Sudan University of Science and Technology

College of Graduate Studies

Investigation the Elemental Composition of Some ‘‘Kohl’’ Samples

تقصي التكوين العنصري لبعض العينات من الكحل

A Thesis Submitted in Partial Fulfilment of the Requirements of theDegree of Master in Chemistry

By

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إستهلال

بسم الله الرحمن الرحيم

(ألم تر أن الله أنزل من السماء ماءً فأخرجنا به ثمرات مختلفاً ألوانها ومن الجبال جدد بيض وحمر مختلف ألوانها وغرابيب سود)

سورة فاطر(آية27) صدق الله العظيم

Dedication

To my parents, my brothers and sister
And to my husband Abdullah Ali.

Acknowledgment

My endless praise is due to Almighty, Allah for giving me healthand strength to perform this work.

My great thanks go to my supervisor Dr. Omer Adam Mohamed Gibla for his continuous encouragement, help and support during his supervision of this work.

I would like to thank my father for his financial support.

My thanks would also extend tothe membersof Sudanese Petroleum Corporation (SPC)and Khartoum University Laboratories for their help during the analysis of the samples.

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Abstract

This study was aimed to investigate the most major elements, in kohl, as a traditional cosmetic material used by Sudanese. Eight Kohl samples from different sources were purchased from Khartoum state markets, and subjected to elaborate analysis by inductively coupled plasma Optical Emission Spectrometry, to detect the presence of a wide range of minerals. The analysis showed the occurrence of twenty seven elements. The lowest concentrations were shown by Boron (<0.001875 ppm) and Lithium (<0.000387ppm). Very higher concentrations were shown by Lead, Iron, Zinc and Manganese. Calcium, Sodium, Magnesium and Potassium contents, were relatively high. Molybdenum, Phosphors and Aluminium showed various concentrations in the eight samples.

المستخلص

تهدف هذه الدراسة إلى لإستقصاء أكثر العناصر المتوفرة في الكحل كمادة تجميلية تقليدية التي يستخدمها السودانيون.تم شراء ثمانية عينات من الكحل من مصادر مختلفة من أسواق ولاية الخرطوم . تم تحليل العينات بمطيافية الإنبعاث الضوئي لبلازما الحث المزدوج للكشف عن وجود مدى واسع للمعادن. أظهر التحليل وجود سبعة وعشرين عنصراً .

أدنى تراكيز أظهرها البورو(0.001875 PPM) والليثيوم 0.000387PPM) (أظهر كل من الرصاص ،الحديد،الزنك والمنغنيز تراكيز عالية جداً .محتوى الكالسيوم ،الصوديوم،الماغنسيوم والبوتاسيوم عالي نسبياً .أظهر كل من المولبيديوم ،الفسفوروالألمونيوم تراكيز مختلفة في العينات الثمانية .

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CHAPTER ONE

Introduction

Chapter one

1. Introduction

1.1 Kohl

Kohl or (Alkohol), is widely used in Sudan, for hundreds of years. It is one of the mostly known traditional cosmetics, as eyeliner. Kohl is used for a variety of reasons e.g. to make the eyes beautiful, to make the eyes appear larger, as an eye medicine for a variety of complaints, as a daily tradition from both cultural and religious backgrounds, and as a preventive for children.

Women use kohl to outline the upper and lower lids of their eyes.A bridegroom may have kohl applied to his eyes for the wedding ceremony, and the same is often done to tiny/new-born babies in the early weeks of life. Black kohl is also used for staining tattoos and facial scars black.

To date, no one has been able to identify the name of the person who invented the kohl, but according to the manuscripts collected from around the world and in different cultures, whether Arab, African or Asian, it was the most visible pharaonic civilization in ancient sculptures, extending from Sudan to the south of Egypt in the north. Some are thought to be important in transitional rituals such as circumcision, marriage, and for those new-borne. According to their beliefs, they are often used as a tool for decoration, since the time of the ancient kingdoms.

Kohl as an ancient eye cosmetic, traditionally made by grinding stibnite (Sb_2S_3). It is widely used in South Asia, the Middle East, North Africa, the Horn

of Africa, and parts of West Africa as eyeliner to contour and/or darken the eyelids and as mascarafor the eyelashes. It is worn mostly usedby women, but also by some men and children. Kohls are prepared in accordance with relevant health standards and can be classified to different types. For example Blue-Kohlis a dark-bluish black pigment composed of both lead-based compounds andantimony compounds. The lead-based compounds in kohl are galena (PbS), dark grey and gloss laurionite (PbCl (OH)), white phosgenite ($(PbCl)_2CO_3$),ancerussite ($PbCO_3$) , blue. The antimony-based compound in kohl is stibnite (Sb_2S_3), blue (Abeer A. Ahmed et al; 2016).

There is an evidence that, submicromolar concentrations of lead (Pb2+) can elicit overproduction of nitrous oxide (N_2O). Kohl was used not only as a cosmetic but also as a medicinal collyrium. Two types of kohl's lead compounds are the lead chlorides laurionite and phosgenite; are not natural to the Nile valley (Abeer A. Ahmed et al; 2016).

It is believed that they were intentionally synthesized by the ancient Egyptians for this purpose. The widespread use of kohl across the mediterranean and the Mid-east attests to its ability to protect the eye from infectious diseases and be used as a cosmetic (Abeer A. Ahmed et al; 2016).

1.1.1 Benefits of Kohl

Regular use of Kohl will keep the eyes cool and clean from dust and pollution to which eyes may be exposed during the day. It should be noted that, after application of kohl at bedtime, in the morning, we may find some particles with Kohl collected at the corners of the eyes, this is all the dirt and dust particles and airborne substances that the Kohl has collected, and washed away.

Some Kohl preparations contain very valuable ingredients which have a property of protection from the glare of Sun, as natural way for UV protection (Hashmi.et al; 2008).

Some Kohl brands with the incorporation of high quality and unique ingredients can actually bring definite therapeutic effects while supplying nutrients to the cells, with healing properties, toning of muscles, maintain proper nerve and muscles functions, antioxidant, strengthening eyesight, ultimately resulting in the maintenance of healthy eyes and eyesight.

Too much continuous stress on our eyes makes them feel burnt and tired, but regular use of a good quality Kohl with finest, hard-to-soft quality ingredients owning the properties to cool and r 2 n your eyes, thus easing out all the stress of a hectic day (Hashmi.et al; 2008).

Regular use of /Kohl protects the eyes from dust and pollution and keeps them cool and clear, and also helps relief tired eyes, eye stress, dry and irritated eyes especially among the youngsters due to (Computer Vision Syndrome, CVS) caused by continuous emission of short wavelength X-rays by the computer screen. Kohl also helps eyes counter electro-magnetic pollution and other forms of harmful environmental energy (Hashmi.et al; 2008).

1.1.2 Hazards of kohl

1.1.2.1 Lead:

Lead compounds are toxic by ingestion, inhalation andskin expire. Children are more susceptible, than adults, to leadpoisoning as adults absorb 5-15 percent of ingested lead, while,children can absorb as much as 41 percent. The toxic effects oflead form a continuum clinical lead level values in childrenbloodgreater than 10 μg/dl are nowconsidered abnormal and it has been shown, that,significant intellectual impairment occurs in young children whohave blood lead levels *below* 10 μg/dl. Previous publication discussed galena's (PbS) particle size with respect to the associated kohl powderbeing "shiny" or "matt" in texture and with respect to its rate ofdissolution in gastric fluid. It was found that at a meanparticle size for galena of about 10 μm the kohl powder (withgalena as the major component) became totally matt in texture. Above this

particle size the sample becomesincreasingly “shiny”. It had previously been found thattreducing the particle size of galena leads to a significantincrease in its rate of dissolution in gastric fluid. Thus a mattgalena-based powder would be much more easily dissolved ingastric fluid than a “shiny”/“very shiny” powder; with the latterperhaps going straight through the body with minimumabsorption and negligible toxicity. Two such samples in that studyare described as “matt” and both were made abroad (SaudiArabia and Pakistan). Thus these two “matt” samples are morelikely than the other galena-based samples to give rise to leadtoxicity(Andrew D.Hardy, 2011).

1.1.2.2 Sulphur:

SulphurExposure does, however, reduce cardiac vagal control, a response thatwould be expected toincrease susceptibility to ventricular arrhythmia**.** Sulphur dioxide (SO_2) is a moderate to strong irritant. Most inhaled (SO_2) only penetrates, as far as, the nose and throat with minimal amounts reaching thelungs unless the person is breathing heavily, breathing only through the mouth (Jonathan N. Townend, 2005).

1.1.2.3 Zinc:

Zinc is found in all parts of the body, in organs, tissues, bones, fluid and cells. Zinc oxide in kohl hasa powerful natural sun block property which may possibly enhance the protective capacity of galena against the glare of the sun. Zinc is important for growing foetus. It is vital in activity growth, high weight and bone development in children. Zinc is also protecting eye from night blindness and preventthe development of cataracts. Excess amount of zinc concentrated in prostate gland was rated to be harmful(Mitchnick. et at; 1999).

1.1.2.4Iron:

Ironis used in the body to produce the red cells of the blood as an essential part of haemoglobin, which, transport oxygen through our bodies’. Low concentration of Iron in the body causes anaemia. Excess iron causes siderosis,

while the high concentration stores in the liver cause's hemochromatosis and lung cancers (Heaney, 2000).

1.1.2.5 Calcium

Calciumis the most abundant mineral in human body. It is responsible for many functions such as muscles, secretir [4] ɔnes and sending massages through the nervous system. Calcium is concentrated in bones and teeth but a small amount circulate in the blood. If the amount of calcium decreases than the original amount**,** it causes osteoporosis especially in women. If the amount of calcium increases, it causes kidney stones and sclerosis of kidney and blood. Also, it causes heart diseases (Heaney, 2000).

1.1.2.6 Arsenic

Arsenicis extremely toxic. It is found in ground water or in water contaminated by industrial or agrochemicalwaste (Epidemiol, 1988).). It enters human body by ingestion, inhalation or skin absorption. After entering the body, it distributes in a large number of organs including lungs, kidney and liver. Poisoningbegins with headaches, severe diarrheal and blood in urine. It is also related to heart diseases, cancer stroke and the final result is the death (AH. Smith.et al 1992)

1.1.3 Kohl in Sudan

Kohl use is a semi-daily beauty practice for women in Sudan. The cosmetic companies have created modern versions of kohl in form of pens, but the old kohl is still the favourite choice for many ladies.

Kohl industry is one of the oldest women's industries, where the frankincense is prepared for incense and burned in a special jar. The burning takes about half an hour until it turns to black powder, packaged in special bottles. Women

usually use small cans of penicillin for the amount of kohl or keep it in copper abrasive many shapes (Fig 1.1).

Figure 1.1. Different shapes of copper abrasive.

In a study curried by Andrew D.Hardy (2011) as the first study in Sudan dealing with kohl as a traditional eye cosmetics, 21 kohl samples were collectedfrom nine local markets in different towns. These ninelocations were: Al Ubayyid, Bahri, Kassala, Khartoum, Malakal,Omdurman, Port Sudan, Wadi Halfa and Wad Madani. The (21) samples were regarded as being representative of the kohl samples readily available in the various souks of Sudan. The analysis showed that, two of these (21) samples were medicines and were not in fact

used as traditional eye cosmetics. Two labelled samples which made in Saudi Arabia and purchased from two different locations, were found to be identical. Ten samples were made in Sudan and (11) were made abroad, (6 in Saudi). Arabia, (4) in India and (1) in Pakistan. Most of the samples were black/grey, or black/silvery-grey in colour; with (3) samples showing various shades of red, (2) white/grey-white and 1 yellow(Andrew D.Hardy, 2011).

Figure 1.2. Some kohl samples available in Sudan.

Eight of them are shown on the map of Sudan Fig (1.3).One location which was not shown is Bahri city.

Figure 1.3 .A map of Sudan before, (2011).

The analysis showed that form the (21) purchased kohl samples 7 had found to be galena (PbS)as the main component, and one sample having it present as a minor component. Two of the 7galena-based samples were matt in texture, and 4 of the remaining 5 samples were described as “shiny”, and one sample being described as “very shiny”. The colours of thesesamples varied between black, grey black and silvery-grey. Six samples were based on amorphous carbon and one was, based on, one or more, unknown amorphous compounds, which were assumed to be carbon-based; and three samples were based on iron compounds, being mixtures of goethite (FeO (OH)) and hematite (Fe_2O_3)). One of the latter samples contained galena as a minor component (21%).Additionally, two samples had calcium carbonate as the major component, as calcite and as

aragonite. Zincate (ZnO) and halite (NaCl) were being the major components of the remaining (2) samples. (Fig1.4) shows the distribution of the main elements as the major components in all the kohl samples studied.

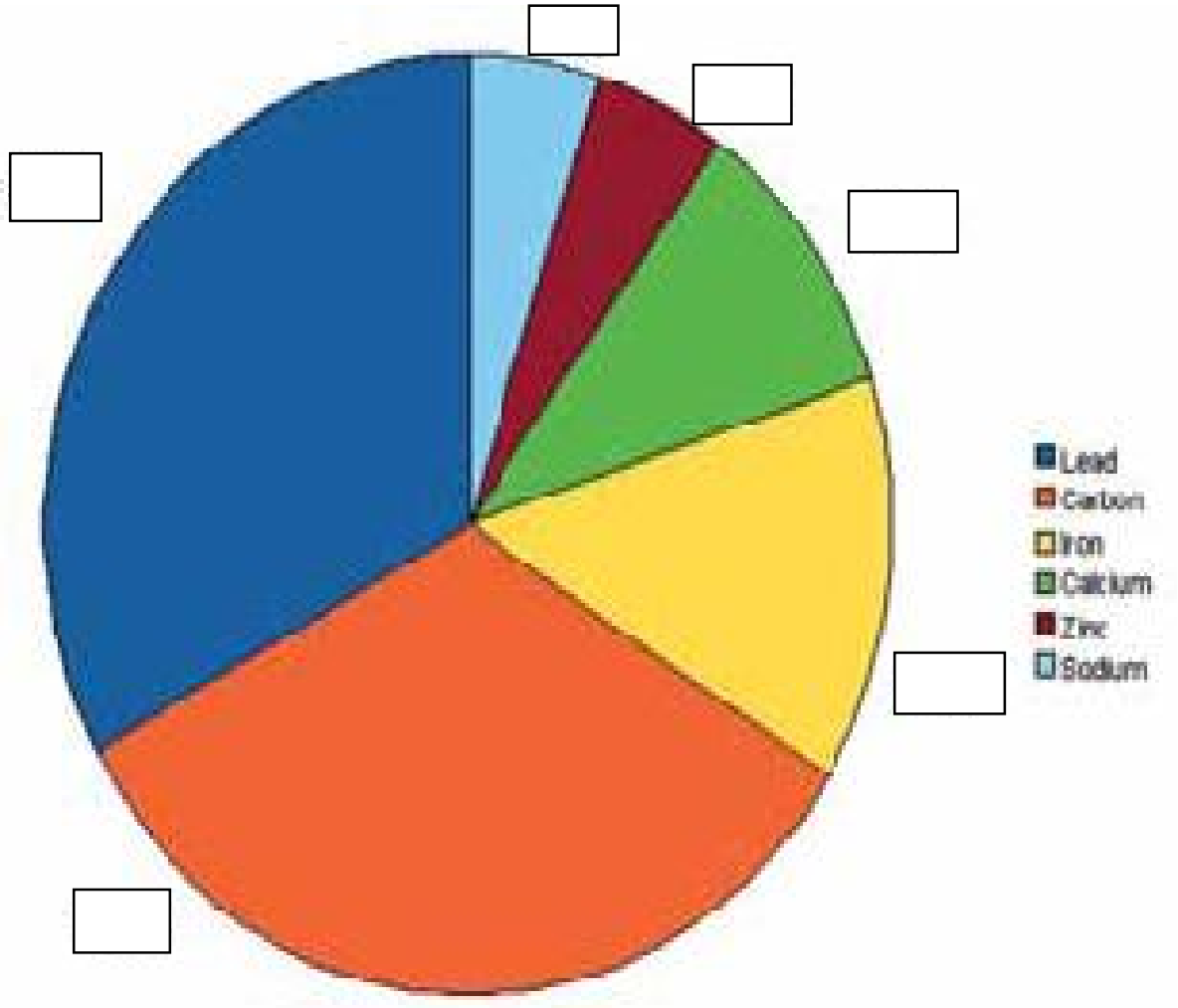

Figure 1.4. Distribution of the main element of the major component in the Sudan kohl samples.

A total of (6) samples were coloured (i.e. *not* black/grey-black/ silvery-grey). The (3) shades-of-red samples were lend to be a mixture of iron compounds goethite and hematite and for the grey-white and white samples the colour was given by the presence of aragonite and halite. The (1) remaining coloured

sample was yellow, its colour may arises from one or more of the currently unknown amorphous organic carbon-based major components. This sample has been tentatively identified as “Gum Arabic”, and it is assumed, that, it is burnt to give amorphous carbon, for making a black kohl. For the (15) samples which, were black/grey black/ silvery-grey thecolour was usuallygiven by their major components that, is amorphous carbon and galena.

For one sample (based on zincate) the black minor components were amorphous carbon and magnetite (Fe_2O_3); and for the other sample based on calcite it was graphite (Andrew D.Hardy, 2011).

1.1.4 Kohl in other countries

In a study conducted in Egypt by N. Bassal, H.H. Mahmoud and M. Fayez-Hassan (2013)X-Ray fluorescence is used to understand theComposition of both natural and industrial kohls,which were taken from different Egyptian markets**.** It was found that the main components of the naturally samples were lead (85 - 89 %) and sulphur (9 - 13 %), while, the industrial samples contain calcium (**92**%, iron 83 % or zinc 96 %. It was found that, some of the natural samples contain traces of radio-active materials such as uranium, thorium and potassium. It is also found, that, one of the samples contains arsenic.

In other study inSaudi Arabia about a toxic traditional eye cosmetic.The results of this study demonstrate that the use ofkohl is part of Saudi culture. Kohl is commonly usedfor cosmetic reasons, and as an eye and umbilicalstump remedy. Some Saudi tribes in differentregions employ it to stop bleeding and aftercircumcision for hygienic measures. Bedouins usekohl (mixed with other colours) for making permanentsigns of beauty on their faces. However, thispractice is confined to some remote desert areas.

Generally, everyone interviewed considered kohl tobe a safe eye cosmetic, while some described itsuse to be a part of prophetic medicine. The dataobtained from this survey revealed that about 81%of kohl sellers believed

that, in addition to its use asan eye cosmetic, kohl also had value for eyeailments; however, 19% thought that there was nolink of kohl use with eye disease.(R.M. Al-Ashban,M. Aslama, A.H. Shah,2003).

In study conducted in India by Mohammed Aleem Pasha, (2016)to know the composition. X-ray study reveals that the composition of kohl stone isgalena. It has been established by several studies that application of kohl does not cause lead poisoning. But recent scientificstudies have reported lead poisoning following traditional lead based medication or kohl application. Similarly, Indiantraditional medicinal texts advocates about the application of anjana (kohl) for curing eye diseases. But it has beenmentioned that the prolonged and persistent use of anjana may cause conjunctivitis and cataract. Hence, the authors are ofthe opinion that application of kohl may be beneficial to eyes but still there may be a possibility of adverse effects onprolonged use.

Study to find Kohl Al-Ethmed, which Prophet Mohammed (Peace beupon him) was using and recommended to use. 16 samples of commonlyused Kohl were analyzed. Atomic Absorption Spectrometer was used todetect minerals presence and its concentrations. Plasma IL-200, Emissionspectrometer was used to detect Antimony. Samples, which found to match the description of Kohl AlEthmed tested for microbial contamination. If thisis negative, its effect on growth of various types of common organisms tothe eye is tested. One sample found to match some of the literature description of Kohl AlEthmed; it is reddish-brownish-black in colour, andhad Antimony (Sb = 0.01%) in it, which is claimed to be the effective gradient of AlEthmed. It has no bacterial contamination, and no inhibitoryeffect on microbial growth in vitro. It contains very low concentration oflead (Pb = 0.01%), which is claimed to be the most hazardous component ofcommonly used brands of Kohl. It contains iron, copper, magnesium,manganese and zinc, which function as cofactors for various enzymes in thetears film. Our sample is safe and matches some of the description of Kohl AlEthmed. Further studies are recommended to fully

understand its effecton eyes and microorganisms in vivo (Osama Badeeb.et al; 2008).

Table (1.1). Lead content of kohl in different countries

Data published country	**Percentage of lead content**
Syria (2010)	90%
Morocco (2010)	80%
Egypt (2009)	50%
Yemen (2008)	80%
Qatar (2008)	20%
UAE (2006)	38%
Egypt (2006)	20%
Egypt (2004)	38%
UAE (2002)	50%
Oman (1998)	38%
Nigeria (1984)	100%
Kuwait (1981)	80%
UK (1979)	60%

Source Andrew D.Hardy-(2011).

1.2 Inductively Coupled Plasma Optical Emission Spectrometer

1.2.1 Principle

Sample solution containing the elements under detecting is aspirated into the plasma generated by inductivity coupled plasma source; the atomized elements produce characteristic emission spectral lines, which are separated by simultaneous optical spectrometer. The intensity of spectral line of an element is proportional to its concentration.(Fig 1.5).

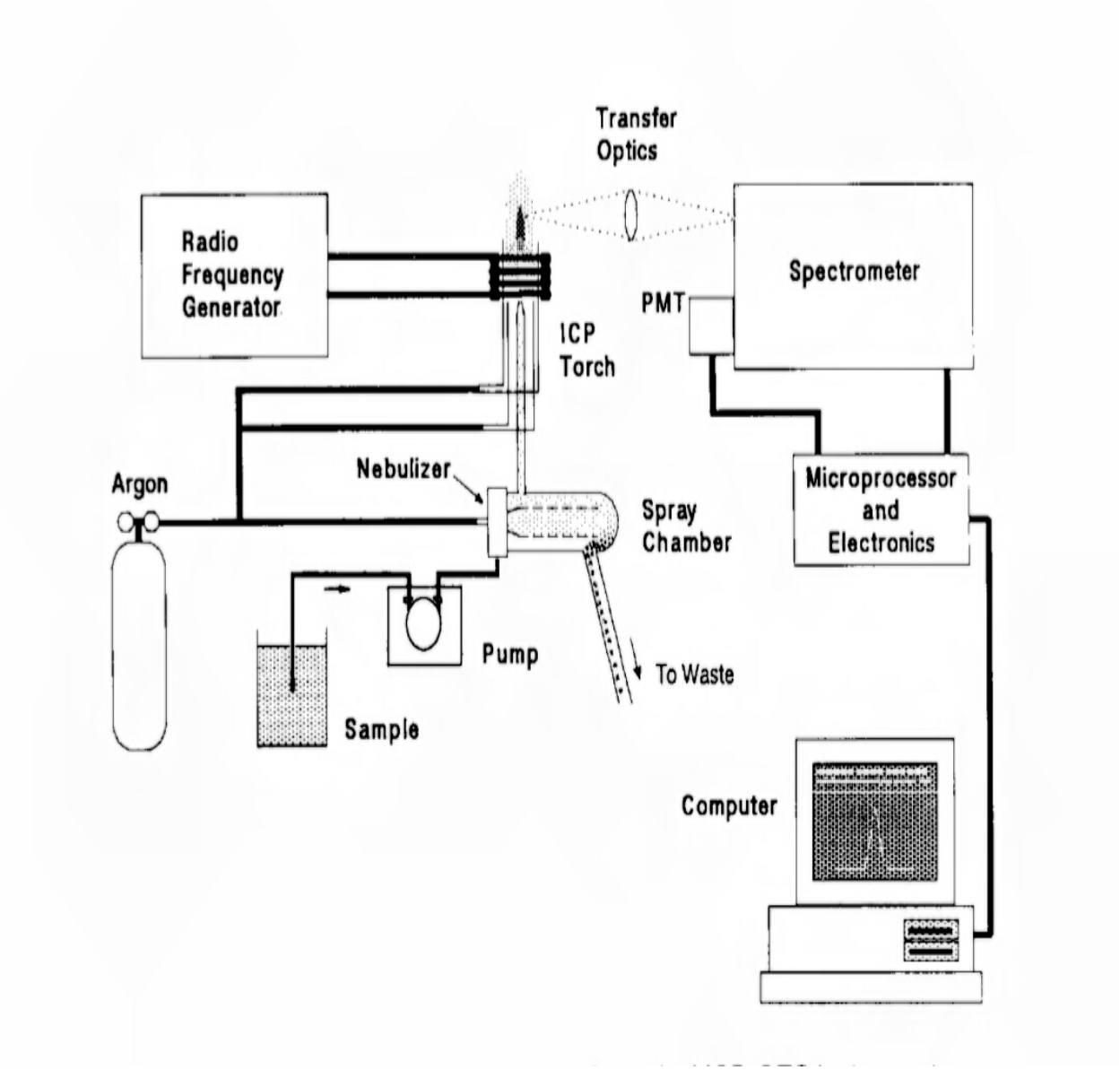

Figure 1.5.Inductively Coupled Plasma Optical Emission Spectrometerdiagram

(Fig 1.5) 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 2 be analyzed contain high levels of particulates or dissolved solids. After that 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. (Charles B. Boss and Kenneth J. Fredeen, 1985)

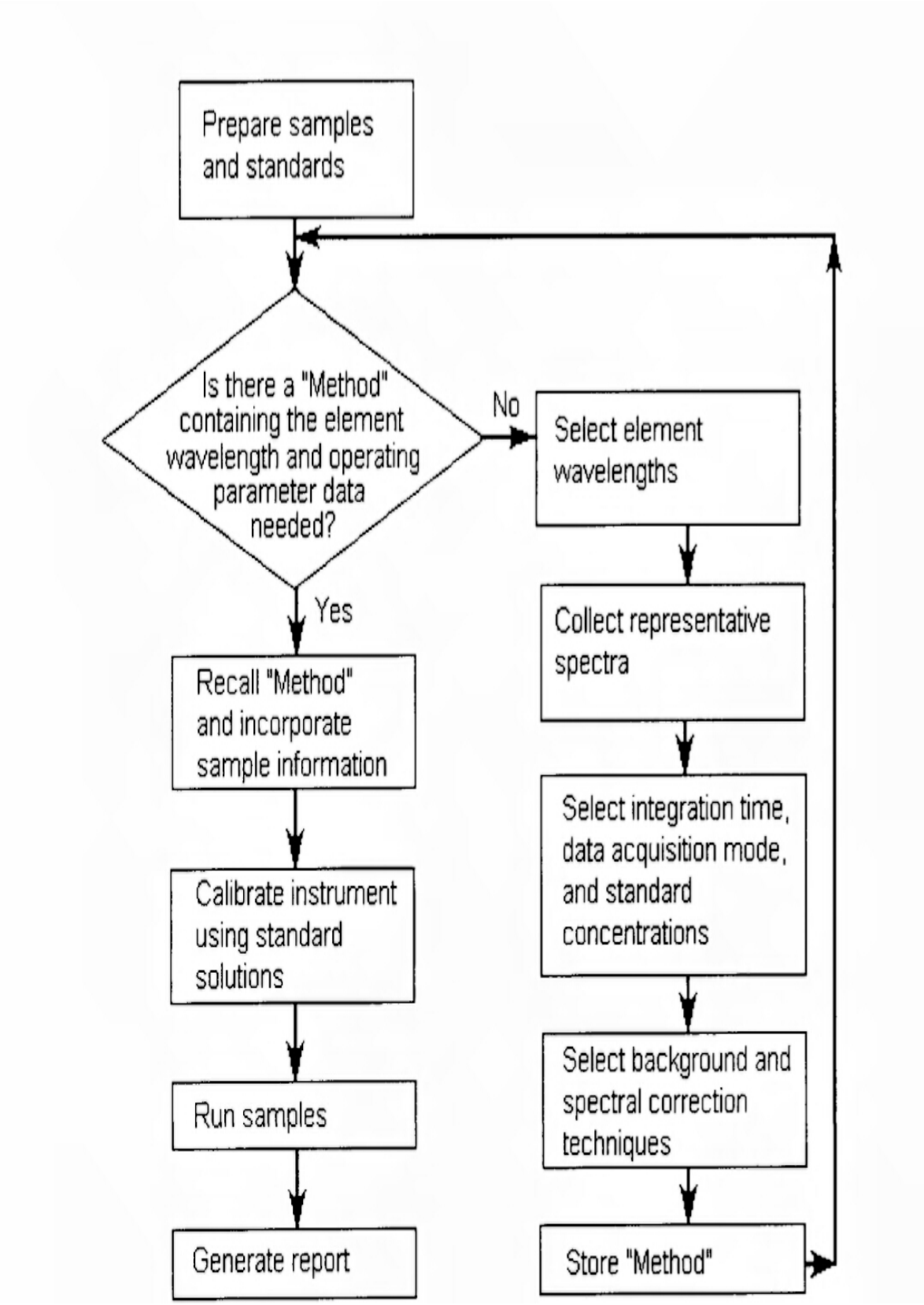

Figure 1.6. Flow chart showing the methodology for a typical ICP-OES analysis

1.2.2ICP Discharge

The inductively coupled plasma discharge used today for optical emission spectrimetric is very much the same in appearance as the one described by Velmer Fassel in the early 1970's. Argon gas is directed through a torch consisting of three concentric tubes made of quartz or some other suitable material. A copper coil, called the load coil, surrounds the end of the torch and is connected to a radio frequency (RF) generator.When RF power (typically 700-1500 watts) is applied to the load coil, an alternating current moves back and forth within the coil, or oscillates, at a rate corresponding to the frequency of the generator. In most ICP instruments this frequency is either 27 or 40 megahertz (MHz) This RF oscillation of the current in the coil causes RF electric and magnetic fields to be set up in the area at the top of the torch with argon gas being swirled through the torch a spark is applied to the gas causing some electrons to be stripped from their argon atoms. These electrons are then caughtup in the magnetic field and accelerated by them. Adding energy to the electrons by the use of a coil in this manner is known as inductive coupling These high-energy electrons in turn collide with other argon atoms, stripping off still more electrons This collisional ionization of the argon gas continues in a chain reaction, breaking down the gas into a plasma consisting of argon atoms, electrons, and argon ions, forming what is known as an inductively coupled plasma (ICP) discharge. The ICP discharge is then sustained within the torch and load coil as RF energy is continually transferred to it through the inductive coupling process (Charles B. Boss and Kenneth J. Fredeen, 1985).

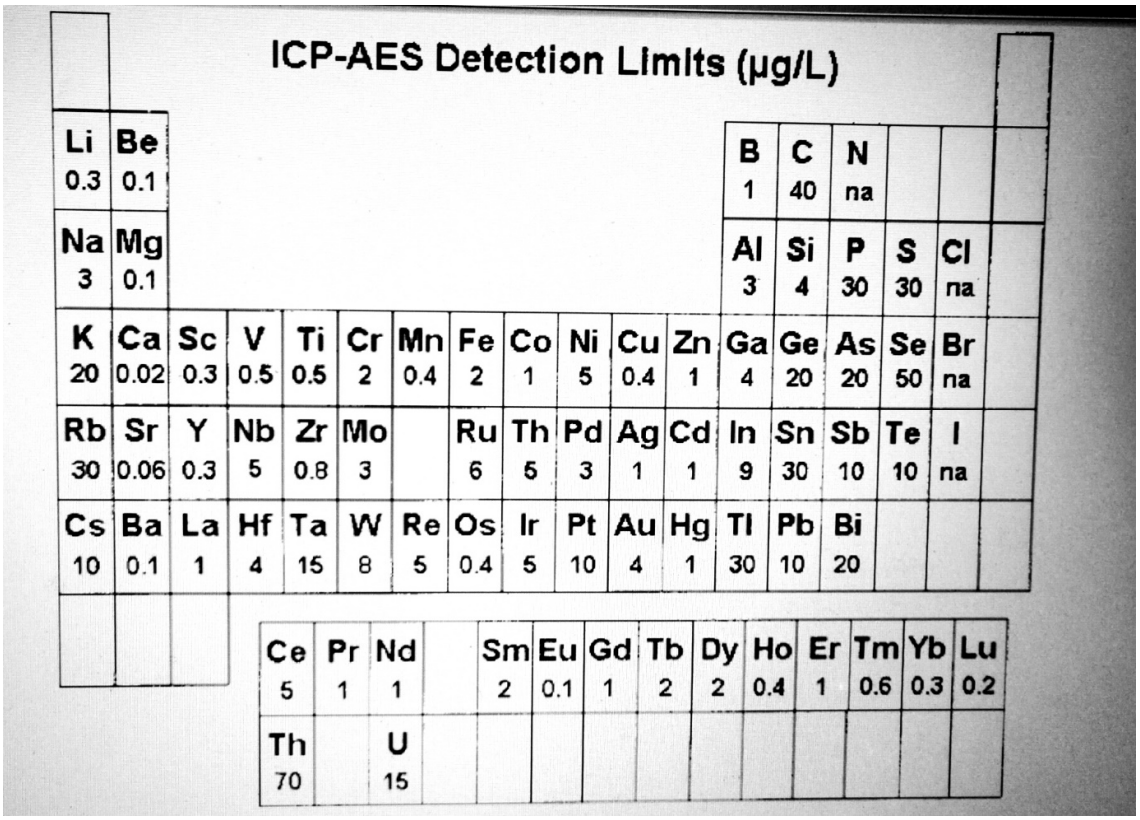

Figure 1.7. Periodic table with ICP-OES detection limits (side-on viewing). All detection limits are reported as 3o and were obtained on a Perkin-Elmer Optima 3000 under simultaneous multi element conditions with a side-viewed plasma Detection limits using an axially-viewed plasma are typically improved by 5-10 times.

1.2.3 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 desolate, 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. Most commercial ICP nebulizers are of the pneumatic type these nebulizers use high-speed gas flows to create an aerosol. The use of pneumatic nebulizers in ICP-OES follows their use and development in flame atomic absorption spectrometry, with one especially important difference in design considerations. In flame atomic absorption a gas flow on the order of ten liters per minute is often employed for nebulization, while the nebulization flow in the ICP is optimal at approximately one liter per minute. Years of research have left us with primarily three pneumatic nebulizers, each with its own advantages (Charles B. Boss and Kenneth J. Fredeen, 1985).

The type of pneumatic nebulizer most commonly used in flame AAS, and thus one of the first nebulizers to be used for ICP-OES, is the concentric nebulizer a typical concentric nebulizer used for ICP-OES. In this nebulizer, the solution is introduced through a capillary tube to a low-pressure region created by a gas flowing rapidly past the end of the capillary The low pressure and high-speed gas combine to break up the solution into an aerosol The much lower sample aerosol carrier flow required for ICP spectrometry forced the designers of concentric pneumatic nebulizers to make the liquid and gas orifices much smaller than those common in flame spectrometers. With these small orifices concentric pneumatic nebulizers can give excellent sensitivity and stability. However, the small orifices can be plagued by clogging problems, often by solutions containing as little as 0.1% dissolved solids. Advances in the design of concentric (Charles B. Boss and Kenneth J. Fredeen, 1985).

Another type of concentric nebulizer, called the micro-concentric nebulizer(MCN), is also available(Figure 9), This compact nebulizer employs a small diameter capillary(polyimide or Teflon) and polyvinyl dine difluoride(PVDF) body to minimize undesirable large drop formation and to facilitate HF tolerance. A very fine aerosol is produced consisting of only very small size droplets while conventional concentric nebulizers have a sample uptake rate of 1-3 mUmin, the MCN is typically less than 0.1 mUmin

permitting analysis of small sample volumes. This low sample uptake is beneficial in extending limited sample volumes so that the long nebulization times encountered with sequential ICPs undertaking multielement analysis may be successfully accomplished. In addition to the small sample volume and low sample uptake rates, the nebulizer also exhibits fast washout times which may particularly critical for samples containing such elements as boron and mercury.

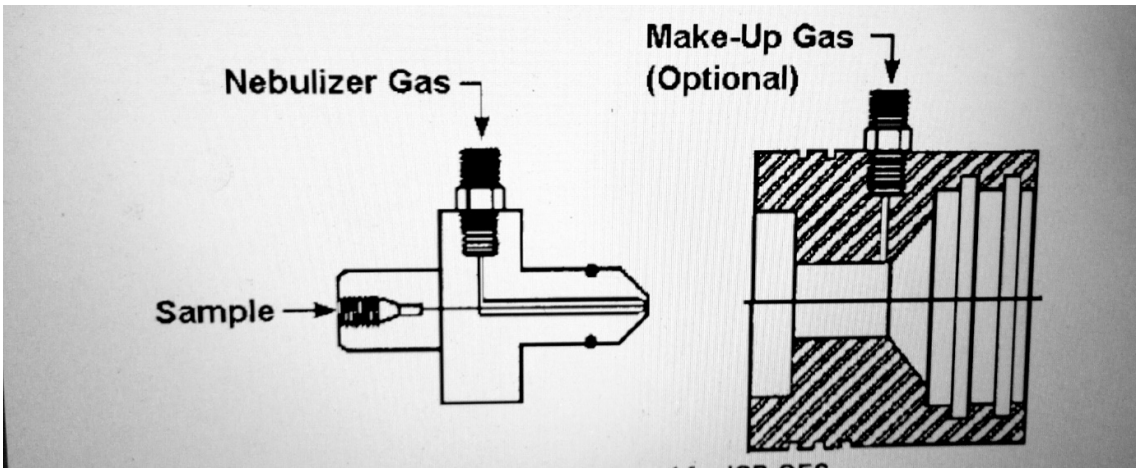

Figure 1.8. Micro nebulizer used for ICP-OES

1.2.4 ICP-OES Interferences-General Considerations

Before moving on to discussions of the specific steps involved in development CP-OES methodology, it is appropriate to discuss interferences in a general sense To the analytical chemist, an interference is anything that causes the signal from an analyte in a sample to be different from the signal for the same concentration of that analyte in a calibration solution Despite the fact that the presence of an interference can be devastating to the accuracy of a determination, there is no analytical technique that is completely free from interferences. However, modern trace elemental analysis instruments have been designed to minimize the interferences. When ICP-OES was first introduced to the analytical community, the claim was often made that the technique was nearly free from interferences. This claim was made because the classic

chemical interferences that were found in flame atomic absorption spectrometry were not observed in ICP-OES Soon after analysts began measuring trace element concentrations in a wide variety of samples, however, the reality of the existence of some interference became apparent The interferences that we know about today in the ICP are spectral in origin. Other interferences are often the result of high concentrations of certain elements or compounds in the sample matrix and are not too severe for most samples. The best way to guard against inaccurate results due to unexpected interferences with ICP-OES (or any other technique for that matter) is an adequate quality control program. The components of quality control will vary with the sample type, the degree of precision and accuracy required, and the penalty anticipated if errors exceed acceptable levels. The most generally applicable quality control procedure is to analyze samples of known composition along with the unknowns. These reference materials should match the sample matrix and the concentration range of the analytic elements (Charles B. Boss and Kenneth J. Fredeen, 1985).

1.2.5 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 . ICP-OES applications have been grouped into six generalized categories. Agricultural and Foods, Biological and Clinical, Geological, Environmental and Waters, Metals, and Organics (Charles B. Boss and Kenneth J. Fredeen, 1985).

The aim of the study:

- To obtain an adequate information about kohl as a traditional material widely used by Sudanese people
- To determine the actual chemical composition of kohl by inductively coupled plasma Optical Emission Spectrometry.
- To determine lead concentration in kohl samples.

CHAPTER TWO

Materials and Methods

Chapter two

2. Materials and Methods

2.1 Collection of samples

Eight samples were collected from local markets ("souks") in Khartoum. The samples include different types of kohl as described below.

Table (2.1)

Samples (No)	Origin	Colour
1	Saudi Arabia (Medina)	Black
2	Saudi Arabia	Dark grey
3	Saudi Arabia	Black
4	India	Black
5	Sudan	Black
6	India	Dark grey
7	Nigeria	Shine grey
8	Saudi Arabia	Shine grey

2.2 Chemicals

- Nitric acid (65%)

2.3Instruments

-Inductively Couple Plasma Optical Emission Spectrometry (ICP)-(OES)

-Computer personal computer (Dell OptiPlex 320) with Laser jet printer (HP 1200).

-Power =1.2 KW

-Plasma Flow =15 L/min

-Aux Flow =1.5 L/min

-Neb Flow =0.75 L/min

-Replicate read time =10 Sec

-Sample Uptake time=30 Sec

-Rinse time =25 Sec

-Pump rate =15 rpm

-Instrument stabilization delay =15 Sec

-Microwave instrument

2.4 Methods of analysis

2.4.1 ICP analysis of kohl samples

0.2 g of kohl was taken in microwave Teflon vessel and 6 ml of concentrated nitric acid (65%) were added. The mixture was placed in microwave instrument (power =950 watt) to complete digestion for 45 minutes. The solution was transferred into 100 volumetric flask and completed the volume till the mark.And placed the sample into (ICP)-(OES) instrument and repeat this steps for all samples.

CHAPTER THREE

Results and discussion

Chapter three
3. Results and discussion

Table (3.1) Concentrations of macro minerals in kohl samples

Samples (No)	**Ca** (mg/L)	**Mg** (mg/L)	**K** (mg/L)	**Na** (mg/L)	**P** (mg/L)
1	**2276**	**735.3**	**651.7**	**586.9**	**643.5**
2	**2955**	**161**	**818**	**408.1**	**131.7**
3	**112000**	**554.1**	**2221**	**501**	**1301.3**
4	**28593**	**5369**	**4268**	**443**	**634.6**
5	**2051**	**661.9**	**554.1**	**341.8**	**634.1**
6	**65647**	**35373**	**774**	**337**	**172.3**
7	**792**	**63.07**	**676.7**	**313.7**	**79.27**
8	**595.2**	**47.53**	**644.9**	**318.2**	**81.13**

3.1 Macro minerals contents of kohl samples:

As shown by (Table 3.1) sample (No.3, 4 and 6) showed significantly high concentrations of calcium, magnesium, sodium, potassium and phosphorus. The lowest calcium, magnesium, sodium and phosphorus concentrations were found in samples (No.7and 8). The lowest magnesium concentration (161 ppm) and the highest potassium content (4268 ppm) were observed in sample (No.4). Samples (No.1 and 5) have moderately high concentration of calcium, magnesium, potassium, sodium and phosphorus with almost similar concentrations in the two samples. In the eight analysed samples calcium is the most available mineral. Sample (No.6) showed significantly high calcium and magnesium concentrations. The highest calcium and phosphorus contents were in sample (No.3).

Andrew D.Hardy (2011) referred to the presence of calcium and sodium in kohl sample in form of calcite, aragonite and halite ($CaCO_3$, NaCl).

Table (3.2) Concentrations of trace minerals in kohl samples (mg/L)

Samples N0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
B	**<0.001875**	**<0.001875**	**<0.0019**	**<0.0019**	**<0.001875**	**<0.0019**	**<0.0019**	**<0.0019**
Se	**<0.003445**	**6.333**	**2.600**	**2.733**	**<0.003445**	**2.733**	**16.13**	**4.133**
Mo	**266.4**	**4.533**	**4.067**	**8.400**	**251.07**	**4.067**	**2.933**	**3.267**
Zn	**1065**	**7780**	**33.00**	**66.20**	**876.0**	**97733**	**78.27**	**55.07**
Ni	**321.5**	**3.667**	**4.467**	**571.0**	**339.9**	**11.07**	**14.60**	**6.133**
Co	**30.93**	**2.93**	**2.33**	**33.67**	**30.60**	**15.47**	**2.133**	**2.333**
Mn	**5140**	**19.00**	**16.87**	**325.2**	**5310.0**	**72.20**	**2.267**	**2.400**
Cr	**1276.0**	**4.333**	**6.467**	**46.07**	**1671**	**13.07**	**2.867**	**2.73**
V	**46.33**	**4.267**	**3.267**	**867.3**	**46.80**	**88.53**	**2.200**	**1.533**
Li	**<0.000387**	**<0.000387**	**<0.000387**	**2.733**	**<0.000387**	**0.2667**	**<0.0004**	**<0.0004**
Cu	**1678**	**520.27**	**24.07**	**35.80**	**1578**	**254.7**	**7.400**	**336.1**
Fe	**453067**	**906.7**	**992.7**	**13227**	**445800**	**6860**	**72.00**	**72.53**
Ti	**322.4**	**9.733**	**6.667**	**518.6**	**314.1**	**95.00**	**3.933**	**4.667**

3.2 Trace minerals contents of kohl samples:

The eight analysed samples showed different concentrations of trace minerals. Boron, lithium and selenium concentrations were very low in all samples except sample (No.7) which showed relatively high selenium content (16.13 ppm).

Sample (No.1) showed high concentrations of molybdenum, copper, zinc, nickel, cobalt, manganese, titanium and significantly high iron content. This may indicate that sample (No.1) is a natural rock sample. This sample contained significantly low lead concentration (Table 3.3). All minerals showed low

concentrations in sample (No.2) except zinc (7780 ppm), copper (520.27 ppm) and iron (906.7 ppm). Trace minerals concentrations in sample (No.3) were generally low except iron (992.7 ppm) followed by zinc (33.0 ppm) and copper (24.07ppm). Sample (No.4) showed the lowest antimony concentration (0.4667 ppm) and the highest nickel concentration (571.0 ppm) as well as relatively high concentrations of iron (13227 ppm) and manganese (325.2 ppm). In sample (No.4) vanadium concentration was significantly high (867.3 ppm). Sample (No.5) showed relatively high content of molybdenum (251.07 ppm), chromium (1671 ppm) and copper (1578 ppm). Iron concentration in sample (No.5) is very high (445800 ppm) resembling that of sample (No.1) which was (453067 ppm). In general view trace minerals composition of sample (No.5) was very similar to that sample (No.1). In sample (No.6) zinc was the highest available trace minerals (97733 ppm) followed by iron (6860 ppm),copper (254.7 ppm), titanium (95.00 ppm), vanadium (88.53 ppm) and manganese (72.2 ppm). All trace minerals showed very low concentrations in sample (No.7) ranging from (2.133 ppm) for cobalt to (78.27 ppm) for zinc. And (72.00 ppm) for iron as the lowest iron content in the eight samples. The lowest concentration of titanium was also shown by this sample (3.933 ppm). In sample (No.8) all the trace minerals showed significantly low concentrations ranging from (1.533 ppm) in vanadium as the lowest concentration to (336.1 ppm) in copper as highest concentration. Iron concentration in this sample is similar to that of sample (No.7)

Which was (72.53 ppm). Concentrations of chromium, molybdenum, cobalt, manganese and titanium were almost similar in samples (No 7 and 8).

Table (3.3) Concentrations of the risky minerals in some kohl samples

Samples (No)	Sn ppm	As Ppm	Sb ppm	Cd ppm	Ba ppm	Pb Ppm	Sr ppm	Be ppm	Al ppm
1	70.33	27.87	63.87	2.467	222	131.4	11.4	1.600	961.3
2	6.33	7.467	261.2	120.0	97.53	971333	242.3	1.533	519.4
3	7.333	2.800	7.933	2.40	181.60	21707	78.33	1.533	120.7
4	2.00	1.333	0.4667	2.07	34466.7	716.7	433.3	1.867	10833
5	70.13	26.67	68.07	2.133	231.4	297.4	9.467	1.600	623.7
6	4.533	4.667	56.20	5.933	142.7	260000	42.67	1.600	2437
7	8.933	2.267	587.5	5.800	3.867	718667	1.800	1.533	68.40
8	9.267	4.400	351.3	11.20	1467	826667	17.80	1.533	63.93

3.3 Risky minerals contents of kohl samples:

Samples (No 1 and 5) showed almost similar concentrations of tin, arsenic, antimony, cadmium, barium, beryllium and strontium. The two samples showed relatively lower concentrations of lead (131.4 ppm) in sample (No.1) and (297.4ppm) in sample (No.5). Because the two samples were from different sources (Table 2.1) they may be of same geochemical formation (Tables 3.1, 3.2). In sample (No.2) the highest concentration was showed by lead (971333 ppm) as the highest concentration in the eight samples. Cadmium as carcinogenic mineral also showed the highest concentration in this sample as (120.0 ppm). Antimony showed relatively high concentration in this sample as (261.2 ppm) compared with the lowest content in sample (No.4) as(0.4667 ppm) and samples (No 7 and 8) as (587.5 ppm) and 351.3) respectively.

Table (3.4) Minerals with significantly high percentage in some samples

Samples No	Fe (%)	Pb (%)	Mg (%)	Ca (%)
		26		
1	**96.47**	**0.027**	**0.157**	**0.485**
2	**0.092**	**98.5**	**0.016**	**0.299**
3	**0.71**	**15.53**	**0.39**	**80.12**
4	**13.00**	**0.70**	**5.3**	**28.1**
5	**96.5**	**0.064**	**0.001**	**0.44**
6	**1.46**	**55.39**	**7.54**	**13.896**
7	**0.0099**	**99.6**	**0.0088**	**0.1**
8	**0.0087**	**99.68**	**0.0057**	**0.0717**

3.4 Minerals with significantly high concentrations in some kohl samples:

Samples (No.1 and 5) were mainly iron based compounds. The lowest lead contents were in samples (No. 1 and 5). Samples (No.2, 6, 7 and 8) may be considered as lead based compounds. Samples (No.3 and 4) were calcium based compounds. Sample (No 6) showed considerable content of zinc (20.82%), calcium (13.896%), and magnesium (7.54%) in addition to lead (55.39%) (Tables 3.1, 3.2, 3.3)

Conclusions

-The analysed commercial kohl samples from Khartoum state were found to be of different elemental composition.

-All the samples showed considerable content of macro elements sodium, potassium, Magnesium, Calcium and phosphorus but the concentrations differ clearly from sample to another.

- Samples (No.1 and 5) were found to be almost identical in their chemical composition, showing similar concentrations of tin, zinc, nickel, molybdenum, manganese, iron, titanium and barium.

-The lowest lead concentrations were shown by these two samples.

- Iron concentrations were significantly high in samples (No.1 and 5). Lead showed very high concentrations in three samples (2, 7 and 8) and moderate concentration in two samples (3 and 6).

-Antimony which is expected to be the major constituent of kohl showed very low concentrations in all samples.

- Samples (No.1 and 5) have considerable content of chromium compared with the other six samples.

- The analysed eight samples of Khartoum states may be described as dominated by calcium, magnesium, potassium, sodium, iron and lead based compounds.

- Samples (No.2, 7 and 8) showed lead content as if they were pure lead powder or crystals.

- O.M.Badeer,et at (2008) found that eight samples out of sixteen have lead content greater than 70%.

-Another study curried by Ali AL-Kaff et al (1993) showed lead concentration of 88% in black stone sample. Andrew D.Hardy (2011), Ragini Vaishnav

(2001), Pervez Habib Allah ef al ;(2010) repeated high lead content in some kohl samples as 85% in Kuwait and 100% in Nigeria. Pasha, M.A., Nallusamy (2016) reported that some kohl samples are 85.5% galena.

Recommendations

- Medical research may also be needed to determine the effect of kohl on human eyes, e.g. the health of the eyes of those who use kohl and those who do not use it, to investigate it there are any real negative side effects of kohl use, as traditional cosmetic widely used in Sudan.
- Commercial kohl samples in Sudanese markets may need to be fairly studied and their origins should be determined.
- More information may need to be collected about kohl preparation in the houses by some women as a gum based kohl.
- Standard specifications may be required for kohl as traditional material used by Sudanese in many areas.
- Further studies may need carried using more wide range of sampling and chemical characterisation.
- Other techniques may be required for more information such as x-ray diffraction and x-ray fluorescence (XRF).

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