected to study the effect of different experimental parameters. These selected finger print wavelengths were (Mn, Cu, Zn, Hg, Pb, Sr and Fe). The elements are indicated on the LIBS spectrum is listed in Table (4.5) to table (4.11). For each data point great extent as compared to the single by XRF and ICPE data as show in table (4.5) to table (4.11).

The important part of this research is to establish the effectiveness of LIBS spectral finger printing technique and two other techniques (XRF, ICPE) for characterizing the composition of any metal (Mn, Cu, Zn, Hg, Pb, Sr and Fe) that may have been applied on the human scalp hairs different samples (16 samples).

An accumulation of 16 sample human scalp hairs, each characterizing by XRF, LIBS and ICPE, and shown in table (4.5) Manganese (Mn) concentration associated with human scalp hairs using (XRF, LIBS and ICPE) techniques. The minimal concentration was 2.63 ppm by ICPE for sample No: B24 and maximal value was 24.4 ppm by XRF for sample No11, but the reference value that say in International Atomic Energy Agency (IAEA) for Manganese (Mn) equal 9.6 ppm.

In fig (4.5) show that Manganese (Mn) concentration in different samples of human scalp hairs used three methods to measurement (XRF, LIBS and ICPE). In table (4.6) Copper (Cu) concentration associated with human scalp hairs measured using (XRF, LIBS and ICPE) Techniques. The minimum concentration was 0.0977 ppm by LIBS for sample No:C9 and maximal value was 78.9 ppm by XRF for sample No:11 but the reference value that say in International Atomic Energy Agency (IAEA) for Copper (Cu) equal 17.6 ppm. In fig (4.6) show that Copper (Cu) concentration in different samples of human scalp hairs used three method to measurement (XRF, LIBS and ICPE) and in fig (4.7) show the relationship between Copper (Cu) concentration and human scalp hairs different samples measured using (XRF, LIBS and ICPE) methods. In table (4.7) Zinc (Zn) concentration associated with human scalp hairs used three methods to measurement (XRF, LIBS and ICPE). The lower concentration was 16 ppm by XRF for sample No:C9 and maximal value was 381 ppm by XRF for sample No:18 but the reference value that say in International Atomic Energy Agency (IAEA) for Zinc (Zn) equal 167 ppm. In fig (4.8) show that Zinc (Zn) concentration in different samples of human scalp hairs obtained from (XRF, LIBS and ICPE) techniques and in fig (4.9) show the relationship between Zinc (Zn) concentration and human scalp hairs different samples using the same spectroscopic techniques.

In table (4.8) Mercury (Hg) concentration associated with human scalp hairs obtained from (XRF, LIBS and ICPE) measurement methods. The lowest concentration was 2.0038 ppm by LIBS for sample No:17 and maximum value was 48 ppm by XRF for sample No:12 but the recommended ratio that say in International Atomic Energy Agency (IAEA) for Mercury (Hg) equal 0.573 ppm. In fig (4.10) shows that Mercury (Hg) concentration in different samples of human scalp hairs measured using (XRF, LIBS and ICPE) methods. In table (4.9) Lead (Pb) concentration associated with human scalp hairs recorded using (XRF, LIBS and ICPE) techniques this figure showed that the minimum concentration was 3.4213 ppm by LIBS for sample No:12 and maximal value was 173.2 ppm by LIBS for sample No:11 but the reference value that say in table (4.4) (Shamberger, 2003) for Lead (Pb) equal 0.97 ppm as shown in fig (4.12) which shows the Lead (Pb) concentration in different samples of human scalp obtained by (XRF, LIBS and ICPE) techniques. In table (4.10), Strontium (Sr) concentration associated with human scalp hairs measured by (XRF, LIBS and ICPE). The results showed that the minimum concentration was 0.01 ppm by XRF for sample No: 9 and maximal value was 12.6567 ppm by LIBS for sample No: 17 but the reference value that say in table (4.4) (Shamberger, 2003) for Strontium (Sr) equal 4.97 ppm as shown in fig (4.14).For Iron (Fe) concentration in human scalp hair of the as shown in fig. (4.16), the Iron Fe was high on each of the samples (No: B24 and No: B3) as the sample No: B24 average concentration 205.14 ppm and the sample No: B3 average concentration180.81ppm, While the recommended ratio of International Atomic Energy Agency (IAEA) 123 ppm.

The higher concentrations for most of the elements are found in XRF due to the fact that the other techniques identify more elements than XRF. Therefore, the concentrations of these elements in these other techniques appear lower.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

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CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion:

The purpose of the work was to determine the elements concentration in hairs of workers in two sites in the industrial area of Omdurman city using XRF analysis and other spectroscopic techniques. Liquid nitrogen was used to grind the hairs at the lower temperature basis of dry weight sample in the fine mode powder form. The results of this assessment show that industrial workshops workers reported higher levels of Mn, Cu, Zn, Hg, Pb and Fe; while in perfume factory the influence of environmental contamination is at increasing level of Fe, Hg and Pb compared to the human hair trace elements of IAEA-086 reference material. Therefore, the results of this analysis show that heavy metals are accumulated in the workers hairs relate to the indoor and outdoor environmental exposure. Consequently, Hg and Pb elements are higher in both situations that may be connected to external contamination exposure in the industrial site. However, the high levels of Mn, Cu and Zn in the hair of the workers in the workshops and the Fe in the perfume factory are connected to the indoor contamination in both sites respectively. The results of this research are assessed using statistical analysis correlation, t-test value and factor analysis to obtain the relation between hairs elements and the sources of pollution that accumulated in the hair that is probably linked to the indoor or outdoor contamination with heavy toxic metals. This assignment has explained the average elements Ca, Cu, Zn, Sr concentrations in hairs of Sudanese workers more strongly coinciding with international data of hairs standards for several countries.

The following is a summary of the conclusions:

- The percentage of manganese Mn contamination was high on each of the samples (No:11, No:18 and No:C9), as the sample No:11 with average concentration 15.499 ppm, the sample No:18 with average concentration 13.31 ppm, and the sample No: C9 with average concentration 12.47 ppm, while the recommended ratio of International Atomic Energy Agency (IAEA) for Mn equals 9.6 ppm.

- The pollution by copper Cu was top on the sample No: 12, average value of 56.43 ppm, while the recommended ratio of International Atomic Energy Agency (IAEA) is 17.6 ppm.
- Zinc (Zn) component was highest in the sample No:18 by medium 370.3 ppm, while the recommended ratio of International Atomic Energy Agency (IAEA) is 167ppm.
- The pollution by mercury Hg was high on each of the samples (No:12, No:B3, No:11and No:B24),as the sample No:12 average concentration was 39.36 ppm, the sample No: B3, average concentration 34.24 ppm, as the sample No:11, average concentration was 21.00 ppm and as the sample No: B24, average concentration was 19.47 ppm and while the recommended ratio of International Atomic Energy Agency (IAEA) for Hg equals 0.573 ppm.
- The largest proportion was enough Lead Pb component of pollution category No: 8 with average 54.64 ppm, while the standard value is 0.97 ppm.
- The largest proportion was enough strontium Sr component of pollution category No: 18 with average 7.364 ppm, while the standard value is 4.97 ppm.
- Iron Fe was high on each of the samples (No: B24 and No: B3) as the sample No: B24 average concentration was 205.14 ppm and the sample No: B3 average concentration was 180.81 ppm, while the recommended ratio of International Atomic Energy Agency (IAEA) is 123 ppm.

The study concluded that most of the samples were suffering from pollution from industrial areas selected elements in a clear disparity study. Therefore, the results of this analysis show that heavy metals are accumulated in the hairs workers related to the indoor and outdoor environmental exposure. Consequently, Hg and

Pb elements are higher in both situations that may be connected to external contamination exposure in the industrial site. However, the high levels of Mn, Cu and Zn in the hair of the workers in the workshops, and the Fe in the perfume factory are connected to the indoor contamination in both sites respectively.

The outcomes of hair analysis have detected toxic metals such as Mn, Fe, Hg and Pb of high concentrations, probably associated with exposure by environmental contaminations, which indicate potential health problems of the workers.

5.2 Recommendations:

In the end of this thesis we recommend the following:

- Create awareness among Workshop workers, Perfume Factories and members of general public to the high levels of heavy elements in the environment and the potential risks of these metals to their health, taking into consideration that industrial area must be far from residential areas.
- Promote the use of human scalp hair as bio-indicator of environmental exposure to toxic metals.
- Encourage decision makers to create long term plans for providing a safe working environment for workers in such areas. This will help reduce the harmful exposure of the workers to heavy metals.
- Commitment to Certified Reference Materials (CRM), creation of reference ranges of toxic metals and essential metals when using various materials.
- More studies are required on the use of the scalp hair to investigate the levels of metals in females who make Sudanese Perfume in their homes.
- Intensification of studies on high risk group for example street children and persons with mental disabilities to providing a data base between different populations throughout Sudan.
- Investigations on comparison of metal levels in paired samples of scalp hair of males and females of the same subjects in adults in different environmental exposure gradients.
- This study recommends expanding the study to include more and other groups working in the workshops of other ages with more accurate information processing. The study also recommends examining the impact of the work time period on increasing pollution.

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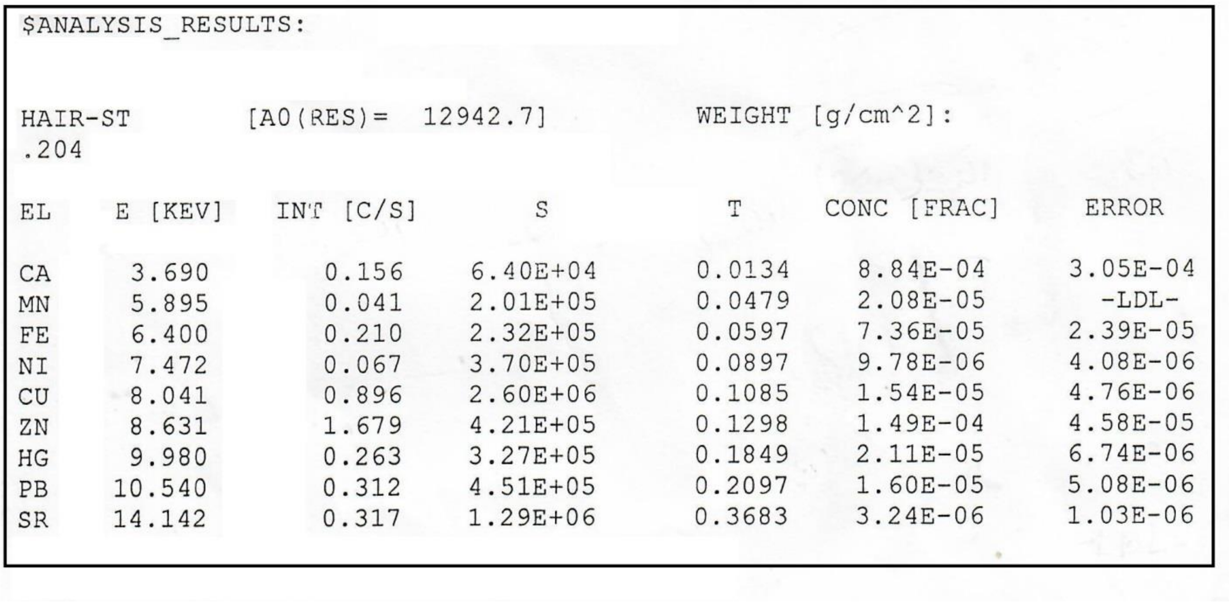
APPENDICES:

APPENDIX A: Some of XRF results:

Standard Results



```
$ANALYSIS_RESULTS:


HAIR-ST        [A0(RES)=  12942.7]        WEIGHT [g/cm^2]:
.204

EL    E [KEV]   INT [C/S]       S           T      CONC [FRAC]     ERROR

CA     3.690       0.156    6.40E+04    0.0134     8.84E-04     3.05E-04
MN     5.895       0.041    2.01E+05    0.0479     2.08E-05      -LDL-
FE     6.400       0.210    2.32E+05    0.0597     7.36E-05     2.39E-05
NI     7.472       0.067    3.70E+05    0.0897     9.78E-06     4.08E-06
CU     8.041       0.896    2.60E+06    0.1085     1.54E-05     4.76E-06
ZN     8.631       1.679    4.21E+05    0.1298     1.49E-04     4.58E-05
HG     9.980       0.263    3.27E+05    0.1849     2.11E-05     6.74E-06
PB    10.540       0.312    4.51E+05    0.2097     1.60E-05     5.08E-06
SR    14.142       0.317    1.29E+06    0.3683     3.24E-06     1.03E-06
```

One-Sample Statistics

	N	Mean	Std. Deviation	Std. Error Mean
Ca	22	1.0534E3	774.19511	165.05895
Mn	22	56.6136	58.07842	12.38236
Fe	22	6.0757E2	595.07711	126.87087
Cu	22	33.4795	22.83393	4.86821
Zn	22	2.0210E2	136.26375	29.05153
Hg	22	13.1859	12.08014	2.57549
Pb	22	60.5768	51.01457	10.87634
Sr	22	3.4123	2.20888	.47093

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	t	Df	Sig. (2-tailed)	Mean Difference	Lower	Upper
Ca	6.382	21	.000	1053.40909	710.1502	1396.6680
Mn	4.572	21	.000	56.61364	30.8631	82.3642
Fe	4.789	21	.000	607.56818	343.7258	871.4106
Cu	6.877	21	.000	33.47955	23.3555	43.6035
Zn	6.957	21	.000	202.10455	141.6886	262.5205
Hg	5.120	21	.000	13.18591	7.8299	18.5419
Pb	5.570	21	.000	60.57682	37.9582	83.1954
Sr	7.246	21	.000	3.41227	2.4329	4.3916

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.415	67.684	67.684	5.415	67.684	67.684
2	.995	12.441	80.125			
3	.668	8.345	88.471			
4	.541	6.760	95.231			
5	.184	2.299	97.530			
6	.106	1.329	98.859			
7	.064	.800	99.659			
8	.027	.341	100.000			

Extraction Method: Principal Component Analysis.

One-Sample Statistics

	N	Mean	Std. Deviation	Std. Error Mean
Ca	20	1.1486E3	1290.96661	288.66891
Fe	20	5.7750E2	845.44268	189.04673
Cu	20	16.1495	16.81289	3.75948
Zn	20	1.5000E2	169.55369	37.91336
Hg	20	15.1065	25.16573	5.62723
Pb	20	22.4380	26.67271	5.96420

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	T	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
Ca	3.979	19	.001	1148.60000	544.4090	1752.7910
Fe	3.055	19	.007	577.49500	181.8156	973.1744
Cu	4.296	19	.000	16.14950	8.2808	24.0182
Zn	3.956	19	.001	150.00000	70.6464	229.3536
Hg	2.685	19	.015	15.10650	3.3286	26.8844
Pb	3.762	19	.001	22.43800	9.9548	34.9212

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.444	74.068	74.068	4.444	74.068	74.068
2	.783	13.043	87.111			
3	.623	10.386	97.497			
4	.105	1.742	99.239			
5	.037	.624	99.863			
6	.008	.137	100.000			

Extraction Method: Principal Component Analysis.

One-Sample Statistics

	N	Mean	Std. Deviation	Std. Error Mean
Ca	42	1.09874E3	1040.018388	160.478321
Fe	42	5.93248E2	716.131544	110.501496
Cu	42	2.52271E1	21.789607	3.362209
Zn	42	1.77293E2	153.383488	23.667586
Hg	42	1.41005E1	19.213898	2.964769
Pb	42	4.24155E1	45.103622	6.959640

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	T	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
Ca	6.847	41	.000	1098.738095	774.64555	1422.83064
Fe	5.369	41	.000	593.247619	370.08532	816.40992
Cu	7.503	41	.000	25.227143	18.43702	32.01726
Zn	7.491	41	.000	177.292857	129.49520	225.09052
Hg	4.756	41	.000	14.100476	8.11300	20.08795
Pb	6.094	41	.000	42.415476	28.36020	56.47075

APPENDIX B: Some of NIST results:

Sample

Element	Wavelength λ (nm)	Intensity (a.u)	$A_{ki}(s^{-1})$	E_i (cm^{-1})	E_k (cm^{-1})
Mn	708.3538	154.01	4.3E5	53698.736	67812.087
	735.3549	157.02	9.6E5	29889.534	43484.664
Cu	419.53590	154.01	1.11E7	122745.9491	146575.101
	483.6799	154.01	4.4E5	116375.406	137044.4647
	496.98062	155.02	1.1E7	116325.9148	136441.817
	657.70812	155.02	1.5E7	136269.9996	151470.113
	775.43688	154.01	9.0E6	122867.7407	135760.1548
	881.0397	156.04	2.4E6	139395.786	150742.896
Hg	755.21	154.04	1.9E6	68886.43	82123.98
	861.87	155.02	1.55E7	71207.296	82805.18
	1012.17	154.02	6.2E5	71207.296	81084.96
Pb	782.9008	155.02	1.88E5	44674.9859	57444.470
	840.93840	154.04	3.06E67	44674.9859	56563.195
Sr	458.2993	155.02	7.6E7	21698.452	43512.1658

Sample

Element	Wavelength λ (nm)	Intensity (a.u)	$A_{ki}(s^{-1})$	E_i (cm^{-1})	E_k (cm^{-1})
Mn	480.686	155.02	4.7E5	43696.217	64494.14
	708.3538	159.02	4.3E5	53698.736	67812.087
	717.4362	154.01	4.6E7	85960.622	99895.291
	735.3549	154.01	9.6E5	29889.534	43484.664
Cu	425.4630	155.02	1.15E7	117747.3504	141244.556
	485.12625	155.02	2.9E7	115662.5622	136269.9996
	505.9418	153.79	6.3E5	133728.0387	153487.668
	543.205	154.04	5.4E6	44544.16	62948.26
	567.0329	154.04	7.4E5	137044.4047	154675.247
	629.6239	163.02	5.72E5	120876.0141	136754.1104
	657.7081	158.04	1.5E7	136269.9996	151470.113
	684.6104	154.23	7.5E6	118991.330	133594.2323
Hg	504.58	154.04	2.92E5	77286.86	97100.23
	755.21	156.04	1.9E6	68886.43	82123.98
Pb	500.65724	154.01	1.09E8	34959.9084	54928.0835
Sr	458.2993	155.02	7.6E7	21698.452	43512.1658

Sample

Element	Wavelength λ (nm)	Intensity (a.u)	$A_{ki}(s^{-1})$	E_i (cm^{-1})	E_k (cm^{-1})
Mn	461.059	154.82	2.9E7	59537.455	81220.63
	464.2795	154.82	9.6E5	38120.18	59652.90
	714.8506	153.8	6.3E5	53781.735	67766.817
Cu	477.29651	154.82	2.11E5	117231.4014	138176.8797
	496.98062	153.98	1.1E7	116325.9148	136441.817
	506.545858	154.65	1.61E8	118483.8135	138219.8605
	522.9518	153.64	9.5E5	118531.9058	137648.800
	653.0082	161.38	2.0E7	136160.6182	151470.130
	662.967	154.73	2.1E7	558119.37	73198.77
	718.2106	154.14	5.6E7	133728.0387	147647.699
	949.2663	153.98	8.3E4	138028.384	148559.958
Hg	702.20	153.73	2.6E6	69516.576	83753.3
	712.00	154.90	4.19E7	181772.41	195814.66
	1050.11	155.74	3.5694E6	71396.073	80916.551
Pb	825.5607	156.00	1.1E6	45443.1710	57552.820
	847.84922	154.73	2.3E7	44809.3636	56600.673
Sr	503.3435	154.23	4.9E6	351385.40	371246.97
	545.5984	154.82	6.9E6	291377.76	309701.00

Sample

Element	Wavelength λ (nm)	Intensity (a.u)	$A_{ki}(s^{-1})$	E_i (cm^{-1})	E_k (cm^{-1})
Mn	420.0280	155.03	2.3E-5	49882.208	73683.44
Cu	949.3808	153.02	1.13E6	125230.061	135760.1548
Fe	671.2438	159.97	4.1E6	40231.336	55124.938
	674.51008	154.02	3.37E2	36940.590	51762.076
	676.3627	153.01	1.3E-1	27620.4033	42401.3198
	1055.3925	153.07	1.32E6	102584.984	112057.539

Sample

Element	Wavelength λ (nm)	Intensity (a.u)	$A_{ki}(s^{-1})$	E_i (cm^{-1})	E_k (cm^{-1})
Mn	722.2648	143.03	2.5E7	86057.625	99899.156
	881.031	143.03	1.6E6	102680.37	114028.11
Fe	425.86109	145.00	8.0E5	22838.228	46313.537
	506.78901	144.03	5.4E7	83308.241	103034.819
	570.32567	143.01	6.2E6	85495.366	103024.341
	1047.68	144.03	2.3E-3	18942.0	28484.3

Sample

Element	Wavelength λ (nm)	Intensity (a.u)	$A_{ki}(s^{-1})$	E_i (cm^{-1})	E_k (cm^{-1})
Fe	419.53288	154.01	1.11E7	26874.550	50703.870
	498.38526	154.01	6.1E5	33095.941	53155.145
	663.6964	155.02	3.44E6	44312.717	48475.686
	990.03169	157.02	4.0E6	103711.610	113809.527
	1055.3925	155.02	1.32E6	102584.984	112057.539
Hg	542.5253	154.04	1.4E8	104984.138	123411.351
Pb	734.66757	156.04	8.5E5	42918.4634	56526.4925

Sample

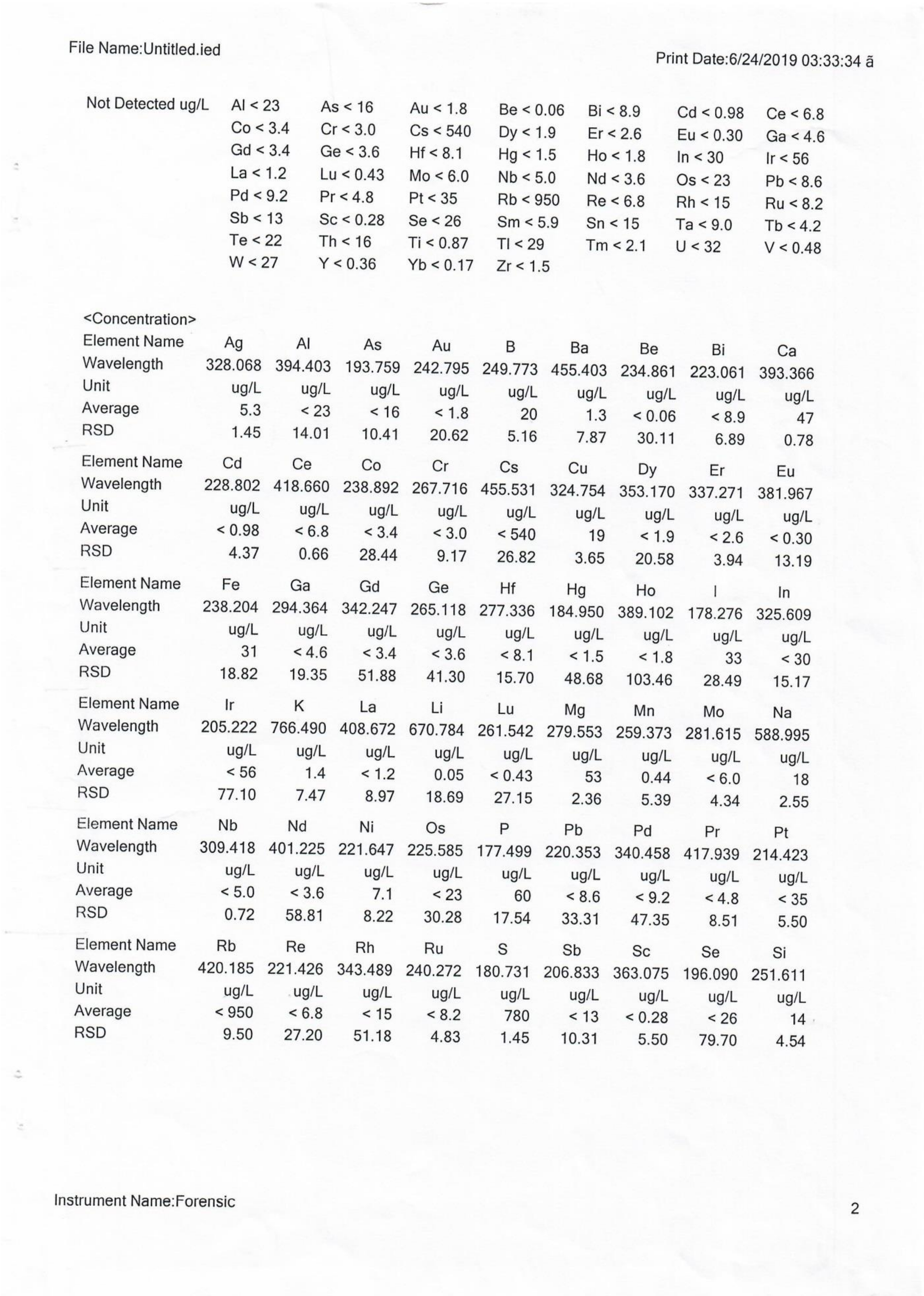
Element	Wavelength λ (nm)	Intensity (a.u)	$A_{ki}(s^{-1})$	E_i (cm^{-1})	E_k (cm^{-1})
Fe	419.53288	155.02	1.11E7	26874.550	50703.870
	806.7506	154.04	7.5E6	68114.577	100506.577
	885.6714	154.04	3.3E7	72524.516	83812.382
	990.03169	157.02	4.0E6	103711.610	113809.527
	1055.3925	155.02	1.32E6	102584.984	112057.539
Hg	636.0199	154.04	4.8E6	126941.844	142660.277
	704.57	155.02	2.2E6	68886.43	83075.9
	708.1901	156.04	2.2E6	62350.325	76466.936
Pb	623.52656	154.01	1.4E7	35287.2244	51320.5981

Sample

Element	Wavelength λ (nm)	Intensity (a.u)	A_{ki}(s^{-1})	E_i (cm^{-1})	E_k (cm^{-1})
Mn	461.059 464.2795 529.433	154.06 153.90 154.40	2.9E7 9.6E5 4.4E7	59537.455 38120.18 79540.93	81220.63 59652.90 98423.63
Cu	630.59712 653.0082 662.967 1057.5703	155.95 153.90 156.50 153.90	5.7E7 2.0E7 2.1E7 3.0E6	120919.5715 136160.61825 58119.37 139028.705	136773.1713 151470.130 73198.77 148481.763
Hg	760.59 861.36	153.98 153.81	1.3E5 5.7E4	69661.803 71207.296	82805.18 82814.5
Pb	607.574	154.57	1.3E7	92515.24	108969.58
Sr	459.2007 858.2112	153.74 154.23	2.7E7 4.67E3	391709.40 269810.66	413480.27 281459.61

APPENDIX C: Some of ICPE results:

Sample



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Not Detected ug/L

Al < 23 As < 16 Au < 1.8 Be < 0.06 Bi < 8.9 Cd < 0.98 Ce < 6.8
Co < 3.4 Cr < 3.0 Cs < 540 Dy < 1.9 Er < 2.6 Eu < 0.30 Ga < 4.6
Gd < 3.4 Ge < 3.6 Hf < 8.1 Hg < 1.5 Ho < 1.8 In < 30 Ir < 56
La < 1.2 Lu < 0.43 Mo < 6.0 Nb < 5.0 Nd < 3.6 Os < 23 Pb < 8.6
Pd < 9.2 Pr < 4.8 Pt < 35 Rb < 950 Re < 6.8 Rh < 15 Ru < 8.2
Sb < 13 Sc < 0.28 Se < 26 Sm < 5.9 Sn < 15 Ta < 9.0 Tb < 4.2
Te < 22 Th < 16 Ti < 0.87 Tl < 29 Tm < 2.1 U < 32 V < 0.48
W < 27 Y < 0.36 Yb < 0.17 Zr < 1.5

<Concentration>

Element Name	Ag	Al	As	Au	B	Ba	Be	Bi	Ca
Wavelength	328.068	394.403	193.759	242.795	249.773	455.403	234.861	223.061	393.366
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	5.3	< 23	< 16	< 1.8	20	1.3	< 0.06	< 8.9	47
RSD	1.45	14.01	10.41	20.62	5.16	7.87	30.11	6.89	0.78

Element Name	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu
Wavelength	228.802	418.660	238.892	267.716	455.531	324.754	353.170	337.271	381.967
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 0.98	< 6.8	< 3.4	< 3.0	< 540	19	< 1.9	< 2.6	< 0.30
RSD	4.37	0.66	28.44	9.17	26.82	3.65	20.58	3.94	13.19

Element Name	Fe	Ga	Gd	Ge	Hf	Hg	Ho	I	In
Wavelength	238.204	294.364	342.247	265.118	277.336	184.950	389.102	178.276	325.609
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	31	< 4.6	< 3.4	< 3.6	< 8.1	< 1.5	< 1.8	33	< 30
RSD	18.82	19.35	51.88	41.30	15.70	48.68	103.46	28.49	15.17

Element Name	Ir	K	La	Li	Lu	Mg	Mn	Mo	Na
Wavelength	205.222	766.490	408.672	670.784	261.542	279.553	259.373	281.615	588.995
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 56	1.4	< 1.2	0.05	< 0.43	53	0.44	< 6.0	18
RSD	77.10	7.47	8.97	18.69	27.15	2.36	5.39	4.34	2.55

Element Name	Nb	Nd	Ni	Os	P	Pb	Pd	Pr	Pt
Wavelength	309.418	401.225	221.647	225.585	177.499	220.353	340.458	417.939	214.423
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 5.0	< 3.6	7.1	< 23	60	< 8.6	< 9.2	< 4.8	< 35
RSD	0.72	58.81	8.22	30.28	17.54	33.31	47.35	8.51	5.50

Element Name	Rb	Re	Rh	Ru	S	Sb	Sc	Se	Si
Wavelength	420.185	221.426	343.489	240.272	180.731	206.833	363.075	196.090	251.611
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 950	< 6.8	< 15	< 8.2	780	< 13	< 0.28	< 26	14
RSD	9.50	27.20	51.18	4.83	1.45	10.31	5.50	79.70	4.54

Instrument Name:Forensic

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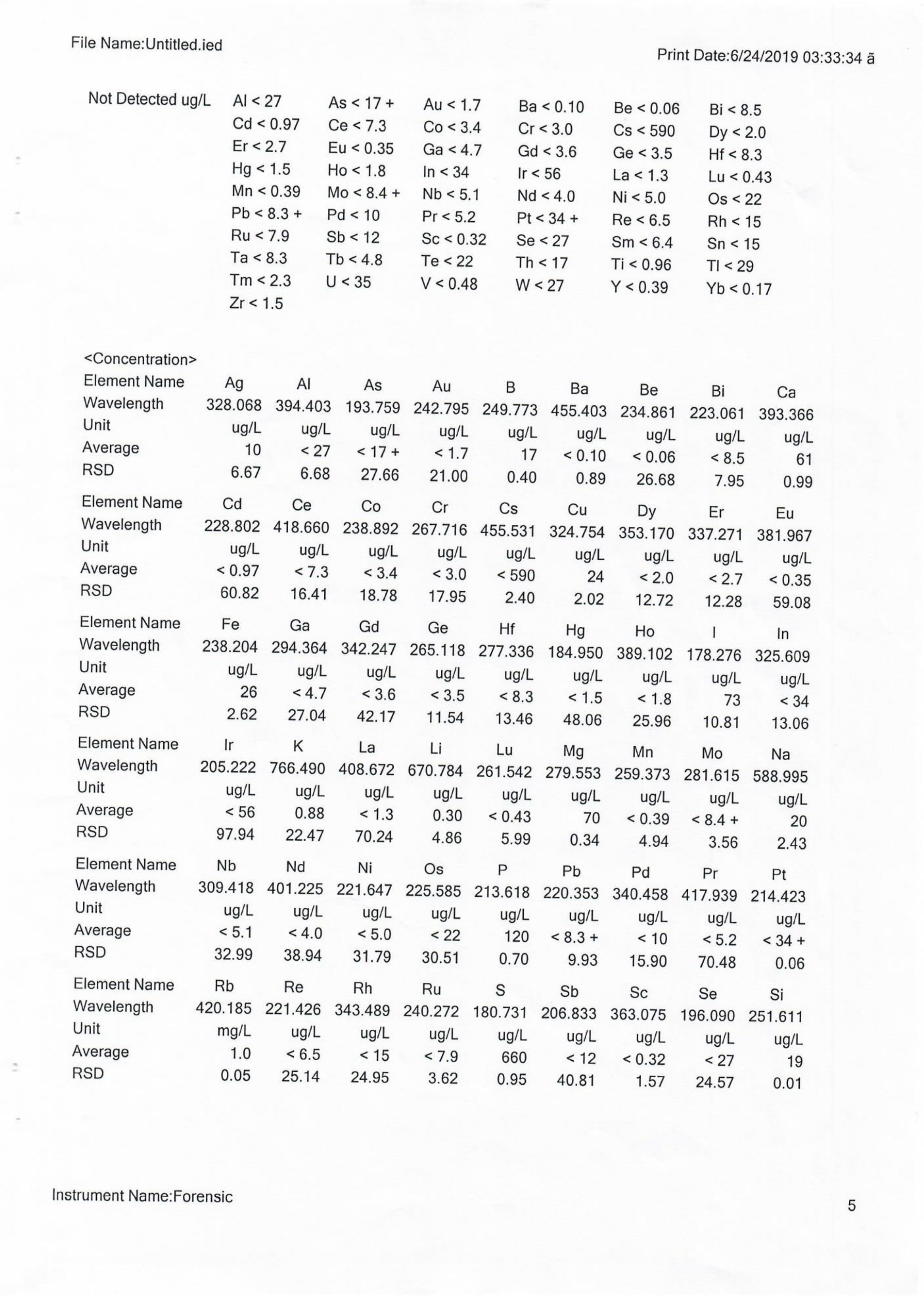
Sample



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Not Detected ug/L	Al < 27	As < 17 +	Au < 1.7	Ba < 0.10	Be < 0.06	Bi < 8.5
	Cd < 0.97	Ce < 7.3	Co < 3.4	Cr < 3.0	Cs < 590	Dy < 2.0
	Er < 2.7	Eu < 0.35	Ga < 4.7	Gd < 3.6	Ge < 3.5	Hf < 8.3
	Hg < 1.5	Ho < 1.8	In < 34	Ir < 56	La < 1.3	Lu < 0.43
	Mn < 0.39	Mo < 8.4 +	Nb < 5.1	Nd < 4.0	Ni < 5.0	Os < 22
	Pb < 8.3 +	Pd < 10	Pr < 5.2	Pt < 34 +	Re < 6.5	Rh < 15
	Ru < 7.9	Sb < 12	Sc < 0.32	Se < 27	Sm < 6.4	Sn < 15
	Ta < 8.3	Tb < 4.8	Te < 22	Th < 17	Ti < 0.96	Tl < 29
	Tm < 2.3	U < 35	V < 0.48	W < 27	Y < 0.39	Yb < 0.17
	Zr < 1.5					

<Concentration>

Element Name	Ag	Al	As	Au	B	Ba	Be	Bi	Ca
Wavelength	328.068	394.403	193.759	242.795	249.773	455.403	234.861	223.061	393.366
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	10	< 27	< 17 +	< 1.7	17	< 0.10	< 0.06	< 8.5	61
RSD	6.67	6.68	27.66	21.00	0.40	0.89	26.68	7.95	0.99

Element Name	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu
Wavelength	228.802	418.660	238.892	267.716	455.531	324.754	353.170	337.271	381.967
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 0.97	< 7.3	< 3.4	< 3.0	< 590	24	< 2.0	< 2.7	< 0.35
RSD	60.82	16.41	18.78	17.95	2.40	2.02	12.72	12.28	59.08

Element Name	Fe	Ga	Gd	Ge	Hf	Hg	Ho	I	In
Wavelength	238.204	294.364	342.247	265.118	277.336	184.950	389.102	178.276	325.609
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	26	< 4.7	< 3.6	< 3.5	< 8.3	< 1.5	< 1.8	73	< 34
RSD	2.62	27.04	42.17	11.54	13.46	48.06	25.96	10.81	13.06

Element Name	Ir	K	La	Li	Lu	Mg	Mn	Mo	Na
Wavelength	205.222	766.490	408.672	670.784	261.542	279.553	259.373	281.615	588.995
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 56	0.88	< 1.3	0.30	< 0.43	70	< 0.39	< 8.4 +	20
RSD	97.94	22.47	70.24	4.86	5.99	0.34	4.94	3.56	2.43

Element Name	Nb	Nd	Ni	Os	P	Pb	Pd	Pr	Pt
Wavelength	309.418	401.225	221.647	225.585	213.618	220.353	340.458	417.939	214.423
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 5.1	< 4.0	< 5.0	< 22	120	< 8.3 +	< 10	< 5.2	< 34 +
RSD	32.99	38.94	31.79	30.51	0.70	9.93	15.90	70.48	0.06

Element Name	Rb	Re	Rh	Ru	S	Sb	Sc	Se	Si
Wavelength	420.185	221.426	343.489	240.272	180.731	206.833	363.075	196.090	251.611
Unit	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	1.0	< 6.5	< 15	< 7.9	660	< 12	< 0.32	< 27	19
RSD	0.05	25.14	24.95	3.62	0.95	40.81	1.57	24.57	0.01

Instrument Name:Forensic

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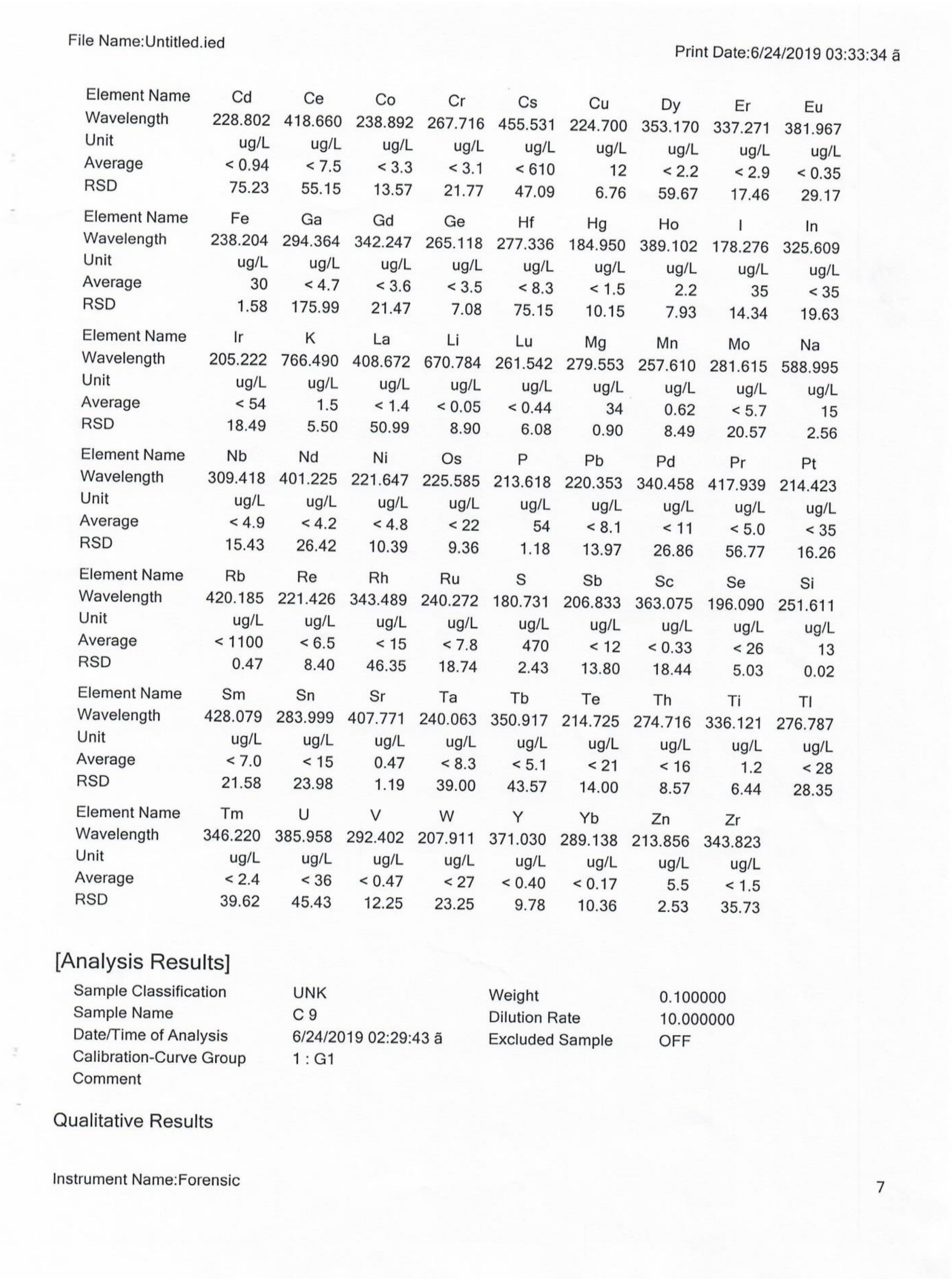
Sample



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Print Date:6/24/2019 03:33:34 ā

Element Name	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu
Wavelength	228.802	418.660	238.892	267.716	455.531	224.700	353.170	337.271	381.967
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 0.94	< 7.5	< 3.3	< 3.1	< 610	12	< 2.2	< 2.9	< 0.35
RSD	75.23	55.15	13.57	21.77	47.09	6.76	59.67	17.46	29.17

Element Name	Fe	Ga	Gd	Ge	Hf	Hg	Ho	I	In
Wavelength	238.204	294.364	342.247	265.118	277.336	184.950	389.102	178.276	325.609
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	30	< 4.7	< 3.6	< 3.5	< 8.3	< 1.5	2.2	35	< 35
RSD	1.58	175.99	21.47	7.08	75.15	10.15	7.93	14.34	19.63

Element Name	Ir	K	La	Li	Lu	Mg	Mn	Mo	Na
Wavelength	205.222	766.490	408.672	670.784	261.542	279.553	257.610	281.615	588.995
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 54	1.5	< 1.4	< 0.05	< 0.44	34	0.62	< 5.7	15
RSD	18.49	5.50	50.99	8.90	6.08	0.90	8.49	20.57	2.56

Element Name	Nb	Nd	Ni	Os	P	Pb	Pd	Pr	Pt
Wavelength	309.418	401.225	221.647	225.585	213.618	220.353	340.458	417.939	214.423
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 4.9	< 4.2	< 4.8	< 22	54	< 8.1	< 11	< 5.0	< 35
RSD	15.43	26.42	10.39	9.36	1.18	13.97	26.86	56.77	16.26

Element Name	Rb	Re	Rh	Ru	S	Sb	Sc	Se	Si
Wavelength	420.185	221.426	343.489	240.272	180.731	206.833	363.075	196.090	251.611
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 1100	< 6.5	< 15	< 7.8	470	< 12	< 0.33	< 26	13
RSD	0.47	8.40	46.35	18.74	2.43	13.80	18.44	5.03	0.02

Element Name	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl
Wavelength	428.079	283.999	407.771	240.063	350.917	214.725	274.716	336.121	276.787
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 7.0	< 15	0.47	< 8.3	< 5.1	< 21	< 16	1.2	< 28
RSD	21.58	23.98	1.19	39.00	43.57	14.00	8.57	6.44	28.35

Element Name	Tm	U	V	W	Y	Yb	Zn	Zr
Wavelength	346.220	385.958	292.402	207.911	371.030	289.138	213.856	343.823
Unit	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Average	< 2.4	< 36	< 0.47	< 27	< 0.40	< 0.17	5.5	< 1.5
RSD	39.62	45.43	12.25	23.25	9.78	10.36	2.53	35.73

[Analysis Results]

Sample Classification	UNK	Weight	0.100000
Sample Name	C 9	Dilution Rate	10.000000
Date/Time of Analysis	6/24/2019 02:29:43 ā	Excluded Sample	OFF
Calibration-Curve Group	1 : G1		
Comment			

Qualitative Results

Instrument Name:Forensic

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