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Identification Of Heavy Metals In Cosmetic Powder Using Inductively Coupled Plasma - Optical Emission Spectroscopy Technique

تحديد المعادن الثقيلة في مساحيق التجميل بإستخدام تقنية مطيافية البلازما المستحثة المزدوجة المقترنة

A thesis submitted for the fulfillment of the requirements for the degree of Doctor of Philosophy in physics

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الآية

قَالَ تَعَالَىٰ:

﴿ٱللَّهُ لَآ إِلَٰهَ إِلَّا هُوَ ٱلۡحَيُّ ٱلۡقَيُّومُۚ لَا تَأۡخُذُهُۥ سِنَةٞ وَلَا نَوۡمٞۚ لَّهُۥ مَا فِى ٱلسَّمَٰوَٰتِ وَمَا فِى
ٱلۡأَرۡضِۗ مَن ذَا ٱلَّذِى يَشۡفَعُ عِندَهُۥٓ إِلَّا بِإِذۡنِهِۦۚ يَعۡلَمُ مَا بَيۡنَ أَيۡدِيهِمۡ وَمَا خَلۡفَهُمۡۖ وَلَا يُحِيطُونَ
بِشَىۡءٖ مِّنۡ عِلۡمِهِۦٓ إِلَّا بِمَا شَآءَۚ وَسِعَ كُرۡسِيُّهُ ٱلسَّمَٰوَٰتِ وَٱلۡأَرۡضَۖ وَلَا يَـُٔودُهُۥ حِفۡظُهُمَاۚ وَهُوَ ٱلۡعَلِىُّ
ٱلۡعَظِيمُ ٢٥٥﴾

سورة البقرة: الاية ٢٥٥

DEDICATION

To my Mother

my Father

My Husband

Sisters and Brothers

My son

My daughter

Acknowledgement

I need to thank my supervisor Professor **Mubarak . Almahal** for his help and support throughout the entire time we've worked together. I am also very thankful to Professor **Ahmed Hassan** for his help and support. I am grateful to all the staff of the Institute of laser in Sudan University of Science and Technology I need to send special thanks to my family and to my **mother** and my **husband** for their support and help all the time.

Abstract

This study aimed to identify the heavy metals in cosmetics powder using the Inductively Coupled Plasma / Optical Emission Spectroscopy technique (ICP-OES). This method gives a clear picture of the powder ingredients of cosmetics. The emission spectra were analyzed using the Atomic Spectrometer Database, published by the National Institute of Standards and Technology. (NIST)

In this technique, liquid samples are injected into the argon plasma using one of the sampling techniques and the sample spray that quickly reaches the plasma is quickly dried and activated. The emission from the plasma is then seen and collected by a lens or mirror and photographed to the input of the wavelength selection device . The principle used in the inductively coupled Plasma Optical Emission Spectroscopy is When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays intensity.

A total of nineteen cosmetic samples marketed under different brand names and widely used by Sudanese women for cosmetic purposes (ICP-OES) were analyzed. The results showed that the samples contain the following elements: Barium, boron, manganese, iron, copper, aluminum, calcium, erbium and zinc. The results also showed no mercury, lead, nickel and cadmium in the test samples Where the results for the first group showed that the common metal in the test samples is calcium. Samples 1 and 2 contain iron, barium, manganese and copper back only in sample 1. The boron appeared only in sample 2, whereas the arbium only appeared in sample 3.

For the second group the results showed that the heavy metals found in some cosmetics are zinc and calcium. While iron is common in samples 1, 2 and 3, samples 1 and 3 cont ain barium, while samples 2 and 3 contain manganese, aluminum is shown only in the third sample.

In summary, this study showed the presence of heavy metals in the cosmetics used in Sudan, which poses a danger to the health of the user must be corrected.

المستخلص

هدفت هذه الدراسة إلى تحديد المعادن الثقيلة فى مسحوق مستحضرات التجميل باستخدام تقنية-Inductively coupled plasma/optical emission spectroscopy (ICP OES) هذه الطريقة تعطي صورة واضحة لمكونات مسحوق مستحضرات التجميل .تم تحليل أطياف الإنبعاث بالاستعانة بقاعدة بيانات الأطياف الذرية الصادرة عن المعهد الوطني للمواصفات والتقانة (NIST) .

في هذه التقنية يتم حقن عينات السائل في بلازما الارجون باستخدام واحدة من تقنيات ادخال العينات و يتم بسرعة تجفيف رذاذ العينة الذي يصل الى البلازما وتنشيطه . وبعد ذلك ينظر الى الانبعاث المنبثق عن البلازما ويتم جمعه بواسطة عدسة أو مرآة ويتم تصويره الى مدخل جهاز اختيار الطول الموجي . المبدأ المستخدم في هذه التقنية هو أنه عندما تُعطى طاقة البلازما إلى عينة تحليل من الخارج ، فإن عناصر المكوِّن (الذرات) تكون متحركة عندما تعود الذرات المثارة إلى موضع منخفض الطاقة ، تُطلق (أشعة الطيف) ويتم قياس أشعة الانبعاث التي تقابل طول موجة الفوتون. يتم تحديد نوع العنصر بناءً على موضع أشعة الفوتون ، ويتم تحديد محتوى كل عنصر على أساس كثافة الأشعة.

تم تحليل ما مجموعه تسعة عشر عينة تجميلية تم تسويقها تحت أسماء تجارية مختلفة واستخدمت على نطاق واسع من قبل النساء السودانيات لأغراض التجميل عن طريق تقنية(ICP-OES). أظهرت النتائج أن العينات تحتوي على العناصر الاتية :الباريوم ،البورون ،المنجنيز ،الحديد،النحاس ،الألمونيوم ، الكالسيوم ،والاربيوم والزنك ،كما أظهرت النتائج عن عدم وجود الزئبق والرصاص والنيكل والكادميوم في عينات الاختبار. حيث

أظهرت النتائج بالنسبة للمجموعة الأولى أن المعدن الشائع في عينات الاختبار هو الكالسيوم. العينات 1 و 2 تحتوي على الحديد، ظهر الباريوم والمنجنيز والنحاس فقط في العينة 1. ظهر البورون فقط في العينة 2 ، بينما ظهر الاربيوم فقط في العينة 3.

بالنسبة للمجموعة الثانية فقد أظهرت النتائج أن المعادن الثقيلة الموجودة في بعض مستحضرات التجميل هي الزنك والكالسيوم. في حين أن الحديد شائع في العينات 1 و 2 و 3،و احتوت العينات 1 و 3 على الباريوم ، في حين احتوت العينات 2 و 3 على المنغنيز، لم يظهر الألمونيوم إلا في العينة الثالثة.

خلاصة القول أن هذه الدراسة أظهرت وجود معادن ثقيلة في مستحضرات التجميل المستخدمة فى السودان والتي تمثل خطراً على صحة مستخدمه يجب تداركه .

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Chapter One

Spectroscopy, Basic Concept

1-1 Introduction:

Spectroscopy is the chief experimental technique of atomic and molecular physics and involves determining the energy states of atoms or molecules by looking at the light absorbed or emitted when they change states. Inductively coupled plasma/optical emission spectroscopy(ICP/OES) is a powerful tool for the determination of metals in a variety of different sample matrices. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity. (Ghosh et al., 2013)

The principle used in the inductively coupled Plasma Optical Emission Spectroscopy is When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays intensity. To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube.(Ghosh et al., 2013)

1-2 The Study Objectives:

The objectives of this Study are:

- The Usage of Inductively coupled plasma/optical emission spectroscopy(ICP/OES) to characterize the components of different types of cosmetic powder, collected from different locations in Sudan.
- The comparison between the types of cosmetic powder after the characterization.

1-3 Thesis Structure:

This thesis consists of four chapters. Chapter one presents an overview of spectroscopy and the objectives of this work. In chapter two, description of Inductively coupled plasma/optical emission spectroscopy(ICP/OES) ; Principles, capabilities, instrumentation and literature review are presented. Experimental setup, components of ICP-OES setup, and the procedure are presented in chapter three. In chapter four results, discussion, conclusions, and Appendixes are presented

1-4 Spectroscopy:

Optical emission spectroscopy, which measures the light emitted from a plasma as a function of wavelength, time, and location, is the most commonly used plasma diagnostic probe for microelectronics fabrication processes. The rate at which such transitions occur is determined by the quantum mechanical similarity of the states. This similarity leads to selection rules that indicate the allowed transitions. The energy of the photons emitted by the plasma, therefore, is characteristic of the composition and energy state of species within the plasma. The spectra can be used to analyze both the chemical species that make up the plasma and their state of excitation. Because it is non-intrusive, inexpensive, and can be easily incorporated into an existing plasma reactor, it quickly gains popularity in the microelectronics industry for monitoring the plasma processing. However, the large information content makes the interpretation of the spectra difficult. For this reason, it is primarily used as a "fingerprint" that is compared with spectra taken while a process is working well to identify the state or drift of the plasma. As a research and development tool, it can be very useful in understanding the basic processes within the plasma. It can be quite effective and quantitative if combined with other measurements.(Samukawa et al., 2012)

1-5 Spectrometry:

The spectroscopic technique used to assess the concentration or amount of a given species. In those cases, the instrument that performs such measurements is a spectrometer or spectrograph.

Spectroscopy/spectrometry is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them.

Spectroscopy/spectrometry is also heavily used in astronomy and remote sensing. Most large telescopes have spectrometers, which are used either to measure the chemical composition and physical properties of astronomical objects or to measure their velocities from the Doppler shift of their spectral lines.

1-5-1Measurement Process:

Most spectroscopic methods are differentiated as either atomic or molecular based on whether or not they apply to atoms or molecules. Along with that distinction, they can be classified on the nature of their interaction:

- Absorption spectroscopy uses the range of the electromagnetic spectra in which a substance absorbs. This includes → atomic absorption spectroscopy and various molecular techniques, such as infrared spectroscopy in that region and nuclear magnetic resonance (NMR) spectroscopy in the radio region.

- Emission spectroscopy uses the range of electromagnetic spectra in which a substance radiates (emits). The substance first must absorb energy. This energy can be from a variety of sources, which determines the name of the subsequent emission, like luminescence. Molecular luminescence techniques include spectrofluorimetry.
- Scattering spectroscopy measures the amount of light that a substance scatters at certain wavelengths, incident angles, and polarization angles. The scattering process is much faster than the absorption/emission process. One of the most useful applications of light scattering spectroscopy is → Raman spectroscopy.

1-6 Common Types:

•Absorption

Absorption spectroscopy is a technique in which the power of a beam of light measured before and after interaction with a sample is compared. When performed with tunable diode laser, it is often referred to as Tunable diode laser absorption spectroscopy (TDLAS).

It is also often combined with a modulation technique, most often wavelength modulation spectrometry (WMS) and occasionally frequency modulation spectrometry (FMS) in order to reduce the noise in the system.

•Fluorescence

Spectrum of light from a fluorescent lamp showing prominent mercury peaks Fluorescence spectroscopy uses higher energy photons to excite a sample, which will then emit lower energy photons. This technique has become popular for its biochemical and medical applications, and can be used for confocal microscopy, fluorescence resonance energy transfer, and fluorescence lifetime imaging.

- **X- ray**

When X-rays of sufficient frequency (energy) interact with a substance, inner shell electrons in the atom are excited to outer empty orbitals, or they may be removed completely, ionizing the atom. The inner shell "hole" will then be filled by electrons from outer orbitals. The energy available in this de-excitation process is emitted as radiation (fluorescence) or will remove other less-bound electrons from the atom (Auger effect). The absorption or emission frequencies (energies) are characteristic of the specific atom. In addition, for a specific atom small frequency (energy) variations occur which are characteristic of the chemical bonding. With a suitable apparatus, these characteristic X-ray frequencies or Auger electron energies can be measured. X-ray absorption and emission spectroscopy is used in chemistry and material sciences to determine elemental composition and chemical bonding.

X-ray crystallography is a scattering process; crystalline materials scatter X-rays at well-defined angles. If the wavelength of the incident X-rays is known, this allows calculation of the distances between planes of atoms within the crystal. The intensities of the scattered X-rays give information about the atomic positions and allow the arrangement of the atoms within the crystal structure to be calculated.

- **Flame**

Liquid solution samples are aspirated into a burner or nebulizer/burner combination, desolvated, atomized, and sometimes excited to a higher energy electronic state. The use of a flame during analysis requires fuel and oxidant, typically in the form of gases. Common fuel gases used are acetylene (ethyne) or hydrogen. Common oxidant gases used are oxygen, air, or nitrous oxide. These methods are often capable of analyzing metallic element analytes in the part per million, billion, or possibly lower concentration ranges.

Light detectors are needed to detect light with the analysis information coming from the flame.

1-7 Types of Spectroscopy:

The spectroscopy mainly classified into two categories these are:

1-7-1 Molecular Spectroscopy:

It deals with the interaction of electromagnetic radiation with molecules. The results in transition between rotational and vibration energy levels in addition to electronic transitions. Molecular spectra may involve transitions between rotational vibration energy levels in addition to electronic transitions. Thus, if an isolated molecule is originally in the ground state electronic energy level (the zero point vibration energy level and in a particular rotational energy level) absorption of a photon may excite the molecule to a higher electronic vibration and / or rotational energy level. There are many transitions that might give rise to absorption, but only those that satisfy certain selection rules are allowed.(Xu et al., 2009)

1-7-2 Atomic Spectroscopy:

The study of transitions, in absorption or emission between electronic states of an atom, is atomic spectroscopy. It deals with the interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state. Atomic spectra involve only transitions of electrons from one electronic energy level to another(Demirbas, 2004). The atomic spectroscopy categorized into two types:

(1) Atomic Absorption Spectroscopy (AAS):

The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analytic element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others. The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms. Aspirating a solution of the sample into a flame aligned in the light beam serves this purpose. Under the proper flame conditions, most of the atoms will remain in the ground state form and are capable of absorbing light at the analytical wavelength from a source lamp. The ease and speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for the determination of metals (Demirbas, 2004).

(2) Atomic Emission Spectroscopy (AES):

The purpose of atomic emission spectroscopy (AES) is to determine the elemental composition of a sample (solid, liquid, or gas). The analysis can range from a simple identification of the atomic constituents of the sample to a more detailed determination of relative concentrations or absolute masses. (Ryan and Deci, 2000).This method uses flame excitation; atoms are excited from the heat of the flame to emit light. This method commonly uses a total consumption burner with a round burning outlet. A higher temperature flame than atomic absorption spectroscopy (AA) is typically used to produce excitation of analytic atoms. Since analytic atoms are excited by the heat of the flame, no special elemental lamps to shine into the Flame are needed. A high resolution polychromatic can be used to produce emission intensity. wavelength spectrum over a range of wavelengths showing multiple element excitation lines, meaning multiple elements can be detected in one run. Alternatively, a monochromator can be set at one wavelength to concentrate on the analysis of a single element at a certain emission line. Plasma emission spectroscopy is a more modern version of this method.(Demirbas, 2004)

(3)Atomic Fluorescence Spectroscopy:

This method commonly uses a burner with a round burning outlet. The flame is used to solvate and atomize the sample, but a lamp shines light at a specific wavelength into the flame to excite the analyte atoms in the flame. The atoms of certain elements can then fluoresce emitting light in a different direction. The intensity of this fluorescing light is used for quantifying the amount of analyte element in the sample. A graphite furnace can also be used for atomic fluorescence spectroscopy. This method is not as commonly used as atomic absorption or plasma emission spectroscopy.

1-7-3 Laser-Induced Fluorescence (LIF):

The phenomenon when the light is absorbed and then re-emitted at another wavelength is called fluorescence; Fluorescence is very often used in practical spectroscopy because of its high sensitivity. Since a wavelength shift occurs, the detection can be made without any disturbance of the excitation light. This is an important feature in contrast to absorption measurements, where scattered light can cause problems, which are due to an Increase of the background signal.(Page and Gautier, 2012).The diagnosis of hydrogen atoms was a typical aim of the laser-induced fluorescence (LIF) technique at the initial stage of its applications to plasma experiments. LIF-technique used to the investigation of the plasma–surface interaction. Measurements of metal atom fluxes, the density of sputtered

particles near plasma facing components, and the velocity distribution of sputtered atoms have been successfully investigated; for most metal atoms in the plasma boundary the LIF-technique can be applied if the density is higher than ~1012 m–3 . Figure (1.3) shows the Setup of fluorescence.

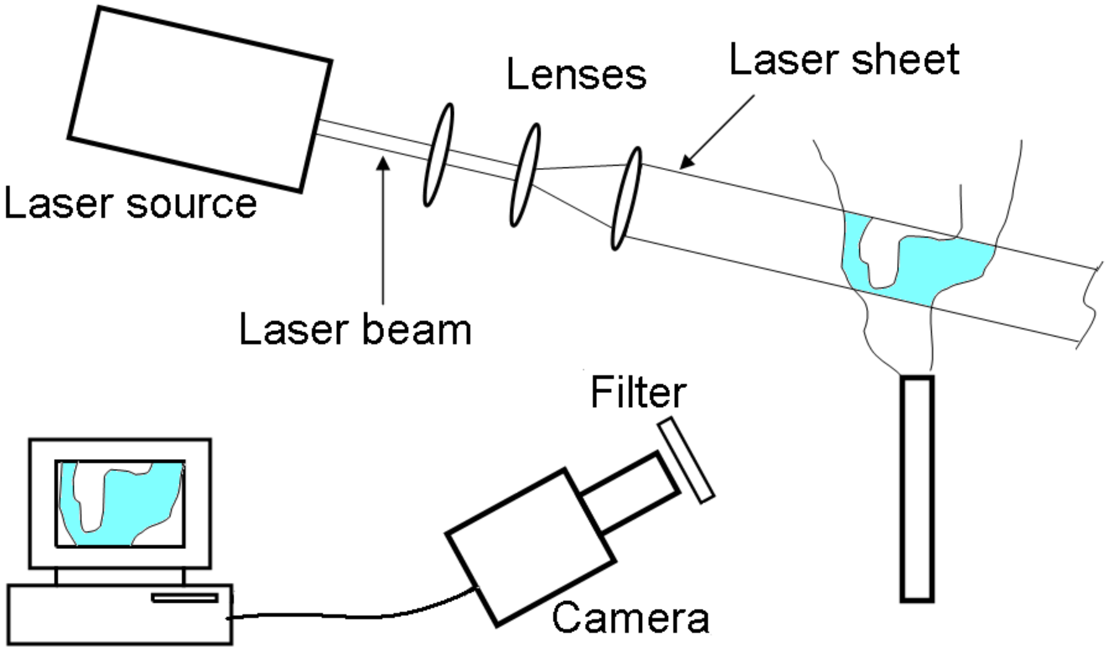


Fig (1.1): The setup of LIF

In the technique of laser-induced fluorescence or LIF, a laser is tuned so that its frequency matches that of an absorption line of some atom or molecule of interest. The absorption of the laser photons by this species produces an electronically excited state which then radiates. The fluorescent emission detected using a filter or a monochromatic followed by a photomultiplier. Because a particular absorption line is selected, the excited state as definite and identifiable vibration, Rotational and fine structure quantum numbers. This clean state has significant advantages for spectroscopic and collision studies, in contrast to the congestion often found in ordinary emission spectra from, for example, a discharge. Since the lower state responsible for the absorption is also definite, considerable selectivity is provided by LIF when used as a diagnostic tool. In addition, its high degree of sensitivity, the spatial and temporal resolution, availability, and its non-intrusive nature is important attributes for this method not possible in non-laser spectroscopy ;, such as two-photon excitation, yield new information and make possible new diagnostic probes. LIF as a whole has had a tremendous impact on the study of the electronic spectra of small molecules,' and it should be noted that the experiments discussed here form but a tiny portion of the many ways LIF has been used to further our knowledge of molecular structure and behavior. None the less, it is hoped that the highly personal selection presented will serve to describe some of the important aspects of this exciting and rapidly progressing technique.(Rideout et al., 2003). Laser-induced fluorescence spectroscopy is based on the electronic excitation of an atom or molecule by laser irradiation. When the electron returns to a lower-lying energy level, the energy maybe released in the form of a photon. This forms the basic principle of fluorescence. The LIF technique is well established, and theoretical, mathematical .(Lui et al., 2008)

1-7-4 Laser-Raman Spectroscopy:

The main spectroscopic methods employed to detect vibrations in molecules are based on the processes of infrared absorption and Raman scattering. They are widely used to provide information on chemical structures and physical forms, to identify substances from the characteristic spectral patterns (‘fingerprinting’), and to determine quantitatively or semi-quantitatively the amount of a substance in a sample. Samples can be examined in a whole range of physical states; for example, as solids, liquids or vapours, in hot or cold states, in bulk, as microscopic particles, or as surface layers. The techniques are very wide ranging and provide solutions to a host of interesting and challenging analytical problems. Raman scattering is less widely used than infrared absorption, largely due to problems with sample degradation and fluorescence. However, recent advances in instrument technology have simplified the equipment and reduced the problems substantially. These advances, together with the ability of Raman spectroscopy to examine aqueous solutions, samples inside glass containers and samples without any preparation; have led to a rapid growth in the application of the technique.

In practice, modern Raman spectroscopy is simple. Variable instrument Parameters are few, spectral manipulation is minimal and a simple interpretation of the data may be sufficient. Raman scattering is an underdeveloped technique, with much important information, often not used or recognized.(Smith and Dent, 2005) The Raman Effect is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system (Der Radiology, et.al. 2009).

When the emitted photon is of lower frequency than the absorbed photon the process is termed stokes scattering, if the emitted photon is of higher frequency the process called anti-stokes scattering (the light has gained energy from the vibrational or rotational state). These two processes are schematically represented in the energy diagrams shown in fig(1.2).

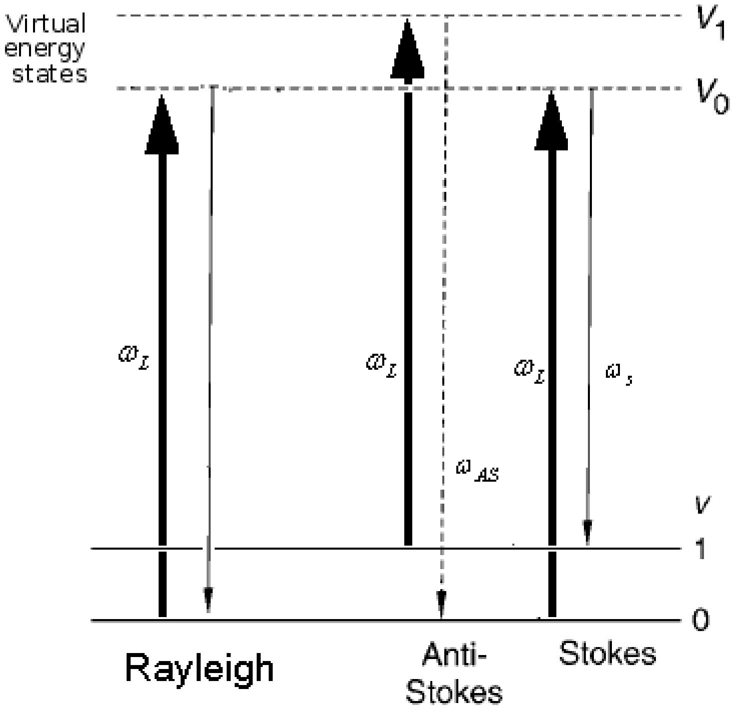


Fig (1.2): Energy-level diagram for spontaneous Raman scattering

The bold arrows indicate the excitation photons at a frequency, ωL while the thin arrows represent the in elastically scattered photon, at frequency ωS or ωAS. Raman spectroscopy is carried out using visible or near UV excitation frequencies. The characteristics of the Raman signal yield a signature dependent on the molecular species, the temperature, and the pressure.

1-7-4-1 Characteristics of Raman Spectroscopy:

Raman spectroscopy is characterized by the following features:

1. Raman spectroscopy permits acquisition of the spectra in situ. Monitoring of a reaction in a flask online, for example, can simply be accomplished by irradiating laser light directly upon the reactant from outside the flask.

2. Raman spectra can be measured irrespective of the state of a substance, that is, regardless of whether the substance is gas, liquid, solution, solid, crystal, fiber, or film. In addition, by measuring spectra of substances in various states one can obtain information about different molecular structures of the given substance in various phases.

3. As lasers are used for exciting the sample and due to high sensitivity of modern detectors, it is possible to obtain Raman spectra from very small amounts of material. This feature is of importance for local analyses and also for instruments equipped with microscopes.

4. Raman experiments can be conducted with optical fibers, which allow the spectrometer to be separated from the sample that might be, say, in a dangerous environment. This feature is very important with respect to Raman spectroscopy as a means of online or outdoor analysis.

5. A valuable application of Raman spectroscopy in fundamental research is for examination of ultrahigh speed phenomena. Raman spectroscopy is, therefore, frequently used to study the excited states of molecules and the structures of reaction intermediates.(McCreery, 2005)

1-7-5 Laser Induced Break Down Spectroscopy:

LIBS is a sensitive technique for analyzing the chemical or atomic compositions of solid or liquid materials. Here a laser pulse is focused onto the surface of a solid or liquid material. Due to the high peak intensity, fast evaporation of a small volume in the focus of the laser pulse occurs. The

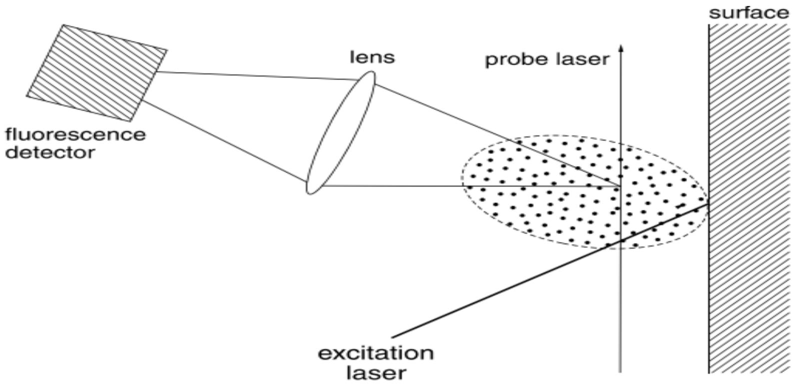


Fig. (1.3) Laser-induced breakdown spectroscopy

gaseous plume ejected from the surface contains molecules, atoms and ions contained in the focal volume.

The fluorescence emitted by the excited species is collected by a lens, focused into an optical fiber and sent to the entrance slit of a spectrograph (Fig. 1.3). If the detector at the exit of the spectrograph is time-gated, the spectra can be recorded at specific times after the generation of the plume. Since the plume cools during its expansion, the ions recombine to excited states of neutral atoms or molecules and the emission from these states is a measure of the concentration of the atoms in the sample. An important application of LIBS is the analysis of samples from a steel converter during the melting process. A small sample is taken from the liquid steel, rapidly cooled and then inspected by LIBS in order to get information on the relative concentrations of the different components in the steel. The whole process takes only a few minutes and therefore the composition of the liquid steel can be corrected before the molten metal solidifies.

LIBS has been also successfully applied to the analysis of geochemical samples. The most accurate information can be obtained for the relative concentrations of different elements in a sample. This is important, for example, for the classification of minerals on earth or in meteorites when it is not clear whether two different samples come from the same source. Also for archeological samples the precise knowledge of elemental composition is very helpful for the exact dating and assignment. The applications of LIBS has benefitted from the use of fiber optics which allows remote sensing, where the laser and detection systems are far away. (Anh Tuan Phungd, 2013)

1-8 Plasma Emission Spectroscopy:

In some ways similar to flame atomic emission spectroscopy, it has largely replaced it.

- Direct-current plasma (DCP)

A direct-current plasma (DCP) is created by an electrical discharge between two electrodes.

A plasma support gas is necessary, and Ar is common. Samples can be deposited on one of
the electrodes, or if conducting can make up one electrode.

- Glow discharge-optical emission spectrometry (GD-OES)
- Inductively coupled plasma-atomic emission spectrometry (ICP-AES)
- Laser Induced Breakdown Spectroscopy (LIBS) (LIBS), also called Laser-induced plasma spectrometry (LIPS)
- Microwave-induced plasma (MIP)

Spark or Arc (Emission) Spectroscopy :

Is used for the analysis of metallic elements in solid samples. For non-conductive materials, a sample is ground with graphite powder to make it conductive. In traditional arc spectroscopy methods, a sample of the solid was commonly ground up and destroyed during analysis. An electric arc or spark is passed through the sample, heating the sample to a high temperature to excite the atoms in it. The excited analyte atoms glow emitting light at various wavelengths which could be detected by common spectroscopic methods. Since the conditions producing the arc emission typically are not controlled quantitatively, the analysis for the elements is qualitative.

Nowadays, the spark sources with controlled discharges under an argon atmosphere allow that this method can be considered eminently quantitative, and its use is widely expanded worldwide through production control laboratories of foundries and steel mills.

•Visible

Many atoms emit or absorb visible light. In order to obtain a fine line spectrum, the atoms must be in a gas phase. This means that the substance has to be vaporised. The spectrum is studied in absorption or emission. Visible absorption spectroscopy is often combined with UV absorption spectroscopy in UV/Vis spectroscopy. Although this form may be uncommon as the human eye is a similar indicator, it still proves useful when distinguishing colours.

•Ultraviolet

All atoms absorb in the Ultraviolet (UV) region because these photons are energetic enough to excite outer electrons. If the frequency is high enough, photo ionization takes place. UV spectroscopy is also used in quantifying protein and DNA concentration as well as the ratio of protein to DNA concentration in a solution. Several amino acids usually found in protein, such as tryptophan, absorb light in the 280 nm range and DNA absorbs light in the 260 nm range. For this reason, the ratio of 260/280 nm absorbance is a good general indicator of the relative purity of a solution in terms of these two macromolecules. Reasonable estimates of protein or DNA concentration can also be made this way using Beer's law.

•Infrared

Infrared spectroscopy offers the possibility to measure different types of inter atomic bond vibrations at different frequencies. Especially in organic chemistry the analysis of IR absorption spectra shows what type of bonds are present in the sample. It is also an important method for analyzing polymers and constituents like fillers, pigments and plasticizers.

•Near Infrared (NIR)

The near infrared NIR range, immediately beyond the visible wavelength range, is especially important for practical applications because of the much greater penetration depth of NIR radiation into the sample than in the case of mid IR spectroscopy range. This allows also large samples to be measured in each scan by → NIR spectroscopy, and is currently employed for many practical applications such as: rapid grain analysis, medical diagnosis pharmaceuticals/medicines, biotechnology, genomics analysis, proteomic analysis, interactomics research, inline textile monitoring, food analysis and chemical imaging/hyper spectral imaging of intact organisms, plastics, textiles, insect detection, forensic lab application, crime detection, various military applications, and so on.

Chapter Two

Spectroscopic Analysis of Cosmetic Solid Powder

2-1General Characteristics Of Inductively coupled plasma /optical emission spectroscopy ICP-OES:

Inductively coupled plasma/optical emission spectroscopy(ICP/OES) is a powerful tool for the determination of metals in a variety of different sample matrices. With this technique, liquid samples are injected into -induced argon plasma using one of a variety of nebulizers or sample introducing techniques.

The sample mist reaching the plasma is quickly dried, vaporized, and energized through collision excitation at high temperature. The atomic emission emanating from the plasma is viewed, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device. Single element measurements can be per for cost effectively with a simple monochromatic / photomultiplier tube (PMT) combination, and simultaneous multi element determinations are performed for up to 70 elements with the combination of a polychromatic and an array detector). The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity.(Ghosh et al., 2013)

The principle used in the inductively coupled Plasma Optical Emission Spectroscopy is When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays intensity. To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube.(Ghosh et al., 2013)

Since the dawn of civilization, cosmetics have constituted a part of routine body care by all set of people. Past few decades has witnessed a rapid growth in cosmetic industries, through production of various types of cosmetics which are needed for care and beautification of skin, hair, nails, teeth and body. Although beauty consciousness of people has set the demand for cosmetics in market, the side effects as well as health consciousness of people have attracted the health practiticians and researchers to find out the probable reason for unusual side effects. Heavy metal contamination is one of the most important reasons addressing problem. Heavy metals like Barium ,Boron ,Aluminum, Manganese ,Copper, Iron ,Zinc, Calcium and Europium are common contaminants in various cosmetic products. This chapter focuses on the analysis of heavy metals using Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES) used in cosmetics and its adverse effects.**(Mayildurai et al., 2015)**

2-2 The ICP discharge:

Inductively coupled plasma (ICP) is a highly ionized gas consist of energetic electrons, ions and atoms. In spite of the high population of ions and electrons it is macroscopically neutral. The plasma is sustained by a continuous supply of energy through electromagnetic induction, or inductive coupling, to a flowing gas. Almost universally used gas for the generation of the plasma is argon, which gives the analytical ICP its unique characteristics. In principle and operation, the ICP is inherently simple, which is evident from the fact that the basic geometry of the plasma torch remains very much the same as that which appeared in the early 1960s when its potential was first demonstrated as an atom source for analytical spectrometry .

A typical configuration of the ICP torch is shown in Figure (2.1), which consists of three concentric circular tubes (outer tube, intermediate tube and inner or injector tube) made of quartz or some other suitable material. The plasma gas, also called the coolant gas, and the auxiliary gas are introduced tangentially to create a vortex flow pattern in the region where the plasma is generated.

The auxiliary gas, which is not essential to maintain a stable plasma, can be used to make slight adjustments in the position of the base of the plasma relative to the quartz torch or the load coil. The central gas flow, which enters through the 'injector tube', is used to transport the analytic into the plasma, commonly as fine aerosol droplets. The same central gas flow typically is used for nebulization of the sample solution to generate the aerosol. A two- or three-turn copper coil (3 mm o.d.), called the load coil,surrounds the top end of the torch, which is water-cooled and carries the

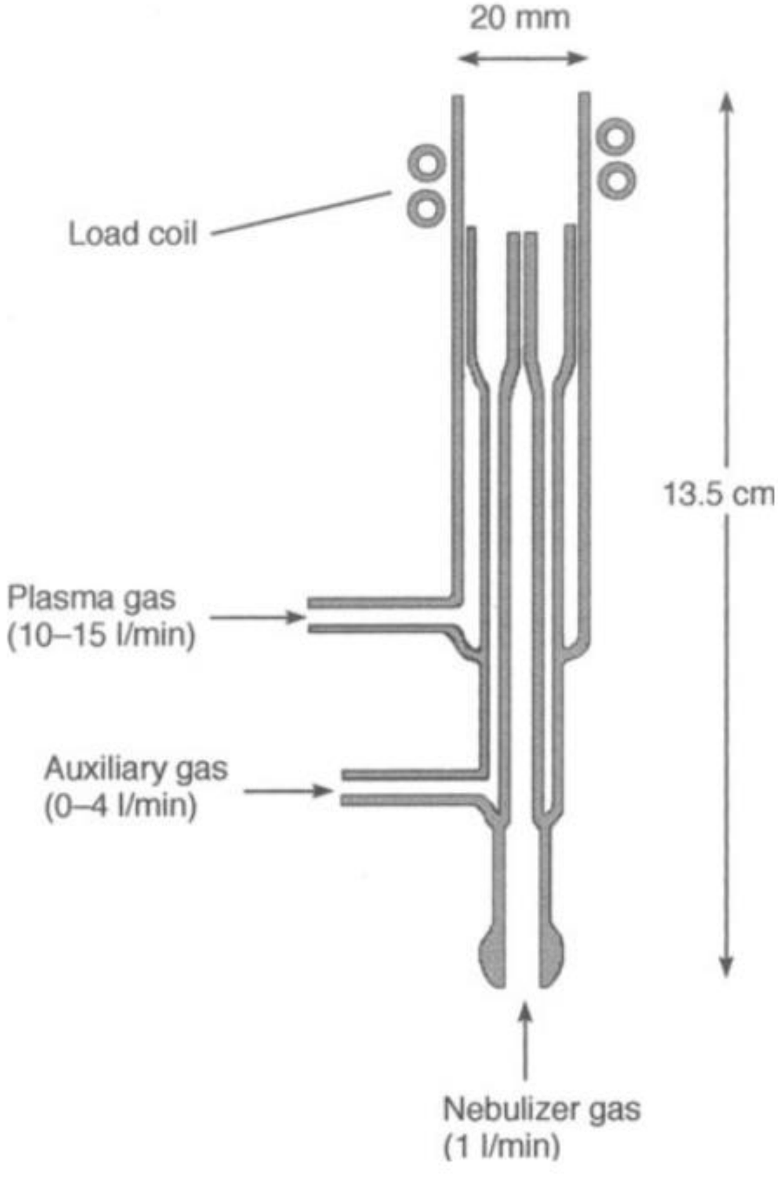


Fig.(2.1) The ICP torch.

alternating current supplied by the radiofrequency (RF) power generator. The most commonly used frequencies are 27.12 or 40.68 MHz. When the RF power is applied typically at 600-1500 W to the load coil, it inducesan oscillating magnetic field inside the torch, which in turn induces an oscillating intense electric field in the vicinity of the load coil. With the argon gas flowing through the torch some electrons are momentarily 'seeded' into the gas by an electrical spark using external means such as a Tesla coil. These electrons get accelerated by the alternating magnetic field and become highly energetic. The collisions between the energetic electrons and argon atoms generate argon ions and more electrons. The process continues as a chain reaction until the gas becomes highly conductive and reaches a steady state where most of the RF energy supplied to the coil is transferred to the gas to self-sustain a high-temperature plasma highly populated with electrons and argon ions. This ignition process takes only a fraction of a second.

2-2-1Detection of Emission:

In ICP-OES, the light emitted by the excited atoms and ions in the plasma is measured to obtain information about the sample. Because the excited species in the plasma emit light at several different wavelengths, the emission from the plasma is polychromatic. This polychromatic radiation must be separated into individual wavelengths so the emission from each excited species can be identified and its intensity can be measured without interference from emission at other wavelengths.

The separation of light according to wavelength is generally done using a monochromator, which is used to measure light at one wavelength at a time, or a polychromator, which can be used to measure light at several different wavelengths at once. The actual detection of the light, once it has been separated from other wavelengths, is done using a photosensitive detector such as a photo-multiplier tube (PMT) or advanced detector techniques such as a charge-injection device (CID) or a charge-coupled device (CCD).

2-3 Basic ICP spectrometric system:

A spectrometric system can be divided into three basic components: (a) sample processor, (b) signal generator and (c) signal processor, as shown in Fig.(2.2). The primary function of the sample processor is to convert the sample into a form that can conveniently be handled by the signal generator. For conventional solution analysis, the sample processor may consist of auto sampler, pump, nebulizer and spray chamber. The signal generator, essentially the plasma, generates photons of specific wavelengths, or ions of specific masses, characteristic to each analytic element from the aerosol droplets. For photon measurement, i.e. in optical emission spectrometry (ICP-ES), the signal processor disperses and separates the photons according to their wavelength and quantitatively measures their intensity. In mass spectrometry (ICP-MS) the ions generated by the plasma are separated according to m/e (mass-to-charge ratio) and the intensity of ions of a desired mass is measured quantitatively.

Even though, in principle, the ICP can also be used as an atom source for atomic absorption and atomic fluorescence, because of its high excitation and ionization efficiency of producing excited atoms and ions, it is primarily used as a source for optical emission and mass spectrometry.(Alfassi, 2012)

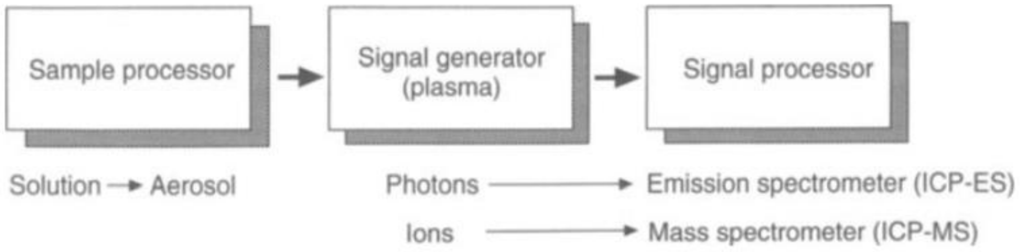


Fig.(2.2) Basic ICP spectrometry system.

2-3-1 Suitability of the ICP as an emission source:

In emission spectrometry the sample is subjected to high enough temperature to dissociate the matrix into atoms or ions and to cause their electronic excitation by collision. The excited atoms or ions relax from the excited state to the ground state by collision with other particles (coalitional relaxation) or by emitting radiation (radiative relaxation) (Figure 2.3). The energy difference between the two energy states, and therefore the wavelength of emitted radiation, is discrete and characteristic to the element.

The intensity of the light emitted at the characteristic wavelength is proportional to the concentration of the particular element One of the main advantages of the high excitation efficiency of the ICP is that it can populate a large number of different excited energy states for a number of elements at the same time under the same set of experimental conditions. This endows the ICP-ES its most notable feature, the capability of simultaneous multi-element determinations. However, by the same token, the emission spectra can also be quite rich in spectral lines and structure, thereby increasing the probability of spectral overlaps, which would demand an optical spectrometer with a high resolving power.

The emission lines can be in the vacuum-ultraviolet (VUV, 120- 190nm), ultraviolet (UV, 190-400 nm), visible (VIS, 400-700 nm) and near-infrared(NIR, 700-850 nm). For practical reasons, the most commonly used spectral regions are UV and VIS. Spectrometers used in the VUV region need to be maintained at a vacuum to avoid absorption of VUV radiation by air, and are used for specialized applications such as sensitive determination of halogens, phosphorus and sulfur. Owing to the high efficiency of matrix decomposition and its inertness, the ICP is virtually free from sample-matrix-induced interferences, which means that calibration can be quickly and easily performed with simple multi-element aqueous standards. It is a constant emission source and its stability is unexcelled, making it capable of performing all day routine determinations with a very few straightforward calibrations. Finally, because it is an optically thin source, ICP has exceptional linearity over a wide range of concentration without being affected by self-absorption.

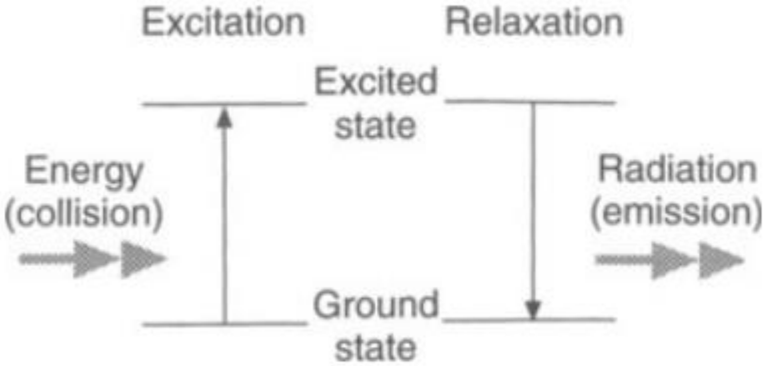


Fig.(2.3) Coalitional excitation and radiative relaxation

This large dynamic range, typically over six orders of magnitude, permits the determination of trace, minor, and major elements in the same sample simultaneously, without the need for serial dilution.

In general these attributes make ICP emission spectroscopy a nearly universal technique for elemental analysis in a variety of applications ranging from geological to clinical fields. (Alfassi, 2012)

2-3-2 Optical Emission Spectroscopy (OES):

This technique is based on the principle that when an element is converted into atoms and ions (atomized), light characteristic for that particular element is emitted; recognition of this phenomenon led to the early development of the technique.

Optical emission spectroscopy (OES) was first applied to archaeological materials in the 1930s. In order to perform this type of analysis, it is necessary for the sample to be either a liquid or in solution; solid samples are often dissolved in a strong Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The next step is nebulization, where the sample solution is converted into an aerosol and then the tiny droplets are sprayed into a heat source, which is often a flame. Depending upon the oxidant and fuel used, flame temperatures between 1700 and 3000◦C can be achieved. At these relatively low temperatures, a portion of the sample is atomized; furnaces sparks, and arcs can be used to produce higher temperatures than flames. Sample atoms are excited through collisions and outer electrons are temporarily lifted to higher energy levels. In order to return to ground state, energy characteristic of the particular element is released. This energy is a well-defined wavelength in the near ultraviolet or visible light range.

(Malainey, 2011)

2-4plasma fundamentals:

2-4-1 Definition of a Plasma:

The word plasma is used to describe a wide variety of macroscopically neutral substances containing many interacting free electrons and ionized atoms or molecules, which exhibit collective behavior due to the long-range coulomb forces. Not all media containing charged particles, however, can be classified as plasmas. For a collection of interacting charged and neutral particles to exhibit plasma behavior it must satisfy certain conditions, or criteria, for plasma existence. These criteria will be discussed in some detail in the next section.
The word plasma comes from the Greek and means something molded. It was applied for the first time by Tonks and Langmuir, in 1929, to describe the inner region, remote from the boundaries, of a glowing ionized gas produced by electric discharge in a tube, the ionized gas as a whole remaining electrically neutral. (Bittencourt, 2004)

2-4-2 Plasma as the Fourth State of Matter:

From a scientific point of view, matter in the known universe is often classified in terms of four states: solid, liquid, gaseous, and plasma. The basic distinction among solids, liquids, and gases lies in the difference between the strength of the bonds that hold their constituent particles together. These binding forces are relatively strong in a solid, weak in a liquid, and essentially almost absent in the gaseous state. Whether a given substance is found in one of these states depends on the random kinetic energy (thermal energy) of its atoms or molecules, i.e., on its temperature. The equilibrium between this particle thermal energy and the inter particle binding forces determines the state.

By heating a solid or liquid substance, the atoms or molecules acquire more thermal kinetic energy until they are able to overcome the binding potential energy. This leads to phase transitions, which occur at a constant temperature for a given pressure.

The amount of energy required for the phase transition is called the latent heat.

If sufficient energy is provided, a molecular gas will gradually dissociate into an atomic gas as a result of collisions between those particles whose thermal kinetic energy exceeds the molecular binding energy.

At sufficiently elevated temperatures an increasing fraction of the atoms will possess enough kinetic energy to overcome, by collisions, the binding energy of the outermost orbital electrons, and an ionized gas or plasma results.

However, this transition from a gas to a plasma is not a phase transition in the thermodynamic sense, since it occurs gradually with increasing temperature. (Bittencourt, 2004)

2-4-3 Plasma Production:

A plasma can be produced by raising the temperature of a substance until a reasonably high fractional ionization is obtained. Under thermodynamic equilibrium conditions, the degree of ionization and the electron temperature are closely related. Although plasmas in local thermodynamic equilibrium are found in many places in nature, as is the case for many astrophysical plasmas, they are not very common in the laboratory.

Plasmas can also be generated by ionization processes that raise the degree of ionization much above its thermal equilibrium value. There are many different methods of creating plasmas in the laboratory and, depending on the method, the plasma may have a high or low density, high or low temperature, it may be steady or transient, stable or unstable, and so on. In what follows, a brief description is presented of the most commonly known processes of photo ionization and electric discharge in gases.

In the photoionization process, ionization occurs by absorption of incident photons whose energy is equal to, or greater than, the ionization potential of the absorbing atom. The excess energy of the photon is transformed into kinetic energy of the electron-ion pair formed. For example, the ionization potential energy for the outermost electron of atomic oxygen is 13.6 eV, which can be supplied by radiation of wavelength smaller than about 91 nm, i.e., in the far ultraviolet. Ionization can also be produced by x-rays or gamma rays, which have much smaller wavelengths.

The Earth's ionosphere, for example, is a natural photo ionized plasma. In a gas discharge, an electric field is applied across the ionized gas, which accelerates the free electrons to energies sufficiently high to ionize other atoms by collisions. One characteristic of this process is that the applied electric field transfers energy much more efficiently to the light electrons than to the relatively heavy ions. The electron temperature in gas discharges is therefore usually higher than the ion temperature, since the transfer of thermal energy from the electrons to the heavier particles is very slow.

When the ionizing source is turned off, the ionization decreases gradually because of recombination until it reaches an equilibrium value consistent with the temperature of the medium. In the laboratory the recombination usually occurs so fast that the plasma completely disappears in a small fraction of a second.(Bittencourt, 2004)

2-4-4 Particle Interactions and Collective Effects:

The properties of a plasma are markedly dependent upon the particle interactions. One of the basic features that distinguish the behavior of plasmas from that of ordinary fluids and solids is the existence of collective effects. Due to the long range of electromagnetic forces, each charged particle in the plasma interacts simultaneously with a considerable number of other charged particles, resulting in important collective effects that are responsible for the wealth of physical phenomena that take place in a plasma.

The particle dynamics in a plasma is governed by the internal fields due to the nature and motion of the particles themselves, and by externally applied fields. The basic particle interactions are electromagnetic in character. Quantum effects are negligible, except for some cases of close collisions.

In a plasma we must distinguish between charge-charge and charge neutral interactions. A charged particle is surrounded by an electric field and interacts with the other charged particles according to the coulomb force law, with its dependence on the inverse of the square of the separation distance. Furthermore, a magnetic field is associated with a moving charged particle, which also produces a force on other moving charges. The charged and neutral particles interact through electric polarization fields produced by distortion of the neutral particle's electronic cloud during a close passage of the charged particle The field associated with neutral particles involves short-range forces, such that their interaction is effective only for inter atomic distances sufficiently small to perturb the orbital electrons. It is appreciable when the distance between the centers of the interacting particles is of the order of their diameter, but nearly zero when they are farther apart. Its characteristics can be adequately described only by quantum-mechanical considerations. In many cases this interaction involves permanent or induced electric dipole moments.

A distinction can be made between weakly ionized and strongly ionized plasmas in terms of the nature of the particle interactions. In a weakly ionized plasma the charge-neutral interactions dominate over the multiple coulomb interactions. When the degree of ionization is such that the multiple coulomb interactions become dominant, the plasma is considered strongly ionized.

As the degree of ionization increases, the coulomb interactions become increasingly important so that in a fully ionized plasma all particles are subjected to the multiple coulomb interactions.(Bittencourt, 2004)

2-5 Advantages/disadvantages:

The primary advantage of optical emission analysis is that it is non-intrusive and can be implemented on an existing apparatus with little or no modification. It provides spatial and temporal resolution of the plasma emission spectra and has very large information content which yields much valuable information about the plasma if analyzed properly. Moreover, it IS relatively inexpensive and can be used on more than one reactor However, its complex spectrum is often difficult to interpret. Therefore, typically only the atomic lines are used in plasma process analysis. Molecular lines of unknown origin are often used to monitor species whose emission changes significantly upon the end point in plasma etching processes. It is reasonably effective as a trouble-shooting tool to identify contamination as water in the process or an air leak, as long as the "normal" processing spectra haven been recorded. One of the most limiting factors of OES as a process diagnostic tool is the maintenance of the optical window. Deposition and/or etching of the window can significantly modify and attenuate the OES signal. (Francis, 2003)

2-6 ICP-OES APPLICATIONS:

The versatility of ICP-OES makes it a good analytical technique for a wide variety of applications. This versatility is due not only to the large number of elements that can be determined rapidly at trace levels but also to the wide variety of sample types that can be analyzed using the ICP-OES technique. In this chapter, ICP-OES applications have been grouped into six generalized categories: Agricultural and Foods, Biological and Clinical, Geological, Environmental and Waters, Metals, and Organics. While an exhaustive review of each of these application areas is beyond the scope of this book, some examples of ICP-OES applications are discussed to give the reader an idea of the types of analyses where this technique has been used successfully. Information regarding general application areas and specific applications can be obtained from a number of sources. Unfortunately, there is no one source that contains all the information needed to perform any and all ICP-OES analyses. For general discussions of applications.(Fredeen, 2004) .

•Agricultural and Foods

The ICP-OES technique has been applied to the analysis of a large variety of agricultural and food materials. Types of samples include soils, fertilizers, plant materials, feedstuffs, foods, animal tissues, and body fluids. Analyses of these materials are required to determine levels of essential nutrients as well as levels of toxic elements in the materials. Most agricultural and food materials are generally not in the form of dilute aqueous solutions nor are they readily soluble in distilled water. Therefore, analyses of these materials by ICP-OES often requires that rigorous sample preparation procedures be carried out prior to analysis. Fortunately for the analyst, the use of modern microwave sample digestion techniques is helping to simplify the sample preparation steps for agricultural and food materials as well as many other sample types.

Some typical applications of ICP-OES in this area include determination of trace metals in beer and wine; analysis of infant formula for Ca, Cu, Fe, Mg, Mn, P, K, Na and Zn; determination of country origin of orange juice through trace element analysis; determination of 14 elements in peanuts; and analysis of soils for toxic metal contamination.

•Biological and Clinical

As research reveals more information regarding the roles and behaviors of trace elements in biological systems, ICP-OES has become an important tool in the area of biological and clinical applications. Determinations by ICP-OES of essential, toxic and therapeutic trace elements are important in the medical research laboratories as well as in the clinical and forensic lab environments. Of significant concern regarding trace element determinations in the biological and clinical fields is the contamination of samples prior to their analysis. While it is always important to consider sources of contamination when performing trace determinations in any field, the biological and clinical area is particularly susceptible to errors due to contamination originating in the sample collection and sample preparation steps. The use of surgical equipment, such as scalpels, needles, scissors, and forceps, often contaminates the sample with trace quantities of the very elements being determined in the sample. Many biological and clinical samples are either too small or contain elemental concentrations too low for ICP-OES analysis using conventional pneumatic sample introduction. In these cases, it is often necessary to turn to alternate sample introduction techniques such as ultrasonic nebulization, electro thermal vaporization, or hydride generation, or pre concentration techniques such as ion exchange or solvent extraction. Examples of ICP-OES analyses of biological and clinical samples include determinations of Cr, Ni and Cu in urine; Al in blood; Cu in brain tissue; Se in liver; Cr in feces; Ni in breast milk; B, P and S in bone; and trace elements in oyster and tuna tissues.

•Geological

Geological applications of ICP-OES involve determinations of major, minor and trace compositions of various rocks, soils, sediments, and related materials. The major use of ICP-OES in this field is for prospecting purposes. The technique is also used for applications such as determining origins of rock formations and for marine geochemistry. Preparation of geological samples for analysis by ICP-OES often involves the use of lithium meta borate fusion reactions, especially for materials containing high levels of silica. Acid dissolutions are also commonly used for many geological materials. Of major concern for geological applications of ICP-OES is the elimination of residues that may be present following acid digestion or dissolution of a fusion bead. Careful selection of the nebulizer used with the ICP instrument can help to reduce problems caused by high salt and residue concentrations. Typical applications of ICP-OES for analysis of geological samples include determination of U in ore grade material; analysis of river sediments for several metals; analysis of carbonate drill cores for major, minor and trace elements; determination of rare earth elements in rock formations; and analysis of plankton for several elements.

•Environmental and Waters

The area of environmental analysis is quite a broad topic, covering many different types of ICP-OES applications. Many of these applications, such as analyses of soils, sediments, and animal and plant tissues, overlap areas covered previously in this chapter and will not be addressed in this section. This still leaves a number of important environmental ICP-OES applications, not the least of which are the analyses of various types of water. Other important environmental ICP-OES applications include analyses of sewage sludge, domestic and industrial refuge, coal and coal fly ash, and dust and other airborne particulates.

The analysis of water can be the simplest of all ICP-OES applications, depending on the type of water being analyzed and the required measurement levels and protocols. Fresh waters generally require only that the sample be stabilized wit a mineral acid before analysis by ICP-OES. Some waters may require filtering to remove particulates. For analyses requiring very low detection levels, it may be necessary to perform some kind of pre concentration step prior to analysis. Ultrasonic nebulizers are also useful for improving sensitivity for such analyses. Analyses of sewage sludge, various refuses, and coal and coal fly ash require more rigorous sample preparation while collection of airborne particulates requires use of air filtering techniques. Examples of environmental ICP-OES applications include various water quality analyses as required by the U.S. Environmental Protection Agency; determination of Fe, Cd, Cu, Mo, Ni, V, and Zn in seawater; determination of phosphorus in municipal wastewater; determination of heavy metals in inner-city dust samples; and trace metal analysis of coal fly ash.

•Metals

ICP-OES is used widely for the determination of major, minor and trace elemental constituents in metals and related materials. The technique is used for analysis of raw materials, production control, and quality control for final products as well as in the developmental lab environment. Sample preparation is generally through acid digestions, except for oxide materials which often require use of fusion techniques. Analysis of metals is also the most likely use of solid sampling techniques such as spark or laser ablation with ICP-OES instruments .A particular difficulty associated with metals analysis by ICP-OES is the potential for a large number of spectral interferences since many metals exhibit very complex emission spectra. Use of a high-resolution spectrometer and spectral interference correction techniques are often required for metals analyses by ICP-OES.Some representative applications of ICP-OES for the analysis of metals and related materials include determination of toxic, trace and major constituents in coal and slags; analysis of low alloy steels for As, B, Bi, Ce, La, P, Sn and Ta; high-precision determination of Si in steels; determination of contaminants in high-purity Al; and analysis of superconducting materials for trace contaminants.(Fredeen, 2004)

•Organics

Analysis of organic solutions by ICP-OES is important not only for analyzing organic-based materials such as petroleum products but also for a wide variety of other applications. For many of the analyses from the other application categories discussed in this chapter, it is necessary to perform sample preparation in which the final form of the analytic is contained in an organic solvent. For example, solvent extraction for the purpose of pre concentrating analytic species is a widely used sample preparation technique for ICP-OES. Also considered under the category of organic analyses would be introduction of organic effluents and vapors from high performance liquid chromatography (HPLC) and gas chromatography (GC) separations. While analysis of organics by ICP-OES is generally straightforward, there are often some special requirements. For example, introduction of organic matrices into the ICP discharge usually requires that the ICP be operated at a higher RF power than is normally required for aqueous samples. Sometimes it is also necessary to use special nebulizers or torch injector tubes. When a peristaltic pump is used to transport the sample to the nebulizer, special consideration must be made regarding the chemical resistance of the

pump tubing used with respect to the organic solvent The analysis of used lubricating oils for trace metal content is one of the more popular applications for organics analysis by ICP-OES. Some other applications include analysis of solvent-extracted geological materials for trace elemental composition; determination of lead in gasoline; determination of Cu, Fe, Ni, P, Si and V in cooking oils; analysis of organophosphates for trace contaminants; and determination of major and trace elements in antifreeze. (Fredeen, 2004)

2-7 Cosmetics :

Cosmetics are products applied to the body for the purpose of beautifying, cleansing or improving appearance and enhancing attractive features . They include a range of products such as tooth paste, shampoo, conditioners, mascara, after shave lotion, styling gel, creams, lotions, powders, perfumes, lipsticks, fingernail and toenail polish, eye and facial make-ups, permanent waves, hair colours, hair sprays and deodorants.

They are articles intended to be rubbed, poured, sprinkled or sprayed on, introduced into, or otherwise applied to the human body or any part thereof for promoting attractiveness, cleansing, beautifying or altering the appearance without affecting the body structure or functions.

The use of cosmetics dates back to around 10000BC .

Many of the present-day beauty rituals such as hair coloration, depilation and exfoliation find their roots in ancient Egyptian culture . In the olden days, the Romans, Greeks and Egyptians used various cosmetics which contain white Lead and Mercury . Scented oils and ointments were used to clean and soften the skin and mask body odour while dyes and natural paints were used to colour the face, mainly for ceremonial and religious occasions . According to, there is a common ancient belief that eye makeup could ward off evil spirits and improve sight. The use of cosmetics today cuts across people of all spheres of life. Facial cosmetics are a necessity in the entertainment industry where hundreds of new recruits are daily added to the huge number of cosmetics users with little or no knowledge of their side effects. Some of the cosmetics used contain different compounds like zincite, cuprite goethite, amorphous carbon, elemental silicon or talc hematite, minimum organic compounds, and even heavy metals such as Lead . Black Antimony which was used as eyeliner in ancient Egypt . Black Antimony, applied to the eyes as ground, fine crystalline powder with the aid of thin stick, is used to draw a straight line on the eyes. The application of these mineral locally to the eyes is believed to serve as treatment of ophthalmologic infections and as an eye cleanser . The use of the local eye liner has been reported as a suspected source of Lead exposure to the ocular system in children and adults .

Cosmetic products contain varieties of different harmful or toxic chemicals capable of attacking the skin. Manufacturers of skincare products do not only use synthetic ingredients but also natural products, such as Shea butter, Rose extract, and cane sugar which are sustainable, cheap and less harmful to the consumer .(Udebuani et al., 2015)

2-7-1TYPES of cosmetics:

The general category of cosmetics includes skin care products. These are creams and lotions to moisturize the face and body, sunscreens to protect the skin from damaging UV radiation, and treatment products to repair or hide skin imperfections (acne, wrinkles, dark circles under eyes, etc.). Cosmetics can be described by the form of the product, as well as the area for application. Cosmetics can be liquid or cream emulsions; powders, both pressed and loose; dispersions; and anhydrous creams or sticks . The various forms of makeup include: Lipstick, lip gloss, lip liner, lip plumper, lip balm, lip luster, lip conditioner and lip boosters; Foundation, used to color the face and conceal flaws to produce an impression of health and youth, usually a liquid, cream, powder or mousse; Powder, or face illuminator used to set the foundation, giving a matte finish; Rouge, blush or blusher cheek stain used to color the cheeks and emphasize the cheekbones that comes in powder, cream and gel forms; Bronzer, used to create a more tanned or sun-kissed look; Mascara and lash extender, lash conditioner used to enhance the eyelashes can be of different colors and even waterproof; Eye liner and eye shadow, eye shimmer and glitter eye pencils as well as different color pencils used to color and emphasize the eyelids (larger eyes are a sign of youth); Eyebrow pencils, creams, waxes, gels and powders are used to fill in and define the brows; Nail polish, used to color the fingernails and toenails; Concealer, a type of thick opaque makeup used to cover pimples, various spots and inconsistencies in the skin .

The term "mineral makeup" applies to a category of face makeup, including foundation, eye shadow, blush, and bronzer, made with loose, dry mineral powders. These powders are often mixed with oil-water emulsions. Lipsticks, liquid foundations, and other liquid cosmetics, as well as compressed make ups such as eye shadow and blush in compacts, are often called mineral makeup if they have the same primary ingredients as dry mineral wakeups. However, liquid makeups must contain preservatives and compressed makeups must contain binders, which dry mineral makeups do not. Mineral makeup usually does not contain synthetic fragrances, preservatives, parabens, mineral oil, and chemical dyes. For this reason, dermatologists may consider mineral makeup to be gentler to the skin than makeup that contains those ingredients . Some minerals are nacreous or pearlescent, giving the skin a shining or sparking appearance. One example is Bi oxychloride .(Ben-Nun)

2-8 Literature Review:

2-8-1 ICP – OES Investigations of Heavy Metal Contents in Cosmetic Products:

Rajagopal Mayildurai1, Alagunambi Ramasubbu2*, Nanjan Velmani2

In 2015 used Inductively Plasma Optical Emission Spectroscopy In a variety of chemicals especially heavy metals used in cosmetics as ingredients has different health effects. The level of heavy elements present viz., arsenic, cadmium, chromium, mercury, nickel, lead, cobalt, copper and zinc in twenty different cosmetic samples. All the samples were digested by suitable protocols and the composition of heavy metals analyzed, quantified on an ICP-OES.

Since the dawn of civilization, cosmetics have constituted a part of routine body care by all set of people1. Past few decades has witnessed a rapid growth in cosmetic industries, through production of various types of cosmetics which are needed for care and beautification of skin, hair, nails, teeth and body2. Although beauty consciousness of people has set the demand for cosmetics in market, the side effects as well as health consciousness of people have attracted the health practiticians and researchers to find out the probable reason for unusual side effects3. Heavy metal contamination is one of the most important reasons addressing problem. Heavy metals

like Lead, Arsenic, Chromium, Nickel, Mercury and Cadmium are common contaminants in various cosmetic products4. This paper focuses on the analysis of heavy metals using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) used in cosmetics and its adverse effects.(Mayildurai et al., 2015)

2-8-2 Inductively Coupled Plasma –Optical Emission Spectroscopy: A Review:

Somsubhra Ghosh1*, V. Laxmi Prasanna1, B. Sowjanya1, P. Srivani1, M. Alagaraja1, Dr. David Banji .In 2013 Reviewed Inductively Coupled Plasma –Optical Emission Spectroscopy is the chief experimental technique of atomic and molecular physics and involves determining the energy states of atoms or molecules by looking at the light absorbed or emitted when they change states. Measuring the frequency of light absorbed or emitted which is determined by the energy difference between the two states, can provide a sensitive probe of interactions which perturb those energy states. Among those in this review we revealed that the principle, instrumentation and applications of inductively coupled plasma optical emission spectroscopy. In this sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulisation. The sample aerosol is then transported to the plasma where it is desolvated, vaporized, atomized, and excited and/or ionized by the plasma. The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information for the analyst.

2-8-3 Determination of Residual Carbon by Inductively-Coupled Plasma Optical Emission Spectrometry with Axial and Radial View Configurations:

In this work it was evaluated the performance of inductively-coupled plasma optical emission spectrometers (ICP-OESs) with axial and radial view configurations for residual carbon content (RCC) determination.

The effects of carbon compound source (urea, l-cysteine, and glucose), sample medium, and internal standards on RCC determination were systematically evaluated. All measurements were carried out with two ICP spectrometers using the carbon atomic emission lines: 247.857 and 193.025 nm. The results obtained using axial and radial configurations showed that both the carbon source and the sample medium did not affect significantly the emission intensities. The sample medium only caused drastic influence when H2SO4 was employed probably due to transport interference that can be corrected employing Y as internal standard. The sensitivity attained using axial view ICP-OES was 20-fold better than that reached using radial view ICP-OES based on the slopes of the analytical curves at the most sensitive wavelength (193.025 nm). Using radial and axial ICP-OESs, high concentrations of Fe (>100 mg l−1) interfered at 247.857 nm wavelength. An addition-recovery experiment was made by adding urea to an acid-digested sample and all recoveries were in the 100±5% range for axial and radial measurements. At this wavelength, R.S.D. <2.0% (n=10) and detection limits of 33 and 34 μg ml−1 C, were measured for ICP-OESs with radial and axial configurations, respectively. Biological samples were acid-digested using a closed-vessel microwave-assisted procedure and RCC was determined using both ICP-OES configurations.(Gouveia et al., 2001)

2-8-4 Inductively Coupled Plasma Optical-Emission Spectroscopy Determination of Major and Minor Elements in Vinegar:

Arzu AKPINAR-BAYIZIT1), Murat Ali TURAN2), Lutfiye YILMAZ-ERSAN1), Nilgun TABAN3) in 2010 used Inductively Coupled Plasma Optical-Emission Spectroscopy for Determination of Major and Minor Elements in Vinegar Minerals play an important role in human nutrition, because they are not synthesized in the body. They can be divided into the following groups: macro-minerals (major elements), such as sodium, potassium, magnesium, calcium and phosphorus, micro-minerals (minor/trace elements) such as iron, copper, zinc and manganese; and ultra-trace elements, such as aluminum, bromine and cadmium. Some elements such as lead, cadmium and mercury, can produce toxic effects at high concentrations. Therefore, in recent years, there has been increasing interest in evaluating the macro- and micro- elements in a variety of food samples.

This study characterizes the mineral content of vinegar samples. The concentrations of Na, K, Ca, Mg and P (major elements) as well as Fe, Mn, Sn, Cu, Ni, Zn, Pb and Cd (minor elements) were determined in 35 commercial vinegar samples using inductively coupled plasma optical-emission spectrometry (ICP-OES). The elements with the highest concentrations were K, Na, Ca, Mg and P. The concentrations of heavy metals in the vinegar samples, including Cd, Ni, Sn and Pb, were n ot considered a health risk.(Akpinar-Bayizit et al., 2010)

Chapter three

Material and methods

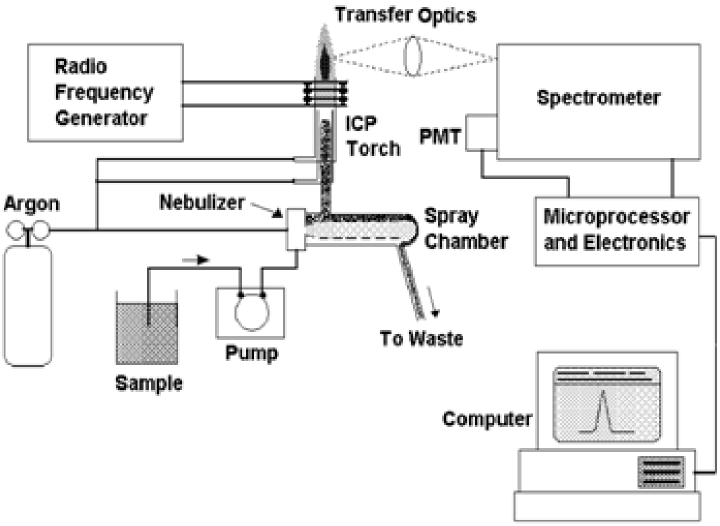
3-1Materials:

Some 0.5% cosmetic powder was taken from the sample and burned at a temperature of 800 ° C for three hours and then dissolved in 10 mL of 10% HCl. The sample was administered in a 500 mL flask and was supplemented by volume with deionized water. The sample was injected into the device.

A total of nineteen cosmetic samples marketed in Khartoum(Sudan) under different commercial names and extensively used by Sudanese women for beautification purposes were purchased from the local market-Khartoum, Sudan.

3-2Instrumentation:

In inductively coupled plasma-optical emission spectrometry, the sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulisation. The sample aerosol is then transported to the plasma where it is desolvated, vaporized, atomized, and excited and/or ionized by the plasma. The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information for the analyst. A representation of the layout of a typical ICP-OES instrument is shown in fig(3-1)



Fig(3-1): Shows the major components and layout of a typical ICP-OES instrument.

3-3the experimental setup:

3-3-1An Overview of ICP-OES Methodology:

Fig(3-2) shows a flow chart for the steps in a typical ICP-OES analysis. The first decision required in developing the methodology for an ICP-OES analysis is which elements are to be determined in the sample. Much of the subsequent methodology is based upon this first decision. Other than making sure that the elements can be determined on the user's instrument, the selection of elements is determined by the user's own requirements for trace elemental analyses. Once that decision has been made, the analyst's goal is to determine the best way to carry out the analysis.

The first step in an analysis is to prepare the samples and standards for introduction to the ICP. This step depends on the physical and chemical characteristics of the samples and runs the gamut from simple dilution to a complex series of chemical reactions and other preparation steps. The next step in the analysis concerns the sample introduction method and hardware to be used. For most ICP-OES analyses, the standard sample introduction system provided with the instrument will suffice.

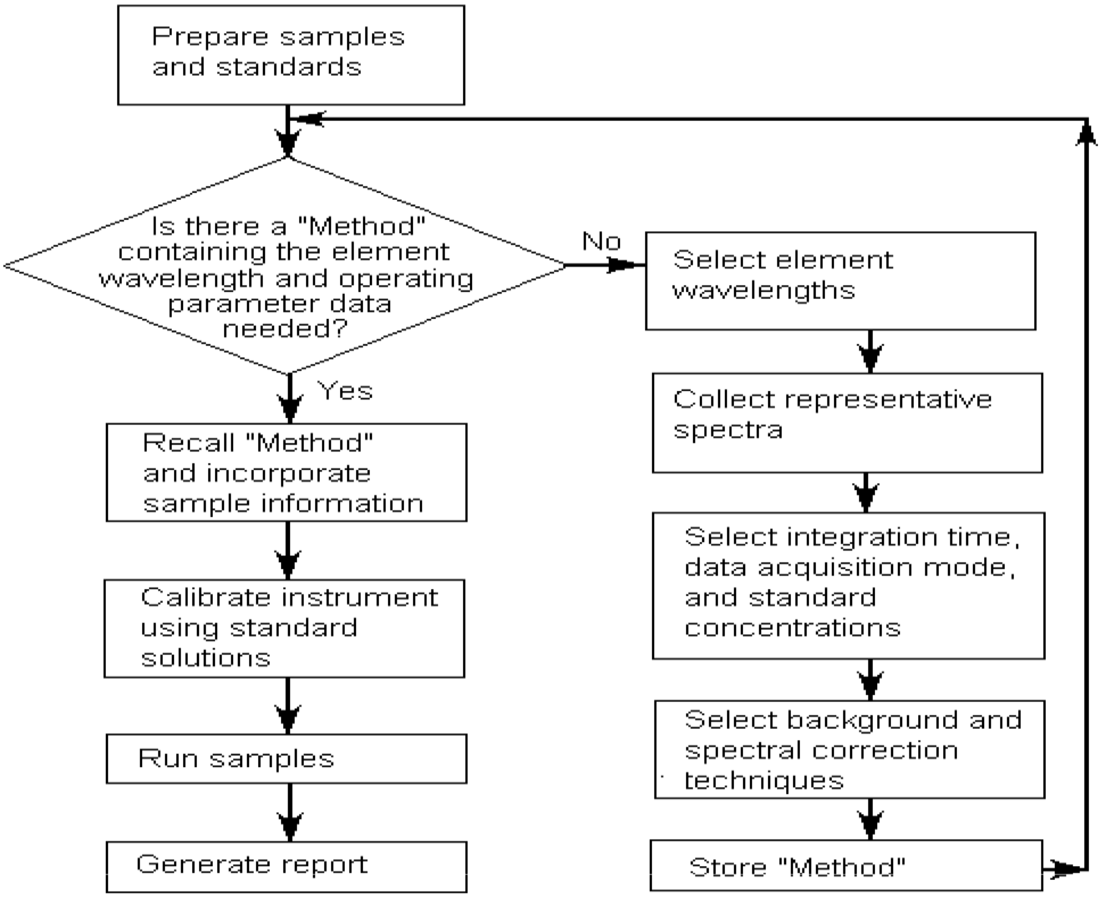
An example of when a nonstandard system might be used is when the solutions to be analyzed contain high levels of particulates or dissolved solids.

The next step in the development of an analysis methodology is to program the instrument, using the computer software provided with the instrument, to perform the data collection and processing steps. To do this, decisions must be made concerning the operating conditions, wavelength selection, instrument calibration, emission measurement, and the actual sample analysis. For many analyses, the default conditions recommended by the instrument manufacturer will provide satisfactory results.

Before making analytical measurements using the instrument, the analyst should take the necessary steps to determine that the instrument is set up and functioning properly. Valuable time and effort, not to mention irreplaceable samples, may be wasted by running an analysis on an instrument that is not set up properly.

Appendix contains some information regarding instrument maintenance and performance verification. The analyst may find this information helpful in assuring that an ICP-OES instrument will provide acceptable analytical results.

Once the samples and standards are prepared, the hardware is set up properly, and the computer is programmed, the analysis may begin. The analyst usually starts by introducing the first standard solution to the plasma and pressing a key on the computer.



Fig(3-2). Flow chart showing the methodology for a typical ICP-OES analysis

Assuming everything is found to be working properly, the analyst continues by introducing further standards (if used) and a blank solution to complete the calibration of the instrument. If no other calibrations or checks are required, the calibration is followed by introduction of samples. Intertwined throughout the analysis may be various solutions used for quality control purposes. Once the analysis of samples is completed, the results can be tabulated and reported as One of the biggest advantages of the general simplicity of ICP-OES methodology is that once a method is developed, the ICP-OES technique lends itself very well to the use of automation. Even for sample preparation, there are a few automated sample preparation systems available. But once analysis begins, relatively little user interaction is generally required. In fact, automation techniques have been developed to the point that the analyst can simply load the unprocessed samples onto a tray, press a few keys on a computer keyboard, walk away from the instrument, and return to find the analysis completed.

3-3-2ICP-OES Methodology:

For most ICP-OES analyses, the standard sample introduction system provided with the instrument will be sufficient. The next step in the development of an analysis methodology is to program the instrument, using the computer software provided with the instrument, to perform the data collection and processing steps. To do this, decisions must be made concerning the operating conditions, wavelength selection, instrument calibration, emission measurement, and the actual sample analysis. For many analyses, the default conditions recommended by the instrument manufacturer will provide satisfactory results. Once the samples and standards are prepared, the hardware is set up properly, and the computer is programmed, the analysis may begin. The analyst usually starts by introducing the first standard solution to the plasma and pressing a key on the computer. Assuming everything is found to be working properly, the analyst continues by introducing further standards (if used) and a blank solution to complete the calibration of the instrument. If no other calibrations or checks are required, the calibration is followed by introduction of samples. Once the analysis of samples is completed, the results can be tabulated and reported as necessary.

3-3-3Sample introduction:

Nebulizers:

Nebulizers are devices that convert a liquid into an aerosol that can be transported to the plasma. The nebulization process is one of the critical steps in ICP-OES. The ideal sample introduction system would be one that delivers all of the sample to the plasma in a form that the plasma could reproducibly desolvate, vaporize, atomize and ionize, and excite. Because only small droplets are useful in the ICP, the ability to produce small droplets for a wide variety of samples largely determines the utility of a nebulizer for ICP-OES.

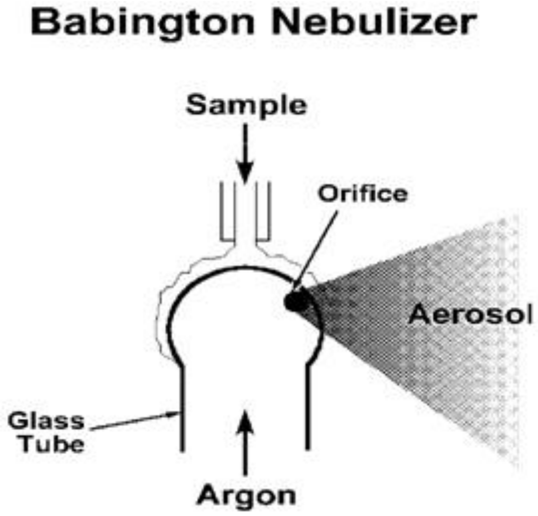
Many forces can be used to break up a liquid into an aerosol; however, only two have been used successfully with an ICP, pneumatic forces and ultrasonic mechanical forces .

Pneumatic nebulizer:

Ex:Babington nebulizer

Babington nebulizer:

The Babington nebulizer, shown in Figure No: 2 works by allowing the liquid to flow over a smooth surface with a small hole in it. High-speed argon gas emanating from the hole shears the sheet of liquid into small drops.



Fig(3-3): **Shows Babington nebulizer**

This nebulizer is susceptible to clogging and can be used for the viscous liquids.

Spray chambers:

Once the sample aerosol is created by the nebulizer, it must be transported to the torch so it can be injected into the plasma. Because only very small droplets in the aerosol are suitable for injection into the plasma, a spray chamber is placed between the nebulizer and the torch. Some typical ICP spray chamber designs. The primary function of the spray chamber is to remove large droplets from the aerosol. A secondary purpose of the spray chamber is to smooth out pulses that occur during nebulisation. In general, spray chambers for the ICP are designed to allow droplets with diameters of about 10 m or smaller to pass to the plasma. With typical nebulizers, this droplet range constitutes about 1 - 5% of the sample that is introduced to the nebulizer. The remaining 95 - 99% of the sample is drained into a waste container. The material from which a spray chamber is constructed can be an important characteristic of a spray chamber. Spray chambers made from corrosion-resistant materials allow to introduce samples containing hydrofluoric acid which could damage glass spray chambers.

Drains:

The drain carries excess sample from the spray chamber to a waste container can have an impact on the performance of the ICP instrument. Besides carrying away excess sample, the drain system provides the backpressure necessary to force the sample aerosol-carrying nebulizer gas flow through the torch’s injector tube and into the plasma discharge. If the drain system does not drain evenly or if it allows bubbles to pass through it, the injection of sample into the plasma may be disrupted and noisy emission signals can result.

Drains for ICP-OES sample introduction systems come in many forms loops, blocks, U-tubes, or even tubing connected to a peristaltic pump. For proper performance, it is important to keep the liquid level within the drain system at the recommended position. Also, when introducing organic-based samples into the ICP, it may be necessary to use drain tubing designated for use with organic solvents.(Ghosh et al., 2013)

3-4the procedure:

3-4-1Wavelength Selection:

Wavelength Selection The selection of wavelengths for measurement of the emission from the analytic elements is done using several criteria. First of all, the wavelengths must be accessible with the instrument being used. In the case of classical PMT-based polychromatic ICP-OES instruments, the wavelength selection may be compromised because of space restrictions, *i.e.*, the juxtaposition of exit slits and PMTs, within the spectrometer. For instruments whose spectrometers do not have vacuum and/or purging capabilities, wavelengths below 190 nm cannot be used.

The second criterion for selection of wavelengths is that the wavelengths selected be appropriate for the concentrations of the elements to be determined. When the analyze concentration falls outside the working range of an emission line, a different emission line should be used. For example, if the manganese concentration in a sample is expected to be about 200 mg/L, then the most sensitive emission line, at 257.610 nm, should not be used since the upper end of its working range is about 50 mg/L. In this case, a less sensitive line, such as the line at 294.920 nm, would be more appropriate.

The final criterion is that the wavelengths be free from spectral interferences.

Because the ICP is so proficient at causing almost any element to emit numerous emission lines, this criterion is sometimes difficult to meet. When freedom from spectral interferences is not possible, lines whose emission intensities can be corrected for spectral interferences should be used. Because correction of spectral interferences is such an important part of ICP-OES methodology.

3-4-2Emission Measurement:

Emission Measurement The method used for the measurement of emission is usually built into the instrument itself and cannot be easily modified by the user. Knowing how the instrument measures emission can be important and may help the analyst to avoid certain problems that may be encountered. The most common two ways to measure emission are to scan the spectrometer over a small wavelength region surrounding the expected emission lines, making a measurement at each step, or to set the spectrometer to a specific wavelength and make measurements only at that wavelength.

With advanced detector methodology, hundreds of ICP-OES emission wavelengths with their associated background are obtained simultaneously. Not only does this permit background correction and spectral interference corrections to be easily applied, the corrections may be made at a later time than the actual analyses which is called *post-processing* of the data. Because all the spectral information is stored,it is even possible to apply the use of internal standardization at some future time if the internal standard lines were included in the method.

While the method of emission measurement is usually fixed for a given instrument, there are certain parameters associated with the emission measurement that can usually be modified to fit the analyst’s needs.(Fredeen, 2004)

3-4-3production of emission:

Torches: the torches contain three concentric tubes for argon flow and aerosol injection. The spacing between the two outer tubes is kept narrow so that the gas introduced between them emerges at high velocity. This outside chamber is also designed to make the gas spiral tangentially around the chamber as it proceeds upward. One of the functions of this gas is to keep the quartz walls of the torch cool and thus this gas flow was originally called the *coolant flow* or *plasma flow* but is now called the "*outer*" gas flow. For argon ICPs, the outer gas flow is usually about 7 - 15 litters per minute. The chamber between the outer flow and the inner flow sends gas directly under the plasma toroid. This flow keeps the plasma discharge away from the intermediate and injector tubes and makes sample aerosol introduction into the plasma easier. In normal operation of the torch, this flow, formerly called the auxiliary flow but now the intermediate gas flow, is about 1.0 L/min. The intermediate flow is usually introduced to reduce carbon formation on the tip of the injector tube when organic samples are being analyzed.

At present, the most popular torches are of the demountable type. These torches can be taken apart so that the tubes can be modified or replaced without replacing the entire torch.

The main advantages of the demountable torch lie in the lower torch replacement costs and the ability to use a variety of injector tubes. Such injectors include corrosion resistant ceramic injectors, narrow-bore injectors for analyses involving organic solvents, and wide-bore injectors for introducing samples with high dissolved solids contents.

Radio Frequency Generators: The radio frequency (RF) generator is the device that provides the power for the generation and sustainment of the plasma discharge. This power ranging from about 700 to 1500 watts, is transferred to the plasma gas through a load coil surrounding the top of the torch. The load coil, which acts as an antenna to transfer the RF power to the plasma, is usually made from copper tubing and is cooled by water or gas during operation. Most RF generators used for ICP-OES operate at a frequency between 27 and 56 MHz. The specific frequency used for an ICP-OES instrument is partially determined by those frequencies that the U. S. Federal Communications Commission (FCC) and similar agencies worldwide have designated for scientific and industrial use. Earlier most of the ICP generators were operated at 27.12 MHz. However, an increasing number of instruments now operate at 40.68 MHz because of improvements in coupling efficiency and reductions in background emission intensity realized at this frequency. Frequencies greater than 40 MHz also have been used but have not been as successful commercially.

There are two general types of RF generators used in ICP instruments. Crystal-controlled generators use a piezoelectric quartz crystal to produce an RF oscillating signal that is amplified by the generator.

(Ghosh et al., 2013)

3-4-4 Computers and Processors :

An important part of any ICP-OES instrument is the computer control incorporated into the instrument. The majority of automated functions of an ICP-OES instrument are directly controlled by an on-board computer. At the simplest level of multi element ICP-OES instrumentation, a computer is needed to handle the massive amounts of data that such an instrument generates. While virtually every commercial ICP-OES instrument available today uses some type of computer to control the spectrometer and to collect, manipulate, and report analytical data, the amount of computer control over other functions of the instrument varies widely from model to model.

3-4-5 Software

ICP-OES instrument would be that it could prepare the standards and samples, develop the analytical method, analyze the samples, report the results, and make decisions based on those results all from a single keystroke.

The objective of a good software package is not only to control the automated features of the instrument during collection of analytical data but to simplify the overall operation of the instrument. Areas in which this is important include not only running an analysis but developing analytical methods and reporting results. The methods development task involves selecting proper operating parameters for an analysis, such as wavelengths, PMT voltages, background correction points, and standards concentrations. The ability to view spectral data displayed graphically with a minimum of effort is indispensable during the selection of these parameters.(Ghosh et al., 2013)

Chapter four

Results and discussion

4-1 Introduction :

Cosmetics industry has grown rapidly over the past decades . Cosmetics refer to those products used by humans to attain attractive features i.e. they are products used for beautification.(Amasa However, beside the expansion in cosmetics market ,which is influence by continual consumers demand , safety in cosmetics has recently become a major concern et al., 2012).(Draelos, 2012)In cosmetics , the most common ingredients are: fragrances , preservatives, ultraviolet absorbers, humectants, emulsifiers and a crylates. (Hamilton and de Gannes, 2011)Such additives are risk factors in many adverse reactions. Some of these fragrances and preservatives are toxic and overexposure is a risk factor in mutation, cancer and endocrine disruption.(Amasa et al., 2012)

Beside fragrances and preservatives , heavy metals are sometimes incorporated to cosmetics .Some of these metals can cause potential damage to the human internal organs. Heavy metals are also associated with various mammalian disorders like respiratory diseases, cancer , kidney failure and intellectual retardation.(Ayenimo et al., 2010)

It is known that the presence of heavy metals as impurities in cosmetics is almost unavoidable due to their ubiquitous nature.(Al-Dayel et al., 2011)Some heavy metal are incorporated in some cosmetics due to their vital fuction.(Volpe et al., 2012) Among heavy metals : lead , mercury, cadmim , nickel, copper and chromium are frequently found in cosmetics. Though , heavy metals occur in cosmetics in trace amount , but due to their long half life, they act as cumulative poison.

In continuation of our interest in safety of cosmetics used by Sudanese women, this study was aimed to analyze some cosmetic articles marketed in Sudan for heavy metal content.

4-2 The Result

In this study a total of nineteen samples of moisturizers marketed in Khartoum and used by Sudanese women for improving appearance have been analyzed by inductively coupled plasma/optical emission spectroscopy(ICP/OES) for heavy metals content. Such metals could be absorbed through the skin causing serious adverse reactions.

The inductively coupled plasma/optical emission spectroscopy(ICP/OES) is a sensitive analytical tool . (ICP/OES) analysis of test samples revealed absence of mercury , lead , nickel and cadmium .

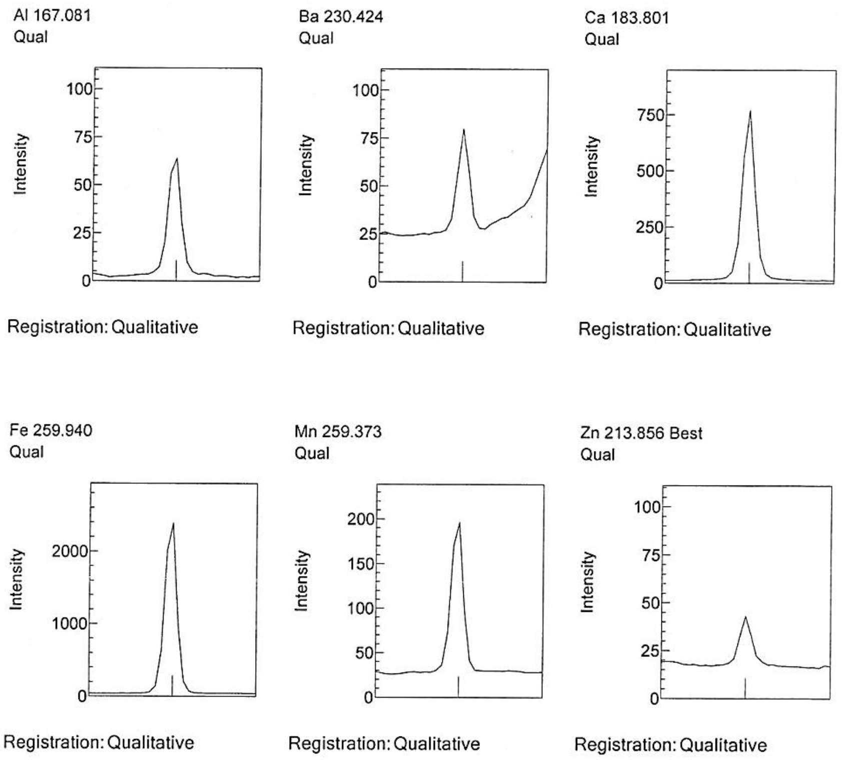


Fig.(4-1): Sample 1 : ICP/OES chromatograms

Table (4.1): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Al	65
Ba	82
Ca	780
Fe	2400
Mn	200
Zn	44

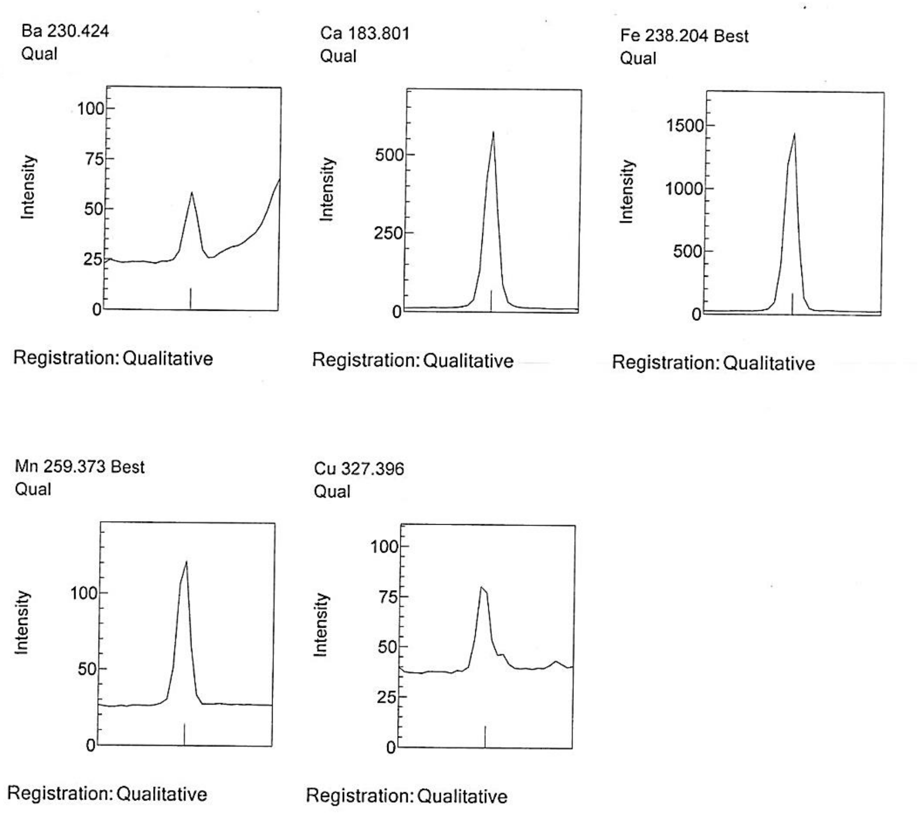


Fig.(4-2): Sample 2 : ICP/OES chromatograms

Table (4.2): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ba	59
Ca	580
Fe	1470
Mn	122
Cu	82

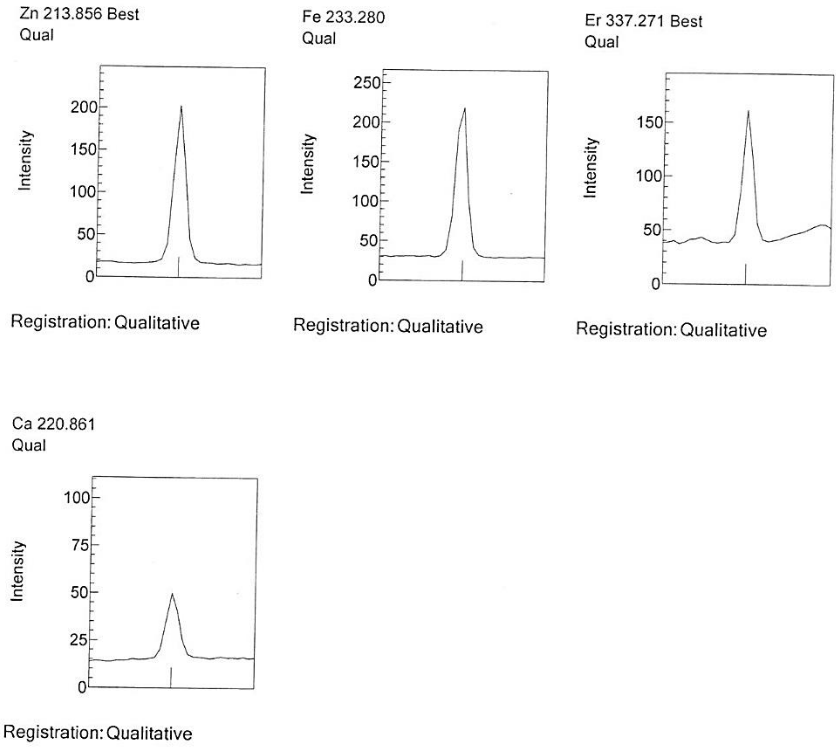


Fig.(4-3): Sample 3 : ICP/OES chromatograms

Table (4.3): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Zn	210
Fe	218
Er	161
Ca	51

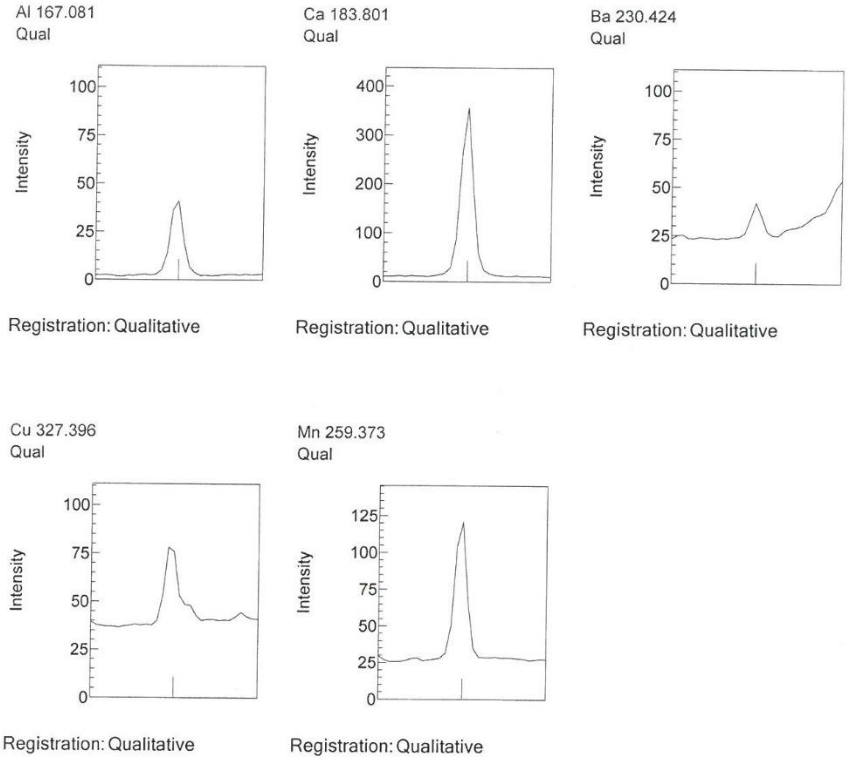


Fig.(4-4): Sample 4 : ICP/OES chromatograms

Table (4.4): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Al	46
Ca	348
Ba	41
Cu	77
Mn	119

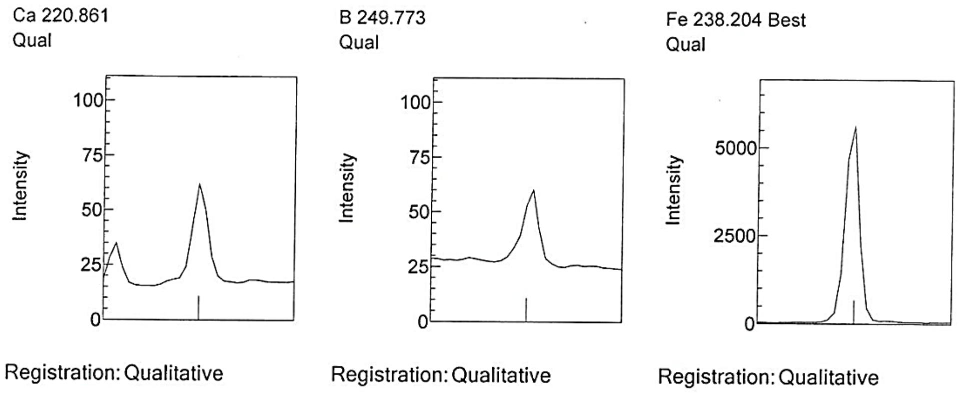


Fig.(4-5): Sample 5 : ICP/OES chromatograms

Table (4.5): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	62
B	60
Fe	5800

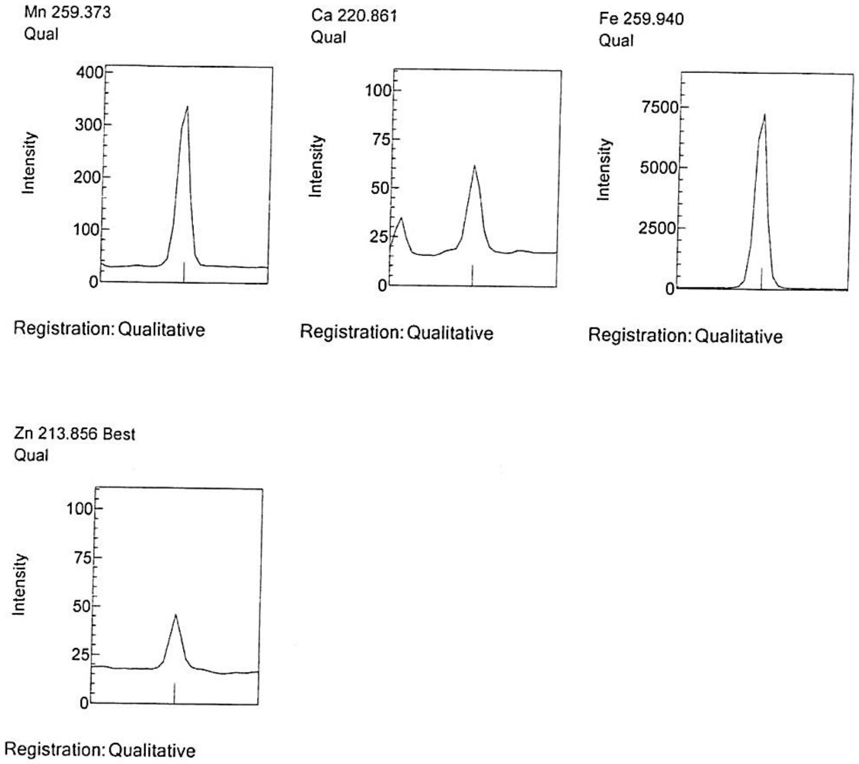


Fig.(4-6): Sample 6 : ICP/OES chromatograms

Table (4.6): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Mn	332
Ca	65
Fe	7400
Zn	45

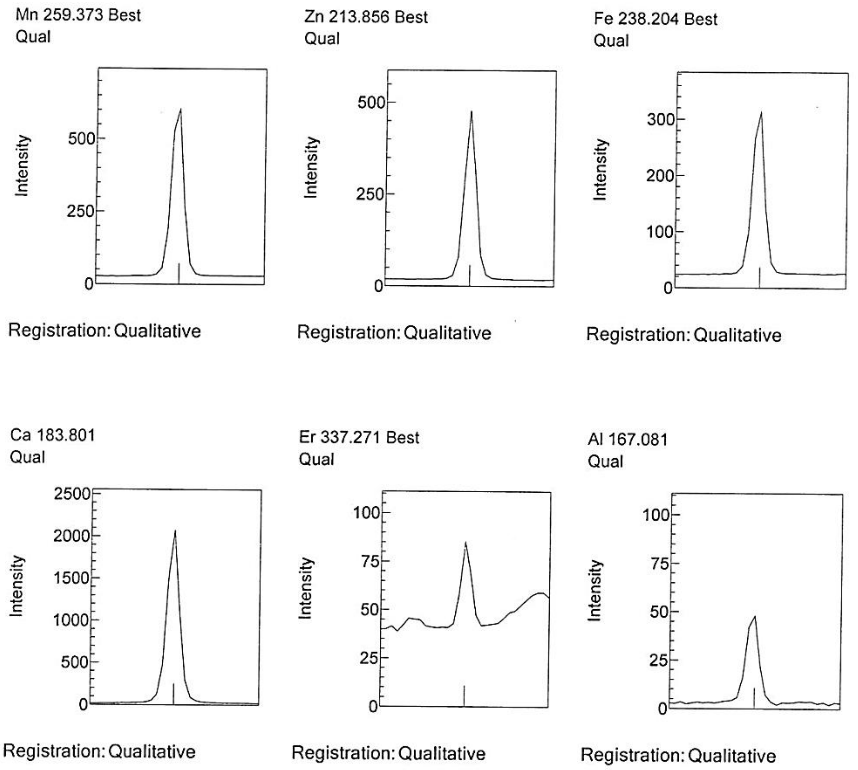
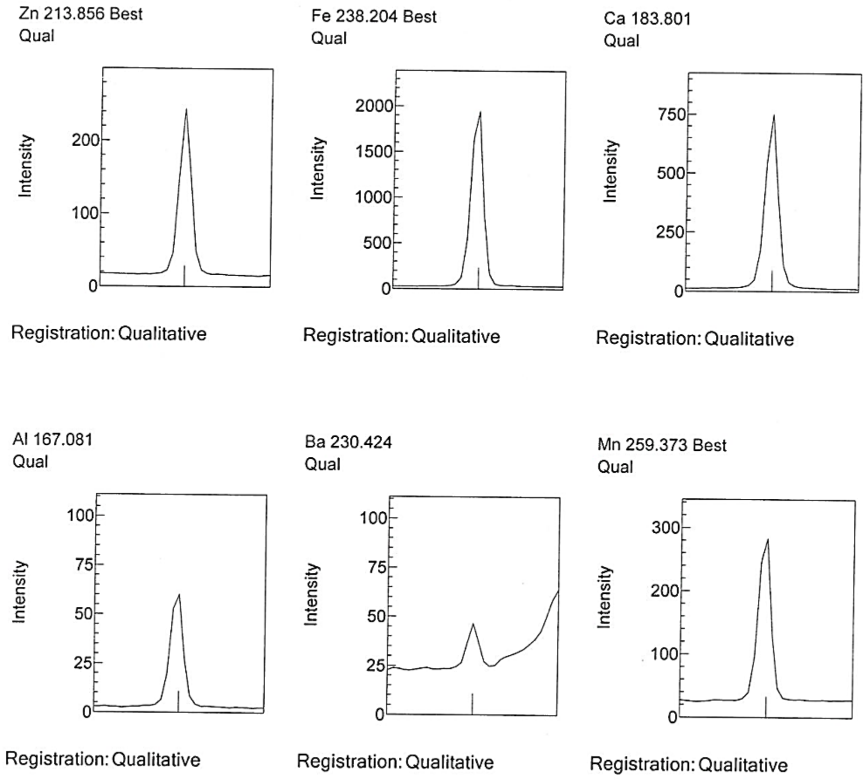


Fig.(4-7): Sample 7 : ICP/OES chromatograms

Table (4.7): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Mn	600
Zn	470
Fe	320
Ca	2100
Er	88
Al	47



Zn 213.856 Best Qual

Fe 238.204 Best Qual

Ca 183.801 Qual

Al 167.081 Qual

Ba 230.424 Qual

Mn 259.373 Best Qual

Fig.(4-8): Sample 8 : ICP/OES chromatograms

Table (4.8): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Zn	244
Fe	1900
Ca	740
Al	58
Ba	45
Mn	280

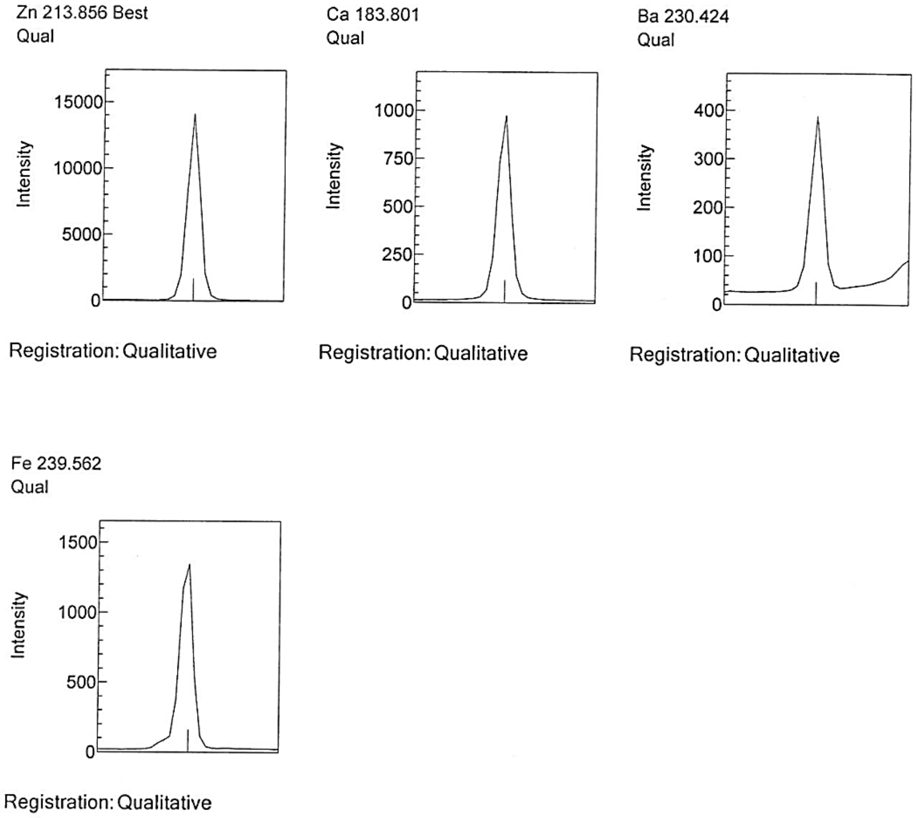


Fig.(4-9): Sample 9 : ICP/OES chromatograms

Table (4.9): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Zn	14400
Ca	980
Ba	380
Fe	1340

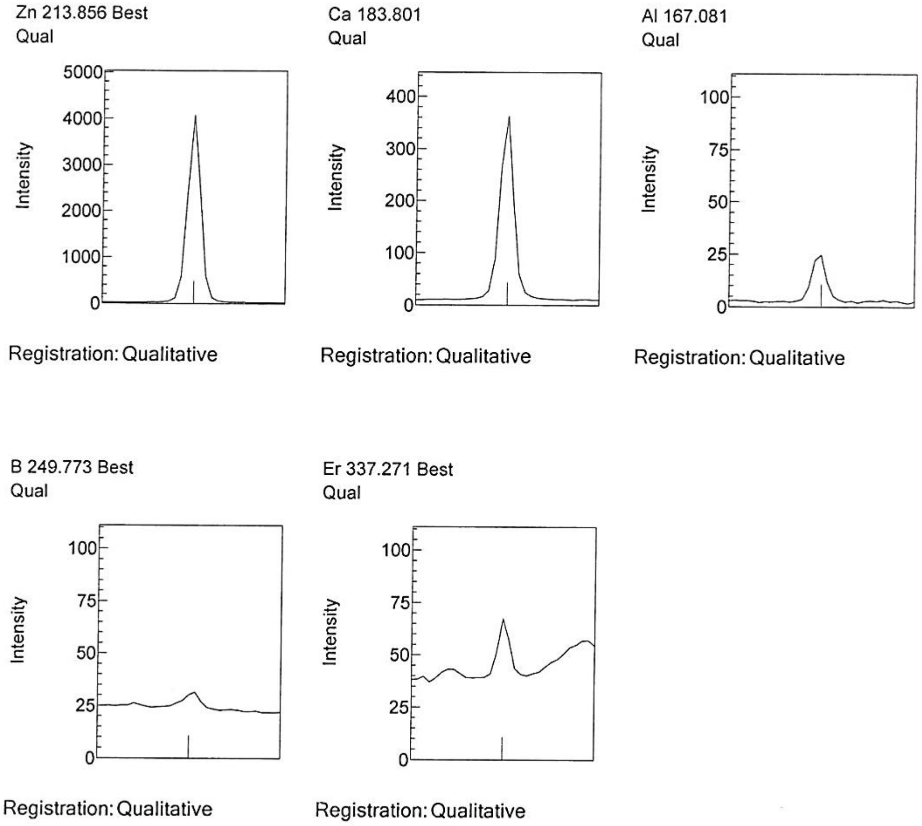


Fig.(4-10): Sample 10 : ICP/OES chromatograms

Table (4.10): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Zn	4200
Ca	360
Al	24
B	30
Er	68

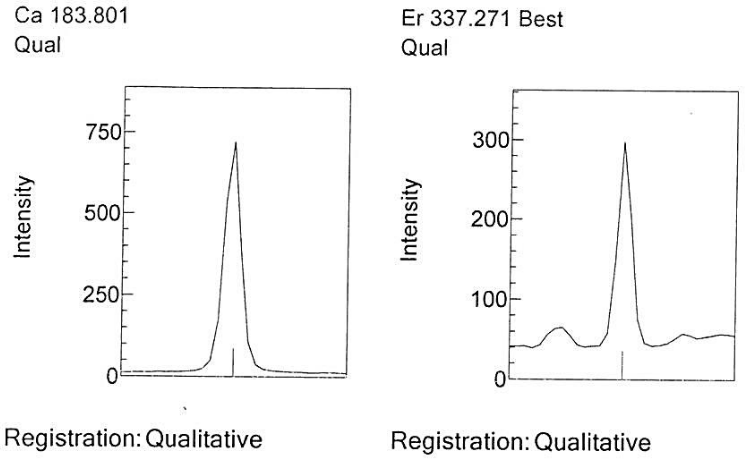


Fig.(4-11): Sample 11 : ICP/OES chromatograms

Table (4.11): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	730
Er	292

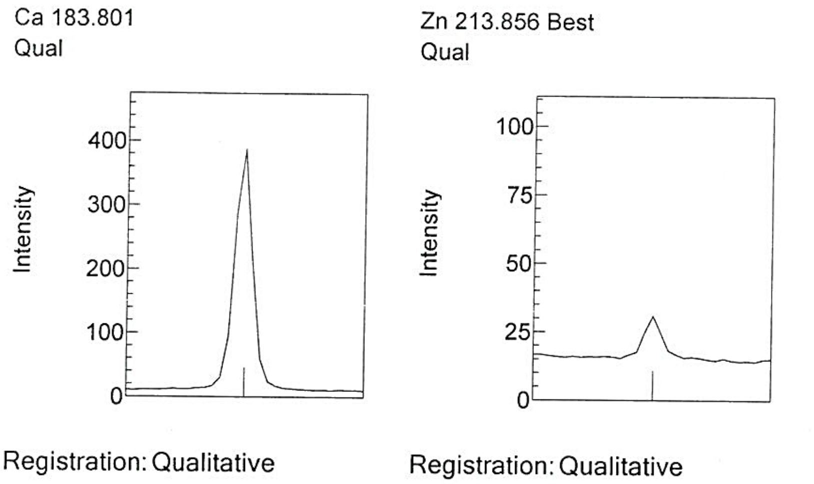


Fig.(4-12): Sample 12 : ICP/OES chromatograms

Table (4.12): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	280
Zn	30

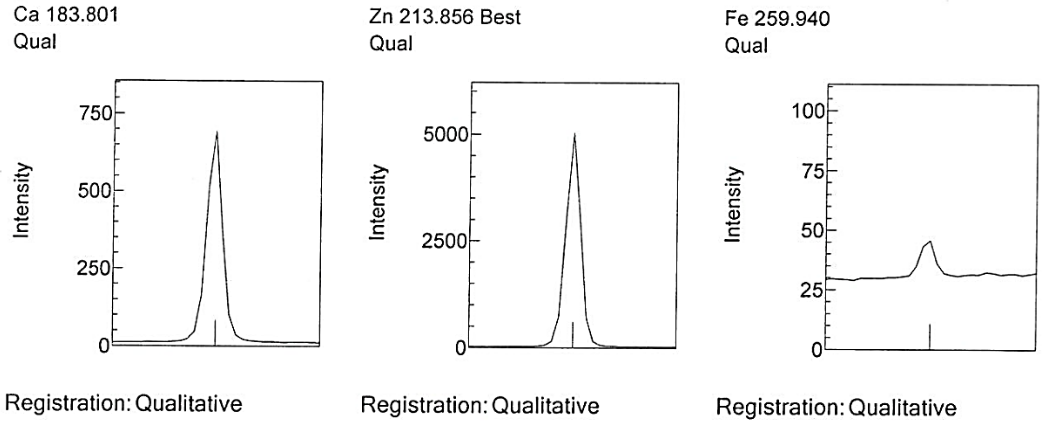


Fig.(4-13): Sample 13 : ICP/OES chromatograms

Table (4.13): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	700
Zn	5100
Fe	45

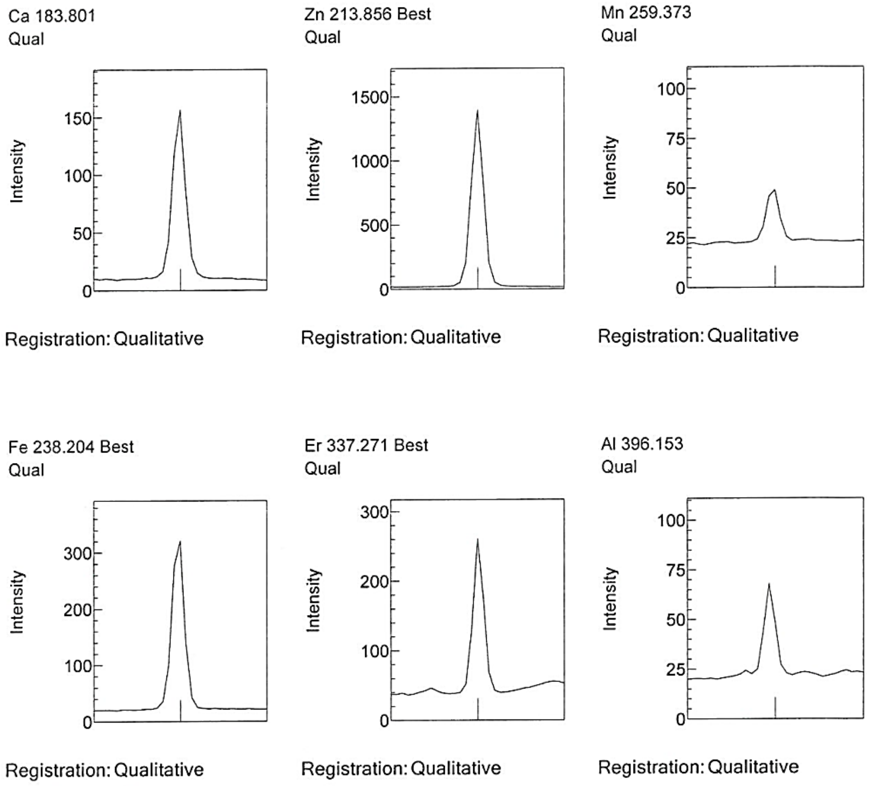


Fig.(4-14): Sample 14 : ICP/OES chromatograms

Table (4.14): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	152
Zn	1400
Mn	48
Fe	320
Er	256
Al	65

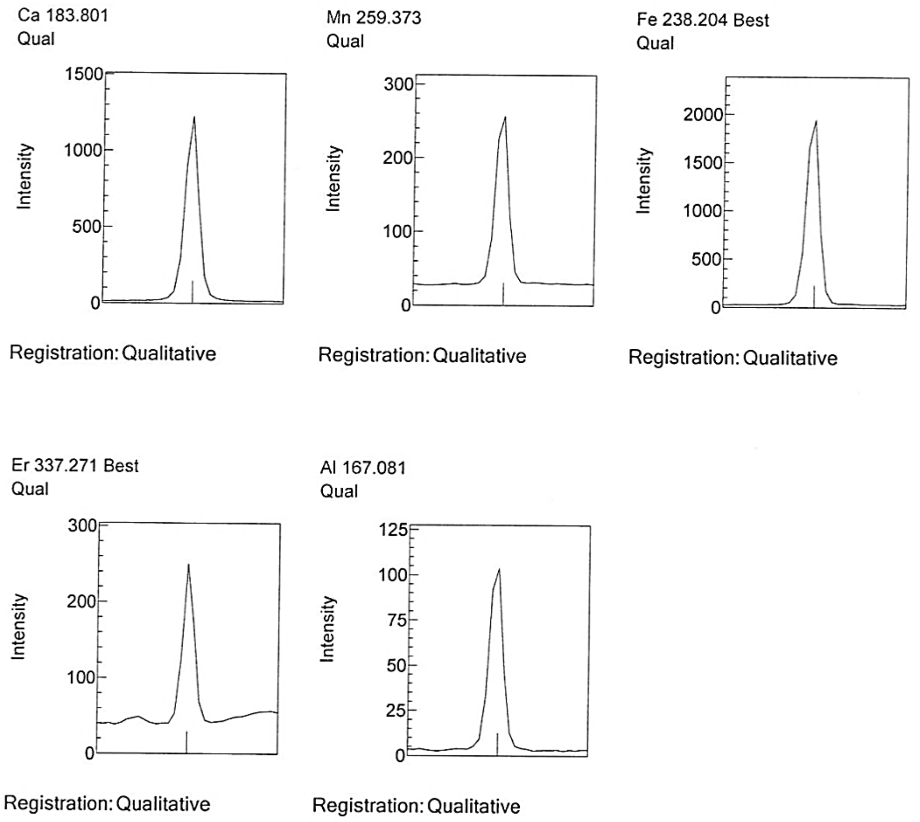


Fig.(4-15): Sample 15 : ICP/OES chromatograms

Table (4.15): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	1200
Mn	256
Fe	1950
Er	252
Al	102

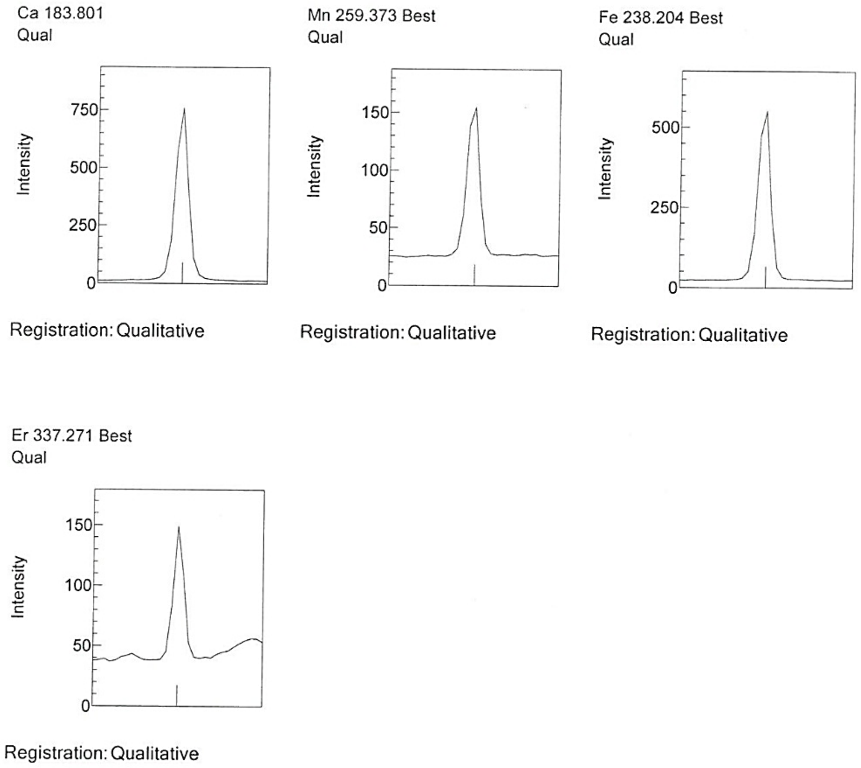


Fig.(4-16): Sample 16 : ICP/OES chromatograms

Table (4.16): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	750
Mn	150
Fe	540
Er	150

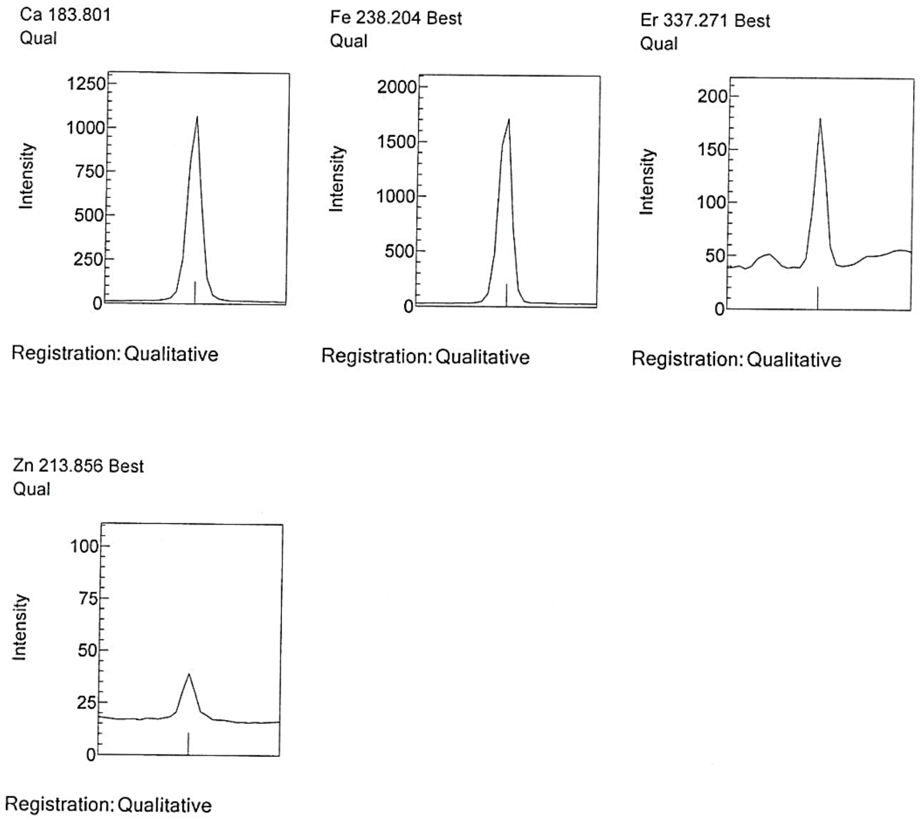


Fig.(4-17): Sample 17 : ICP/OES chromatograms

Table (4.17): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	1050
Fe	1700
Er	178
Zn	38

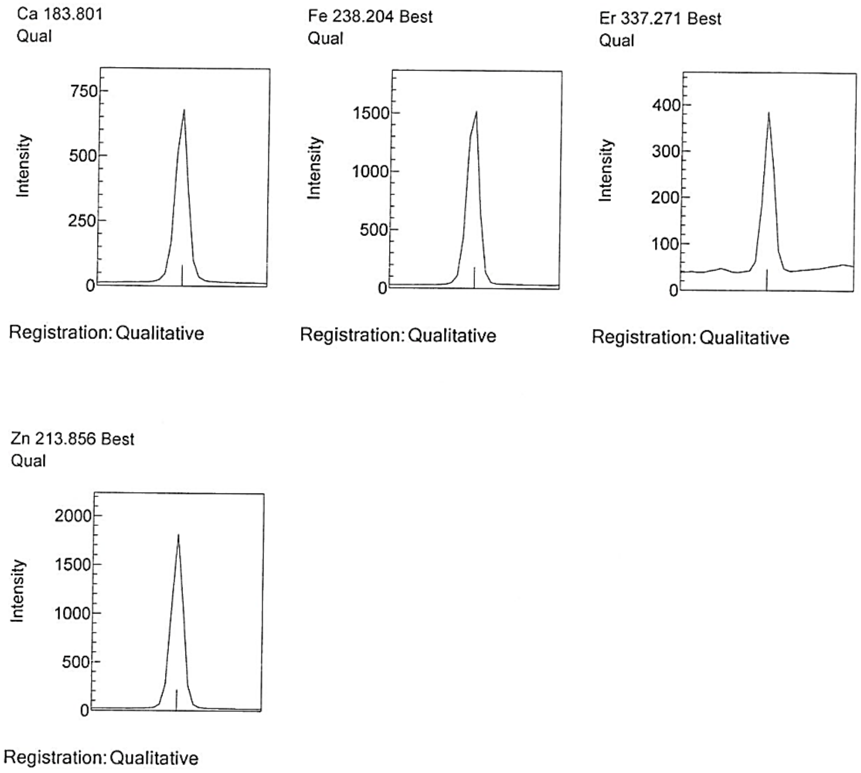


Fig.(4-18): Sample 18 : ICP/OES chromatograms

Table (4.18): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	680
Fe	1500
Er	380
Zn	1800

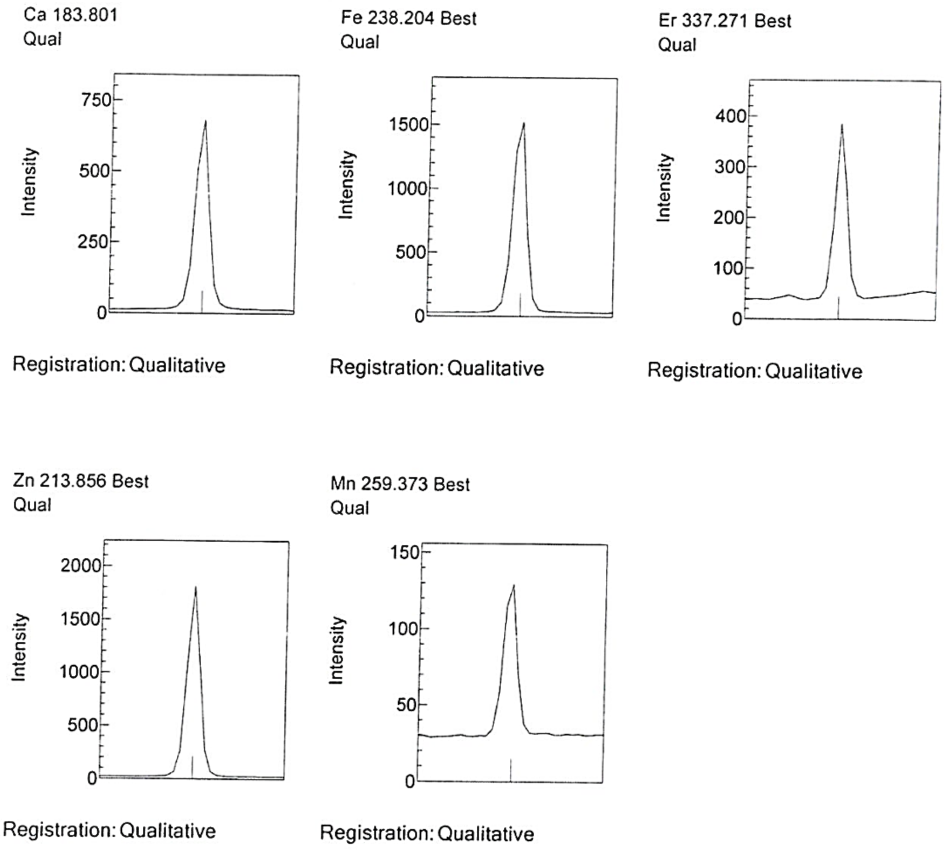


Fig.(4-19): Sample 19 : ICP/OES chromatograms

Table (4.19): The analyzed data of sample collected from different locations in Khartoum(Sudan)

Element	Emission intensity
Ca	698
Fe	1560
Er	390
Mn	1800
Zn	126

4-3 Analysis of the results:

4-3-1 The result of ICP/OES Analysis of Some Conditioners Marketed in Sudan for Heavy Metal Content:

In this study 3 cosmetic samples marketed in Khartoum(Sudan) as conditioners and used extensively by young Sudanese women for improving appearance have been analyzed for heavy metals content using the inductively coupled plasma/optical emission spectroscopy(ICP/OES) . Such heavy metals are classified as cumulative poison.
The inductively coupled plasma/optical emission spectroscopy(ICP/OES) is a sensitive analytical tool . (ICP/OES**)** analysis of test samples revealed absence of mercury , lead , nickel and cadmium . However it showed that a common metal in test samples is calcium. Samples 1 and 2 contained iron. Barium , manganese and copper appeared only in sample 1. Boron appeared only in sample 2 ,while europium appeared only in 3 (see Table 20 and Figures 20-22).

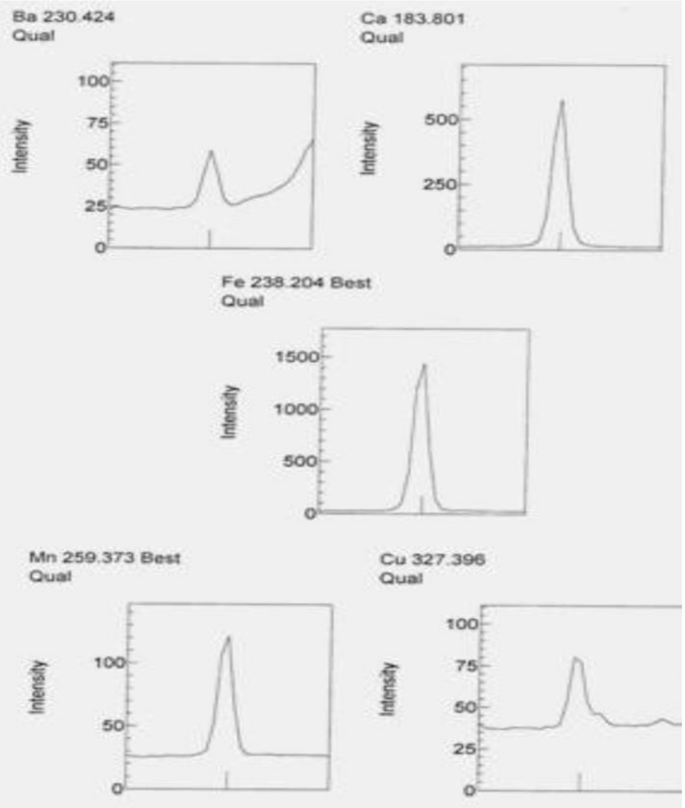


Fig.(4-20): Analysis **Sample 1 : ICP/OES chromatograms**

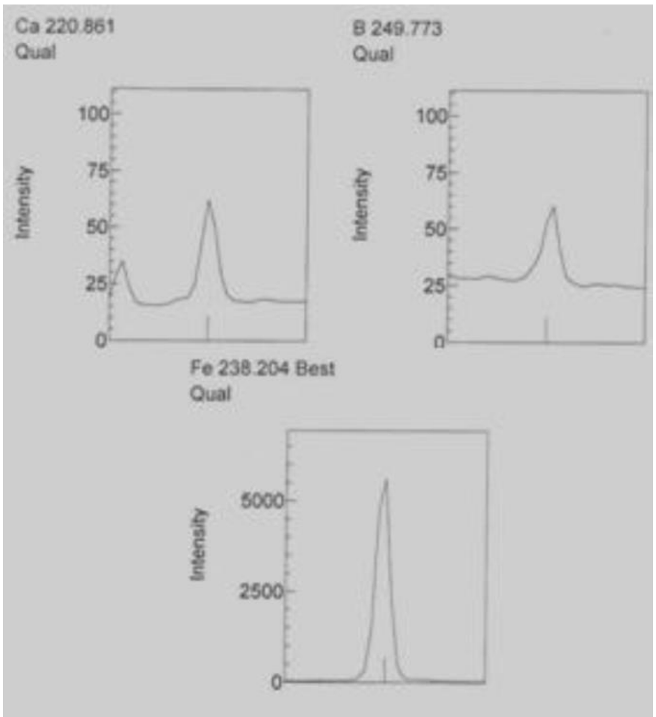


Fig.(4-21): Analysis **Sample 2 : ICP/OES chromatograms**

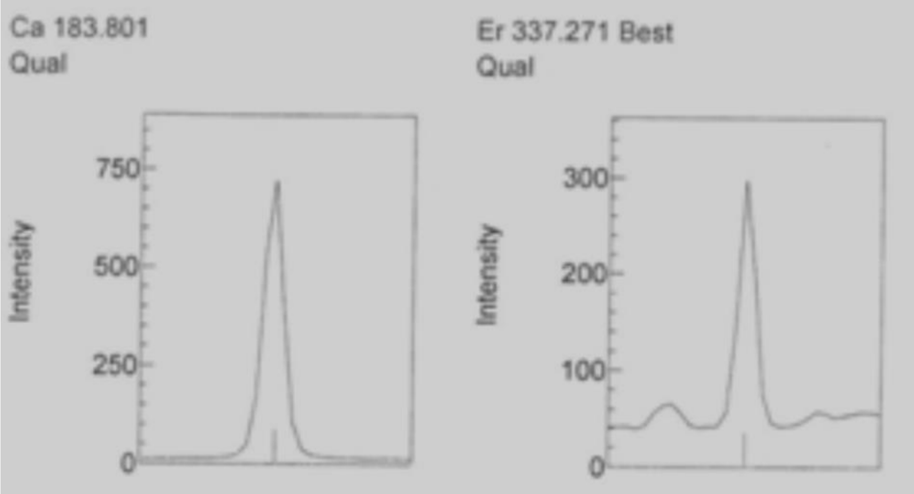


Fig.(4-22): Analysis **Sample 3 : ICP/OES chromatograms**

Table 20: Heavy metals in test analysis samples

Sample No.	Heavy metal						
1	Ba	Ca	Fe	Mn	Cu	-	-
2	-	Ca	Fe	-	-	B	-
3	-	Ca	-	-	-	-	Er

4-3-2 The result ICP/OES Analysis of Some Moisturizers Marketed in Sudan for Heavy Metal Content :

In this study a total of four samples of moisturizers marketed in Khartoum and used by Sudanese women for improving appearance have been analyzed by inductively coupled plasma/optical emission spectroscopy(ICP/OES) for heavy metals content. Such metals could be absorbed through the skin causing serious adverse reactions.

The inductively coupled plasma/optical emission spectroscopy(ICP/OES) is a powerful analytical tool. (ICP/OES**)** analysis of test samples revealed absence of mercury , lead , nickel and cadmium . However it showed that common heavy metals in test samples are: zinc and calcium. whereas iron is common in samples 1,2 and 3.Samples 1 and 3 contained barium , while samples 2 and 3 contained manganese. Aluminum appeared only in sample 3(see Table 21 and Figures 23-26).

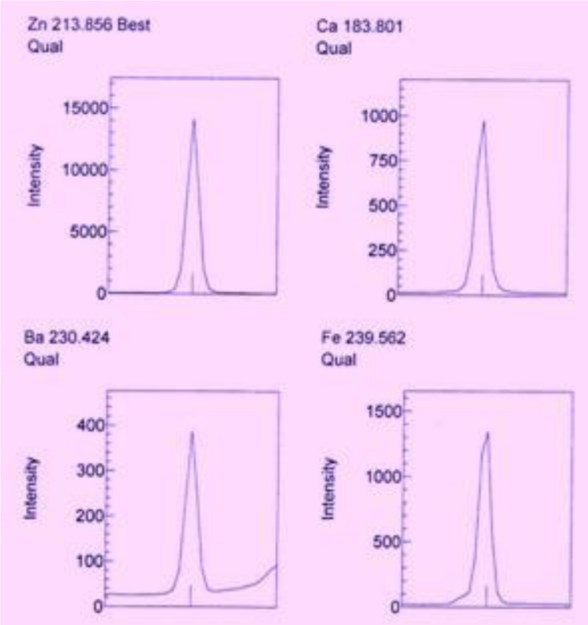


Fig.(4-23): Analysis Sample 1 ICP/OES chromatograms

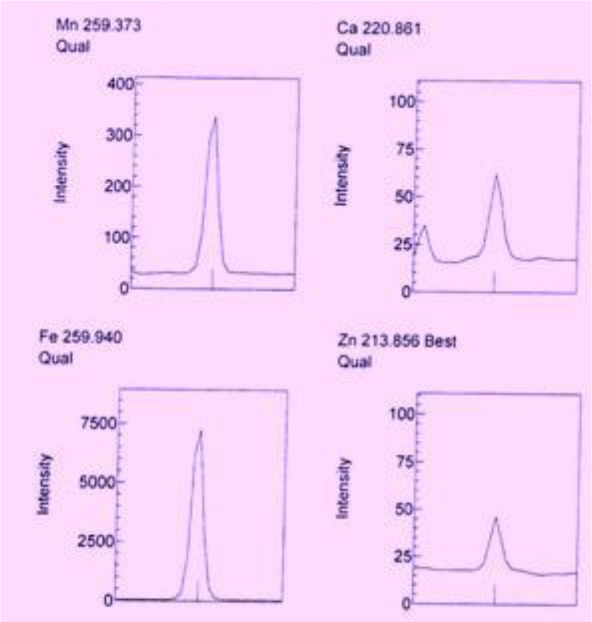


Fig.(4-24): Analysis Sample 2 ICP/OES chromatograms

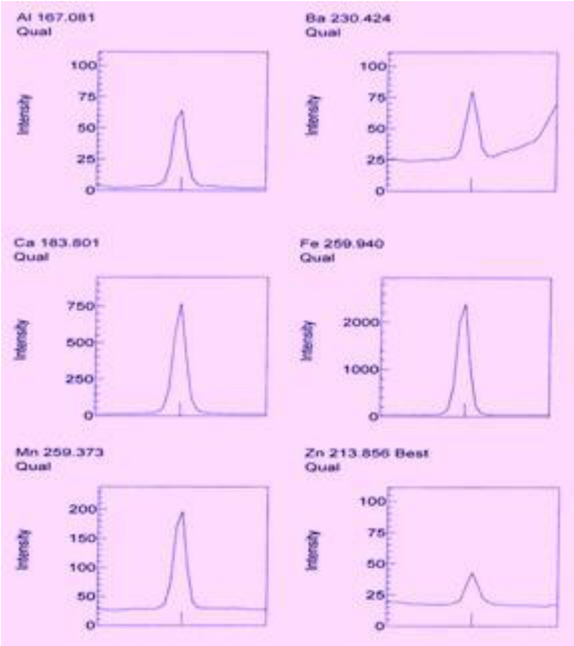


Fig.(4-25): Analysis Sample 3 ICP/OES chromatograms

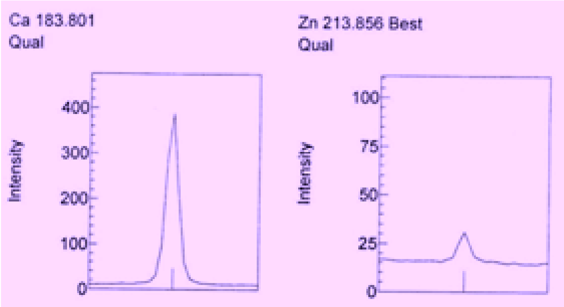


Fig.(4-26): Analysis Sample 4 ICP/OES chromatograms

Table 21: Heavy metals in test analysis samples

Sample No.	[redacted]					
1	Zn	Fe	Ba	Ca	-	-
2	Zn	Fe	-	Ca	Mn	-
3	Zn	Fe	Ba	Ca	Mn	Al
4	Zn	-	-	Ca	-	-

4-4 Discussion:

The health hazards associated with heavy metal-containing cosmetics have been outlined. The accumulation of heavy metals in human body is a risk factor in cancer, reproductive disorders, cardiovascular diseases and kidney failure. Heavy metals can cause vomiting, nausea, brittle hair, lung damage, headache and contact dermatitis. They could be absorbed through the skin and over-exposure can cause serious adverse reactions. The health hazards associated with heavy metal-containing cosmetics have been outlined.(Popoola et al., 2013) It is known that the accumulation of heavy metals in human body is a risk factor in reproductive disorders, cardiovascular diseases, cancer, kidney and liver damage.(Sainio et al., 2000) Cadmium, lead, mercury and nickel implicated in some cosmetics are classified as known carcinogenic agents. They are absorbed via dermal contact and are stored in liver and kidney. High levels of lead in human may cause severe contact dermatitis.(Fisher et al., 2013) Lead is associated with increased blood – lead level in women using leaded eye-powders. Lead overexposure is a risk factor in menstrual irregularities, reduced fertility, and hormonal changes. (Demtröder, 2015)Some cosmetics contain nickel . Nickel and its alloys which are incorporated in some cosmetics are classified as possible carcinogenic agents. On the other hand , mercury-containing cosmetics may cause kidney damage . It has been reported that mercury can reduce skin resistance towards microbial infections.

Europium is a soft metal possessing the lowest density among all lanthanides . It is the most reactive rare earth element. Though, europium salts could be mildly toxic by ingestion, the toxicity of europium has not been fully investigated. (Kassem et al., 2016)

Copper is an essential trace element, but excessive intake of copper is associated with gastrointestinal problems, anemia and allergic dermatitis.(Ababneh et al., 2013) There is a limited data on the toxicity of boron .The limited data on this topic has only been obtained from human poisoning cases and toxicity studies on animals However , clinical symptons of boron toxicity have been outlined.(Bakirdere et al., 2010)

Manganes toxicity is evidenced primarily in the central nervous system and in lung tissue following inhalation exposure, cardiovascular and liver, as well as reproductive and developmental.

Barium is an alkaline earth metal with wide industrial applications. However, accumulation of barium in human body poses serious health hazards including : pulmonary edema , respiratory paralysis, gastric hemorrhages, cardiac failure and kidney damage. (Kravchenko et al., 2014) Many reports addressed the adverse effects associated with ingestion of aluminum in humans. The accmulation of this metal in the body has been linked with Alzheimer and Parkinsson diseases.(Shaw and Tomljenovic, 2013) Also the effect of manganese in the central nervous system has been studied. (Crossgrove and Zheng, 2004)

Iron is found in human body and it is an essential trace element . As far as excessive amount of iron is avoided, this metal does not pose serious adverse effects.(Martin and Griswold, 2009) Also zinc is an essential trace element , but zinc over-exposure can maintain homeostasis .

(Plum et al., 2010)

Cadmium, lead, mercury and nickel implicated in some cosmetics are absorbed via dermal contact and are stored in liver and kidney. Such heavy metals are classified as known carcinogenic agents. Lead is a constituent of leaded eye-powders and is associated with increased blood –lead level in women using such products. Accmalation of lead in human body is a risk factor in reduced fertility, menstrual irregularities and hormonal changes. Some cosmetics contain nickel . Nickel and its alloys are classified as possible carcinogenic agent. High levels of lead may cause severe contact dermatitis.

In skin-lightening agents , mercury is a common ingredient. The major adverse effect of mercury-containing cosmetics is kidney damage .This metal can reduce skin resistance towards microbial infections.(Biebl and Warshaw, 2006)

4-5 Conclusions:

The result of this work showed agreement with the standard sample in National Institute of Standard and Technology (NIST). The results showed that heavy metals by using inductively coupled plasma optical emission spectroscopy (ICPOES)technique . were toxic even if were present in small quantities. However, it is feared that the continued use of cosmetics products contaminated with these heavy metals may cause these minerals to enter the human body and cause harmful effects to consumers over time. The widespread use of such metals should be avoided until the situation is fully clarified.

4-6 Future work:

By the end of research we can suggest the following:

1-The usage of inductively coupled plasma optical emission spectroscopy (ICPOES)technique to determine the concentration in cosmetics powder.
2-Applying of inductively coupled plasma optical emission spectroscopy (ICPOES)technique in all production manufacture in Sudan
3- The usage of inductively coupled plasma optical emission spectroscopy (ICPOES)technique to determine the Cadmium, lead, mercury and nickel.

Reference

ABABNEH, F. A., ABU-SBEIH, K. A. & AL-MOMANI, I. F. 2013. Evaluation of allergenic metals and other trace elements in personal care products.

AL-DAYEL, O., HEFNE, J. & AL-AJYAN, T. 2011. Human exposure to heavy metals from cosmetics. *Oriental Journal of Chemistry,* 27**,** 1-11.

AMASA, W., SANTIAGO, D., MEKONEN, S. & AMBELU, A. 2012. Are cosmetics used in developing countries safe? Use and dermal irritation of body care products in Jimma Town, Southwestern Ethiopia. *Journal of toxicology,* 2012.

AYENIMO, J., YUSUF, A., ADEKUNLE, A. & MAKINDE, O. 2010. Heavy metal exposure from personal care products. *Bulletin of environmental contamination and toxicology,* 84**,** 8-14.

BAKIRDERE, S., ORENAY, S. & KORKMAZ, M. 2010. Effect of boron on human health. *The Open Mineral Processing Journal,* 3.

BIEBL, K. A. & WARSHAW, E. M. 2006. Allergic contact dermatitis to cosmetics. *Dermatologic clinics,* 24**,** 215-32, vii.

CROSSGROVE, J. & ZHENG, W. 2004. Manganese toxicity upon overexposure. *NMR in Biomedicine: An International Journal Devoted to the Development and Application of Magnetic Resonance In Vivo,* 17**,** 544-553.

DEMTRöDER, W. 2015. Laser Spectroscopy 2 Experimental Techniques 5th Edition. *Springer-Verlag Berlin Heidelberg*.

DRAELOS, Z. D. 2012. Are cosmetics safe? *Journal of cosmetic dermatology,* 11**,** 249-250.

FISHER, M., ARBUCKLE, T. E., WADE, M. & HAINES, D. A. 2013. Do perfluoroalkyl substances affect metabolic function and plasma lipids?—analysis of the 2007–2009, Canadian Health Measures Survey (CHMS) Cycle 1. *Environmental research,* 121**,** 95-103.

HAMILTON, T. & DE GANNES, G. C. 2011. Allergic contact dermatitis to preservatives and fragrances in cosmetics. *dermatitis,* 14**,** 16.

KASSEM, M. A., ALTHAGAFI, I. I. & AHMED, S. A. 2016. Sensitive Spectrofluorimetric Study of the Interaction between Europium (III) and 1, 2-Phenylenebis (azan-1-yl-1-ylidene) bis (methan-1-yl-1-ylidene) diphenol Schiff Base. *Journal of fluorescence,* 26**,** 2087-2093.

KRAVCHENKO, J., DARRAH, T. H., MILLER, R. K., LYERLY, H. K. & VENGOSH, A. 2014. A review of the health impacts of barium from natural and anthropogenic exposure. *Environmental geochemistry and health,* 36**,** 797-814.

MARTIN, S. & GRISWOLD, W. 2009. Human health effects of heavy metals. *Environmental Science and Technology briefs for citizens,* 15**,** 1-6.

PLUM, L. M., RINK, L. & HAASE, H. 2010. The essential toxin: impact of zinc on human health. *International journal of environmental research and public health,* 7**,** 1342-1365.

POPOOLA, O., BISI-JOHNSON, M., ABIODUN, A. & IBEH, O. 2013. Heavy metal content and antimicrobial activities of some naturally occurring facial cosmetics in Nigeria. *Ife Journal of Science,* 15**,** 637-644.

SAINIO, E. L., JOLANKI, R., HAKALA, E. & KANERVA, L. 2000. Metals and arsenic in eye shadows. *Contact Dermatitis,* 42**,** 5-10.

SHAW, C. & TOMLJENOVIC, L. 2013. Aluminum in the central nervous system (CNS): toxicity in humans and animals, vaccine adjuvants, and autoimmunity. *Immunologic research,* 56**,** 304-316.

VOLPE, M., NAZZARO, M., COPPOLA, R., RAPUANO, F. & AQUINO, R. 2012. Determination and assessments of selected heavy metals in eye shadow cosmetics from China, Italy, and USA. *Microchemical Journal,* 101**,** 65-69.

AKPINAR-BAYIZIT, A., TURAN, M. A., YILMAZ-ERSAN, L. & TABAN, N. 2010. Inductively coupled plasma optical-emission spectroscopy determination of major and minor elements in vinegar. *Notulae Botanicae Horti Agrobotanici Cluj-Napoca,* 38**,** 64-68.

ALFASSI, Z. B. 2012. *Instrumental multi-element chemical analysis*, Springer Science & Business Media.

BEN-NUN, L. MEDICAL EFFECTS OF COSMETICS.

BITTENCOURT, J. A. 2004. Fundamentals of Plasma Physics Third Edition. *Springer Science+Business Media New York*.

FRANCIS, J. 2003. Lecture Notes On Principles Of Plasma Procissing. *Springer Science+Business Media*.

FREDEEN, C. B. B. A. K. J. 2004. Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry. *2004 PerkinElmer, Inc.*

GHOSH, S., PRASANNA, V. L., SOWJANYA, B., SRIVANI, P., ALAGARAJA, M. & BANJI, D. 2013. Inductively coupled plasma–optical emission spectroscopy: a review. *Asian J. Pharm. Ana,* 3**,** 24-33.

GOUVEIA, S. T., SILVA, F. V., COSTA, L. C. M., NOGUEIRA, A. R. A. & NóBREGA, J. A. 2001. Determination of residual carbon by inductively-coupled plasma optical emission spectrometry with axial and radial view configurations. *Analytica Chimica Acta,* 445**,** 269-275.

MALAINEY, M. E. 2011. Atomic and Emission Spectroscopy. *A Consumer's Guide to Archaeological Science.* Springer.

MAYILDURAI, R., RAMASUBBU, A. & VELMANI, N. 2015. ICP—OES investigations of heavy metal contents in cosmetic products. *J. Pharm. Res,* 9**,** 27-30.

UDEBUANI, A., EZEJI, E., OBASI, K. & NNOLI, M. 2015. Possible Health Implications Associated with Cosmetics: A. *Science,* 3**,** 58-63.

DEMIRBAS, A. 2004. Combustion characteristics of different biomass fuels. *Progress in energy and combustion science,* 30**,** 219-230.

GHOSH, S., PRASANNA, V. L., SOWJANYA, B., SRIVANI, P., ALAGARAJA, M. & BANJI, D. 2013. Inductively coupled plasma–optical emission spectroscopy: a review. *Asian J. Pharm. Ana,* 3**,** 24-33.

RYAN, R. M. & DECI, E. L. 2000. Self-determination theory and the facilitation of intrinsic motivation, social development, and well-being. *American psychologist,* 55**,** 68.

SAMUKAWA, S., HORI, M., RAUF, S., TACHIBANA, K., BRUGGEMAN, P., KROESEN, G., WHITEHEAD, J. C., MURPHY, A. B., GUTSOL, A. F. & STARIKOVSKAIA, S. 2012. The 2012 plasma roadmap. *Journal of Physics D: Applied Physics,* 45**,** 253001.

XU, D. M., VAN DER ZAAG-LOONEN, H. J., OUDKERK, M., WANG, Y., VLIEGENTHART, R., SCHOLTEN, E. T., VERSCHAKELEN, J., PROKOP, M., DE KONING, H. J. & VAN KLAVEREN, R. J. 2009. Smooth or attached solid indeterminate nodules detected at baseline CT screening in the NELSON study: cancer risk during 1 year of follow-up. *Radiology,* 250**,** 264-272.

Appendixes

1- ICP/OES analysis of some conditioners marketed in Sudan for heavy metal content

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Abstract

The safety of cosmetics is becoming nowadays a current issue. This study was designed to detect heavy metals in some conditioners marketed in Sudan for beautification. Three cosmetic articles marketed under different commercial names and extensively used by Sudanese women were analyzed by inductively coupled plasma/optical emission spectroscopy (ICP/OES). (ICP/OES) analysis of test samples revealed absence of potentially harmful mercury, lead, nickel and cadmium. However it showed that a common metal in test samples is calcium. Samples 1 and 2 contained iron. Barium, manganese and copper appeared only in sample 1. Boron appeared only in sample 2, while europium appeared only in 3.

Keywords: health hazards, cosmetics, conditioners, ICP/OES analysis, heavy metals.

2-ICP/OES ANALYSIS OF SOME MOISTURIZERS MARKETED IN SUDAN FOR HEAVY METAL CONTENT

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ABSTRACT

This study was designed to detect heavy metals in some moisturizers marketed in Khartoum(Sudan) for beautification purposes. A total of four cosmetic samples marketed under different commercial names and extensively used by Sudanese women for beautification purposes were analyzed by inductively coupled plasma/optical emission spectroscopy (ICP/OES). The analysis revealed absence of the potentially harmful mercury, lead, nickel and cadmium in test samples. However it showed that common heavy meals in test samples are: zinc and calcium. whereas iron is common in samples 1, 2 and 3. Samples 1 and 3 contained barium, while samples 2 and 3 contained manganese. Aluminium appeared only in sample 3.

KEYWORDS: Health hathards, Cosmetics, Moisturizers, Analysis, Heavy metals