State of Libya
Ministry of Higher Education and Scientific Research
Alasmarya Islamic University
College of Science / Department of Chemistry

MSc. Project titled

Determination of some trace elements in hair dye samples available in Libyan markets by induction plasma emission spectroscopy

Submitted by

Hanin Salah Abdalla Milad

Under Supervision

Prof. Abdelsalam Ali Asweisi **Dr. Khalifa Abdualsalam Alfallous**

A thesis submitted in fulfillment of the requirement for the Master's Degree in analytical chemistry

Academic year: (2023 – 2024)

الإقـــــــــرار

أُقر أنا الطالبة حنين صالح عبد الله ميلاد بأن ما اشتملت عليه الرسالة إنما هو إنتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أي درجة علمية، أو بحث علمي لدى أي مؤسسة تعليمية أو بحثية أخرى، وللجامعة حق توظيف الرسالة أو الأطروحة والاستفادة منها مصدراً مرجعيا للمعلومات، لأغراض الاطلاع أو الإعارة أو النشر بما لا يتعارض وحقوق الملكية الفكرية المقررة بالتشريعات النافذة.

التوقيع: _____

التاريخ: 29 / 10 / 2023

Declaration

I HANIN SALAH ABDALLA MILAD confirm that the work contained in this thesis is the researcher's own work, and has not been previously submitted to meet requirements of an award at this University or any other higher education or research institution, I furthermore, cede copyright of this thesis in favour of Alasmarya Islamic University.

Student name: HANIN SALAH ABDALLA MILAD

Signature:

Date: 29 / 10 /2023

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(وقُــل رَّبِّ زِدْنـــِي عِلْمًا)

صدق الله العظيم

سورة طـــه : الآية (114)

إهـــــــــداء

بعد التوفيق من عند الله أهدي ثمرة نجاحي إلى أعز الناس وأقربهم إلى قلبي إلى والدتي العزيزة ووالدي العزيز اللذان كانا عوناً وسنداً لي، وكان لدعائهما المبارك أثر كبير في تسيير أمور البحث حتى أكملت هذا المشوار الصعب

إلى من ساندني وخط معي خطواتي، ويسر لي الصعاب؛ إلى زوجي العزيز التي تحمل الكثير وأعانني حتى وقوفي في هذا المكان، وما كان ليحدث لولا العون من الله ثم تشجيعه المستمر لي، فجزاه الله عني كل خير وبارك لي فيه

إلى زهراتي وفلذات كبدي؛ أولادي الاعزاء وابنتي الغالية الذين قصرت في حقهم طيلة الفترة التي قضيتها في إعداد هذا البحث

إلى أساتذتي وأهل الفضل الذين قدموا لي كامل الاحترام والتقدير والنصيحة والتوجيه والإرشاد

إلى كل هؤلاء أهديهم هذا العمل المتواضع، أسأل الله العلي القدير أن ينفعنا به ويوفقنا لما هو خير لنا

حنين صالح عبد الله ميلاد

شــكر وتقـــــدير

أشكر الله عز وجل الذي بتوفيق منه وبفضل منه مكنني من إنجاز هذه الرسالة وأمدني بالصبر والقوة فالحمد لله حمدا كثيرا طيبا مباركا فيه

أتقدم بالشكر الجزيل والامتنان إلى مشرفيّ على الرسالة

الأستاذ الدكتور الفاضل: عبد السلام علي سويسي

والدكتور الفاضل: خليفة عبد السلام الفلوس

على كل الملاحظات والتوجيهات لي، وكذألك على صبرهم طيلة إشرافهم على هذه الرسالة رغم تعدد التزاماتهم

وأيضا أتقدم بخالص الشكر للمؤسسة الوطنية للنفط معهد النفط الليبي لما قدموه لي من مساعدات كبيرة في تحليل عيناتي فلهم مني جزيل الشكر

وأتقدم بجزيل الشكر والعرفان لشركة سكاي تك للاتصالات والتقنية – زليتن لما قدموه لي من خدمات متميزة وتسهيل عملية مناقشة السيمنار الثاني بقاعة الاجتماعات بمقر الشركة بزليتن عبر تقنية (ZOOM)

كما أتوجه بالشكر إلى كافة أساتذتنا الكرام بقسم الكيمياء وكافة موظفي كلية العلوم بالجامعة الأسمرية الإسلامية لما قدموه لي من مساعدات طيبة

الباحثة: حنين صالح عبد الله ميلاد

TABLE OF CONTENT

LIST OF TABLES vii
LIST OF FIGURES viii
Abstract: x
Chapter I xiv
INTRODUCTION 1
1.1 Background: 1
1.2 problem Statement of the study: 5
1.3 The aim of the study 5
1.4 Objectives of the study: 6
1.5. Study subject: 6
Chapter II 7
LITERARURE REVIEW 8
2.1 Nature hair dyes: 8
2.2 Classified hair dyes into four categories as follows 8
2.3 Trace Elements Definition: 11
2.4 The effect of Trace elements on human health: 11
2.5. Trace elements: 12
2.5.1. Lead (Pb): 12
2.5.2 Cadmium (Cd): 16
2.5.3 Iron (Fe): 19
2.5.4 Cobalt (Co): 22
2.5.5Chromium (Cr): 24
2.5.6 Arsenic (As): 27
2.5.7 Stannum (Tin) (Sn): 31
2.5.8 Potassium (K): 34
2.5.9 Magnesium (Mg): 35
2.6 Heavy metals in hair dyes: 36

CHAPTER III 39
Experimental 40
3.1. Reagent and Apparatus: 40
3.1.1 Sample Collection: 40
3.1.2 Sample preparation: 40
3.1.3 Chemicals: 41
3.1.4. Glassware cleaning: 42
3.1.5 Preparation of Sample: 42
3.1.6 Blank solution: 43
3.1.7 Analytical Methods and Instrumentation 43
3.2 Preparation of aqueous standard solutions: 59
3.2.1 Calibration curves of standard solutions for the studied elements 60
3.2.2Calibration curve of Magnesium Standard: 61
3.2.3 Calibration curve of Arsenic Standard: 62
3.2.4 Calibration curve of Potassium Standard: 63
3.2.5 Calibration curve of Chromium Standard: 64
3.2.6 Calibration curve of Iron Standard: 65
3.2.7 Calibration curve of Cobalt Standard: 66
3.2.8 Calibration curve of Cadmium Standard 67
3.2.9 Calibration curve of Lead Standard: 68
3.3. Physical tests of samples: 69
3.3.1. preparation of the Sample: 69
Chapter IV 70
RESULTS & DISCUSSION 70
4.1 Results: 71
4.2 Physical tests of samples 71
4.2.1. Conductivity(σ) values results: 71

4.2.2 pH value results 73
4.2.3 TDS value results: 75
4.2.4 Salinity value results: 77
4.3. Trace elements concentration of hair dyes: 79
4.3.1 Iron concentration: 79
4.3.2 Chromium concentration: 79
4.3.3 Potassium Concentration: 80
4.3.4 Magnesium Concentration: 81
4.3.5 Stannum (Tin) concentration: 82
4.3.6 Lead, Cadmium, Cobalt and Arsenic concentration: 83
5. Suggestions and Recommendations: 85
6. Conclusions: 86
7. Summary: 88
References: 91

LIST OF TABLES

Table (3.1) Samples of hair dyes colors from different manufacturers 41

Table (3.2) Magnesium Standard Calibration 61

Table (3.3) Arsenic Standard Calibration 62

Table (3.4) Potassium Standard Calibration 63

Table (3.5) Chromium Standard Calibration 64

Table (3.6) Iron Standard Calibration 65

Table (3.7) Cobalt Standard Calibration 66

Table (3.8) Cadmium Standard Calibration 67

Table (3.9) Lead Standard Calibration 68

Table (4. 1) σ Conductivity test of samples at 22 T/C^{O} : 72

Table (4. 2) pH Physical test of samples at 25 T/C^{O} 74

Table (4. 3)TDS Physical test of samples at 22.5 T/C^{O} 76

Table (4. 4) Salinity Physical test of samples at 22.5 T/C^{O} 78

Table (4. 6) Trace elements concentration 84

LIST OF FIGURES

Figure(1.1) Pathway of heavy metals sources and exposure to humans. 4

Figure(3.1) Sample preparation…….…….40

Figure (3.2) Sample digestion…….……..…….……43

Figure (3.3) Components of ICP Optical Emission Spectrometry Equipment46

Figure (3.4) Chematic of a typical inductively coupled plasma-optical emission spectrometry (ICP-OES) system..... 46

Figure (3.5) Front and side of the ICP-OES instrument 47

Figure (3.6) Parts of pH meter 54

Figure (3.7) Measurement of the two-electrode conductivity 58

Figure (3.8) Both coils are encased in a single sensor body and over molded with plastic. The coils must be completely submerged in the process liquid..59

Figure (3.9) Calibration curve of Magnesium 61

Figure (3.10) Calibration curve of Arsenic Standard..... 62

Figure (3.11) Calibration curve of Potassium Standard..... 63

Figure (3.12) Calibration curve of Chromium Standard..... 64

Figure (3.13) Calibration curve of Iron Standard 65

Figure (3.14) Calibration curve of Cobalt Standard 66

Figure(3.15) Calibration curve of Cadmium Standard 67

Figure (3.16) Calibration curves of Lead Standard..... 68

Figure (3.17) Physical tests of Samples…….……..……69

Figure (4.1) Conductivity Physical test of Samples. at 22 T/C^{O}……..…72

Figure (4.2) pH Physical test of samples at 25 T/C^{O}…….……..74

Figure (4.3) TDS Physical test of samples at 22.5 T/C^{O}……..…76

Figure(4.4) Salinity Physical test of samples at 22.5 T/C^{O}……....….78

Figure (4.5) The concentrations of the Iron metal in studied hair dyes..... 79

Figure (4.6)The concentrations of the Chrome metal in studied hair dyes..... 80

Figure (4.7) The concentrations of the Potassium metal in studied hair dyes

..... 81

Figure(4.8) The concentrations of the Magnesium metal in studied hair dyes

..... 82

Figure (4.9) The concentrations of the Stannum metal in studied hair dyes .. 83

Abstract:

The U.S. Food and Drug Administration defines products cosmetics (hair dyes) like “goods that are used on our bodies to change hair color, remove gray hair, improve attractiveness, or change appearance.” This includes a large number of hair dyes that have become a part of the routine life modern, especially in women. These products usually consist of a mixture of chemical components derived from natural and synthetic sources that are not without traces of the presence of toxic elements (trace elements) resulting from a mixture of the same components or environmental pollution. These substances, due to their forced use, may be carcinogenic, mutagenic or mineral components that may adversely affect human health. Due to the lack of extensive and sufficient studies on this subject, so this research focused to determine the concentrations of some trace elements in some hair dyes imported and locally manufactured in the Libyan markets. Collected 23 samples of Henna and hair dyes from 11 brands, 6 brands of chemical hair dyes consist of 3 colors, 1 brand of hair bleach and 4 brands of Henna dyes, we applied the normal digestion method, weighed 1.0 g of each sample of hair dye and 0.5 grams of each sample of Henna. The samples were mixed with highly concentrated acids putted it on a hot plate until getting the digested and the acidic solutions were filtrated and Samples

were dilute with deionized water. Concentration of Iron, Lead, Cobalt, Cadmium, Chromium, stannium, Magnesium, Potassium and Arsenic in hair dyes using an was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The results showed that the concentration of trace elements was (<0.001-0.07 mg L-1), (0.53-95.9 mg L-1), (71.4-0.09 mg L-1), (62.2-0.07 mg L-1) and (1.28-0.15 mg L-1) for Cr, K, Mg, Fe and Sn respectively, While the concentrations of the remaining elements of Co, Cd, Pb and as the results were less than the detection limit. The standard deviation of the samples was (12.423, 0.0157, 30.791, 23.489, 0.344, 0.000, 0.000, 0.000, 0.000) for Fe, Cr, K, Mg, Sn, Co, Cd, Pb and As. also for the physical analyzes (conductivity, pH, TDS and salinity) found that some values exceeded the normal limit for permissible aqueous solutions it globally as for the Libyan product (Rajhi Henna) the results did not show any significant difference between it and other non-local products.

المستخلص:

تُعرّف إدارة الغذاء والدواء الأمريكية مستحضرات التجميل (صبغات الشعر) بأنها "سلع تُستخدم على أجسامنا لتغيير لون الشعر أو إزالة الشعر الرمادي أو تحسين الجاذبية أو تغيير المظهر. وهذا يشمل عددًا كبيرًا من صبغات الشعر التي أصبحت جزءًا من روتين الحياة الحديثة وخاصة عند النساء. تتكون هذه المنتجات عادة من خليط من المكونات الكيميائية المشتقة من المصادر الطبيعية والاصطناعية التي لا تخلو من آثار لوجود العناصر السامة (العناصر النزرة) الناتجة عن خليط من نفس المكونات أو التلوث البيئي. قد تكون هذه المواد، بسبب استخدامها القصري، مسببة للسرطان ومسببة للطفرات أو مكونات معدنية قد تؤثر سلبًا على صحة الإنسان، ونظرا لعدم وجود دراسات مستفيضة وكافية حول هذا الموضوع، بالإضافة إلى حقيقة وخطورة العناصر النزرة من المواد السامة على جسم الإنسان، لذلك ركز هذا البحث على تحديد تركيزات بعض العناصر النزرة في بعض صبغات الشعر المستوردة والمصنعة محلياً في الأسواق الليبية. جمعت 23 عينة من صبغات الحناء والشعر من 11 علامة تجارية، 6 ماركات من أصباغ الشعر الكيميائية تتكون من 3 ألوان، ماركة واحدة من مبيض الشعر و4 أنواع من أصباغ الحناء، طبقنا طريقة الهضم الحمضية العادية، وزن 1 جرام من كل عينة شعر صبغ و0.5 جرام من كل عينة من الحناء، ثم خلط العينات بأحماض مركزه عالية النقاوة على الصفيح الساخن حتى تم هضمها، وبعد ذلك تم ترشيحها وتخفيف العينات بواسطة ماء منزوع الأيونات. تم قياس تركيز الحديد والرصاص والكوبالت والكادميوم والكروم والقصدير والمغنيسيوم والبوتاسيوم والزرنيخ في صبغات الشعر باستخدام مقياس طيف الانبعاث البصري للبلازما المقترن بالحث (ICP-OES). أظهرت النتائج أن تركيز العناصر النزرة في العينات كانت (0.07-<0.001 mg L^{-1}) ، (95.9-0.53 mg L^{-1}) ، (71.4-0.09 mg L^{-1}) ، (62.2-0.07 mg L^{-1}) ، (1.28-0.15 mg L^{-1}) لكل من Sn, Fe, Mg, K, Cr على التوالي. بينما تركيزات العناصر المتبقية لكل من Co، Cd، Pb وAs فكانت النتائج أقل من حد الكشف للجهاز. قيم الانحراف المعياري للعينات كانت (12.423، 0.0157، 30.791، 23.489،

0.344، 0.000، 0.000، 0.000، 0.000) Fe، Cr، K، Mg، Sn، Co، Cd، Pb وAs على التوالي. أما بالنسبة للتحليلات الفيزيائية (التوصيلية ودرجة الحموضة والمواد الصلبة الذائبة والملوحة) فقد وجدت أن بعض القيم تجاوزت الحد الطبيعي للمحاليل المائية المسموح بها عالميا، أما بالنسبة للمنتج الليبي (حنة الراجحي) فلم تظهر النتائج أي فرق معنوي بينه وبين غيره من منتجات الحناء الغير محلية.

Chapter I

INTRODUCTION

INTRODUCTION

1.1 Background:

The practice of changing hair colour is called 'hair colouring'. The main purpose of this process is cosmetic, which includes covering weak and white hair, changing to a nice colour considered more fashionable and civilized, or restoring the original hair colour after it has been discoloured due to hair-styling operations or solar bleaching. Hair dyeing, an ancient art, involves treating damaged hair with various chemicals and natural[1]. Hair dyes have been used by humans since ancient times and were used by ancient civilizations in most parts of the world. Some of these cultures, such as the ancient Egyptians, Greeks, Persians, Chinese, and early Hindu peoples, all mention the use of hair dyes for colouring. Hair dyes were made from plant leaves, metallic colouring compounds, or a mixture of them. Natural rock alum, tree wood ash and quicklime were used for bleaching hair in ancient Roman times. Preparations included ingredients such as birch bark, mullein, saffron, myrrh, turmeric and Henna, which was known worldwide for producing a reddish hair dye[2]. In Egypt more than 4,000 years ago, black dyes were routinely used to dye hair. The dyes were made from a mixture of Lead oxide and Calcium hydroxide. This recipe made the hair wet; Within four days, the hair became very black [3]. In the last century, hair colouring was so routine for everyone that people were not afraid of the negative effects of these chemicals. In the late quarter of the twentieth century,

scientists noticed that there are trace elements whose descendants are in dyes, cosmetics, in general, as impurities from the ingredients of cosmetics or as additives in these cosmetics, and these are increasing in industrialized countries[4], Although our bodies require some trace elements in varying quantities and very little interaction with each other for vital functions in the body, frequent and excessive exposure to heavy metals can cause disease[5]. Hair colouring cosmetics are widely used worldwide. specifically, by the women about 35% over 18 years of age, and 10% of men to 40 years of age in all countries of the world, especially developed countries [6]. In an some of try to ensure that hair dyes contain only safe materials, the European Commission has Adopt guidance 2012/21/EU which limits the use of around 45 chemicals in hair dyes colours and European Union Make-up Directives 76/768/EC. (EC) No. 1223/2009[7], Most mercantile hair dyes have a complex formula, also Contains dozens of ingredients, and the formulas vary widely from product into product and large, hair dyes contain dye agents, modifiers, antioxidants, alkalis, soap, ammonia composite, high wetting agents, fragrances, and a host of other chemicals that have been used in small amounts to impart special qualities to hair (like smooth texture)[8]. Oxidative hair dyes are one of the most important groups of hair dye products and their market share in the United States of America (USA) or the European Union (EU) is close to 80%. The

Oxidative hair dyes consists of two ingredients that are packed apart and mixed together prior to application which Lead s to chemical interaction of the hair dye[9], Trace elements are a term that includes chemical elements with very similar chemical properties, and some of these Trace elements may be harmful if their concentrations are higher than the normal limit[10], Trace elements are one of the oldest toxic elements and compounds known to humans and a subject of important scientific research because of their real toxic effects[11]. Fine Chemical analysis is so important to know the accumulation concentration of trace elements and then their effect on the organism[12]. Trace elements are found naturally in different concentrations in the surrounding environment such as soil, water and rocks. Also, some rare metals are considered toxic in low concentrations, while others are non-toxic except in high concentrations[13], The toxicity of metals relies on the dose absorbed, the mode of exposure and the duration of exposure[5]. Trace elements are one of the most serious environmental pollutants, some of them, at very low values can pose a danger to human health because they have a long biological half-life, are non-degradable, and are very toxic at low concentration[14][15]. Due to the extent and frequency of human contact with hair colouring products, hair dye ingredients should not be harmful to human health under normal or expected conditions of use[16]. In general, the toxicity of metal ions to mammalian systems is due to the chemical

interaction of ions with enzymatic cellular proteins, enzyme systems and membranes. The target organs for specific metal toxicity may be those organs in which the highest concentrations of metals accumulate in vivo. This often depends on the route of exposure and the chemical compound of the metal, i.e., its symbiotic state, its volatility, its solubility in fats, etc. Today scientists are most concerned about the potential for cancer-causing metal compounds like Nickel and Chromium, which have low concentration and have been linked to a number of human cancers [17].

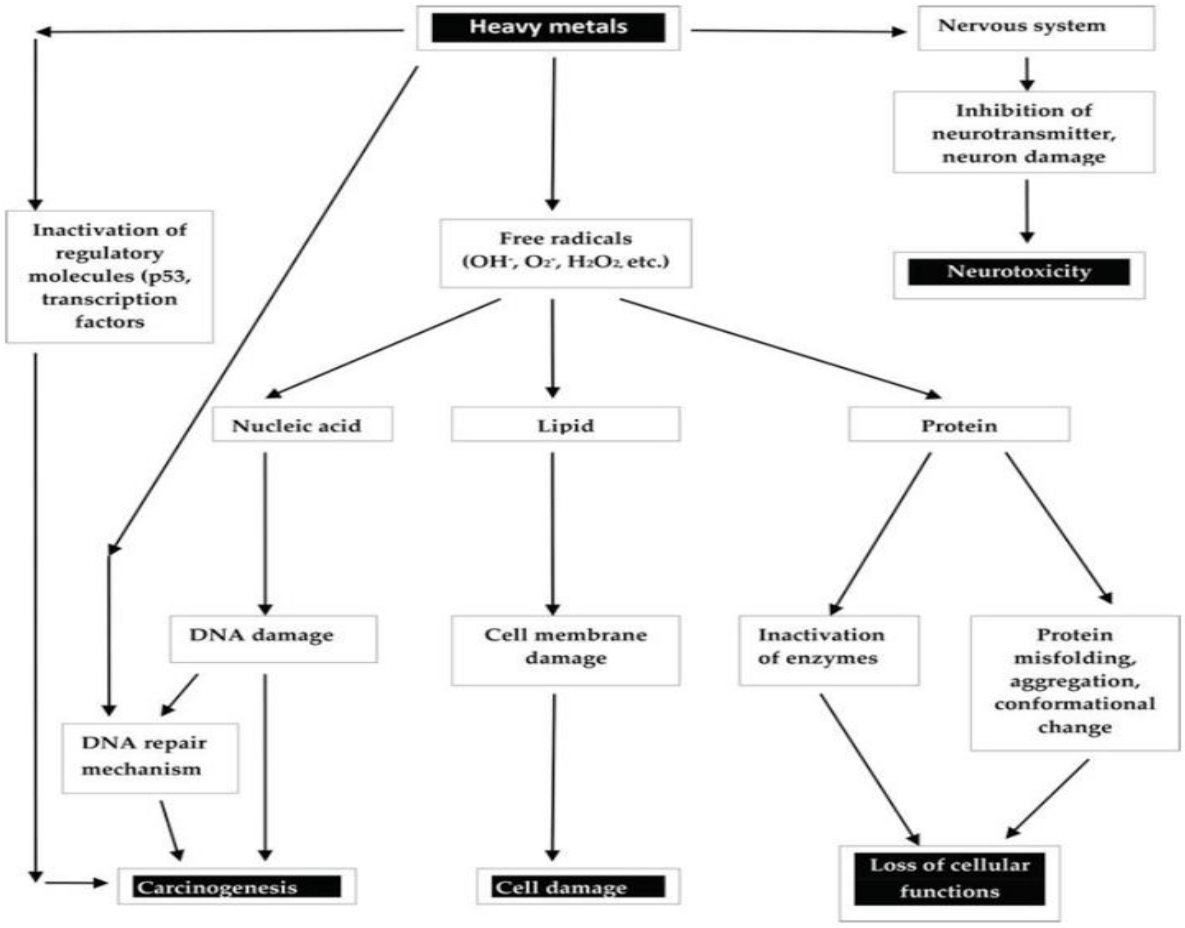


Figure (1.1) Pathway of heavy metals sources and exposure to humans.

1.2 problem Statement of the study:

Trace elements have a significant impact on our environment and Its presence is difficult to avoid and their effect on the human body, some of them be necessary for the human organism, Others are highly toxic in very low concentrations to humans.

The trace elements contained in hair dyes may threaten the health of the consumer.

Trace elements have the ability to penetrate through the human skin and hair roots and therefore their deposition in the body in varying concentrations may cause great damage to the vital organs.

Due to the excessive consumption the cosmetics, particularly hair dyes in Libya, finite studies have measured human exposure to trace elements from these products.

It is important to determine the content of some trace elements in the products of different manufacturers of hair dyes and natural hair dye called (Henna) used in the Libyan market (Tripoli).

1.3 The aim of the study

The aim of this study is to determine some of trace elements concentrations by Inductively Coupled Plasma Emission Spectrometry (ICP-OES) in 23 types of different manufacturing companies' hair dyes are sold in

different markets in Tripoli with the aim of evaluating the possible dangers these dyes could cause to customers.

1.4 Objectives of the study:

1. Determination of some trace elements content in hair dyes and (Hanna) available in Libyan market.
2. Identifying the trace elements with the highest concentration in hair dyes and knowing how harmful they are to human health.
3. Recommend strategies that can be taken to reduce human exposure to high concentrations of trace elements.

1.5. Study subject:

In this study, several types of hair dyes that are most sailed in the Libyan market and different in the countries of manufacture were selected, as they were chosen equally between the European, Arab and local industries. Hair dyes are one of the sources that can cause harm to the human body due to the adoption of the application of these chemicals directly to the skin of the head, where the danger is that the skin can run out of heavy metals that are dangerous to human health, causing their accumulation inside the human body, causing poisoning or suffer from multiple diseases.

Chapter II

LITERARURE REVIEW

LITERARURE REVIEW

2.1 Nature hair dyes:

Graying of scalp hair is an inevitable physiological process with age. Due to this process, pigment-forming melanocytes are lost from primary hair follicles, reflecting the loss of melanocyte stem cells in ageing hair follicles[18].

2.2 classified hair dyes into four categories as follows:

- Metal salts.
- Direct (temporary or semi-permanent) dyes
- Oxidative (permanent) dyes
- Natural dyes

Oxidative hair dyes are the most important group and have a market share in the EU or the US of 80%[19].

Hair consists of the root hair trunk. Where the column consists of three layers. The cuticle consists of well-packed colourless cells, the cortex also contains natural colour pigments that determine the colour of his hair and the cortex has a hollow core. Larger particles of temporary hair dye do not have the ability to penetrate and the combination of oxidizing and alkaline agents causes swelling of the hair scalp. It facilitates the spread of the colourless substance in the cortex of his hair, which Lead s to bleaching of the natural

melanin pigment of his hair. Ultimately, the oxidation of the colourless precursor moves large colour molecules to be trapped within the hair coat[20], Thus, the hair shaft can preserve oxidative damage by using permanent hair dye. The level of damage is increased with dark pigments (e.g., black, dark brown and dark red) because dark pigments need high concentrations of precursors [21].

Permanent hair dyes are damaging nature, especially those of a dark colour. According to international associations, there is a possible link between these dyes and human cancer. Also, semi-permanent hair colour contains an alkalizing agent other than ammonia (such as Sodium carbonate and ethanolamine) with a lower level of hydrogen peroxide (relative to permanent hair colour) [22] [23], It differs from other dye classes because it consists of two mixtures of ingredients prior to use and production. Chemical processes deposit colour on or in the hair. Modern oxidative dyes include a variety of important components[23].

Primary intermediates: Among them are para-phenylenediamine (PPD), Para-toluendiamine (PTD), Substituted Para diamin, Ortho or Para-Aminophenol. Oxidation of these substances and conjugation with the modifiers result in coloured reaction products. Content From the main mediators in hair dyes ranges from 0.050% (light colours) to 1.50% (dark pigments).

Couplers or modifiers: Among them are substitutions include meta-Aromatic derivatives such as m-phenylene-diamine, m-aminophenol, resorcinol or others. Couplers are contained in an approximate 1:1 molar ratio.

Oxidants: Hydrogen peroxide, Urea peroxide, Sodium Percarbonate or perborate.

Alkalinizing agents: Aminomethylpropanol or monoethanolamine, ammonia.

Direct dyes represent the second category of economically important hair dyes, and contain colours that are transient and semi-permanent. Temporary colouring agents include azo-, triphenylmethane-, anthraquinone- or indamine pigments, whereas some azo dyes, nitro-aminophenols, and nitro-phenylenediamines are found in semi-permanent colouring compounds. Mineral salts are mainly used to cover gray hair. The hair is generally based on Lead acetate and other heavy metals, which are restricted to the EU maximum of 0.60% of content Lead reship[16]. Plant-based natural dyes are made of relative value Small but increasingly economically important. The majority of natural dyes employ (Henna), which is made from the leaf extract of the North African plant (Lawsonia inermis) or its pure chromosomal component (Lawsone; 2-hydroxy-1,4-naphthoquinone)[16].

Background Henna is Lawsonia inermis, family Lythraceae is a naturally occurring plant grown throughout Africa and Asia. Marketed Henna is a natural powder derived from the dried and crushed leaves of the plant. Henna is very popular in many parts of Libya because it is part of the culture and traditions.

2.3 Trace Elements Definition:

A chemical element required in minute quantities by an organism to maintain proper physical functioning, Metals as trace elements Metals are generally solid materials at room temperature, have luster, high electrical conductivity, ductility, and can lose electrons and form positively charged ions. According to their position in the periodic table, they are composed of transition metals, alkali metals, alkaline earth metals, and rare earth metals[24].

2.4 The effect of Trace elements on human health:

Trace elements metals can seriously poison the enzyme systems, increase the production of free radicals and replace or mix them with the necessary elements that make up the enzyme-mineral mixtures and combine them with impregnations of food minerals, as Lead acetate is used as the colour additive in "gradual" hair-dyeing products[25].

Pregnant women and infants are particularly vulnerable to this because easy driving can cross the placenta and enter the fetus's brain, it can also be transmitted to infants through breastfeeding[26].

Heavy elements ions are absorbed upon petition with human skin and form a few compounds inside the body, which Lead to erratic or fatal function of cells and produce various diseases, to amine (-NH2), carboxylic acid (-COOH) and thiol (-SH) proteins[27]. Long-range exposure to certain trace elements may cause disorders, including cancer, cardiovascular disease, reproductive and developmental disorders, lung damage, neurological disease, kidney and liver problems, cardiovascular disease and hair fall or breakage. In particular, Nickel, Cobalt and Chromium act like strong skin stimulators; anyway, Arsenic, Lead, mercury, Antimony, and Cadmium, are highly toxic and have long-lasting effects[28].Some scientists believe that hair dyes can Lead to cancer, especially when using dark colours [29].

2.5. Trace elements:

2.5.1. Lead (Pb):

- **Exposure sources:**

Lead is one of the oldest known historically heavy metals. The ancient Babylonians, Greeks and Egyptians were involved in the manufacture and welding of water pipes. Lead compounds are abundant in the earth's crust. Lead is mainly used in the manufacture of storage batteries, electrical wires,

and industry Shields protection from X-ray and rumors that emit nuclear reactors. Lead compounds are also heavily involved in the synthesis of paint pigments (Lead sulphate is white, Lead sulfate is black, Lead Chromate is yellow and Lead carbonate is white and in the manufacture of Ceramics and pesticides [30].

- **Physiological role:**

Lead is a metal that is toxic to the body and does not have any important physiological role[30].

- **Toxicokinetic:**

a. Absorption: Lead is absorbed through the digestive tracts, but its bioavailability depends on its intake with food, where its absorption decreases in the presence of food becomes 12% or less, while without food it is absorbed by 23%[31], Digestive absorption is affected by several factors such as age Absorption in children is higher than in adults), fasting the presence of food in the digestive tract reduces the absorption of water-soluble Lead), normal diet (the presence of Iron reduces the absorption of digestive Lead , and the presence of Calcium and phosphorous also reduces absorption). Its absorption increases during pregnancy), by dose, and by the size of the particles ingested[32] [30]. It is also absorbed when it enters the respiratory system, and its skin absorption is in a small amount.

b. Distribution: Lead is distributed in the plasma where it is found in the blood – mainly in the red blood cells account for 33% of the total, and it is

distributed in the soft tissues in a basic way as well. It is present in high concentrations in the liver, lung, spleen and soft tissues and then redistributed to accumulating emulate in the bones. That is, Lead is not distributed in the bones in a basic way, but rather accumulates within them due to the effectiveness of Calcium in them[31].

c. Metabolism: Organic Lead compounds are metabolized in the liver by oxidative dealkylation by cytochrome 450CYP enzymes. As for the inorganic Lead compounds, they are not metabolized or bio transformed, but rather form complexes with different proteins[31]**.**

d. Excretion: It is excreted by the kidneys in the urine as soluble salts or through the bile conjugated with organic compounds[31]. In addition to secondary elimination pathways such as sweat, saliva, nails, hair and breast milk[30].

- **Mechanism of toxicity**:

The toxic effects of Lead include all parts and systems of the body, due to the ability of Lead to inhibit or mimic the action of Calcium and to bind to important proteins in the body by binding to sulfhydryl groups, amine groups, phosphate groups, and carboxyl groups, Lead increases the intracellular Calcium concentration in blood vessels, nerve cells (neurons), liver cells and various arteries, which Lead s to smooth muscle contraction and thus an increase in arterial pressure.

The circulating level, Lead interferes with the biosynthesis of heme through its inclusion in ferro chelatase, ALAS (aminolaevulinic acid synthetase) and ALAD (aminolaevulinic acid dehydrase) enzymes.

The bone level, Lead causes a change in the levels of 1.05-dihydroxyvitamin D (1.25-dihydroxyvitamin D), causing a change in Calcium homeostasis in the bones and a change in osteoblast function.

At the level of the nervous system, Lead replaces Calcium, which acts as a second messenger in the neurons, blocking the voltage-related Calcium channels, inhibiting Calcium flow, releasing neurotransmitters later. As a result, synaptic transport is inhibited. Lead also inhibits the process of glutamate uptake and the activity of the enzyme glutamate synthetase in astrocytes Lead Ing to inhibition of glutamate regeneration and high excitability in neurotransmission[31].

On the molecular level, Lead causes carcinogenicity but the gear mechanism is completely clear.

- **Acute toxicity**:

Excessive exposure to Lead results in cramping, abdominal pain, and constipation. This may be associated with nausea, vomiting, and bloody stools. Patients initially show signs of fatigue, apathy, pain of unknown cause in the digestive tract which later turn into neurological symptoms[31].

- **Chronic toxicity:**

  Chronic exposure to Lead causes anemia and jaundice, due to acute hemolysis. Examination of the gums also shows the appearance of blue-gray pigmentation "Lead streaks".

- **Treatment**

Acute poisoning is treated by injection of chelating agents from Dimerco Bal and EDTA-2CaNa together to reduce Lead absorption.

It is permissible to take it orally for the treatment of poisoning in children when the concentration of Lead in the blood more than 15µg /dl[31].

2.5.2 Cadmium (Cd):

- **Routes of exposure:**

Cadmium is used as an astringent, and it is also included in the composition of number of an important adhesive substance. The presence of Cadmium is due to the environment from coal combustion, waste burning, metal smelters, and the use of phosphate chemical fertilizers. Cadmium exposure is product from drinking water, from cigarette smoke, and from food as the U.S.EPA in foodstuffs in cereals, potatoes and leafy vegetables having the highest content of Cadmium. On average, a person consumes about 32.0µg of Cadmium daily and 3.0µg daily if he is a smoker[31].

- **Physiological role**

Cadmium has no physiological role in the body[33]**.**

- **Toxicokinetic:**

a. **Absorption:** Its absorption depends on the way it enters the body. Its intestinal absorption is small (less than 3% of the dose of Cadmium ingested in the gastrointestinal tract). As for pulmonary absorption, it may exceed 32% as it enters through the alveolar epithelium and then enters the bloodstream.
b. **Distribution**: Cadmium is distributed through the blood to a number of tissues and is concentrated in them, especially in the acacia and rind because it contains a large amount of metallothionine.
c. **Metabolize:** The direct metabolic method, such as oxidation, reflux, or alkylation, was not known. However, the Cadmium ion is bound to anionic groups, especially sulfhydryl protein groups, especially albumin and metallothionine and their protein molecules.
d. **Excretion:** Most of the unabsorbed Cadmium ingested orally or by inhalation is transported to the gastrointestinal tract through mucosal cilia and is excreted in the feces. As for the absorbed Cadmium, it is very slowly excreted in the urine and feces, with a half-life of more than 2 years in humans[30] .

- **Mechanism of toxicity**:

Cadmium is dangerous for two reasons: Its biological half-life (20-30 years) and its accumulation in tissues. Acute poisoning rare, with Cadmium causing lung damage. It damages the intestinal mucosa, while in high doses it causes liver damage showed hepatic necrosis with inflammatory cell infiltration. As for chronic nephrotoxicity, harmful pathogens accumulate in the proximal tubules of the renal nephron, which is represented by severe proteinuria, as a result of reduced reabsorption of low molecular weight proteins. Cadmium toxicity – acute hepatocellular and chronic renal – is due to the molecular level to the binding of Cadmium to sulfhydryl groups, especially in the complex metallothioneine (MT), in the form of the Cadmium-metallothionine complex (Cd-MT), which is excreted from the liver into the kidneys. The tubular lumen accumulates in the epithelial cells of the proximal tubule cells, releasing the academia with lysosomal degeneration. In 1993, Cadmium became a human carcinogen, occupational exposure to it was inflicted on those prone to prostate and lung cancer by a very clear mechanism[31].

- **Acute toxicity**

It usually counteracts acute Cadmium poisoning by exposing Cadmium or mononitrate. Its salts are heated, and we have Cadmium oxide fumes, which you inhale and give rise to two Symptoms are similar to spray

infection, while severe exposure to such causes fumes that cause lung damage[31].

- **Chronic toxicity**

Chronic exposure to Cadmium affects the kidneys, lungs, and bones. What is the price It contributes to cancer at the kidney level and to pulmonary hemorrhage Emphysema Osteoporosis and osteoma Acia[31].

- **Treatment**

There is no cure for Cadmium poisoning, especially if Cadmium ions accumulate in the body However, administration of Calcium and Zinc compounds stimulates the synthesis. This may have led to competition with Cadmium for enzymatic binding sites. This is why tender Zinc and Calcium supplementation may reduce Cadmium nephrotoxicity[31][30].

2.5.3 Iron (Fe):

- **Routes of exposure**:

Iron exposure is mainly through food, especially in people with a genetic predisposition to increased Iron absorption. There are many foods that contain Iron, such as liver and dark green leafy vegetables. Mineral water is also another source of Iron as well as soil (because it is the most abundant mineral in the earth's crust), as well as the use of Iron-containing pharmaceuticals as nutritional supplements[34].

- **Physiological role:**

Iron is an important element in the body, as it is involved in the formation of hemoglobin. Myoglobin is also a necessary component of oxidative phosphorylation because it is a component, of cytochromes and Iron-containing proteins. It also requires the neutralizing enzyme Myeloperoxidase to function fully Suitable[35].

Iron deficiency anemia is the most common cause of anemia. Where A third of the world's population suffers from it. Because Iron is necessary for the body to enter it, Normal composition is one of the important vital components and its deficiency leads to serious effects on the cellular functions of many organs [34][36].

- **Toxicokinetic**:

a. **Absorption**: Iron is usually poorly absorbed; only 10% of Blacksmiths are consumed medicinally, but in the cases of severe need, the percentage of blacksmiths increases. Absorption percentage up to 30%.
b. **Distribution:** The absorbed Iron travels to the liver and bone marrow to produce hemoglobin and myoglobin, and various tissues to enter the synthesis of proteins and enzymes Cytochromes.
c. **Excretion:** is mainly excreted in the feces, and it is excreted in very small quantities in the feces Paul[35].

- **Toxicity Mechanism:**

Acute Iron intake Leads to cell damage and organ damage; it affects the beta cells of the heart, liver and pancreas, due to its induction of glycogenesis, free radicals (Fenton reaction). Their accumulation in particles makes them sensitive to rupture and thus limits the release of their enzymes into the cytoplasm Acute phagocytosis and acute cell death programmed cell death, necrosis[35] [37].

- **Acute toxicity:**

Acute poisoning is divided into several clinical stages, namely:

a. Gastrointestinal poisoning

b. Circulatory shocks and metabolic acidosis

c. liver toxicity

d. gastrointestinal scarring[35]

- **Chronic toxicity**:

Symptoms of chronic poisoning include disturbances in liver function due to depression and Iron in hepatocytes[35] [37].

- **Treatment:**

Treatment aims to remove Iron from the digestive tract by inducing vomiting. Deferoxamine is an Iron chelating compound and is one of

the Treatment options in cases of acute Iron poisoning. Phlebotomy can be used as a treatment for Iron poisoning Where 02 mg of Iron is eliminated in this way[35].

2.5.4 Cobalt (Co):

- **Routes of exposure:**

Cobalt is found widely and in low concentrations in the environment, so it may limit poisoning Exposure to Cobalt through food, drinking water, or air channels. May also limit exposure through skin contact with soil or water or its waste.

However, food is the main source of Cobalt, with an average individual eating 0.11 mg L^{-1} of Cobalt per day in his diet, including vitamin B12 content and Cobalt intake[38].

As for occupational poisoning, it is limited to metal miners by inhaling large amounts of it[39].

Cobalt is an important mineral element because it is included in the vitamin B12 complex. It is Necessary in maintaining human health (its deficiency causes anemia), (as Cobalt is sometimes used to treat anemia) 0.16-0.1 mg L^{-1} of body weight[40][36].

- **Toxicokinetic**:

a. **Absorption:** The amount of hydrated Cobalt ranges between 5- 45% and depending on the state of health, the amount eaten and the period of time taken while taking Cobalt. Cobalt absorption also increases when it is deficient the body's need for it. It also absorbs Cobalt if it enters the respiratory tract[41]. With skin contact, especially damaged skin[30].

b. **Distribution:** Absorbed Cobalt is distributed to all tissues of the body, but mainly in the liver, kidneys and bones[38] The excretion of slowly absorbed Cobalt is excreted mainly in the urine. Part of it is excreted through feces[42].

- **Mechanism of toxicity**:

Cobalt generates free radicals, including peroxides, in addition to its ability to formation of toxic oxygen species, Lead in to increased and emergence of oxidative stress and its toxic effects on the lungs in particular[30].

- **Chronic toxicity**

Symptoms of poisoning appear on a number of parts of the body, including:

a. dermatitis[43].
b. Increase in the number of red blood cells RBCs[33].

c. Respiratory effects include coughing, wheezing, shortness of breath, decreased function, lung and respiratory infections, asthma and pulmonary fibrosis [30]
d. goiter[30].

- **Treatment**:

The patient is treated by inducing vomiting and performing procedures for him. A chelating agent is also used in treatment N-acetylcysteine (NAC) is the most effective chelating agent in the treatment of poisoning Cobalt [30].

2.5.5Chromium (Cr):

- **Routes of exposure**:

Food is a major source of Chromium exposure, such as meat and vegetables Acidic foods in contact with stainless steel bowls or utensils Rust has higher levels of Chromium due to its exudation compared to stainless steel. Since Chromium is a component of the earth's scale, large amounts of it are transferred to the water and soil. The presence of Chromium in phosphate fertilizers may be responsible for Its presence in water, soil and some dirt[30][44].

It is also exposed professionally by inhaling or touching the dust it contains skin[45].

- **Physiological role**:

Strengthening the interaction between insulin and its receptors on cell surfaces as a component Glucose tolerance factor (GTF) has a synergistic effect with insulin in improving it Metabolism, as a result, Chromium deficiency causes an increase in blood sugar and an imbalance in endurance Glucose[30].

- **Toxicokinetic**:

a. **Absorption** :Only 1-2% of Chromium is taken orally. Professionally, it sucks Dust containing Chromium is respiratory, and Chromium penetrates the skin especially in the presence of skin damage.
b. **Distribution:** The largest distribution of Chromium is found in the lung, spleen, liver, kidney and bone. As such Chromium crosses the placental barrier in fetuses.
c. **Excretion**: The excretion is excreted mainly in the urine and partly in the Stool, hair and nails It is also excreted in breast milk[30] [44] [45].
d. **Mechanism of toxicity**:

The Mechanism of toxicity of Chromium depends on the oxidation state of the Chromium atom Hexavalent is more toxic than Chromium because it has a higher oxidation capacity and more able to enter cells[30] [44]. The toxic effect of hexa-Chromium is due to its feedback products entering the ring Oxidative stress is associated with the formation of reactive oxygen

tables that cause oxidative stress, which interact with the presence of proteins and DNA, there are a number of harmful effects in it and thus in its generation of cancers[46].

- **Acute toxicity**:

Acute exposure to Chromium causes many diseases, including the following:

At the level of the kidneys, renal tubule necrosis may occur, and death may occur if it exceeds the dose, it is 5 g. At the level of the liver, diffuse hepatic necrosis appears within 10 hours if it is the dose is 5 g. Severe gastrointestinal bleeding, Neurotoxicity, Bloody urine, At the level of the respiratory system, this causes tingling in the airways, jaundice, dysuria Appearance of albumin in urine[47][48].

- **Chronic toxicity**:

Chronic occupational exposure to hexa-Chromium usually results in localized lesions.

Include the following:

1. A corrosive reaction in the nasal septum appears with severe ulcerations of the nasal septum, and Lead s to ulceration on both sides. Cartilage necrosis eventually Leads to perforation of the nasal septum.
2. Local effects in the lungs (pneumonia).

3. Chromium ulcers caused by Chromium corrosion Hexagonal, allergic eczematous dermatitis, Carcinogenic effects of chronic occupational exposure to carcinogenic Chromium compounds lung[48][49].

- **Treatment**:

In cases of digestive poisoning with Chromium compounds, vomiting occurs through the procedure of Gastric bypass but if Chromium is absorbed into the body, the poisoned person is given chelating agents such as Ca-EDTA, in cases of severe poisoning, Chromium toxins should be excreted by inhalation in the open air While monitoring for respiratory distress, this is accompanied by the administration of oxygen and medication bronchodilator[48][50].

2.5.6 Arsenic (As):

- **Routes of exposure:**

One of the most significant heavy metals that is unsettling the environment and human health is Arsenic. It is widely available as oxides, sulphides, or salts of Iron, Sodium, Calcium, Copper, and other elements, has a semi-metallic quality, and is noticeably poisonous and carcinogenic.

It is most common element on earth, Arsenic, is toxic to both the environment and living things in its inorganic forms, such as Arsenic and arsenate compounds[51] Natural geological processes and human actions

both contribute to Arsenic contamination. Human activities like mining and ore processing are sources of Arsenic. also, Arsenic can be released throughout the smelting process, whether ancient or modern, into the air and soil[52].

Arsenic is a common ingredient in paints, dyes, soaps, metals, semiconductors, and medications. In addition, some pesticides, fertilizers, and methods of feeding animals release more Arsenic into the environment. It has been determined that Arsenic in its inorganic forms, such as Arsenic and Arsenic compound, poses a greater threat to human health. They are extremely carcinogenic and can result in skin, bladder, lung, and liver cancer. Arsenic exposure in humans occurs through food, drink, and the air. One of the Lead in causes of Arsenic poisoning in more than 30 nations throughout the world is drinking water contamination[53]. Health risks to people can arise if groundwater levels of Arsenic are 10-100 times higher than what the WHO recommends for drinking water (10 µg/L)[54].

- **Physiological role**

Arsenic is a metal that is toxic to the body and does not have any important physiological role.

- **Toxicokinetic**:
- Arsenic is the twenty-first most common element on Earth, and both the environment and living things are killed by its inorganic forms,

such as Arsenic and Arsenic compounds. Arsenic may be ingested by people naturally, through industrial sources, or by accidental sources. Pesticides containing Arsenic, naturally occurring mineral deposits, or incorrect disposal of Arsenic compounds might all contaminate drinking water[55]. It is a highly toxic and carcinogenic substance, and it is widely available in the form of oxides, sulphides, or salt of Iron, Sodium, Calcium, Copper, etc.

- **Mechanism of toxicity**:

inorganic Arsenic (iAs) is a carcinogen that ranks the 20th in terms of frequency of elements in the earth's crust with an average of 1.8 mg/kg. It is naturally found in the oxidation state of As V (arsenate) and As III (arsenite), the latter being about 60 times more toxic than the former[56]

The biotransformation pathway of As involves several changes in oxidative state, oxidative methylation, and production of at least four metabolites. When this metalloid enters the body, iAs is metabolized from arsenate to Arsenite and then metabolized by oxidative methylation to monomethyl Arsenic (MMA). After the conversion from arsenate to Arsenite, at the final methylation stage, dimethylarsinic acid (DMA) is produced [57][58]

iAs (V) ⟶ iAs (III) ⟶ MMA (V) ⟶ MMA (III) ⟶ DMA (V)

- **Acute toxicity:**

Intentional consumption of Arsenic in the event of suicide attempts or accidental consumption, in children, may also Lead to severe poisoning[59]

- **Chronic toxicity**:

Chronic Arsenic poisoning in humans has cutaneous manifestations due to its specificity in diagnosis. Pigmentation and keratosis are specific skin lesions indicative of chronic Arsenic poisoning[60]. Labelled "raindrops on a dirt road" (bone marrow; non-neoplastic, benign and toxic changes to Arsenic, available from dermatological lesions caused by Arsenic poisoning

Vascular damage can result from exposure to low doses of Arsenic. Vomiting, nauseousness, and irregular pulse, decreased production of red blood cells, white blood cells, Tingling sensation in hands and legs. Skin lesions, internal malignancies, neurological issues, lung disease, peripheral vascular disease, hypertension, cardiovascular disease, and diabetes can all develop as a result of prolonged exposure[61].

- **Treatment:**

Bio-methylation is the detoxification process and its end products are inorganic methyl Arsenic such as MMA (V) and DMA (V), which are excreted through the urine, and is a biomarker of chronic Arsenic exposure.

But, MMA (III) is not secreted and remains inside the cell as an intermediate product. Monomethyllarsonic acid (MMA III), an intermediate the product is highly toxic compared to others including Arsenic which is potentially responsible for inducible Arsenic Carcinogenesis[55]Chronic Arsenic poisoning Lead to many irreversible changes in the vital organs of the human body and the mortality rate is higher. Despite the magnitude of this potentially fatal toxicity, it has been concluded that there is no effective treatment for this disease[59].

2.5.7 Stannum (Tin) (Sn):

Grasping cellular physiology and pathology requires a thorough understanding of the mechanisms driving selective toxicity. The molecular mechanisms causing specific toxicity are classified as such because they directly impart protective and cellular damage-promoting effects. Organotin compounds are among the top selective cytotoxic agents that cause cell damage[62]. In particular, the three-substituted organic tin shows different tissue cellular damage patterns that depend on the alkyl chain length. The substituent groups on Hazardous effects are caused by groups like ethyl, methyl, and butyl on the tin atom, to some extent directly. It causes myelin swelling and cerebral edema, and TMT salts also Lead to rapid selective apoptosis in certain peripheral regions of the mammalian nervous system,

and many specific subsets of cells of the immune system[63]. As opposed to that, tributyltin (TBT) T cell apoptosis is triggered by salts[64].

- **Physiological role:**

There is no known biological role for tin in living organisms. It is also difficult to absorb humans and animals easily. It is still unclear, but the possibility of organotin toxic substances activity concurrent biological processes that differ from Sn's typical biological function[65].

- **Toxicokinetic**:

Tin can get into when you consume contaminated food or drink polluted water, it enters your body. Tin can be ingested, touched, or inhaled when exposed to air, water, or soil pollutants, or it can be found in some soils. Tin in food is ingested in trace amounts, which pass through the digestive tract and enter the bloodstream. The majority of the tin passes through your intestines and is excreted in your stool. Urine from some people contains your body. Tin dust or fumes may be caught in your lungs if you breathe them in, although this won't stop you from breathing if the amount is minimal. Most inorganic tin may be eliminated by your body in less than a month, but not all of it remains in your body for two to three months. The dangers of tin are becoming increasingly important due to the increased use of tin in plasticizers, fungicides, mollusks It remains in your body for two to

three months. the dangers of tin and antitumor agents and the resulting increased human exposure to organic and inorganic tin compounds.

- **Acute toxicity:**

Exposure to a large amount in a short period of time to organotin compounds causes respiratory tract irritation, irritation of the skin and eyes, gastrointestinal effects, and neurological problems. After the poisoning, certain neurological issues lasted for years. After ingesting extremely high amounts, fatal occurrences have been observed. Animal tests have revealed that organic tin is safe primarily affects the body's immune and nervous systems.

- **Chronic toxicity:**

Inorganic tin compounds enter the human body and quickly leave it after breathing or ingestion. Typically, they don't have any negative effects. However, anemia, liver and renal issues, as well as stomach distress, have been reported in humans who were exposed to significant doses of inorganic tin during studies. Animal studies with inorganic tin have revealed outcomes resembling those seen in people. There is no proof that substances containing inorganic tin alter birth abnormalities, genetic changes, or reproductive functions. Cancer-causing organotin chemicals are not known to exist. Some organotin compounds have been proven to have negative effects on humans when inhaled (through breathing), orally (through eating or drinking), or

topically (through skin contact). However, the principal effect will vary depending on the particular organotin compound.

- **Treatment:**

Tin itself is not actually a toxic metal, as there are no recorded cases of poisoning by tin, its oxides, or any of its inorganic salts, but some organotin compounds are highly toxic, close to that of cyanide[66], The allowable limit for exposure to metallic tin in the workplace has been set by the US Occupational Safety and Health Administration (OSHA) at 2 mg/m3 during a period of eight working hours; the same amount as a suggested value by the US National Institute for Occupational Safety and Health; but at levels greater than 100 mg/m3, so metallic tin is dangerous to living organisms[67].

2.5.8 Potassium (K):

Is a crucial part of cations in extracellular and intracellular fluids. Together, they serve a crucial physiological role in regulating bodily fluid balance as well as membrane potential, contraction, and muscle contractions. It has a significant impact on health, including blood pressure (BP), cardiovascular disease (CVD), arrhythmia and glucose disease (CVD), stomach cancer, osteoporosis, Asthma, kidney stones, sclerosis and muscle weakness[68].

The average daily Potassium intake ranged from 90 to 120 mmol. Increased Potassium intake did not appear to have any negative effects on lipid levels, renal function, or catecholamine concentrations. These BP findings concur with a prior meta-analysis of 33 randomized controlled trials (26 participants) [69]

Individuals who have high levels of blood pressure, high levels of potassium, and high urinary sodium excretion will have an easier time lowering their blood pressure when potassium consumption increases[67]

2.5.9 Magnesium (Mg):

Is naturally present in bone tissue and is necessary for human metabolism[70] [71] ,It ranks as the fourth most abundant cation in the human body, the proportion of 1 mole of Magnesium stored in the body of a normal adult being about 70 kg, approximately half of the total physiological Magnesium stored in bone tissue [70] ,Magnesium is a cofactor for many enzymes in the body, and it stabilizes DNA and RNA structures[71] The level of Magnesium in extracellular body fluids ranges between 0.7 and 1.05 mmol/L, so Kidneys and intestines maintain equilibrium [70]. But levels of Magnesium in the blood that exceed 1.05 mmol/L can Lead to severe muscle paralysis in the body, hypotension, severe shortness of breath[72] and cardiac arrest if the serum level is extremely high

of 6-7 mmol/l, The occurrence of hypermagnesemia is rare due to the large and active excretion of the element in the urine[70] [72] [73].

2.6 Heavy metals in hair dyes:

Hair dyes have been in use for at least 4000 years. Where they found it in the hair of Egyptian mummies, it was dyed with Henna. In the days of the ancient Roman Empire, Lead combs dipped in vinegar were permanently used to darken white hair to gray. Today, humans use large numbers of hair dyes. Due to the constant human desire to improve our appearance, these products play a major role in our quality of life[16]. Thus, the traceability of the presence of these metals in food, water and other habitats is significant for the study of chemistry, ecology, and human health, and is very important and necessary for public safety[74]. Prior to 1960, it was widely believed that skin could not absorb personal care items. As a result, some local consequences among consumers of such goods raise questions about public safety, and it was later shown in some studies that some of them are capable of penetrating the skin[75]. Since hair dyes in general are cosmetics, Regulation (EC) in the European Union No. 2009.1223 states that their components must adhere to a number of severe standards. According to the list of forbidden substances in cosmetic compounds, restricted minerals in the case of cosmetics include As, Cd and Cr, Co, Hg, Ni, Pb, and tin[76]. As a result of Health Canada's (HC) recent publication of a cosmetic hot list in

2015, some minerals like As, Cr, Cd, Sb, Hg, and Pb (and their components) are now restricted or forbidden from use in cosmetics[77]. Furthermore, Canada defined the average percentage of impurities in heavy metals in cosmetics as 10µg/g of As, Hg, Cd, 10µg/g of Pb, and 5µg/g of Sb[78]. The rate of heavy metal impurities in cosmetics was also specified by the German federal government as follows: 15 µg/g of As, 120 µg/g of Hg, 120 µg/g of Pb, and 110 µg/g of Sb[79]. Various amounts of this mineral density have been found in various hair dye brands, according to several researchers from Saudi Arabia, Iran, India, Turkey, Nigeria, and Brazil[80]. Thus, before going on the market, this kind of cosmetics and its contents must be thoroughly and comprehensively assessed and be safe for use under typical conditions. As a result, investigations were conducted on the levels of heavy metals in both natural and chemically treated hair in various marketplaces across various nations. For instance, quantities of Lead, Copper, Iron, and Cadmium in Iraq were found to be between 0.41 to 0.91 mg L^{-1}, 0.26, 0.31, 0.11and 0.16 mg L^{-1} respectively[81]. Additionally, in a different investigation on natural hair colouring in Nigeria, levels of Copper, Lead, Chromium, Nickel and Zinc were reported in the ranges <0.03-20.5, <0.03-3.5, <0.1-9, 1.33-8.4 and <0.03-298mg L^{-1}. The millionth. million moreover, they discovered that Al, Cd, and Co concentrations were below the detection limit[82]. Furthermore, the levels of Cadmium, Lead and Nickel were checked on both natural hair dyes and the dye sold in the Turkish market.

The concentrations for the two natural hair colours, the simultaneous hair dyes had acceptable Pb, Cd, and Ni values in the ranges of LOD-0.56 mg g^{-1}, LOD-0.011 ng g^{-1}, and 0.030-0.37 mg g^{-1}. 0.033-0.065 ng g^{-1}, 0.60-0.93 mg g^{-1}, and 0.49-1.06 mg g^{-1}, respectively[83]. There is a study that made it clear the average Fe defined in hair made from hair is 209.8 mg/kg [14]. In another study on WA hair dyes, they were reported as 20.3x103mg/kg and 10.2 x103mg/kg, respectively [84].In a previous study mentioned that the concentration of Cr in 12 brands of preparations (L4 to L13, L22 and L23) was below the detectable limit. The maximum concentration of Cr was determined at L20 (0.69 ± 0.02 mg L-1) [85] relatively, Also in a previous study it was the Potassium and magnesium concentrations in hair dye samples ranged between for K (8.33-3.67 mg L-1) [86]and magnesium ranged between (2.71-1.44 mg L-1) [86] .Sn According to the World Health Organization, it is assumed an MRL of 0.3 mg/kg/day has been derived for intermediate duration oral exposure (15–364 days) to inorganic tin [87] In another study on the element Cobalt, Lead and Cadmium, the results of Cobalt concentration ranged between (44.52 ± 0.9µg /g)[85] Lead and Cadmium (0.07-0.18µg/g) and (0.012-0.13µg/g) respectively[88] Unfortunately, no study has been conducted on the concentration levels of these dangerous substances in Industrial hair dyes used in Libyan markets (Tripoli).

CHAPTER III

EXPERMENTAL

Experimental

3.1. Reagent and Apparatus:

3.1.1 Sample Collection:

Dye samples were collected from different stores in the Libyan market in Tripoli. The selected dye types were of the most common types used by consumers in the market.

3.1.2 Sample preparation:

instructions attached to the leaflet in each dye box. The samples were prepared according to the can of dye cream mixed with the oxygen canister according to the percentage specified in the leaflet for each dye, and then a soft dye cream that can be applied to the hair was formed.

Figure(3.1) Sample preparation

No	Dye name	Type of colour	Source
S1	Loreal	Black	French
S2	Loreal	Red	French
S3	Loreal	Blonde	French
S4	Beauty	Black	Bulgarian
S5	Beauty	Red	Bulgarian
S6	Beauty	Blonde	Bulgarian
S7	Sea Colour	Black	Turkish
S8	Sea Colour	Red	Turkish
S9	Sea Colour	Blonde	Turkish
S10	Syoss	Black	German
S11	Syoss	Red	German
S12	Syoss	Blonde	German
S13	Farmavita	Black	Italia
S14	Farmavita	Red	Italia
S15	Farmavita	Blonde	Italia
S16	Farmcolor	Black	Tunisia
S17	Farmcolor	Red	Tunisia
S18	Farmcolor	Blonde	Tunisia
S19	White Touch	White	Syria
S20	Royal Henna	Red	India
S21	Taj Henna	Red	Sudan
S22	Kase Alkalije Henna	Red	Pakistan
S23	Rajhi Henna	Red	Libya

Table (3.1)Samples of hair dyes colours from different manufacturers

3.1.3 Chemicals:

In this study, we used chemicals to digest the samples, as we used concentrated (nitric acid 69.5% for analyse CARLO ERBA), as well as (Hydrogen peroxide 30%, (Perhydrol™) for analysis EMSURE ISO), All the solutions were prepared in deionized water.

3.1.4. Glassware cleaning:

All glassware was soaked first with nitric acid (1:1) for 24 hours, then washed well with deionized water, and placed appropriately to dry it from the water.

3.1.5 Preparation of Sample:

1.0 g of dyes(0.5 g Henna) was placed in 80ml of beakers, for each dye sample added 10ml of 69.5% nitric acid and 4.0 ml of 30% peroxide were added to the sample Inside the hood, The samples were stirred well with a glass stem and put on the heating plate for at least half an hour, stirring each 10 minutes until the sample is completely dissolved and so that the samples do not leak from the cups, after half an hour you notice that the sample has evaporated and the digestion process is not complete due to the presence of colour in the solution and sediment. Another 10ml of nitric acid was added and continued to stir over the fire for another half an hour, and the digestion process continued until about 5 ml of the sample solution remained. After the samples were cooled for 10 min, they were filtered with No.41-filter paper, and the filter solution was diluted with deionized water to 25 ml. All samples were collected and sent to the ICP-OES device laboratory.

Figure (3.2) Sample digestion

3.1.6 Blank solution:

In an 80ml beaker, was added 20ml of concentrated nitric acid and 4ml of concentrated peroxide inside the hood, the ingredients were mixed with the spoon glassy well and put in the heating plate for at least half hour, stirring every 10 minutes so that did not leak from the beakers After half an hour, it was observed that the sample had evaporated and about 5ml of the blank solution remained. After cooling for 10 min, I filtered the solution, and diluted the plank solution with deionized water to 25ml. Finally, they were sent with the dye samples to the ICP-OES instrument lab for analysis.

3.1.7 Analytical Methods and Instrumentation

There are many classical, analytical techniques and tools for identifying minerals, each has its own advantages and disadvantages. In this study, inductively coupled optical plasmon emission spectrometry (ICP-

OES) is used to determine the trace metals, also. the pH-meter and conductivity meter devices are used in the physical analyses of hair dye samples.

1) **inductively coupled plasma optical emission spectrometry (ICP-OES):**

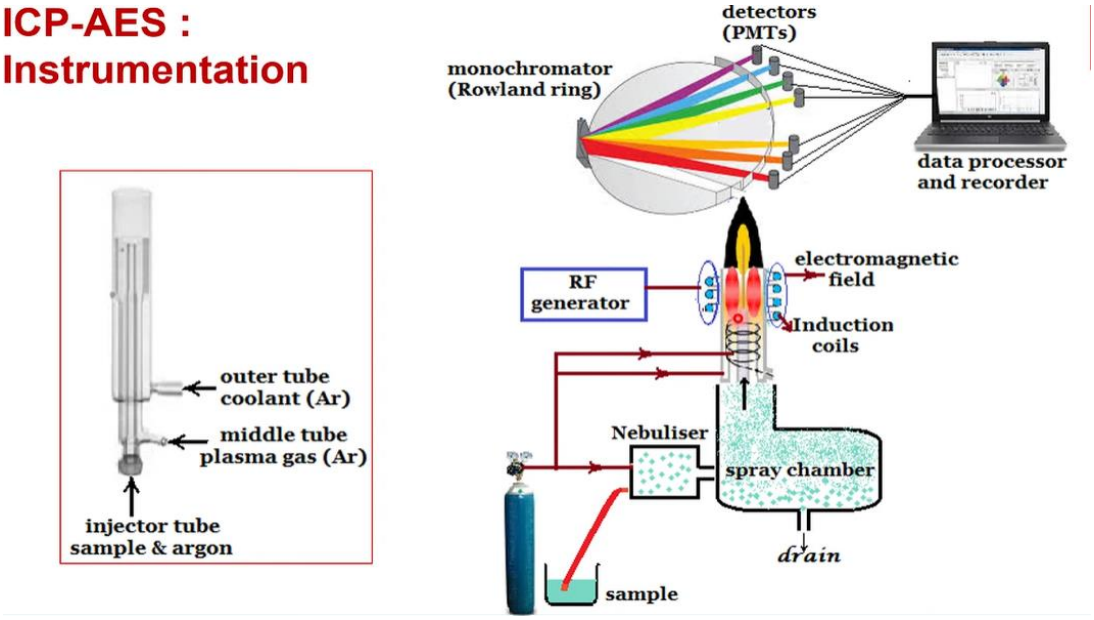
- **Instruments description:**

Plasma Instruments Of all the different instruments used for elemental analysis over the past 25 years, inductively coupled plasma (ICP) has been the most popular and important influence in the field of atomic spectroscopy. Other plasmas, such as microwave induced plasma (MIP), direct current plasma (DCP) and post-auroral discharge, have been discovered to be useful for spectrochemical analysis. However, ICP is the primary source used for assay and mineral analysis at a minimum and with high accuracy [89]**.** Since its commercial introduction in the middle of the 1970s, inductively coupled plasma optical emission spectrometry (ICP-OES), also referred to as inductive coupled plasma atomic emission spectrometry (ICP-AES), has developed into a rapidly expanding and widely accepted instrument in many mineral identification applications in a wide variety of samples. Figure (3.3) illustrates a typical ICP-OES instrument[89].

- **The working principle of the instrument:**

Inductively coupled plasma (ICP), which was first produced in the middle of the 1960s by Fassel and colleagues at Iowa State University and Greenfield and co-workers at Albright and Wilson Ltd. in England, is the most popular and used plasma source today. In the middle of the 1970s, it spread widely and was made commercially available. ICP is an acronym for "inductively coupled plasma", and it is considered one of the methods of optical emission spectrometry. When the plasma energy is given to an analysis sample from the outside, the components of the sample (atoms) are excited, and when the excited atoms return to the lower and lower energy modes, Emission rays (spectrum rays) are emitted, emission rays corresponding to the wavelength of the photon for which the type of element is selected are measured by the position of the photon rays, and the content of each element is determined based on the intensity of the rays. The source of this energy is heat from a plasma of argon gas operating at 10,000 K[90].

An optical emission spectrophotometer, a light source unit, a detector, and a data processing unit make up the ICP optical emission spectrometry apparatus. Because the detector and spectrophotometer vary, there are several types of equipment[90] The most typical type is depicted in Figure (3.3)



Figure(3.3) Components of ICP Optical Emission Spectrometry Equipment

- **Sensitivity for ICP- OES:**

The detection limit is inversely correlated with the (ICP-OES) sensitivity. However, a variety of variables can influence the detection limit for a specific isotope in a given sample. Sensitivity, background noise, interference, and calibration standards are some of these elements and often overlooked sources of variations[90]

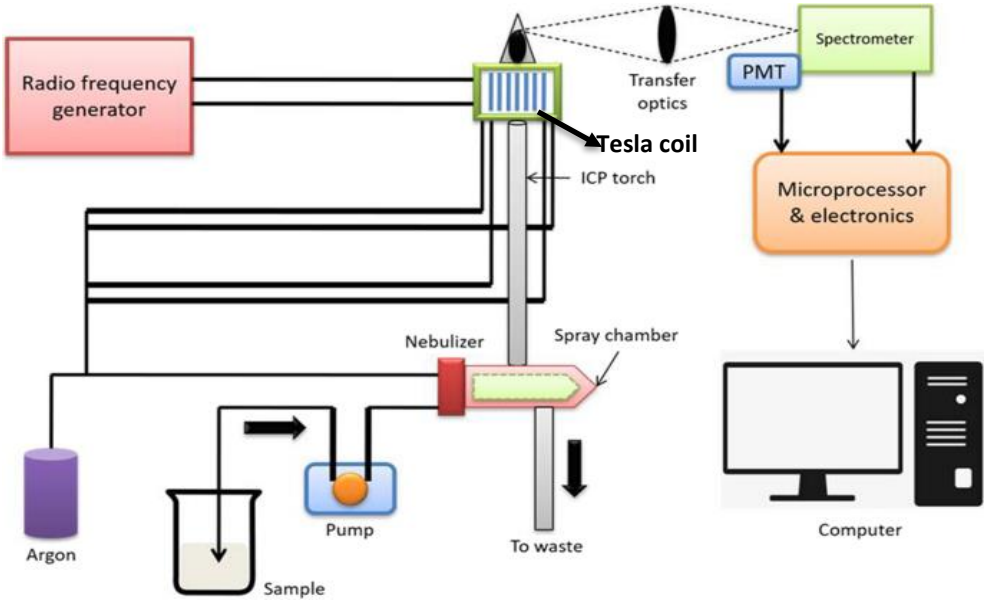


Figure (3.4) Schematic of a typical inductively coupled plasma-optical emission spectrometry (ICP-OES) system

Agilent ICP-OES Instrument Overview

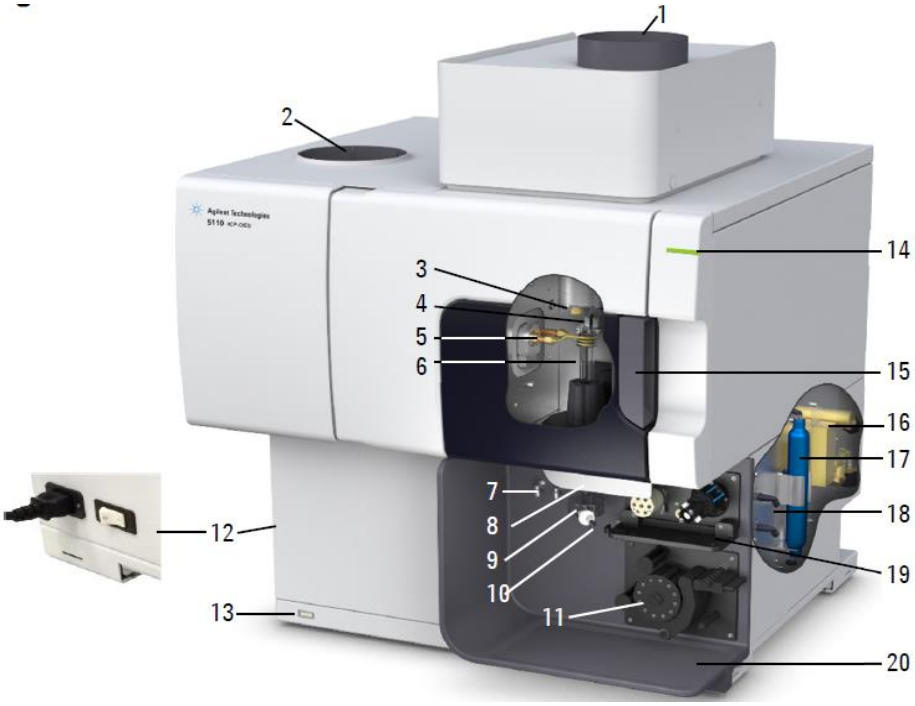


Figure (3.5) Front and side of the ICP-OES instrument

1. Exhaust
2. Air inlet filter
3. Cone and axial pre-optics window (not shown)
4. Snout and radial pre-optics window (not shown)
5. Induction coil
6. Torch
7. Nebulizer and make up gas connections
8. Torch loader handle
9. Spray chamber
10. Nebulizer
11. Peristaltic pump
12. Mains power switch and cable connection
13. Front panel power button
14. LED instrument status indicator
15. Torch compartment handle
16. Water assembly
17. Optics purge filter for argon or nitrogen
18. Gas supply assembly
19. Optional AVS 4, AVS 6 or AVS 7 Switching Valve accessory location
20. Drain for liquid overflow

Argon is normally injected into the torch at a flow rate of between 1.0 and 2.2 L per minute, and the RF field is operated between 5 and 51 MHz, frequently 27.00 MHz, with a forward power of 1.2 to 5 kW, typically 1.35 kW. An average spark from the Tesla coil is used to create electrons and ions "seed" in this area, which is surrounded by intense magnetic fields. The

argon gas is significantly heated as a result of the generated current running continuously in a closed circular route, which generates a strong stream of ions. ICP's temperatures are thought to range from 8100 to 10000K. Higher temperatures call for quick cooling, which is delivered to the outer tubes using argon at flow rates that can reach 17 L/min. Using a field nebulizer, the sample is delivered to the ICP, preferably as an aqueous solution. In order to view the solution from a distance of 5 to 20 mm above the coil, the solution is first turned into a spray and delivered through the inner tube. ICP has a number of benefits, including being optical, having a much higher temperature have very extended dwell durations and having very few or no molecular species[90].

- **Plasma gas flow:**

The cross-flow design began with a design that allowed for the adjustment of the two capillary tubes that are set at right angles to each other (5). The criticality of the capillary positioning led to the commercial production of the fixed cross-flow design. The fixed cross-flow is used with the Scott spray chamber, will provide moderate to good sensitivity, and is generally better than the concentric design for high solids. It is available in construction materials that resist chemical attack. It is not as delicate as the concentric nebulizer and often is used in laboratories where the optimum in precision

and detection limit is of less importance than having a large sample load capability. It is not recommended if suspended particles are present [90].

- **sample uptake:**

Sample introduction can be a significant source of random and systematic error in the measurement of samples by inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP mass spectrometry (ICP-MS) systems. Consequently, texts devoted to ICP have given sample introduction considerable attention, Samples are most commonly introduced as liquids. The considerations made in selecting a liquid introduction system include dissolved solids content, suspended solids presence, presence of hydrofluoric acid or caustic, detection limit requirements, precision requirements, sample load requirements, sample size limitations, and operating budget. The analyst is left with the task of choosing the best introduction components [90].

- **Pneumatic Nebulizers:**

The term “pneumatic” is defined as “of or relating to or using air or a similar gas.” The word “nebulizer” is derived from the Latin “nebula,” meaning mist and is defined as “an instrument for converting a liquid into a fine spray.” Therefore, a pneumatic nebulizer is literally an instrument for converting a liquid into a fine spray that uses a gas as the driving force. The most popular

types of ICP pneumatic nebulizers are concentric, fixed cross-flow, and high solids [90].

- **Concentric nebulizers:**

This basic type of nebulizer can be made from glass or plastics such as PFA and (depending upon design) is capable of handling a sample solution introduction rate of between 0.01 and 3 mL/min. Therefore, the "micro concentric" nebulizer (0.01–0.1 mL/min) should be considered when the sample size is limited to 1 mL. They are typically used with cyclonic spray chambers but can also be used with the Scott spray chamber (an adaptor is needed in this case).

The metal atoms in the plasma transform the light they emit into an electrical signal that can be measured. Grooved diffraction decomposes light into radiation that is often formed for the subsequent measurement of the intensity of the emitted light using a photomultiplier tube. The past decade has seen significant efforts in evaluating and understanding ICP, with many studies conducted to analyse the mechanisms and characterize differences in the system used[90].

ICP rotation through (to some extent)90 to improve the quality of detection limits, as well as the development of sample insertion systems in various forms like laser ablation and electrothermal evaporation (ETV) solid

sampling, are all examples of the accelerated developments that are still occurring in ICP-OES, unknowns are usually compared to standards using standard calibration curves, Consequently, proper sample preparation still plays a crucial role in ICP-OES[90].

Inductively coupled optical plasmon emission spectrometry (ICP-OES) samples were introduced employing radially viewed nebulizers for direct hydride generation (DHGN) [91]. This straightforward hydride production device, which the authors built in their lab, needs plasma operating conditions similar to those seen in typical nebulizer chamber configurations. This work focused on evaluating essential analytical numbers of merit for the determination of As, Cr, Co, K, Mg, Cd, Pb, Fe, and Sn as well as optimizing the operating parameters for hydride formation. Additionally, the excitation conditions of an ICP-OES device using DHGN were investigated. The new system outperformed traditional nebulizer systems in terms of analytical performance for the determination of As, Sb, and Se. With less sensitivity than traditional nebulizer systems, DHGN also makes it possible to detect components that do not form volatile hydrates. The plasma strength analysis revealed that the gases produced during the hydride production have no discernible impact on the plasma discharge. The analysis using DHGN was vulnerable to non-spectral interferences induced by transition metals, just like with traditional hydride generation methods

Finally, actual ICP-OES investigations have shown the value of DHGN in identifying trace elements in a common reference material for hair dye texture[90].

- **Analytical chemical properties of ICP-OES:**

The ICP-OES differs from an atomic absorption spectrometer used for similar purposes in that it has the following characteristics. the potential for sequential and simultaneous investigation of many aspects. An analytical curve with a large linear area, and minimal chemical or ionization interference allows for the investigation of high-matrix materials. extremely sensitive (minimum detection for the majority of elements is 10mg L^{-1} or less), Numerous quantifiable components - Stable analyses of elements that are challenging to analyse with an atomic absorption spectrometer, such as Zr, Ta, rare earths, P, and B, are simple. The structure and characteristics of the plasma light source are the source of the bulk of the aforementioned attributes.

2) pH-METER:(THERMO-ELECTRONIC / USA / AN005750):

A pH meter has a pH probe to conduct the electrical signals to the pH meter, which then displays the pH value of the solution. The pH probe contains two electrodes, namely a sensor electrode and a reference electrode. One is filled with a pH 7 buffer and the other with a saturated Potassium chloride

solution. The sensor electrode bulb comprises a porous glass membrane coated with metal salts and silica.

When the probe is submerged in a sample solution to measure the pH, hydrogen ions build up around the bulb and take the place of the metal ions. Similarly, some metal ions transfer from the glass (sensor) electrode to the sample solution. Because of low sensitivity to pH changes or complete insensitivity to pH changes, the reference electrode potential offers a constant voltage. This generates some electricity captured by the silver wire by generating a potential difference (hydrogen-ion activity). The pH meter converts the voltage of this electric flow into a pH value by comparing the generated voltage to the reference electrode.

Increasing the solution's acidity results in a higher concentration of hydrogen ions, which raises the voltage. The pH measurement on the pH meter decreases due to the increased voltage. Similar to how an increase in alkalinity reduces hydrogen ions, an increase in the concentration of hydroxyl ions also reduces the voltage and raises the pH reading on a pH meter[92].

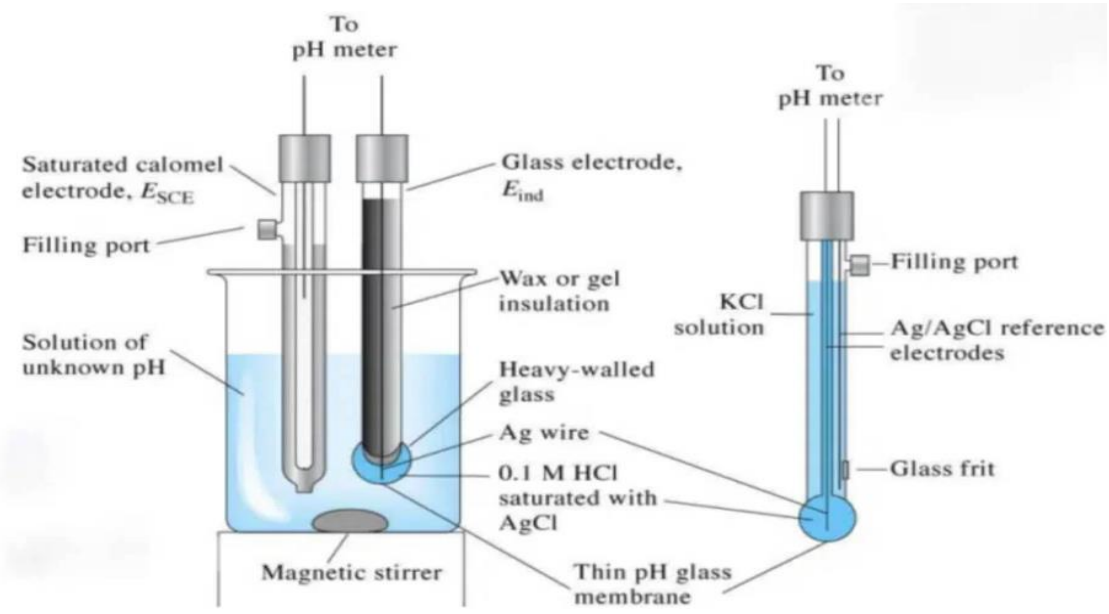


Figure (3.6) Parts of pH meter

- **A high input impedance meter**:

This is the key component that holds the microprocessor that processes extremely small electrode voltages and displays measurements in pH units on display. The microchip reads the pH of the solution, calculates the measurement temperature, and translates the amplifier voltage value.

- **The combined electrode:**

It consists of two electrodes, where the actual measurement takes place. It is the most expensive, sensitive, and consumable component of the meter and needs to be handled carefully. A reference electrode and a measuring electrode or sensor electrode, both submerged in the same solution, make up the combination electrode. The reference electrode must have a defined stable voltage independent of the measured solution to produce a defined pH value.

Reference electrode: A reference electrode is made up of a reference material (such as mercury, mercury chloride, or a saturated solution of Potassium chloride) submerged in a specific electrolyte which needs to be interacting with the measured solution most frequently through a porous ceramic junction, have a low electrical resistance due to a high ion concentration and adequate stability across a broad temperature range. It has a known and constant potential.

pH glass electrode: It is a glass bulb sensitive to hydrogen ions, and when the relative concentration of hydrogen ions within and outside the bulb changes, so does the millivolt output. It is also known as a sensor electrode or indicator electrode.

- **Amplifier**:

An amplifier, also known as a voltage amplifier, plays a vital role in measuring pH value. The amplifier will increase the accuracy of the pH reading in the same way that a thermometer increases calculations concerning temperature. To precisely measure the amount of acidity, basicity, and neutrality in a solution, this component will ensure that the voltage count is in the pH range of 0–14.

- **Thermometer probe**

Some pH meters can measure the temperature of the solution being sampled and incorporate that information into the meter reading (the temperature of

the solution directly influences pH). This feature is termed “Automatic Temperature Compensation (ATC)”[92].

3) CONDUCTIVITY METER: (Wissenschaftlisch Technisch Werkatten WTW Germany Ser-No01120020):

Conductivity is a measure of how well a solution conducts electricity. To carry a current a solution must contain charged particles, or ions. Most conductivity measurements are made in aqueous solutions, and the ions responsible for the conductivity come from electrolytes dissolved in the water. Salts (like Sodium chloride and Magnesium sulphate), acids (like hydrochloric acid and acetic acid), and bases (like Sodium hydroxide and ammonia) are all electrolytes. Although water itself is not an electrolyte, it does have a very small conductivity, implying that at least some ions are present. The ions are hydrogen and hydroxide, and they originate from the dissociation of molecular water. Conductivity is not specific. It measures the total concentration of ions in solution. It cannot distinguish one electrolyte or ion from another. Not all aqueous solutions have conductivity. Solutions of non-electrolytes, for example sugar or alcohol, have no conductivity because neither sugar nor alcohol contain ions nor do they produce ions when dissolved in water.

The units of conductivity are siemens per cm (S/cm). Derived units are µS/cm (one millionth of a S/cm) and mS/cm (one thousandth of a S/cm). S/cm is the same as the older unit mho/cm [93].

- **measurement of conductivity**:

There are two types of conductivity measurement: contact and inductive. The choice of which to use depends on the amount of conductivity, the corrosiveness of the liquid, and the amount of suspended solids. Generally, the inductive method is better when the conductivity is high, the liquid is corrosive, or suspended solids are present[94]

- **Contacting Conductivity:**

Most contacting conductivity sensors consist of two metal electrodes, usually stainless steel or titanium, in contact with the electrolyte solution. See Figure (3.7) The analyser applies an alternating voltage to the electrodes. The electric field causes the ions to move back and forth producing a current. Because the charge carriers are ions, the current is called an ionic current. The analyser measures the current and uses Ohm's law to calculate the resistance of the solution (resistance = voltage/current). The conductance of the solution is the reciprocal of the resistance. The ionic current depends on the total concentration of ions in solution and on the length and area of the solution through which the current flows. The current path is defined by the sensor geometry, or cell constant, which has units of 1/cm (length/area).

Multiplying the conductance by the cell constant corrects for the effect of sensor geometry on the measurement. The result is conductivity, which depends only on the concentration of ions[95].

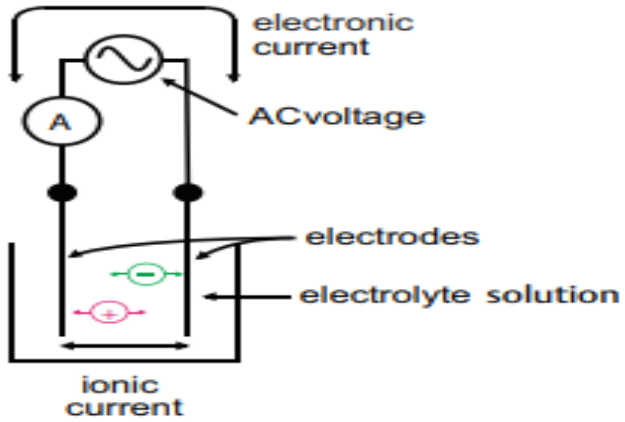


Figure (3.7) measurement of the two electrode conductivity

- **Inductive Conductivity:**

Inductive conductivity is sometimes called toroidal or electrodeless conductivity. An inductive sensor consists of two wire-wound metal toroids encased in a corrosion-resistant plastic body. One toroid is the drive coil, the other is the receive coil. The sensor is immersed in the conductive liquid. The analyser applies an alternating voltage to the drive coil, which induces a voltage in the liquid surrounding the coil. The voltage causes an ionic current to flow proportional to the conductance of the liquid. The ionic current induces an electronic current in the receive coil, which the analyser measures. The induced current is directly proportional to the conductance of the solution. See Figure (3.8). For accurate results, the user must calibrate

the sensor in place in the process piping. inductive sensors are ideal for measuring solutions having high conductivity. High conductivity solutions produce a large, easily measured induced current in the received coil. Inductive sensors do have drawbacks. Chiefly, they are restricted to samples having conductivity greater than about 15 µS/cm. They cannot be used for measuring low conductivity solutions[96]

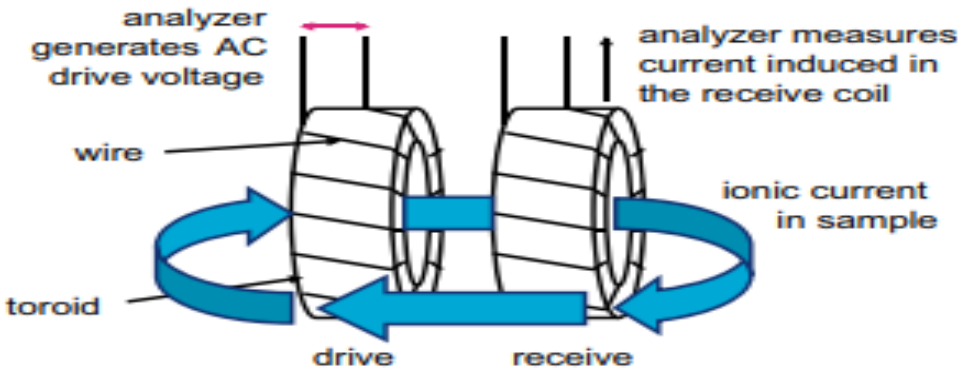


Figure (3.8) Both coils are encased in a single sensor body and over molded with plastic. The coils must be completely submerged in the process liquid.

3.2 Preparation of aqueous standard solutions:

Aqueous buffer solutions have been prepared of dilution of standard concentrated stock solutions as follows**:**

The standard solutions were Prepared daily by diluting stock solution according to Moore's law to prepare solutions $N*V=N_1*V_1$ where Initially, a standard solution of 100mg L^{-1} for each element was prepared, take 10 mL

of the mother standard solution in a 100 mL volumetric flask, and complete the volume with deionized distilled water.

The calibration blank and std. prepared for each element as shown in the following figures (3.9-3.16).

3.2.1 Calibration curves of standard solutions for the studied elements:

Typical calibration curves for the studied items were linear and passed through the origin. The following figures show typical calibration graphs where the Correlation coefficient ranges from 1.0000 to 0.99915.

The calibration curve for all trace elements was prepared, the analytical properties were showed in figures (3.9- 3.16), The elements were analyzed by the ICP.OES, Calibration at levels (0.0, 0.1, 0.5, 1.0, 5.0, 10.0) was presented in tables (3.2-3.9).

3.2.2Calibration curve of Magnesium Standard:

Mg (279.553nm), Intensity = 839284.65396464* concentration+ 7007.67848390

Correlation coefficient: 0.99994

Standards	Intensity	Method concentration	Calculated concentration	% Error
Blank	**2674.44**	**0.00**	**-0.01**	**N/A**
Standard1	**92305.16**	**0.10**	**0.10**	**1.63**
Standard2	**420752.51**	**0.50**	**0.49**	**1.41**
Standard3	**824063.67**	**1.00**	**0.97**	**2.65**

Table (3.2)Magnesium Standard Calibration

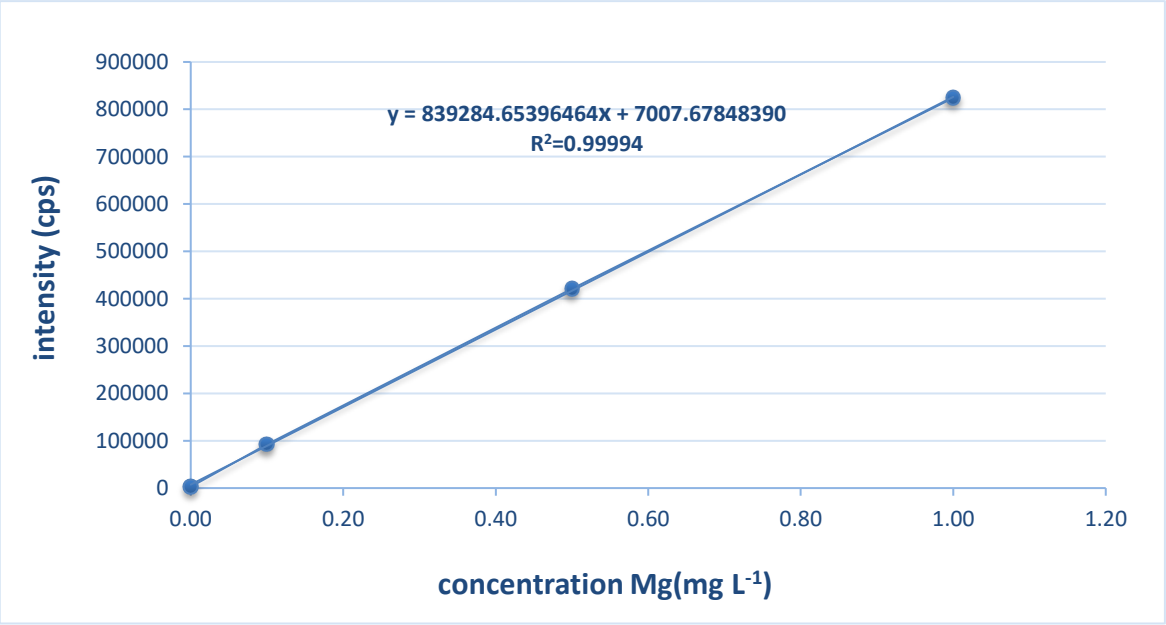


Figure (3.9) Calibration curve of Magnesium Standard

3.2.3 Calibration curve of Arsenic Standard:

As (193.696 nm)

Intensity = 1699.18330845* concentration+ 18.20972296

Correlation coefficient: 0.99915

Standards	Intensity	Method concentration	Calculated concentration	% Error
Blank	**12.37**	**0.0**	**0.00**	**N/A**
Standard1	**188.41**	**0.10**	**0.10**	**0.17**
Standard2	**876.92**	**0.50**	**0.51**	**1.07**
Standard3	**1719.97**	**1.00**	**1.00**	**0.15**
Standard4	**8841.10**	**5.00**	**5.19**	**3.85**
Standard5	**16251.94**	**10.00**	**9.55**	**4.46**

Table (3.3)Arsenic Standard Calibration

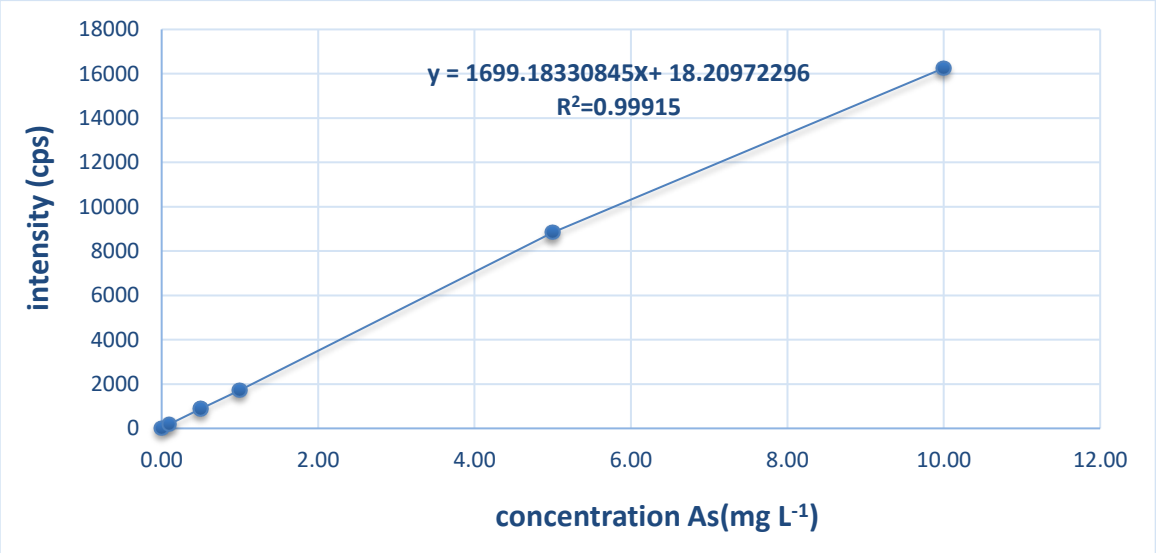


Figure (3.10) Calibration curve of Arsenic Standard

3.2.4 Calibration curve of Potassium Standard:

K (766.491 nm)

Intensity = 2833.33596844* concentration+ 611.54298861

Correlation coefficient: 1.00000

Standards	Intensity	Method concentration	Calculated concentration	% Error
Blank	**654.09**	**0.00**	**0.02**	**N/A**
Standard2	**2024.43**	**0.50**	**0.50**	**0.27**
Standard3	**3486.92**	**1.00**	**0.01**	**1.48**
Standard4	**14785.91**	**5.00**	**5.00**	**0.05**
Standard5	**28926.82**	**10.00**	**9.99**	**0.06**

Table (3.4) Potassium Standard Calibration

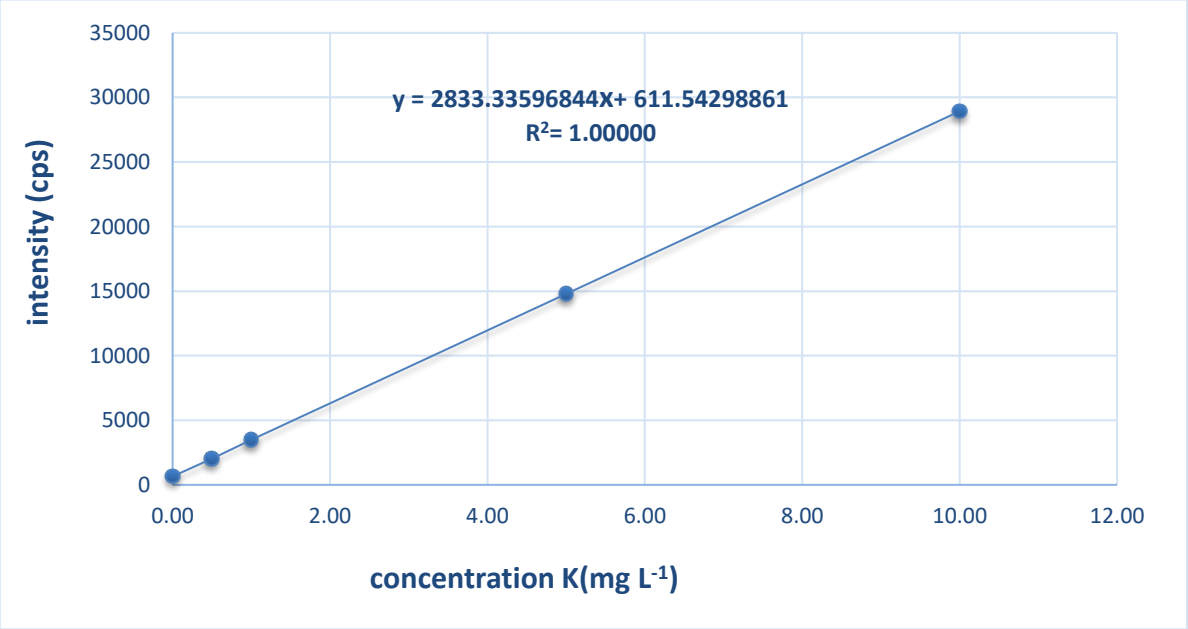


Figure (3.11) Calibration curve of Potassium Standard

3.2.5 Calibration curve of Chromium Standard:

Cr (267.716 nm)

Intensity = 57054.64201526* concentration+ 5.50158590

Correlation coefficient: 1.00000

standards	intensity	Method concentration	Calculated concentration	% Error
blank	**5.38**	**0.00**	**0.00**	**N/A**
Standard2	**28533.88**	**0.50**	**0.50**	**0.00**
Standard3	**57027.95**	**1.00**	**1.00**	**0.06**

Table (3.5) Chromium Standard Calibration

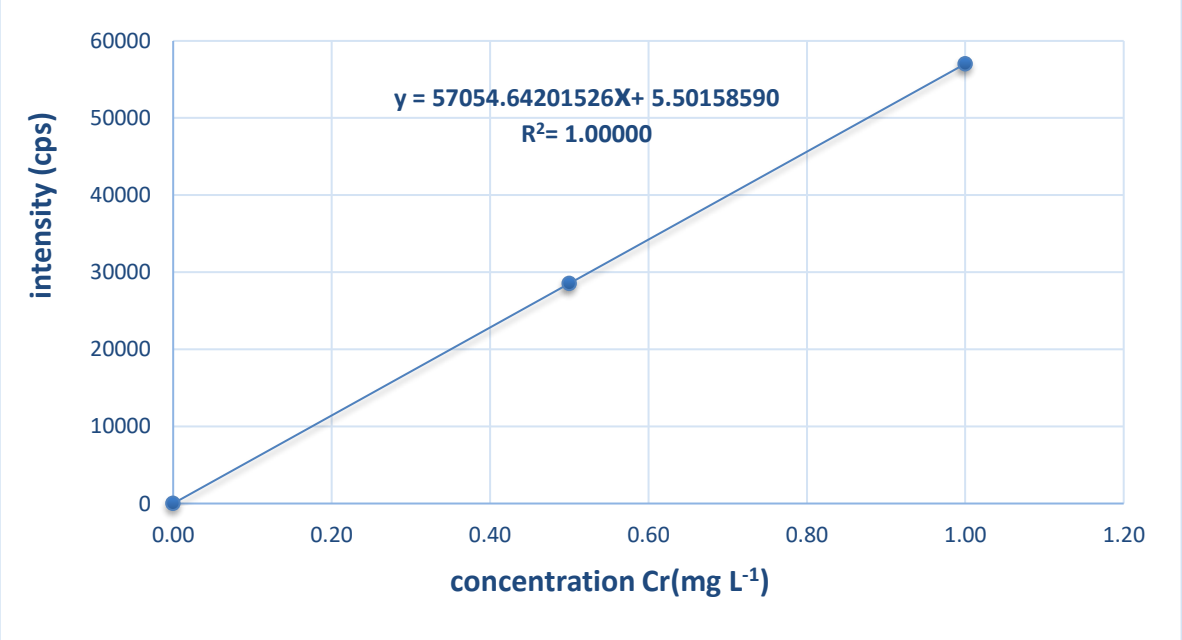


Figure (3.12) Calibration curve of Chromium Standard

3.2.6 Calibration curve of Iron Standard:

Fe (259.940 nm)

Intensity = 26098.78860402* concentration+ 61.66332987

Correlation coefficient: 0.99999

Standards	intensity	Method concentration	Calculated concentration	% Error
Blank	**31.13**	**0.00**	**0.00**	**N/A**
Standard1	**2766.35**	**0.10**	**0.10**	**3.63**
Standard2	**13311.07**	**0.50**	**0.51**	**1.53**
Standard3	**26284.07**	**1.00**	**1.00**	**0.47**
Standard4	**128993.12**	**5.00**	**4.94**	**1.20**

Table (3. 6) Iron Standard Calibration

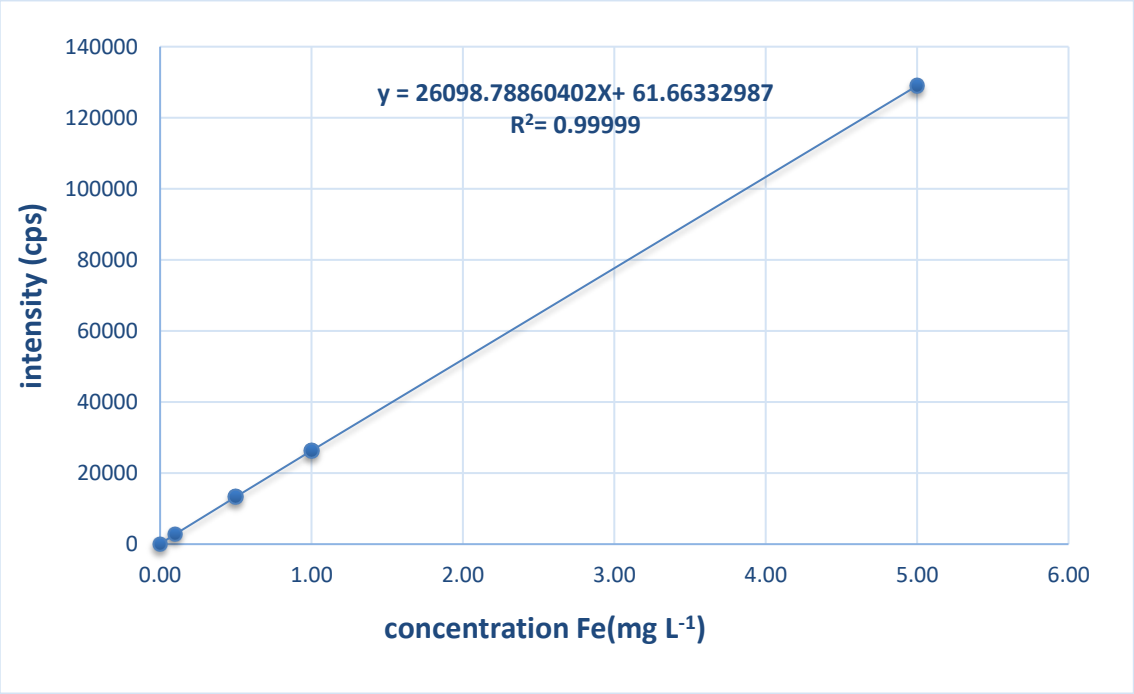


Figure (3.13) Calibration curve of Iron Standard

3.2.7 Calibration curve of Cobalt Standard:

Co (238.892 nm)

Intensity = 17034.69671769* concentration+ 112.28409541

Correlation coefficient: 0.99998

standards	intensity	Method concentration	Calculated concentration	% Error
blank	20.19	0.00	-0.01	N/A
Standard1	1820.90	0.10	0.10	0.30
Standard2	8567.91	0.50	0.50	0.72
Standard3	17156.58	1.00	1.00	0.06
Standard4	83145.72	5.00	4.87	2.51

Table (3.7) Cobalt Standard Calibration

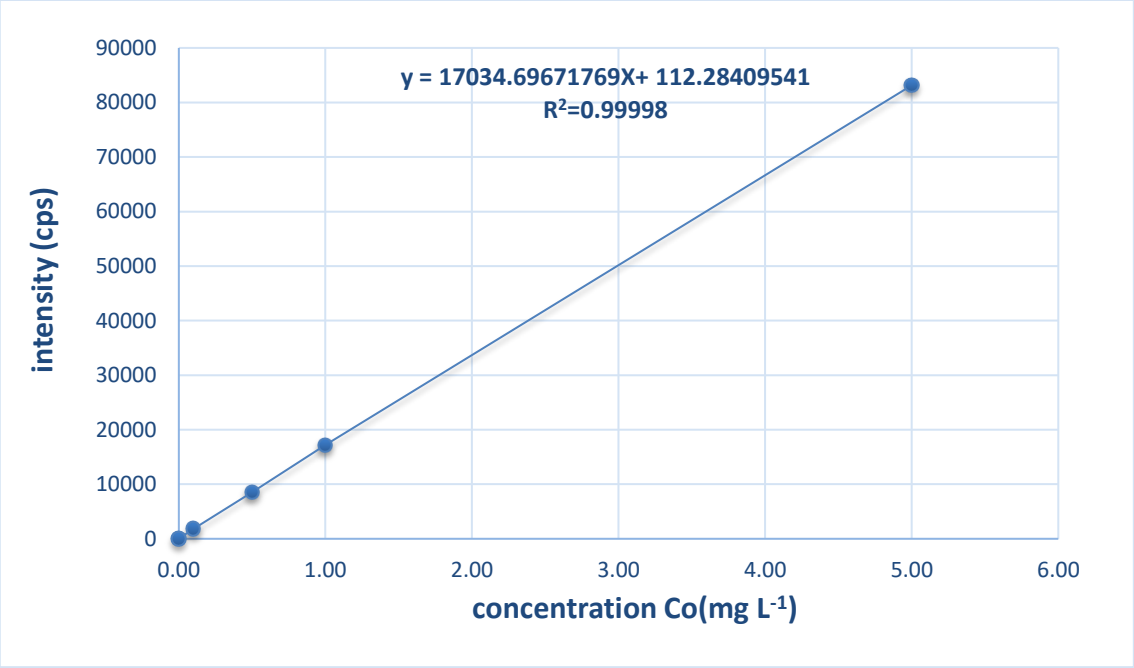


Figure (3.14) Calibration curve of Cobalt Standard

3.2.8 Calibration curve of Cadmium Standard

Cd (228.802 nm)

Intensity = 36941.59417594* concentration+ 23.91741738

Correlation coefficient: 0.99972

standards	Intensity	Method concentration	Calculated concentration	% Error
blank	**23.81**	**0.00**	**0.00**	**N/A**
Standard2	**18970.57**	**0.50**	**0.51**	**2.58**
Standard3	**38076.99**	**1.00**	**1.03**	**3.01**
Standard4	**185751.00**	**5.00**	**5.03**	**0.55**
Standard5	**354350.95**	**10.00**	**9.59**	**4.08**

Table (3.8) Cadmium Standard Calibration

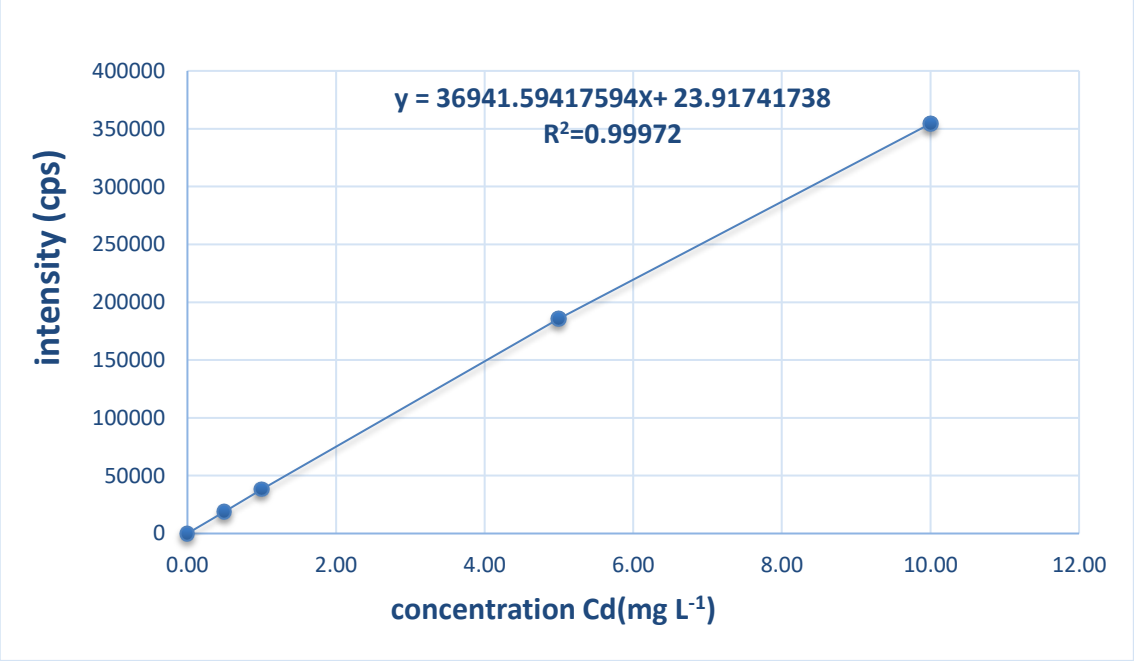


Figure (3.15) Calibration curve of Cadmium Standard

3.2.9 Calibration curve of Lead Standard:

Pb (217.000 nm)

Intensity = 862.32413115* concentration+ 13.23426941

Correlation coefficient: 0.99999

standards	intensity	Method concentration	Calculated concentration	% Error
Blank	13.60	0.00	0.00	N/A
Standard1	99.98	0.10	0.10	0.59
Standard2	443.78	0.50	0.50	0.14
Standard3	890.80	1.00	1.02	1.77
Standard4	4342.22	5.00	5.02	0.40
Standard5	8607.49	10.00	9.97	0.34

Table (3.9) Lead Standard Calibration

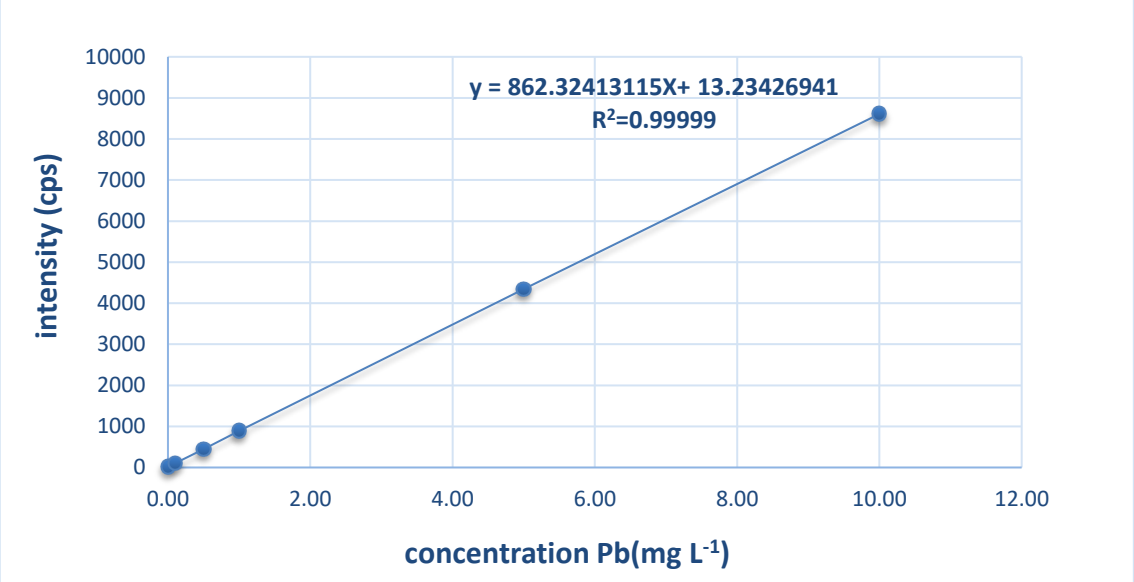


Figure (3.16) Calibration curves of Lead Standard

3.3. Physical tests of samples:

3.3.1. preparation of the Sample:

The hair dyes were prepared as indicated in the leaflets attached to each dye. Approximately 1.5 g of each dye was taken into test tubes, diluted to 25 ml with deionized water, closed tightly, agitated for 2 minutes and left for 4 days. After samples were prepared, pH, TDS, electrical conductivity and SAL were measured and the results were recorded at 22°C.

Figure (3.17) Physical tests of samples

Chapter IV

RESULTS & DISCUSSION

RESULTS and DISCUSSION.

4.1 Results:

The experiments were focused on the determination of elements in hair dyes.

Table No (4.5) shows the concentrations of trace elements in all hair dyes represented in Figures (4.5-4.9). The analytical data of the measuring conductivity pH, TDS, electrical conductivity and SAL were presented in tables No (4.1 - 4.4).

4.2 Physical tests of samples

4.2.1. Conductivity(σ) values results:

We note that the conductivity values of samples (S19) were the highest in the results with a conductivity value higher than 5720 µs /cm, while those of samples (S8, S9, S15, S17 and S18) were much lower because they were less than 1000 µs /cm in the samples, As shown in TABLE (4.1). The remaining values were approximately close to each other, This is attributed to the difference in the amounts of dissolved ions present in the dye solution.

NO	σ µs/cm
S1	1156
S2	1288
S3	/
S4	2590
S5	2320
S6	/
S7	1665
S8	845
S9	730
S10	3700
S11	2570

NO	σ µs/cm
S12	2870
S13	1370
S14	2330
S15	649
S16	2020
S17	702
S18	430
S19	5720
S20	1155
S21	1541
S22	2410
S23	1337

TABLE (4. 1) σ Conductivity test of samples at 22 T/C^{O} :

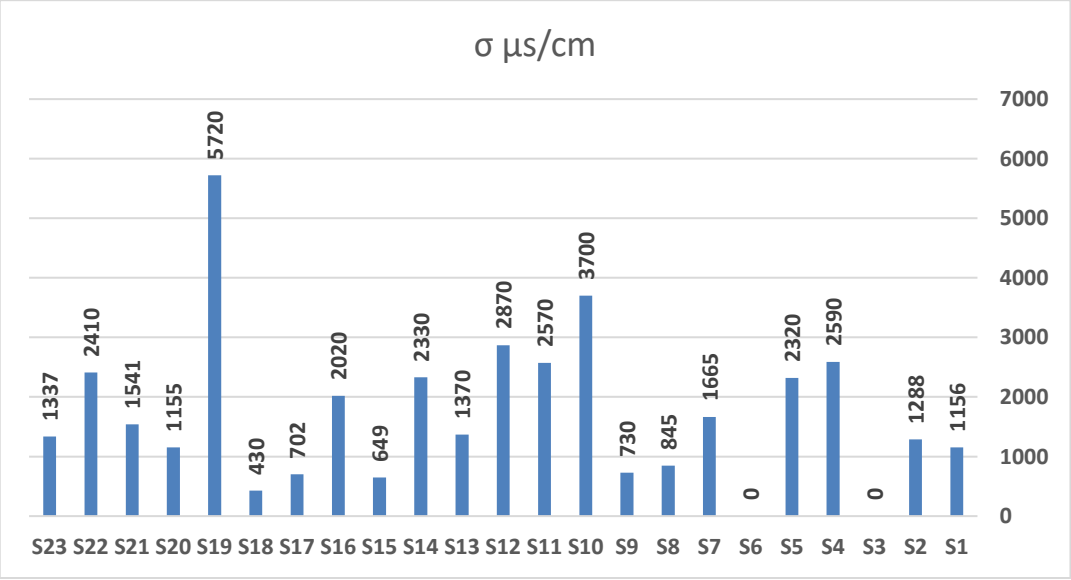


Figure (4.1) Conductivity Physical test of samples. at 22 T/ C^{O}

4.2.2 pH value results

The samples (S20, S21, S22, S23) had a pH ranging between (4.05-4.57) as it is the closest to the natural pH of the scalp which is between (4.5-5.5) and in the sample (S19) it was the highest number among all the samples with a pH number(10.05), and the rest of the samples ranged between (7.1-9.57) as shown in Table(4.2), since these high values are not good for the scalp The head causes problems such as itching and eczema and is a suitable medium for the growth of bacteria and fungi on the scalp.

NO	pH at 25CO
S1	8.44
S2	9.19
S3	/
S4	9.13
S5	9.03
S6	/
S7	7.10
S8	8.50
S9	9.34
S10	7.61
S11	9.37

NO	pH at 25CO
S12	9.18
S13	7.10
S14	8.83
S15	9.52
S16	8.30
S17	9.34
S18	9.57
S19	10.05
S20	4.29
S21	4.57
S22	4.13
S23	4.05

TABLE (4. 2) pH Physical test of samples at 25 T/C^{O}

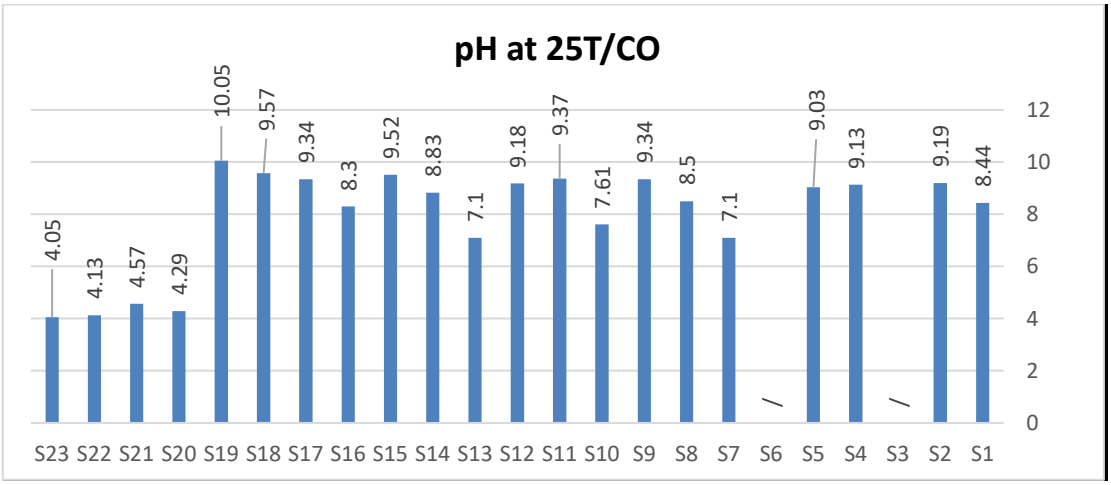


Figure (4.2) pH Physical test of samples at 25 T/ C^{O}

4.2.3 TDS value results:

TDS (Total dissolved solids) expresses the amount of organic and inorganic substances contained in a liquid, whether they are suspended substances in a molecular or ionic form. It was noticed from the results of the TDS measurement that the sample S19 was the highest at 8005mg/l and it is classified as one of the very high solutions in the TDS scale, while the samples S9, S15, S17, S18 are considered averages in concentration TDS because they are less than 800mg/l, while the rest of the samples range between (840-4050mg/l)[97]where this value is considered high in the sample solutions as shown in the TABLE (4.3).

NO	TDS mg/l
S1	1116
S2	1310
S3	/
S4	2820
S5	20580
S6	/
S7	1630
S8	840
S9	717
S10	4050
S11	3445

NO	TDS mg/l
S12	3750
S13	1370
S14	2900
S15	639
S16	1950
S17	705
S18	426
S19	8005
S20	1136
S21	1515
S22	2600
S23	1326

Table (4. 3)TDS Physical test of samples at 22.5 T/C^{O}

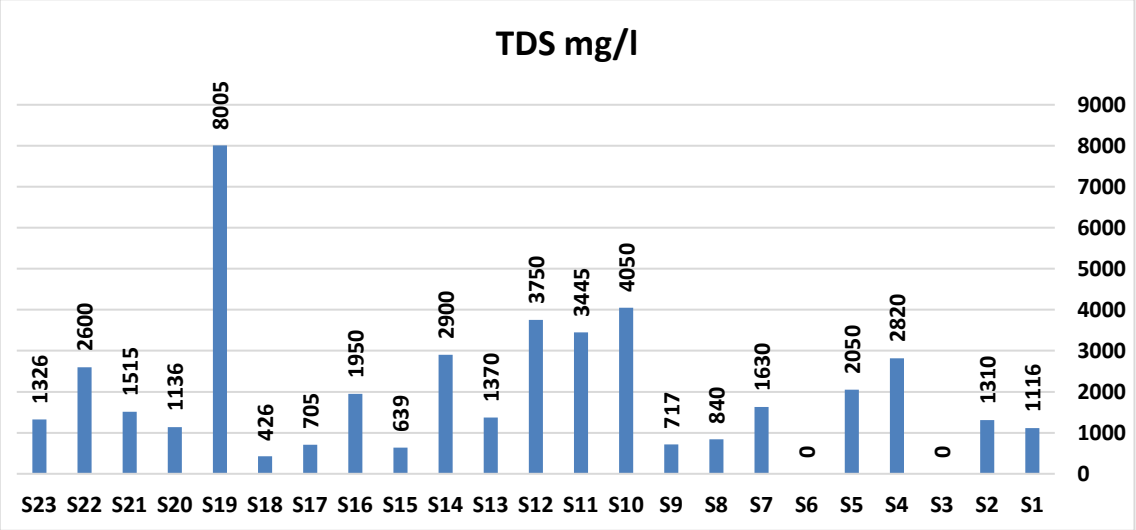


Figure (4.3) TDS Physical test of samples at 22.5 T/ C^{O}

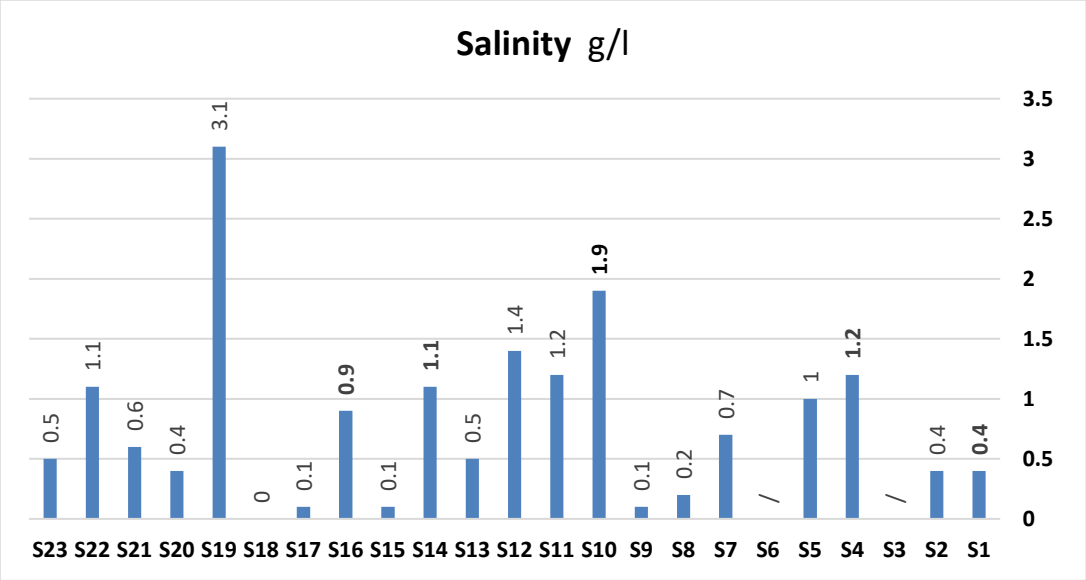
4.2.4 Salinity value results:

Sample (S19) had the largest salinity value of (3.1 g/l), which is considered a high value compared to the rest of the samples, and sample (S18) had a very low salinity value by a value by a value (0.0g/l), while the rest of the samples ranged (0.1-1.9g/l) As shown in Table (4.4), It is considered a harmless value for the scalp, but a high value causes problems such as itching and hair loss due to high salinity.

NO	SAL g/l
S1	0.4
S2	0.4
S3	/
S4	1.2
S5	1.0
S6	/
S7	0.7
S8	0.2
S9	0.1
S10	1.9
S11	1.2

NO	SAL g/l
S12	1.4
S13	0.5
S14	1.1
S15	0.1
S16	0.9
S17	0.1
S18	0.0
S19	3.1
S20	0.4
S21	0.6
S22	1.1
S23	0.5

TABLE (4. 4) Salinity Physical test of samples at 22.5 T/C^{O}



Figure(4.4) Salinity Physical test of samples at 22.5 T/ C^{O}

4.3. Trace elements concentration of hair dyes:

4.3.1 Iron concentration:

The determination of the Iron in the samples presented in figure (4.5) showed that the Iron concentrations ranged from (0.05 - 62.2) mg L^{-1} in different colours and brands. The highest percentage of Iron was in the sample of S23, and in general, the four Henna dyes S20, S21, S22 and S23 had the highest percentage of Iron compared to the rest of the dyes (9.06, 40.35, 44.1, 62.2 mg L^{-1}), respectively. The samples (S2, S3, S4, S9, S11, S13, S14, S18) with concentrations (0.09, 0.05, 0.07, 0.08, 0.07, 0.09, 0.07, 0.09 mg L^{-1}) respectively, had very low concentrations and their value been less than the internationally permissible value. Vomiting, dizziness, nausea, loss of appetite, severe headache, and sudden weight loss are some of the complications of Iron overload. High levels of Iron increase the risk of cancer through the rapid stimulation of oxygen radicals in cells[98].

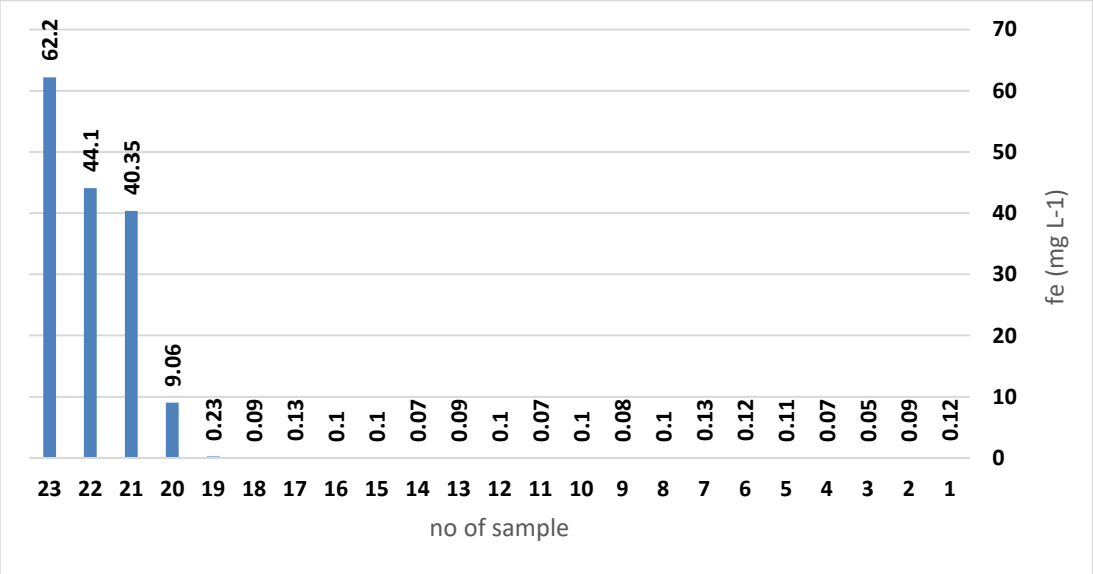


Figure (4.5) The concentrations of the Iron metal in studied hair dyes

4.3.2 Chromium concentration:

The results showed that the maximum concentration of Cr was determined in sample (S5) (0.07 mg L^{-1}), and the concentration of Chromium

in one sample (S11) with a concentration (<0.001 mg L^{-1}) of Hair dye level was less than the detectable limit. and nearly the rest of the samples results were similar in concentrations, As shown in the Figure (4.6). however, Cr was within the safe limit of 50 mg/kg set by the Food and Drug Administration[99].

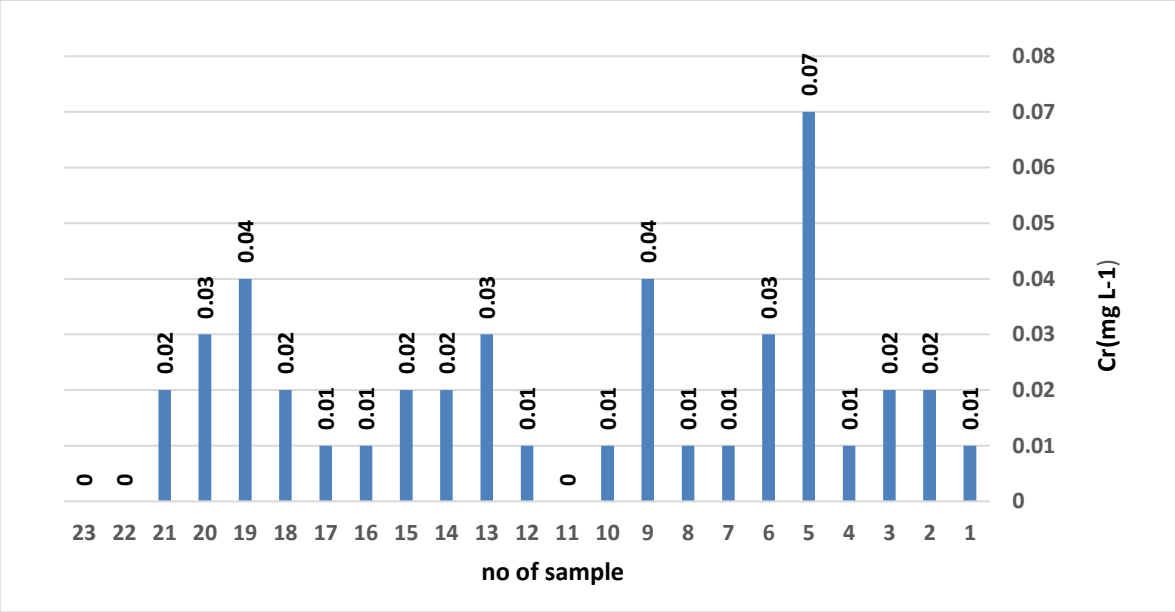


Figure (4.6) The concentrations of the Chromium metal in studied hair dyes

4.3.3 Potassium Concentration:

Potassium results ranged between (0.35-95.9 mg L^{-1}), and the highest concentration of Potassium was in the samples (S10 , S11 and S12) (95.9-95.4-73.5 mg L^{-1}), respectively, as these concentrations were for the same brand of product with its three colours (blond, red and black), which are considered very high concentrations compared to other samples of hair dyes, and the Samples (S8 and S9) with concentrations (0.35 and0.37 mg L^{-1})

respectively, have very low concentrations and their value is less than the internationally permissible value As shown in Figure (4.7)

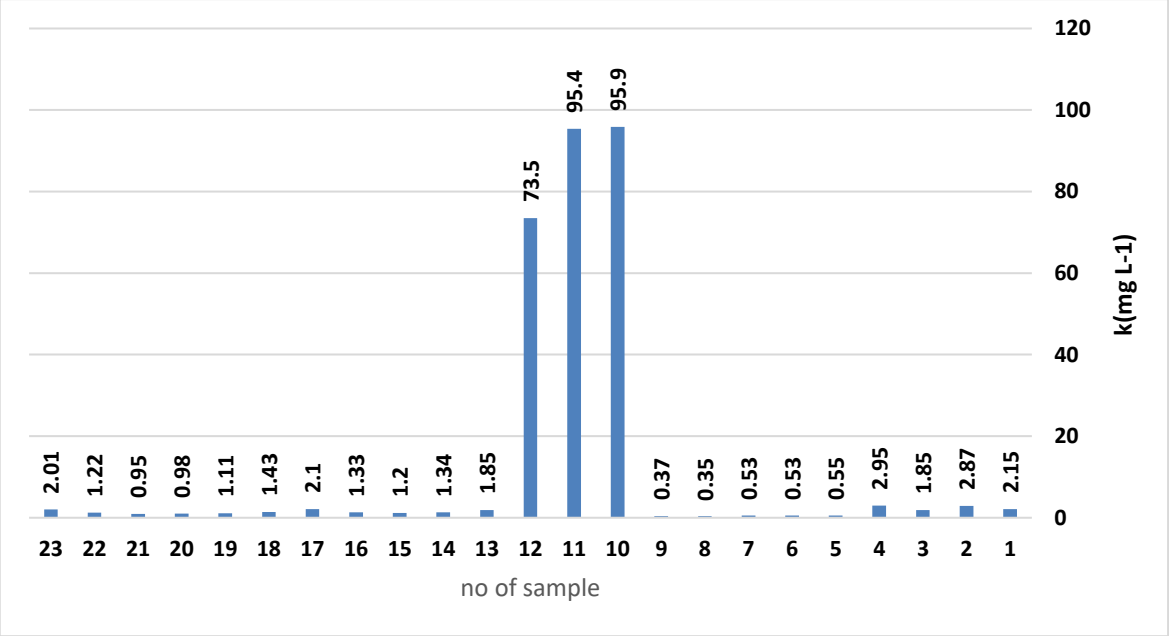


Figure (4.7) The concentrations of the Potassium metal in studied hair dyes

4.3.4 Magnesium Concentration:

Magnesium results ranged between (0.09-71.4 mg L^{-1}). Where the highest concentrations were in samples (S19, S20, S21, S22 and S23) (54.3-59.1-63.1-62.4-71.4 mg L^{-1}) respectively, which is a very high percentage compared to the rest of the other samples, the Samples (S3) with concentrations (0.09 mg L^{-1}) have very low concentration and their value is less than the internationally permissible value, As shown in Figure (4.8).

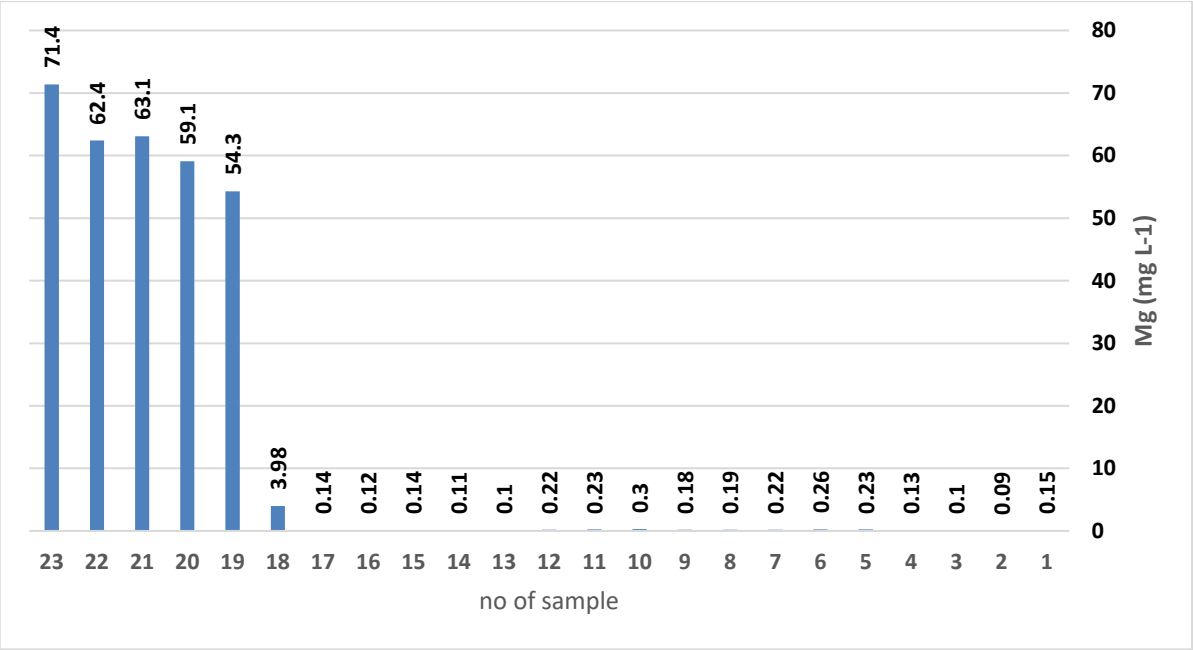


Figure (4.8) The concentrations of the Magnesium metal in studied hair dyes

4.3.5 Stannum (Tin) concentration:

The results of Sn ranged between (0.15-1.28 mg L^{-1}), where the highest concentrations were in samples (S16, S9, S12 and S3) (1.28, 1.21, 1.19 and1.05mg L^{-1}) compared to the rest of the samples which are higher concentrations than permitted internationally, and the Samples (S20, S21, S22, S23) with concentrations (0.15, 0.16, 0.17, 0.19mg L^{-1}) respectively, have very low concentrations and their value is less than the internationally permissible value, As shown in Figure (4.9), Unfortunately, no guidelines on the element tin in hair dyes.

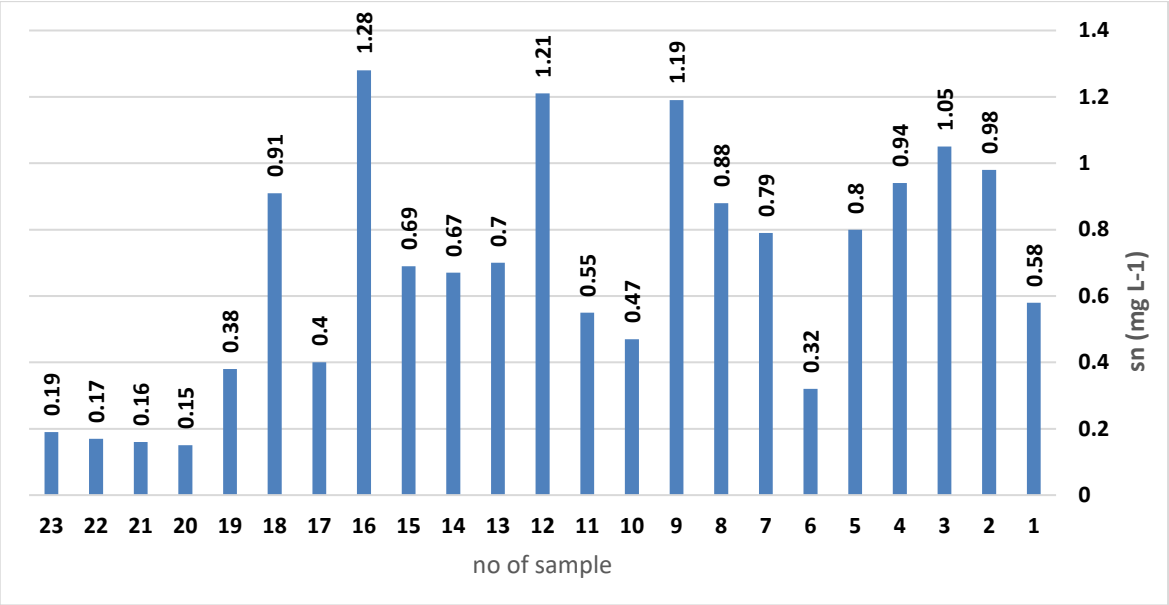


Figure (4.9) The concentrations of the stannum metal in studied hair dyes

4.3.6 Lead, Cadmium, Cobalt and Arsenic concentration:

The elements Lead, Cadmium, Cobalt and Arsenic when measured, found that their concentration were below the detection limits of the device and this is good for hair dyes, As for Arsenic, there is no guidelines on its concentration in hair dyes.

- **Co** detection limit was below <0.001The limit allowed globally 0.002 mg L^{-1} [100]
- **Cd** detection limit was below <0.01The limit allowed globally 0.0003 mg L^{-1} [101].
- **Pb** detection limit was below <0.003 The limit allowed globally 0.3 mg L^{-1} [101]
- **As** detection limit was below <0.02 The limit allowed globally 0.04 mg L^{-1} [101]

NO	Fe mg L^{-1}	Cr mg L^{-1}	K mg L^{-1}	Mg mg L^{-1}	Sn mg L^{-1}	Co mg L^{-1}	Cd mg L^{-1}	Pb mg L^{-1}	As mg L^{-1}
1	0.12	0.01	2.15	0.15	0.58	<0.001	<0.01	<0.003	<0.02
2	0.09	0.02	2.87	0.09	0.98	<0.001	<0.01	<0.003	<0.02
3	0.05	0.02	1.85	0.10	1.05	<0.001	<0.01	<0.003	<0.02
4	0.07	0.01	2.95	0.13	0.94	<0.001	<0.01	<0.003	<0.02
5	0.11	0.07	0.55	0.23	0.80	<0.001	<0.01	<0.003	<0.02
6	0.12	0.03	0.53	0.26	0.32	<0.001	<0.01	<0.003	<0.02
7	0.13	0.01	0.53	0.22	0.79	<0.001	<0.01	<0.003	<0.02
8	0.10	0.01	0.35	0.19	0.88	<0.001	<0.01	<0.003	<0.02
9	0.08	0.04	0.37	0.18	1.19	<0.001	<0.01	<0.003	<0.02
10	0.10	0.01	95.9	0.30	0.47	<0.001	<0.01	<0.003	<0.02
11	0.07	<0.001	95.4	0.23	0.55	<0.001	<0.01	<0.003	<0.02
12	0.10	0.01	73.5	0.22	1.21	<0.001	<0.01	<0.003	<0.02
13	0.09	0.03	1.85	0.10	0.70	<0.001	<0.01	<0.003	<0.02
14	0.07	0.02	1.34	0.11	0.67	<0.001	<0.01	<0.003	<0.02
15	0.10	0.02	1.20	0.14	0.69	<0.001	<0.01	<0.003	<0.02
16	0.10	0.01	1.33	0.12	1.28	<0.001	<0.01	<0.003	<0.02
17	0.13	0.01	2.10	0.14	0.40	<0.001	<0.01	<0.003	<0.02
18	0.09	0.02	1.43	3.98	0.91	<0.001	<0.01	<0.003	<0.02
19	0.23	0.04	1.11	54.3	0.38	<0.001	<0.01	<0.003	<0.02
20	9.06	0.03	0.98	59.1	0.15	<0.001	<0.01	<0.003	<0.02
21	40.35	0.02	0.95	63.1	0.16	<0.001	<0.01	<0.003	<0.02
22	44.1	<0.02	1.22	62.4	0.17	<0.001	<0.01	<0.003	<0.02
23	62.2	<0.02	2.01	71.4	0.19	<0.001	<0.01	<0.003	<0.02
SD	12.423	0.0157	30.791	23.489	0.3444	0.000	0.000	0.000	0.000

TABLE (4. 5) Trace elements concentration

5. Suggestions and Recommendations:

- Strict laws must be put in place to limit the acceptable limit of potential pollutants and toxic substances in Cosmetics and skin care products by international bodies and organizations in general the local concerned authorities and the control center, in particular, taking into account the difference in the toxicity of metals among them.
- Imposing good manufacturing rules for local factories to apply hair dyes
- Monitoring cosmetic products including hair dyes and others imported or manufactured locally and present in the Libyan market by taking random samples by the concerned authorities and conducting periodic checks on them.
- Awareness that the price of the product is a mold that is related to its quality, and therefore not to be reckless in buying such These inexpensive products may be harmful to the body if applied frequently and permanently to the skin.
- Spreading a culture of awareness about the possibility and dangers of some toxic substances in cosmetic products.
- must protect children and pregnant women from exposure.

6. Conclusions:

Libya is one of the countries with a consumer market for cosmetics in the Arab world, Chemical hair dyes are among the most popular cosmetics in Libya, Since they are considered Trace elements are among the most important elements found in living organisms, but in very small proportions, and their high levels in the body may expose a person to health problems that vary according to their concentration in the body and the place of their accumulation, although there are not many studies on the heavy substance contamination of these products. In the present research, the most popular hair colours in Tripoli markets were analyzed in 23 samples to check for heavy metal contamination. Next, the health risks related to the consumption of these products were evaluated. The trace elements were measured in the samples from several brands of hair dyes, whereby each brand took three colours (blond, red and black), one sample of bleaching and four samples of Henna, by using concentrated acid, dyes samples were digested, and these samples were filtered, diluted, and sent to the device laboratory (ICP.OES) to complete the trace elements assessment process. The results recorded in this study showed that there was a discrepancy in the concentrations of trace elements, as the concentrations of trace elements were different according to the different types of dye, as it ranged in Chromium (0.07- <0.001mg L^{-1}), Potassium (0.35-95.9mg L^{-1}), Magnesium it ranged between (0.09-71.4mg

L^{-1}), Iron (0.05-62.2mg L^{-1}) and Sn (0.15-1.28mg L^{-1}) . But in the rest of the trace elements, they were not detected because of their very low concentrations below the device's ability to measure and they were As (<0.02mg L^{-1}), Co (<0.001mg L^{-1}), Cd (<0.01mg L^{-1}) and Pb (<0.003mg L-1), The standard deviation of the samples was (12.423, 0.0157, 30.791, 23.489, 0.344, 0.000, 0.000, 0.000, 0.000) for Fe, Cr, K, Mg, Sn, Co, Cd, Pb and As. for the physical results (conductivity, pH, TDS and salinity), the conductivity showed results that ranged between (430-5720µs/cm) and the results of pH were between (4.05-10.05) and the results of TDS were between (426-8005mg/l) and the results of salinity were also between (0-1.9mg/l).

7. Summary:

The US Food and Drug Administration defines cosmetics as substances that are applied to the human body for the purpose of purifying, enhancing its attractiveness, beautifying it, or changing its appearance. This includes a large number of products, including hair dyes, which have become an integral part of the daily life of modern man, and their routine application and use begin after a certain period. These preparations usually consist of a mixture of chemical compounds derived from natural or industrial sources that are not without the slight presence of some toxic substances resulting from contamination of the components or from pollution of the environment, which may adversely affect human health, such as carcinogenic, mutagenic or metallic substances. And due to the lack of sufficient studies on this subject in addition to the fact that heavy metals are toxic to the human body, especially if they are ingested or exposed continuously, this research was conducted on some hair dyes and Henna to determine the concentrations of some trace elements such as Chromium, Potassium, Magnesium, Iron, Stanium , Arsenic, Cobalt and Cadmium. The Lead in these products available in the Libyan market, where 23 samples of hair dyes were analysed, samples were taken from 11 brands of dyes of different colours (blond, red, black, Henna). 5 gm of Henna dye for each sample. The samples were digested and treated with concentrated nitric acid and highly purified acid

peroxide. The samples were filtered after digestion, diluted with deionized water and transported to the laboratory for analysis using the. ICP-OE device. Where the results of some samples such as Iron, Chromium, Potassium , Magnesium and Stanium were higher than the permissible limit, and some other trace elements such as Arsenic, Cobalt , Cadmium and Lead were less than the detectable limit, and the results of physical analyses of hair dye samples (conductivity, pH, TDS salinity), some of which were higher than the safe normal levels for the solutions. From the results as a whole, the samples for the studied dyes in general, in terms of trace elements, are not significantly dangerous to health, but in terms of physical, they may cause problems on the scalp in some samples.

7. الملخص:

تُعرّف إدارة الغذاء والدواء الأمريكية مستحضرات التجميل بأنها مواد يتم وضعها على جسم الإنسان بغرض تنقيته أو تعزيز جاذبيته أو تجميله أو تغيير مظهره. ويشمل ذلك عددًا كبيرًا من المنتجات، بما في ذلك صبغات الشعر، والتي أصبحت جزءًا لا يتجزأ من الحياة اليومية للإنسان الحديث، ويبدأ تطبيقها واستخدامها بشكل روتيني كل فترة معينة. تتكون هذه المستحضرات عادة من خليط من المركبات الكيميائية المشتقة من مصادر طبيعية أو صناعية لا تخلو من وجود طفيف لبعض المواد السامة الناتجة عن تلوث المكونات أو من تلوث البيئة، والتي قد تؤثر سلبًا على صحة الإنسان، مثل المواد المسببة للسرطان, والمواد المسببة لطفرات الجينية والمواد المعدنية السامه، ولعدم وجود دراسات كافية حول هذا الموضوع بالإضافة إلى حقيقة أن المعادن الثقيلة سامة لجسم الإنسان خاصة إذا تم تناولها أو تعرض لها بشكل مستمر، لذلك تم إجراء هذا البحث على بعض صبغات الشعر والحناء لتحديد كمية التركيزات لبعض العناصر النزرة مثل الكروم والبوتاسيوم والمغنيسيوم والحديد والقصدير والزرنيخ والكوبالت والكادميوم والرصاص في هذه المستحضرات المتوفرة في السوق الليبي, حيث تم تحليل 23 عينة من صبغات الشعر، أخذت عينات مكونة من 11 ماركة أصباغ مختلفة الألوان (أشقر، أحمر، أسود، حناء), طبقت طريقة الهضم الحمضي وهي عبارة عن وزن 1.0 جم لصبغات الشعر و0.5 جم لصبغات الحناء لكل عينة, تم هضم العينات ومعالجتها بحمض النيتريك المركز وتركيز بيروكسيد حامض عالي النقاوة, تم ترشيح العينات بعد الهضم وتخفيفها بمياه منزوعة الايونات ونقلها إلى المختبر لتحليلها باستخدام جهاز ICP-OES , حيث كانت نتائج بعض العينات مثل الحديد و الكروم والبوتاسيوم والمغنيسيوم والقصدير أعلى من الحد المسموح به وكانت بعض العناصر النزرة الأخرى مثل الزرنيخ والكوبالت والكادميوم والرصاص أقل من الحد القابل للكشف, كما أن نتائج تحاليل الفيزيائية لعينات صبغات الشعر(التوصيلية، الأس الهيدروجيني، المواد الصلبة الذائبة، الملوحة) كانت بعضها أعلى من المعدلات الطبيعية الأمنه للمحاليل. ومن النتائج ككل فإن

العينات للأصباغ المدروسة بصفه عامه من ناحية العناصر النزرة فهي ليست بالخطيرة على الصحة بشكل كبير وأما من ناحية الفيزيائية فهي في بعض العينات قد تسبب مشاكل على فروة الرأس.

.

References:

[1] J. J. Wecker, *Eighteen Books of the Secrets of Art & Nature: Being the Summe and Substance of Naturall Philosophy, Methodically Digested*. Simon Miller, 1978.

[2] H. Dye, 'How hair dye is made - ingredients of, making, used, parts, composition, product, industry', Accessed: [Online]. Available: http://www.madehow.com/Volume-3/Hair-Dye.html

[3] O. J. X. Morel and R. M. Christie, 'Current trends in the chemistry of permanent hair dyeing', *Chem Rev*, vol. 111, no. 4, pp. 2537–2561, Apr. 2011, doi: 10.1021/CR1000145.

[4] H. A. M. Ahmed, K. M. A. Al-Qahtani, H. Emara, M. N. Janjua, N. Alhafez, and M. B. Al-Otaibi, 'Determination of Some Heavy Metals in Eye Shadows Cosmetics.', *Asian Journal of Chemistry*, vol. 29, no. 7, 2017.

[5] M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew, and K. N. Beeregowda, 'Toxicity, mechanism and health effects of some heavy metals', *Interdiscip Toxicol*, vol. 7, no. 2, p. 60, 2014.

[6] B. Bocca, A. Pino, A. Alimonti, and G. Forte, 'Toxic metals contained in cosmetics: a status report', *Regulatory Toxicology and Pharmacology*, vol. 68, no. 3, pp. 447–467, 2014.

[7] P. UNION, 'Regulation (EC) No 1223/2009 of the european parliament and of the council', *Official Journal of the European Union L*, vol. 342, p. 59, 2009.

[8] E. Pehlić, H. Nanić, H. Jukić, and A. Aldžić, 'Determination of Heavy Metals in Hair Dyes by the Atomic Absorption Spectrophotometry', in *International Conference "New Technologies, Development and Applications"*, Springer, 2018, pp. 561–567.

[9] G. J. Nohynek, E. Antignac, T. Re, and H. Toutain, 'Safety assessment of personal care products/cosmetics and their ingredients', *Toxicol Appl Pharmacol*, vol. 243, no. 2, pp. 239–259, 2010.

[10] S. R. Rasool, W. Al-Dahhan, A. J. Al-Zuhairi, F. Hussein, K. E. Rodda, and E. Yousif, 'Fire and Explosion Hazards expected in a Laboratory', *J Lab Chem Educ*, vol. 4, no. PNNL-SA-118942, 2016.

[11] S. S. Deshpande, *Handbook of food toxicology*. CRC press, 2002.

[12] K. Chojnacka, H. Górecka, A. Chojnacki, and H. Górecki, 'Inter-element interactions in human hair', *Environ Toxicol Pharmacol*, vol. 20, no. 2, pp. 368–374, 2005.

[13] T. McIntyre, 'Phytoremediation of heavy metals from soils', *Phytoremediation*, pp. 97–123, 2003.

[14] E. O. Amartey, A. B. Asumadu-Sakyi, C. A. Adjei, F. K. Quashie, G. O. Duodu, and N. O. Bentil, 'Determination of heavy metals concentration in hair Pomades on the Ghanaian

market using atomic absorption spectrometry technique', *British Journal of Pharmacology and Toxicology*, vol. 2, no. 4, pp. 192–198, 2011.

[15] B. Djahed, M. Taghavi, M. Farzadkia, S. Norzaee, and M. Miri, 'Stochastic exposure and health risk assessment of rice contamination to the heavy metals in the market of Iranshahr, Iran', *Food and chemical toxicology*, vol. 115, pp. 405–412, 2018.

[16] G. J. Nohynek, R. Fautz, F. Benech-Kieffer, and H. Toutain, 'Toxicity and human health risk of hair dyes', *Food and Chemical Toxicology*, vol. 42, no. 4, pp. 517–543, 2004.

[17] G. A. Engwa, P. U. Ferdinand, F. N. Nwalo, and M. N. Unachukwu, 'Mechanism and health effects of heavy metal toxicity in humans', *Poisoning in the modern world-new tricks for an old dog*, vol. 10, 2019.

[18] J. E. Kim, H. D. Jung, and H. Kang, 'A survey of the awareness, knowledge and behavior of hair dye use in a Korean population with gray hair', *Ann Dermatol*, vol. 24, no. 3, pp. 274–279, 2012.

[19] J. F. Corbett, 'An historical review of the use of dye precursors in the formulation of commercial oxidation hair dyes', *Dyes and Pigments*, vol. 41, no. 1–2, pp. 127–136, 1999.

[20] U. N. Kashyap, V. Gupta, and H. V Raghunandan, 'Comparison of drug approval process in United States & Europe', *Journal of pharmaceutical sciences and research*, vol. 5, no. 6, p. 131, 2013.

[21] W. Bonefeld, 'Abstract labour: Against its nature and on its time', *Capital & Class*, vol. 34, no. 2, pp. 257–276, 2010.

[22] C. van Gorp, 'Toxicity of hair dyes in human keratinocytes Effects of Basic Yellow 57 in combination with Resorcinol and Hydrogen Peroxide', *MaRBLe*, vol. 2, 2014.

[23] A. Sinha, V. Ignatchenko, A. Ignatchenko, S. Mejia-Guerrero, and T. Kislinger, 'In-depth proteomic analyses of ovarian cancer cell line exosomes reveals differential enrichment of functional categories compared to the NCI 60 proteome', *Biochem Biophys Res Commun*, vol. 445, no. 4, pp. 694–701, 2014.

[24] B. Halliwell and J. M. C. Gutteridge, *Free radicals in biology and medicine*. Oxford university press, USA, 2015.

[25] L. David, T. Jardin, and A. Farcy, 'On the non-intrusive evaluation of fluid forces with the momentum equation approach', *Meas Sci Technol*, vol. 20, no. 9, p. 95401, 2009.

[26] 'Toxicological Profiles | ATSDR'. Accessed: Nov. 12, 2021. [Online]. Available: https://www.atsdr.cdc.gov/toxprofiledocs/index.html?id=96&tid=

[27] H. Ullah *et al.*, 'Comparative study of heavy metals content in cosmetic products of different countries marketed in Khyber Pakhtunkhwa, Pakistan', *Arabian Journal of Chemistry*, vol. 10, no. 1, pp. 10–18, 2017.

[28] R. Mayildurai, A. Ramasubbu, and N. Velmani, 'ICP–OES investigations of heavy metal contents in cosmetic products', *J. Pharm. Res*, vol. 9, pp. 27–30, 2015.

[29] M. Gago-Dominguez, J. E. Castelao, J. Yuan, M. C. Yu, and R. K. Ross, 'Use of permanent hair dyes and bladder-cancer risk', *Int J Cancer*, vol. 91, no. 4, pp. 575–579, 2001.

[30] U. S. D. of H. and H. Services, 'Agency for Toxic Substances and Disease Registry-ATSDR.', 1999.

[31] F. A. Barile, *Clinical toxicology: principles and mechanisms*. CRC Press, 2003.

[32] C. Sessa, C. Steuer, D. Quintero Balbas, G. Sciutto, S. Prati, and H. Stege, 'Analytical studies on commercial artists' colour charts from Das Deutsche Farbenbuch (1925)—identification of synthetic and natural organic colourants by Raman microscopy, surface-enhanced Raman spectroscopy and metal underlayer ATR-FTIR spectroscopy', *Herit Sci*, vol. 10, no. 1, pp. 1–19, 2022.

[33] U. A. Boelsterli, *Mechanistic toxicology: the molecular basis of how chemicals disrupt biological targets*. CRC press, 2002.

[34] G. F. Nordberg, B. A. Fowler, and M. Nordberg, *Handbook on the Toxicology of Metals*. Academic press, 2014.

[35] U. Atsdr, 'Toxicological profile for lead (Atlanta, GA: US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), Public Health Service)', *US EPA (2006) Air quality criteria for lead*, 2007.

[36] T. K. Dutta and V. Mukta, 'Trace elements', *Medicine*, vol. 22, pp. 352–357, 2012.

[37] G. Papanikolaou and K. Pantopoulos, 'Iron metabolism and toxicity', *Toxicol Appl Pharmacol*, vol. 202, no. 2, pp. 199–211, 2005.

[38] D. T. Del Rio, 'Biossorção de cádmio por leveduras Saccharomyces cerevisiae.' Universidade de São Paulo, 2004.

[39] M. Behl *et al.*, 'Comparative toxicity and carcinogenicity of soluble and insoluble cobalt compounds', *Toxicology*, vol. 333, pp. 195–205, 2015.

[40] J. F. Diehl, *Safety of irradiated foods*. CRC Press, 1995.

[41] G. J. Kullman, C. B. Doak, D. G. Keimig, R. J. Cornwell, and R. P. Ferguson, 'Assessment of respiratory exposures during gilsonite mining and milling operations', *Am Ind Hyg Assoc J*, vol. 50, no. 8, pp. 413–418, 1989.

[42] R. Alexandersson, 'Blood and urinary concentrations as estimators of cobalt exposure', *Archives of Environmental Health: An International Journal*, vol. 43, no. 4, pp. 299–303, 1988.

[43] L. R. Payne, 'The hazards of cobalt', *Occup Med (Chic Ill)*, vol. 27, no. 1, pp. 20–25, 1977.

[44] K. J. Irgolic and A. E. Martell, *Environmental inorganic chemistry*. Wiley-VCH, 1985.

[45] K. S. P. Kumar and E. C. N. Peter, 'Adsorption of chromium (vi) from aqueous solutions by different admixtures–a batch equilibrium test study', *J Eng Sci Technol*, vol. 9, no. 4, pp. 410–422, 2014.

[46] A. D. Dayan and A. J. Paine, 'Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000', *Hum Exp Toxicol*, vol. 20, no. 9, pp. 439–451, 2001.

[47] U. EPA, 'Toxicological review of hexavalent chromium', *Washington, DC*, 1998.

[48] G. F. Nordberg, B. A. Fowler, M. Nordberg, and L. T. Friberg, 'Handbook on the Toxicology of Metals (2007)'. Academic Press, 2011.

[49] R. Flegal, J. Last, E. McConnell, M. Schenker, and H. Witschi, 'Scientific review of toxicological and human health issues related to the development of a public health goal for chromium (VI)', *Chromate toxicity review committee, Sacramento, Available via: http://www. oehha. ca. gov/public_info/facts/pdf/CrPanelRptFinal901. pdf*, 2001.

[50] S. Wilbur, H. Abadin, M. Fay, D. Yu, B. Tencza, and L. Ingerman, 'Toxicological Profile for Chromium. Atlanta (GA): US Department of Health and Human Services', *Public Health Service, Agency for Toxic Substances and Disease Registry*, vol. 24049864, 2012.

[51] M. S. Sankhla, M. Kumari, M. Nandan, R. Kumar, and P. Agrawal, 'Heavy metals contamination in water and their hazardous effect on human health-a review', *Int. J. Curr. Microbiol. App. Sci (2016)*, vol. 5, no. 10, pp. 759–766, 2016.

[52] J. Matschullat, 'Arsenic in the geosphere—a review', *Science of the Total Environment*, vol. 249, no. 1–3, pp. 297–312, 2000.

[53] U. K. Chowdhury *et al.*, 'Groundwater arsenic contamination in Bangladesh and West Bengal, India.', *Environ Health Perspect*, vol. 108, no. 5, pp. 393–397, 2000.

[54] M. A. Hoque, W. G. Burgess, M. Shamsudduha, and K. M. Ahmed, 'Delineating low-arsenic groundwater environments in the Bengal Aquifer System, Bangladesh', *Applied Geochemistry*, vol. 26, no. 4, pp. 614–623, 2011.

[55] N. Singh, D. Kumar, and A. P. Sahu, 'Arsenic in the environment: effects on human health and possible prevention', *J Environ Biol*, vol. 28, no. 2, p. 359, 2007.

[56] M. Touzandejani, A. Soffianian, N. Mirghafari, and M. Soleimani, 'Assessment of arsenic contamination probability of groundwater in Hamedan-Bahar Basin using geostatistical methods', *Water and Soil*, vol. 31, no. 3, pp. 874–885, 2017.

[57] A. Scott, 'Hamilton and Hardy's Industrial Toxicology'. Oxford University Press UK, 2016.

[58] A. Scott, 'Hamilton and Hardy's Industrial Toxicology'. Oxford University Press UK, 2016.

[59] D. N. Guha. Mazumder, 'Chronic arsenic toxicity & human health.', *Indian Journal of Medical Research*, vol. 128, no. 4, p. 436+, 2008.

[60] S. Martin and W. Griswold, 'Human health effects of heavy metals', *Environmental Science and Technology briefs for citizens*, vol. 15, pp. 1–6, 2009.

[61] D. S. Smith *et al.*, 'Regulation of cytoplasmic dynein behaviour and microtubule organization by mammalian Lis1', *Nat Cell Biol*, vol. 2, no. 11, pp. 767–775, 2000.

[62] M. A. Philbert, M. L. Billingsley, and K. R. Reuhl, 'Mechanisms of injury in the central nervous system', *Toxicol Pathol*, vol. 28, no. 1, pp. 43–53, 2000.

[63] C. D. Balaban, J. P. O. Callaghan, and M. L. Billingsle, 'Trimethyltin-induced neuronal damage in the rat brain: comparative studies using silver degeneration stains, immunocytochemistry and immunoassay for neuronotypic and gliotypic proteins', *Neuroscience*, vol. 26, no. 1, pp. 337–361, 1988.

[64] A. Saito *et al.*, 'A study of the clinical effects of clindamycin on respiratory infections-Focusing on inhibition of β-lactamase production', *Chemotherapy*, vol. 41, no. 11, pp. 1232–1245, 1993.

[65] S. S. Chadwick, 'Ullmann's encyclopedia of industrial chemistry', *Reference Services Review*, 1988.

[66] J. M. Kassaian, 'Ullmann's Encyclopedia of Industrial Chemistry'. Wiley-VCH: Weinheim, Germany, 2002.

[67] P. K. Whelton *et al.*, 'Effects of oral potassium on blood pressure: meta-analysis of randomized controlled clinical trials', *JAMA*, vol. 277, no. 20, pp. 1624–1632, 1997.

[68] F. J. He, J. Li, and G. A. MacGregor, 'Effect of longer term modest salt reduction on blood pressure: Cochrane systematic review and meta-analysis of randomised trials', *Bmj*, vol. 346, 2013.

[69] P. M. Kearney, M. Whelton, K. Reynolds, P. Muntner, P. K. Whelton, and J. He, 'Global burden of hypertension: analysis of worldwide data', *The lancet*, vol. 365, no. 9455, pp. 217–223, 2005.

[70] J. L. Lewis III, 'Water, electrolyte, mineral and acid–base metabolism', *The Merck Manual of Diagnosis and Therapy. Merck Research Laboratories: Whitehouse Station, NJ*, pp. 120–164, 1999.

[71] A. Hartwig, 'Role of magnesium in genomic stability', *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis*, vol. 475, no. 1–2, pp. 113–121, 2001.

[72] N.-E. L. Saris, E. Mervaala, H. Karppanen, J. A. Khawaja, and A. Lewenstam, 'Magnesium: an update on physiological, clinical and analytical aspects', *Clinica chimica acta*, vol. 294, no. 1–2, pp. 1–26, 2000.

[73] J. Vormann, 'Magnesium: nutrition and metabolism', *Mol Aspects Med*, vol. 24, no. 1–3, pp. 27–37, 2003.

[74] S. Kilic, M. Kilic, and M. Soylak, 'The determination of toxic metals in some traditional cosmetic products and health risk assessment', *Biol Trace Elem Res*, vol. 199, no. 6, pp. 2272–2277, 2021.

[75] O. Al-Dayel, J. Hefne, and T. Al-Ajyan, 'Human exposure to heavy metals from cosmetics', *Oriental Journal of Chemistry*, vol. 27, no. 1, p. 1, 2011.

[76] B. C. DIRECTIVE, 'of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products', 2003.

[77] H. C.-S. C. HC-SC, 'Cosmetic Ingredient Hotlist. Available at':, *taylor francis online*, 2011.

[78] H. Canada, 'Guidance on heavy metal impurities in cosmetics'. Health Canada Ottawa, 2012.

[79] BfR, 'Kosmetische Mittel : BfR empfiehlt Schwermetallgehalte über Reinheits-anforderungen der Ausgangsstoffe zu regeln', no. 025, pp. 1–4, 2006.

[80] K. Sharafi, N. Fattahi, M. Pirsaheb, H. Yarmohamadi, and M. Fazlzadeh Davil, 'Trace determination of lead in lipsticks and hair dyes using microwave-assisted dispersive liquid–liquid microextraction and graphite furnace atomic absorption spectrometry', *Int J Cosmet Sci*, vol. 37, no. 5, pp. 489–495, 2015.

[81] H. J. Hussein, 'Evaluation of the concentration of some heavy metals in hair dyes in Baghdad', *Int J Sci Res*, vol. 4, no. 2, pp. 687–691, 2015.

[82] C. M. A. Iwegbue, S. O. Onyeloni, F. I. Bassey, G. O. Tesi, R. O. Ogboru, and B. S. Martincigh, 'Safety evaluation of metal exposure from commonly used hair dyes and tattoo inks in Nigeria', *J Environ Health*, vol. 78, no. 6, pp. 26–31, 2016.

[83] N. Ozbek and S. Akman, 'Determination of lead, cadmium and nickel in hennas and other hair dyes sold in Turkey', *Regulatory Toxicology and Pharmacology*, vol. 79, pp. 49–53, 2016.

[84] F. A. Ababneh, K. A. Abu-Sbeih, and I. F. Al-Momani, 'Evaluation of allergenic metals and other trace elements in personal care products', *Jordan Journal of Chemistry*, vol. 146, no. 897, pp. 1–12, 2013.

[85] H. Arshad, M. Z. Mehmood, M. H. Shah, and A. M. Abbasi, 'Evaluation of heavy metals in cosmetic products and their health risk assessment', *Saudi Pharmaceutical Journal*, vol. 28, no. 7, pp. 779–790, 2020.

[86] W. H. Al-Dahhan, 'Determination of heavy metals in natural hair dye selected from Iraqi plants', *Noble Int. J. Sci. Res*, vol. 4, no. 2, pp. 11–16, 2020.

[87] M. R. Schroeder, 'Period histogram and product spectrum: New methods for fundamental-frequency measurement', *J Acoust Soc Am*, vol. 43, no. 4, pp. 829–834, 1968.

[88] A. M. Ali, H. S. Mohammed, and H. M. Idress, 'Determination and Assessment of Ammonia and Some Heavy Metals in Some Hair Dye Samples.', 2022.

[89] J. NÖLTE, *ICP Emission Spectrometry: a practical guide*. John Wiley & Sons,., 2021.

[90] J. Sneddon and M. D. Vincent, 'ICP-OES and ICP-MS for the determination of metals: application to oysters', *Anal Lett*, vol. 41, no. 8, pp. 1291–1303, 2008.

[91] I. Rojas, M. Murillo, N. Carrión, and J. Chirinos, 'Investigation of the direct hydride generation nebulizer for the determination of arsenic, antimony and selenium in inductively coupled plasma optical emission spectrometry', *Anal Bioanal Chem*, vol. 376, pp. 110–117, 2003.

[92] Prakriti Karki, 'pH Meter- Principle, Parts, Procedure, Types, Uses, Examples'.

[93] J. Del Coso, E. Estevez, R. A. Baquero, and R. Mora-Rodriguez, 'Anaerobic performance when rehydrating with water or commercially available sports drinks during prolonged exercise in the heat', *Applied Physiology, Nutrition, and Metabolism*, vol. 33, no. 2, pp. 290–298, 2008.

[94] W. Liu and M. Asheghi, 'Thermal conductivity measurements of ultra-thin single crystal silicon layers', 2006.

[95] S. F. Oboudi, M. T. A. Nabi, W. A. Al-Taa'y, R. M. Yusop, D. Derawi, and E. Yousif, 'Dispersion Characterization of conductive polymer', *Int J Electrochem Sci*, vol. 10, no. 2, pp. 1555–1562, 2015.

[96] J. Luo *et al.*, 'Energy Environ. Sci., 2015, 8, 1276;(b) SM Haile, DA Boysen, CRI Chisholm and RB Merle', *Nature*, vol. 410, p. 910, 2001.

[97] 'TDS'.

[98] R. G. Stevens, D. Y. Jones, M. S. Micozzi, and P. R. Taylor, 'Body iron stores and the risk of cancer', *New England Journal of Medicine*, vol. 319, no. 16, pp. 1047–1052, 1988.

[99] J. Yu, Z. Zhou, J. Tay-Sontheimer, R. H. Levy, and I. Ragueneau-Majlessi, 'Risk of clinically relevant pharmacokinetic-based drug-drug interactions with drugs approved by the US Food and Drug Administration between 2013 and 2016', *Drug metabolism and disposition*, vol. 46, no. 6, pp. 835–845, 2018.

[100] 'scholar 2222'.

[101] A. Moravcsik, 'Reassessing legitimacy in the European Union', *JCMS: journal of common market studies*, vol. 40, no. 4, pp. 603–624, 2002.