# ANALYSIS OF HEAVY METAL CONCENTRATIONS IN COATINGS OF SCRATCH LOTTERY CARDS AND SCRATCH PHONE RECHARGE CARDS IN ETHIOPIA USING FLAME ATOMIC ABSORPTIONS SPECTROSCOPY

**MSC IN LASER SPECTROSCOPY PHYSICS**

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**JUNE, 2024**

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**A THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS,**

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# ADVISORS' APPROVAL SHEET

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Name of advisor Signature Date

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We, the undersigned members of that the Board of Examiners of the final open defense by kedir Edao have read and evaluated his thesis entitled "Analysis of heavy metal concentrations in coatings of scratch lottery cards and scratch phone recharge cards in Ethiopia using flame atomic absorptions spectroscopy" and examined the candidate. This is, therefore, certifying that the thesis has accepted in partial fulfillment of the requirements for the degree.

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Declaration I hereby declare that this MSc specialty or equivalent thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

**Name**: Kedir Edao

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This MSc Specialty or equivalent thesis has been submitted for examination with my approval as thesis advisor.

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**Signature**: _________________________________

**Place and Date of Submission:** Collage of Natural and Computational Science department of Physics.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| AAS | Atomic absorptions spectroscopy |
| FAAS | Flame atomic absorptions spectroscopy |
| UV | ultra violet |
| PPM | Parts per million |
| PIN | Personal Identification Number |
| EMR | Electromagnetic radiations |
| EMW | Electromagnetic wave |
| BGC | Back ground corrections |
| STPF | Stabilized Temperature Platform |
| EMS | Electromagnetic spectrum |
| CCD | Charge Coupled Device |
| HCL | Hollow Cathod Lamp |
| A=Y | Absorbance |
| C =x | Concentrations |
| WHO | World health organizations |

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## *ABSTRACT*

*This research work was focused on the presence and level of heavy metals in coatings of scratch mobile cards and lottery cards in Ethiopia using flame atomic absorptions spectroscopy .The study mainly stressed on heavy metals such as Copper, Lead, Manganese, Chromium, and Nickel, so that the coatings of this scratch mobile cards and lottery cards were acidic digested for the determinations of the presence and levels of heavy metals concentrations. According to the laboratory results the concentrations of heavy metals in certain amounts in all these heavy metals indicated above and when we saw the levels and concentration of this heavy metals one by one with a value Cu(0.954,1.07) ,Pb(0.085,0.071), Mn(0.084,0.055), Cr(0.073,0.060) and Ni(0.051,0.041) in ppm respectively for both mobile recharge and lottery cards. This indicated that heavy metals Cu had the largest value as we compared with heavy metals and heavy metals Ni had the least and the rest heavy metals were next to the copper metal respectively for both mobile recharge cards and lottery cards and the calibrations of concentration to absorbance would obtained the result and the concentration of heavy metals in coatings of scratch mobile recharge cared and lottery cards in standards solution and its within* $R^2$ *(0.994-0.999). Although the concentrations of all this heavy metal in the scratch cards are low, over time they can accumulate on the environment if not properly disposed, and can cause health problems as they are poisonous and dangers to human health when taken above the limit set by WHO. Therefore public awareness become advised not to use finger nails to scratch mobile recharged card and lottery cared rather it is advisable to use sharp edge materials in order to scratch this mobile recharge cards and lottery cards .*

*Keywords: Mobile phone recharges card coating, heavy metals, scratch lottery card coatings, FAAS*

# CHAPTER ONE

# 1. INTRODUCTIONS

## 1.1Back ground of the study

Heavy metals have been shown to abound in several environmental matrices including water [1], plants [2,3],soil air particulates [4], cosmetics [5] and even biological tissues and organs [6]. Some of these heavy metals are essential elements for human growth and development, but could pose serious health problems at very high concentration in the body. For example, zinc (Zn) is important for the physiological functions of living tissue and regulates many biochemical processes but too much Zn can cause imminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia [7]. Copper (Cu) does essential work in animal metabolism but excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death [8]. Nickel (Ni) exceeding its critical level might bring about serious lung and kidney problem aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis; Ni is also known as a human carcinogen [9]. High concentrations of mercury (Hg) cause impairment of pulmonary and kidney function. .

The major routes of heavy metal uptake by human are food, water and air. Although some metals such as Cu Zn and Mn are essential for growth and well-being of living organisms including human, they are toxic at higher concentrations [10].Infarct, epidemiological evidence revealed that pollutants such as metals at even normal concentrations have adverse effects on human health. Other metals such as Pb, Cd and Hg are non-essential for metabolic activities and are toxic [11]. Heavy metals such as Ag, Cd, Pb, Zn,Mn, Cu, Fe and Cr are found to be the major cause of nephritis, anural and extensive lesions in kidneys [12]. Since many people use their fingers nails to scratch the film.

Rapid industrialization and urbanization have polluted the environment with heavy metals, and the rate of migration and transport of these metals in the environment has increased dramatically since the 1940s [13]. Pollution due to heavy metals poses an environmental threat and is currently a major concern [14] and [15]. Rapid industrial development has resulted in a serious concern for natural resources such as soil and water in many countries [16]. Industries are one of the anthropogenic activities that have contributed to increase concentrations of many heavy metals in the environment [17].

They are not biodegradable and remain in the environment. They contaminate the food chain and cause various health problems in animals and humans due to their toxicity [18] About one-fourth of human diseases are due to exposure to environmental pollutants [19] Heavy metals such as cadmium (Cd), lead (Pb), arsenic (As) and mercury (Hg) constitute one of the main environmental pollutants that can cause a critical problem for all organisms, such as soil microbial populations, plants as well as human [20].

One major source of heavy metals can be materials that are used in coatings. Specially, some cards such as mobile cards and instant lottery cards use materials that are suspected to heavy metal content. These cards are coated with glossy water-resistant material, which protect the text printed in infrared ink from fading or being washed off easily. The card is layered with a 'silver' coating which when scratched off, reveal a PIN (Personal Identification Number) printed underneath. A scratch card is a card designed for competitions, often made of thin card stock or plastic to conceal PINs. The silver coatings have been shown to contain heavy metals such as lead, copper, cobalt, nickel, and manganese. Some of the particles contaminate the air around, while in most cases, larger percentage are returned into the ground where they are subjected to a number of processes that influences their mobility in the soil as well as their potential to contaminate ground water. Further transformations may lead to contamination of farm products and fresh water plants and animals, and finally get into the food chain. Thus, the human health implication cannot be overemphasized. Heavy metals describe their composition, forms of association, ionic types and concentration in a given matrix. The significance of chemical analysis for the environmental sciences lies in its usefulness as a tool for the interpretation of chemo dynamics, properties and toxicity of chemical compounds.

Relatively few attempts have been made to evaluate the analysis of heavy metals in different matrices including recharge cards silver coatings. In this MSc research work the presence and concentrations of heavy metals in these matrices will be investigated and it will be used as a criterion to assess their potential effects in the environment. To determine the presence and concentration of these heavy metals, spectroscopic technique, particularly AAS will be used.

Atomic absorption spectrometry (AAS) detects elements in either liquid or solid samples through the application of characteristic wavelengths of electromagnetic radiation from a light source Individual elements will absorb wavelengths differently, and these absorbance are measured against standards. In effect, AAS takes advantage of the different radiation wavelengths that are absorbed by different atoms. In AAS, analyses are first atomized so that their characteristic wavelengths are emitted and recorded. Then, during excitation, electrons move up one energy level in their respective atoms when those atoms absorb a specific energy. This energy corresponds to a specific wavelength that is characteristic of the element. Depending on the light wavelength and its intensity, specific elements can be detected and their concentrations measured. In a typical atomic absorption spectro photometric determination, the radiation of hollow cathode lamp is made to fall on the sample of the analyses aspirated into the flame, where a part of it is absorbed. The transmitted radiation is then dispersed by a monochromatic and sent to the detector.

## 1.2 Statement of the problem

One of the present day exposure routes to heavy metals is through the use of scratch cards such as mobile phone recharge cards and lottery scratch cards which are becoming increasingly popular among the young and the old. It has been observed that most people use their fingernails to scratch off the thin film opaque substance in order to reveal the PIN on these cards. Mostly, these acts of scratching are done subconsciously or trivially without resorting to washing and with clean water and soap. Therefore, it becomes necessary to investigate the presence and levels of heavy metals such as Lead (Pb),Manganese (Mn), Copper (Cu), Chromium (Cr) and Nickel (Ni) in mobile phone and lottery scratch cards and compare the levels of heavy metals with permissible limits.

Assessing the health risk associated with these metals is important since it is a common habit among people using recharged cards to use their finger nails to scratch the recharge card coating without proper washing of the nails there by contributing a direct dermal contact with the heavy metal content of the coating films. Also in the course of removing the coating or scratching, the scratched particles are carelessly dispersed in the environment. Some of the particles contaminate the air around, while in most cases, larger percentage are returned into the ground where they are subjected to a number of processes that influences their mobility in the soil as well as their potential to contaminate ground water. Further transformations may lead to contamination of farm products and fresh water plants and animals, and finally get into the food chain [21]**.** The contamination of river water by heavy metals is also a serious worldwide ecological problem in general and Ethiopian ecological problems in particular as some of them like Hg, Cd and Pb are toxic even at low concentrations, are non-degradable and can bioaccumulation through food chain.

These assessments are carried out by using spectroscopic technique known as atomic absorption spectroscopy (AAS). Atomic absorption spectrometry is an analytical technique that measures the concentrations of elements qualitatively and quantitatively. If light of just the right impinges on a free, ground state atom, the atom absorbs the light as it enters an excited state in a process known as atomic absorptions.

## 1.3 Objective of the study

### 1.3.1 General objectives

The general objectives of the study had been evaluated the concentrations of heavy metals in scratch lottery cards and scratch phone recharge cards in Ethiopia using flame atomic absorptions spectroscopy.

### 1.3.2Specific objectives

To achieve the main objectives the study would be addressed the following specific objectives.

To investigate the presence and levels of heavy metals Copper (Cu), Chromium (Cr), Lead (Pb), Manganese (Mn) and Nickel (Ni) in coatings of mobile phone and lottery scratch cards

To explain the impact or the health implications associated with heavy metals concentrations in coatings of scratch lottery cards and scratch phone recharge cards.

## 1.4 Research questions

The research questions for this intended research will therefore originates from the practical problems that initiated this study in this research study while the broad issue is about the heavy metals concentrations of coatings in scratch lottery cards and scratch phone recharge cards.
The following questions will be developed for this intended research based on the following

1. What is the presence and levels of heavy metals concentrations of coatings in scratch lottery cards and scratch phone recharge cards?
2. What are the health implications of heavy metals concentrations of coatings in scratch lottery cards and phone recharge cards?
3. What is the difference and similarities between the heavy metals concentrations of coatings in scratch lottery cards and scratch phone recharge cards?
4. What conclusions can be drawn from the above information on heavy metals concentrations of coatings in scratch lottery cards and scratch phone recharge cards?

## 1.5 Scope of the study

The study will be limited both in scope and depth to manageable size based on the researchers time availability budget and other factors on the basis of this situations the scope of the study will delimit to analysis of heavy metal concentrations of coatings in scratch lottery cards and scratch phone recharge cards in the Shashemane and Dodola town administration in Oromia Ethiopia. This is because it will be observed that shashemae and Dodola town administration is a good representative of the other in terms of locations as well as availability of resources and expected materials such as lottery cards and phone recharge cards, etc.

## 1.6 Significance of the research study

The main goal of this study will first evaluate the heavy metal concentrations of coatings in scratch lottery and scratch phone recharge cards are becoming increasingly popular among the young and the old. The results of this work will give awareness for both the users and the authorities about the content and concentration of heavy metals on the coatings of these scratch cards. For example, for the users, the result may give information to use caution during scratching by avoiding skin contact with the coatings. And also, once they used the cards, they have to dispose the used cards properly. Awareing the heavy metal contents of these coatings, the authorities also have a responsibility to monitor and take action on the proper disposal of these cards after use.

# CHAPTER TWO

# 2 THEORETICAL BACKGROUND

## 2.1Optical spectroscopy

Optical Spectroscopy is the study of the interaction between *matter* and *electromagnetic radiation [22]*. It uses the absorption, emission, or scattering of electromagnetic radiation by matter to qualitatively or quantitatively study the matter or to study physical processes. The matter can be atoms, molecules, atomic or molecular ions, or solids. The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules.

Atomic absorption/emission spectroscopes involve electrons changing energy states these transitions should result in *very narrow* absorbance bands at wavelengths highly characteristic of the difference in energy levels of the absorbing species

### 2.1.1Electromagnetic Radiation (EMR)

EMR is a form of energy whose behavior is described by the properties of both wave and particle. Some aspects of an experiment are best explained by the wave concept, but others by the particle concept [23]. Some properties of electromagnetic radiation, such as its refraction, diffraction, reflection are explained best by describing light as a *wave*. Other properties, such as absorption, emission and scattering are better described by treating light as a *particle*.

Light is considered wave-like in nature as it consists of oscillating electric ($E$) and magnetic ($M$) fields. These fields are at right angles to each other, and travel at a constant velocity in a given medium. Invacuum, this velocity is$3x10^8$ m/s. An electromagnetic wave is characterized by several fundamental properties, including its *velocity*, *amplitude*, *frequency*, *phase angle*, *polarization*, *wave length*, etc

The particle nature of light are expressed in terms of packets of energy called *photons*.

$$E = h\mathrm{v}$$

*where*, $E$= Energy ($J$),$h$ =Planck's constant (6.62 $x10^{-34}Js$),and $v$= Frequency ($s^{-1}$) or ($Hz$)

Frequency is related to wavelength and wave number by:

$$v = \frac{c}{\lambda} = h\tilde{v} \Rightarrow \boldsymbol{E} = \frac{\boldsymbol{hv}}{\boldsymbol{\lambda}} = \boldsymbol{hv} = \boldsymbol{hc\tilde{v}}$$

Where, c= Speed of light (3x$10^8$ $m/s$) ,$\lambda$ =Wavelength ($m$) and$v$=Wave number ($cm^{-1}$)

The types of electromagnetic radiations are include radio wave, micro waves, infrared, visible light, ultraviolet, X ray and gamma rays all of which are part of the electromagnetic spectrum

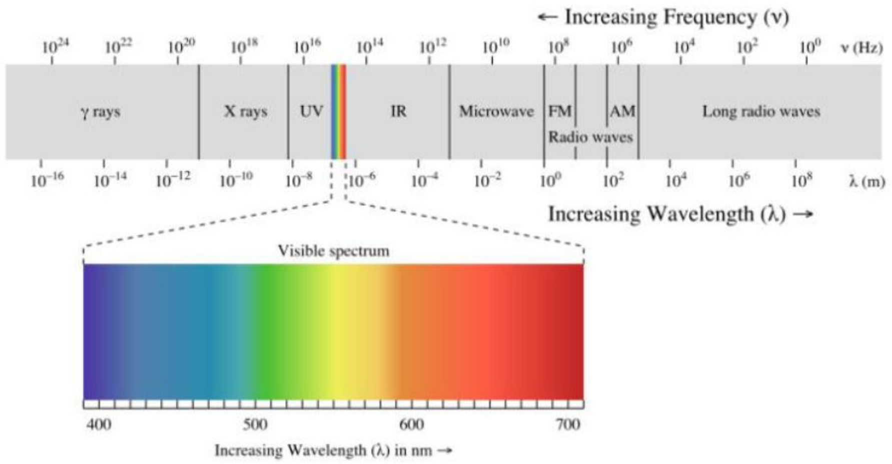


**Figure 2.1Electromagnetic spectrum**

### 2.1.2 Laser

A laser is a device that emits light through a process of optical amplification based on the stimulated emission of electromagnetic radiation [24]. The word laser is that originated as light amplification by stimulated emission of radiation. Lasers are normally categorized as gas, liquid or solid state, depending on the nature of the active medium. In the following subsections, representative examples of each type of laser are described.

Some of the common properties of these lasers are :coherent, monochromatic, uni-directional and high intensity.

The working principles of laser are based on some important features such absorptions, stimulated emission, population inversion, and amplification ,Population inversion refers to a situation where electrons populate a higher energy shell while the lower energy shells are not completely filled. That is an unstable state, and eventually those electrons will “fall” into the lower energy shells. The energy difference is discharged as a photon, whose energy (read: frequency/wavelength) corresponds to the energy difference between the shells. Laser action the stimulating emission triggers a chain reaction in which the radiation from one atom stimulates another in succession until all the excited atoms in the system have returned to normal. In doing so, coherent monochromatic light (light of a single wavelength) is emitted. Stimulate population inversion can be achieved by optical pumping in which the atoms in the ground state are excited to higher states by absorption of pump light. The electrons in the excited levels decay by non-radioactive transitions to a Metal stable level which is the upper laser level. Laser action the stimulating emission triggers a chain reaction in which the radiation from one atom stimulates another in succession until all the excited atoms in the system have returned to normal. In doing so, coherent monochromatic light (light of a single wavelength) is emitted.

The three components required for laser action are:

**Active medium/ Gain medium:** - which can support population inversion high radiation density/ amplification.

**An energy pump**:- to create population inversion in the active medium and

**An optical resonator/ Cavity**: - to create high radiation density/ amplification

The two important conditions to obtain population inversion are pumping and nature of gain medium

Pumping: in order for an assembly of atoms to amplify an incident light, pump energy must be supplied to the atoms in order to derive the atoms out of thermal equilibrium and preferentially populate upper energy level $N1>N0$Pumping can be achieved by either Optically or Electrically flash lamp, Hg arc lamps and Electric discharge in gas, and semiconductor lasers Nature of gain medium respectively. A gain medium plays a central role in laser action to help achieve population inversion. .

### 2.2Atomic Spectrum

Atomic spectrum is plot of a particular property of matter against wave length , frequency, energy or wave number of radiations [25] . It is methodology that studies properties of matter through its interaction with different frequency components of the electromagnetic spectrum. All atoms and molecules absorb and emit light at certain wavelengths so we can identify and read their properties. In essence, every element has a unique atomic "fingerprint".

## 2.3 Transition probability

If the initial (stationary) state of the system has $\psi_k$ and Eigen value $E_k$, and the final state of the system has wave function $\psi n$ and Eigen value $E_n$ then the transition probability per unit time and per unit radiation density is given by $B_{kn}$, the Einstein coefficient for induced absorption. $B_{kn}=D^2{}_{/6}\varepsilon_0\hbar^2$.$B_{kn}$ is a measure of the probability of producing the transition. The term $D$ is the transition moment integral and is related to the wave functions through D= $\psi_k\mu\psi_n d_\tau$ Einstein's coefficient, Oscillator strength, and Integrated absorption coefficient.$B_{kn}=D^2{}_{/6}\varepsilon_0\hbar^2$takes the form of a set of wavelengths, or a spectrum. The Einstein coefficients are related to wave function $\psi_1$ and $\psi_2$ of the combining states through the transition moment $D$, given by$D= \int\psi_2{*}\mu\psi_1 d_\tau$ For interaction with electric component of the radiation $\mu$ is electric dipole moment operator, and given by$\mu= q_i r_{ii}$ q - charge $r_i$ - position vector of i$^{th}$ particle. The square of the magnitude of $D$ is the transition probability and relatedto$B_{12.}$ .$B_{12}=8\pi^3/(4\pi\varepsilon_0)D_2$ The transition probability $D_2$ is related to selection rules in spectroscopy$D_2 = 0$ for bidden transitions $D \neq 0$ for allowed transitions electric dipole selection.

## 2.4Atomic absorptions spectroscopy

Atomic absorption/emission spectroscopes involve electrons changing energy states. These transitions should result in *very narrow* absorbance bands at wavelengths highly characteristic of the difference in energy levels of the absorbing species [26]. These energy states have well defined energies and electrons moving between them must absorb or emit energy equal to the difference between them. Unique wavelengths exist for each absorption / emission of energy from the atom since every element has a unique electronic structure, the wavelength of light emitted is a unique property of each individual element Provided we have atoms present in a sample it is possible to analyze them spectroscopic ally using either absorption of emission measurement.

One problem is that most samples we analyze do not consist of atoms but instead consist of molecules with covalent or ionic bond atomic spectra are mostly in UV and visible regions of the EM spectrum As the orbital configuration of a large atom may be complex, there are many electronic transitions which can occur, each transition resulting in the emission of a characteristic wavelength of light. The level and quantities of energy supplied to excite electron's can be measured & studied in terms of the frequency and the intensity of light studied by the *absorption spectroscopy*. The level and quantities of energy emitted by excited electron's, as they return to their ground state, can be measured & studied by means of the *emission spectroscopy*.

The level & quantities of energy absorbed or emitted (frequency& intensity of light) are specific for a substance Quantities can be determined from the measured signal which is proportional to top number of atoms and it can be characterize by Boltzmann Distribution$N_iN_0=exp-.^{EiKT}$

### 2.4.1Flame atomic absorptions spectroscopy ( FAAS)

FAAS is a very popular analytical technique that has been employed by researchers for the elemental analysis of trace metals in a variety of samples [27] . FAAS analyses after either wet aching or dry aching sample pretreatment and it is a simple, robust, and easy to implement tool for the analysis of digests and calibration can typically be accomplish using aqueous standards. The detections limits are in the sub-ppm range, making this method suitable for a wide range of elements (including Cr, Cu, Ni ,Mn, ,Pb) in various sample matrices system.

In the 1990s, so-called STPF (stabilized temperature platform furnace) conditions established by Slaving were almost universally adopted. STPF conditions call for the use of platform atomization, matrix modification rapid heating (1500 °C s−1 or more), prolifically coated tubes, fast digital electronics, integrated absorbance measurements (peak area), argon (stop-flow during atomization), and Zeeman (or Smith–Heftier) background correction.

Methods developed with these criteria in mind will facilitate straight forward quantization using aqueous standards to make external calibration curves, in most cases minimizing matrix interference effects and reducing the need for using the method of additions. Analytical figures of importance include sensitivity/characteristic mass, detection limit, accuracy, and precision

When a beam of radiation (light) passes through a substance or a solution, some of the light may be absorbed and the remaining transmitted through the sample the transmittance ($T$) is often expressed as the percent transmittance (%$T$), which is simply the transmittance multiplied by
100% Transmittance

$$T = \frac{I}{I_0} \qquad \text{or} \qquad T = \left(\frac{I}{I_0}\right) \cdot 100\%$$

Andthe absorbance (*A*) of a sample is the negative logarithm of the transmittance.

**Absorbance** $A = -\log_{10} T$

Beer Lambert law states that absorbance and path length are directly proportional and it was stated by *Johann Heinrich Lambert*. It states that concentration and absorbance are directly proportional to each other and it was stated by *August Beer*. The law states that, absorbance (*A(λ)*) of a species at a particular wavelength of light (λ) is proportional to the concentration (*c*) of the absorbing species and to the length of the path of the light through the sample containing the absorbing species. $A(\lambda) = \varepsilon(\lambda)\, l\, c$

Beer-Lambert law is an empirical relationship that relates the *absorption of light* [28] .to the *properties of the material* through which the light is traveling the proportionality constant $\varepsilon(\lambda)$ is called the *absorptive* of the species at the wavelength, $\lambda$. [$\varepsilon(\lambda)$ is called the molar absorptive if the concentration is measured in moles/lit].The portion of light absorbed by a transparent medium is independent of the intensity of the incident light. Each successive unit of thickness of the medium absorbs an equal fraction of the light passing through it.

### 2.4.2 Instrumentations of atomic absorptions spectroscopy (AAS)

The basic component of spectroscopic instrumentation is a stable source of radiant energy (sources of radiation) which is transparent container for holding the sample (sample cell) [29] .A device that isolates a restricted region of the spectrum for measurement (wavelength selector, monochromatic or grating).Radiation detector which converts radiant energy to a usable electrical signal. A signal processor and readout, which displays the transducer signal. Although the instruments for measuring each differ somewhat in configuration, most of their basic components are remarkably similar the common infrared sources are inert solids heated to 1500 to 2000 K. Continuum sources emit radiation that changes in intensity only slowly as a function of wavelength It is widely used in absorption and fluorescence spectroscopy. For the ultraviolet region, the most common source is the deuterium lamp. High pressure gas filled arc lamps that contain argon, xenon, or mercury serve when a particular intense source is required For the visible region of the spectrum, the tungsten filament lamp is used universally.

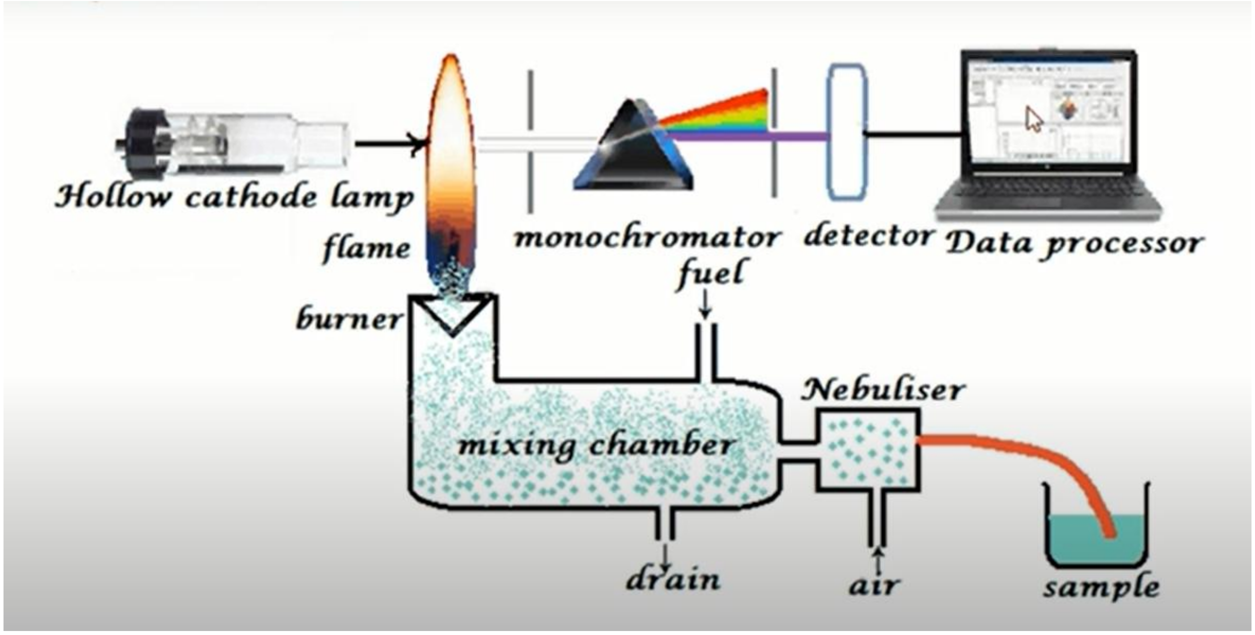


**Figure 2.2Flame atomic absorption spectroscopy**

**I  Light source, hallow cathode lamp (HCL):** The Sources of radiation is of two type's line source and continuum source the ideal wavelength selector has a high intensity of radiation and a narrow band width [30]. A narrow effective bandwidth provides a higher resolution, with spectral features separated by more than twice the effective bandwidth being resolved. Although for many experiments in laser spectroscopy these instruments can be replaced by monochromatic tunable lasers, they are still indispensable for the solution of quite a number of problems in spectroscopy.

**II Atomization:** Atomization is the process of converting analyses to a free gaseous atom and it is converting an aqueous analysis into a free atom requires that we strip away the solvent, volatilize the analyses, and, if necessary, dissociates the analyses into free atoms[31] Atomization involves separating particles into individual molecules (spectrophotometers typically include a flame burner to atomize the sample (most commonly a hollow cathode lamp), a monochromatic, and a photon detector vaporization) and breaking molecules into atoms. It is usually accomplished by exposing the analyses (the substance being measured) to high temperatures in a flame or plasma

**III Monochromatic:** The simplest method for isolating a narrow band of radiation is to use an absorption or interference filter Absorption filters work by selectively absorbing radiation from a narrow region of the electromagnetic spectrum and It an optical dispersing device that is used to select a narrow band of light and It is a mechanism that emits monochromatic light from a light source. A dispersive element, generally a prism or diffraction grating, is used to optical radiation).It is the process of converting an analyses to a free gaseous atom is called atomization or converting an aqueous analyses into a free atom requires that we strip away the solvent, volatilize the analyses, and, if necessary, dissociate the analyses into free atoms Example, a piece of colored glass and Band width 30 – 250 nm[32]. The color we see is transmitted while all other colors are absorbed Interference filters use constructive and destructive interference to isolate a narrow range of wavelengths The prism disperses and resolves the radiation, which is focused by lens 2 onto a detector. If wavelengths $\lambda$ and $\lambda+d\lambda$ are just observably separated then $d\lambda$, or the corresponding frequency interval $d\nu$ or wave number interval $d\bar{\upsilon}$, is the resolution which is obtained by$R=\lambda\Delta\lambda=\nu\Delta\nu=\nu\ \Delta\nu$.

The resolving power R of a dispersing element is defined as Prisms can be used to disperse ultraviolet, visible, and infrared radiation A diffraction grating is an optically reflecting surface consists of a series of parallel grooves ruled on a hard glassy or metallic material the general equation for diffraction by a grating is $m\lambda=d(\sin i+\sin r)$ where I and r are the angle of incidence and reflection, respectively, both measured from the normal to the surface, *d* is the groove spacing, $\lambda$ the wavelength, and *m* (0, 1, 2, . . .) the order of diffraction. The grooves are extremely closely spaced, a spacing of the order of 1 mm being not unusual. Gratings are usually coated on the ruled surface with a reflecting material such as aluminum.

.IV **Detector or radiation transducer**: is any device that converts an amount of radiation into some other measurable phenomenon. Ultimately, most of these other measurable phenomena will be tied to an electrical signal. There are two main types of detectors: photon detectors and thermal detectors .Photon detectors are usually used in UV-Visible spectroscopy and are classified into four types, namely Photomultiplier tube Phototube Diode array detector and charge coupled device (CCD) and thermal detectors are also categorized as Thermocouples which change *voltage* difference as the temperature changes Bolometer which change their *resistance* as temperature changes Pyroelectric which change *color* when the temperature changes The detectors gather clues about the particles including their speed, mass and charge –

from which physicists can work out a particle's identity the process requires accelerators, powerful electromagnets, and layer upon layer of complex sub detectors.

Background corrections used to distinguish background absorption from elemental absorption, thus returning more accurate results there are many ways to correct background absorption [33] - this article looks at two of the most commonly used methods detectors from Field Guide to background Correction (BGC) is an essence part of spectrometric analysis.

Typically a non-specific signal, the spectral background, is superimposed on the analyses-specific signal and needs to be excluded to obtain the metal analyses signal background Correction methods include Beam Chopping or Electrical Modulation, Deuterium Correction Method, and Zeeman Effect. Moreover, detection limits analyzed by various techniques for elements are also explained Deuterium background correction is the oldest and still most commonly used technique, particularly in flame AAS. In this technique, a separate source (deuterium lamp) with broad emission is used to measure background absorption over the entire width of the exit slit of the spectrometer Correction in AAS.

### 2.5Reviews of related Literature

Only few studies have been performed concerning heavy metal contents of coatings from mobile recharge cards and lottery cards. Some of these studies are revised as follows [34].Studies about the concentration of heavy metals in mobile phone recharge cards commonly used in Iraq. This was designed to study the content of silver film coating materials on mobile recharge cards in Iraq, especially 79.17 % of the mobile users used their fingers nails to scratch the film in order to reveal the Personal Identification Number PIN as well as, about 7% of these users have different dermatological signs during the use of mobile cards, also, about93%of the consumers wanted to know the chemical composition of coating materials. The concentrations of heavy metals Fe, Zn, Pb, Cu, Ni, Mn and Cr in mobile phone recharge cards of two major companies (designated as A and B).Coating materials were carefully scratched using a scraper into a special plastic tubes. The coatings were acid digested for total metals concentrations by Atomic Absorption Spectrophotometer (AAS) technique.

The total metals concentrations (in part per million ppm) were as follow Fe (142.803, 101.349 ppm), Zn (7.039, 9.126 ppm), Ag (4.706, 1.750 ppm), Cu (0.674, 0.303 ppm), Ni (0.380, 0.190

ppm),Mn(0.136, 0.075 ppm), and Cr (0.026, 0.003 ppm) for samples A and B respectively. For both the coatings analyzed, Iron and Silver elements had the highest concentration, while Cr metal had the lowest concentration. The content of metals was found to be in the order of Fe> Zn> Ag > Cu > Ni > Cd >Cr. Our results revealed that Iron and Silver concentrations were more than the recommended limit. As well as, it should be noted that Cu, Zn, Ni, Cr as well asCd metals were present in the substances and despite their low concentrations they may have a toxic effect when ingested frequently, with children being at higher risks. Therefore, the uses of silver coated recharge cards pose serious concern to humans and the environment through adhering of silver coatings on mobile cards on nails or under the fingers so, public awareness on proper handling and disposal of recharge scratch cards was recommended. Other studies performed by [35] in Nigeria, indicates that the levels of heavy metals exposure from silver coatings of mobile phones recharge cards of three major companies (designated as A, B and C) with price denominations 100, 200 and 400 from companies A, B and C respectively, which were carefully scratched using a plastic scraper into a glass tube. The coatings were acid digested for total metal concentration, while speciation experiment for Mn, Cu, Cd and Pb was carried out. Total metals and speciation analysis were done using AAS and XRF techniques.

The total metal concentration from XRF analysis was in the range: Ca (70–2140 μg/g), K (20–4930 μg/g), Sc (80–270 μg/g), Ti (1530–12,580 μg/g),Fe (50–6660 μg/g), Ni (20–2040 μg/g), Cu (20–850 μg/g) and Zn (40–460 μg/g). Cr had the lowest concentration (10 μg/g) in A ( 400) while Ti had the highest concentration(12,580 μg/g) in C ( 500) for all the coatings analyzed. AAS and XRF results agreed closely except for Fe with higher concentration. A ( 100) contained high concentration of the metals compared with others. Speciation study identified Mn as the most mobile element when present in the environment.

# CHAPTER THREE

## 3. MATERIALS AND METHODS

### 3.1 Sample collection and preparation

Mobile phone recharge cards and lottery cards from two major scratch cards distributing centers of telecommunication and lottery cards from local lottery administration office in Shashamane and Dodola administration town are used for this study.

The recharge cards commonly and commercially available are in the price denominations of 5 10, 15 25, 50,100 and three scratch lottery cards of price denominations 10, 15, 25 and two (National, and Bingo) lottery cards are most purchased by a greater percentage of the population. So that the researcher of this study would be used these price denominations as one sample of the study for phone recharge cards and two lottery cards as another sample of the study and the sellers and retail shops in sample center and care will be taken during sample collection in order to avoid cross contaminations.

The samples were later analyzed for their metal composition using flame atomic absorptions spectroscopy (FAAS) techniques.

### 3.2 Chemicals and reagents used

$HNO_3$, and distilled water.

### 3.3 Instrumentation and apparatus

#### Apparatus

The following apparatus were used in order to perform the research work.

Different size beakers, measuring cylinders, micropipette, volumetric flasks, burettes, funnel, test tubes, thermometer, stopwatch, oven, electronic-mill, plastic bottles, Erlenmeyer flask (different sizes), refrigerator, filter papers.

#### Instrumentation

Digital analytical balance used for all measurements of samples and chemicals.

FAAS will used to determine the concentrations of heavy metals Mn, Cr, Cu, Pb and Ni.

**Table 3.1**Instrumental Operating Conditions for Determination of Selected Metals Using FAAS

| **Metals** | **Wave length (nm)** | **Slit width (nm)** | **Lamp current (mA)** | **Energy (eV)** | **Instrumental detection limit (mg/L)** |
|---|---|---|---|---|---|
| Cr | 357.9 | 0.7 | 2.0 | 2.712 | 0.040 |
| Ni | 341.5 | 0.2 | 7.0 | 2.624 | 0.020 |
| Cu | 324.7 | 0.7 | 1.5 | 3.938 | 0.005 |
| Pb | 283.2 | 0.7 | 2.0 | 2.874 | 0.040 |
| Mn | 279.5 | 0.7 | 3.0 | 3.913 | 0.030 |

### 3.4Sample preparation

Determination of trace metals concentration was done by using FAAS (BUCK SCIENTIFIC MODEL 210VGP). Intermediate standard solutions (10 mg/L) of metals of interest were prepared from the 1000 mg/L standard stock solutions. These solutions were diluted to the desired concentrations to calibrate the instrument (A 10 ppm) multi-element solution containing Cr, Cu, Mn, Ni and Pb, was utilized to prepare elemental calibration solutions. This multi-element solution was diluted with 2% nitric acid to obtain working standards for each metal of interest. These intermediate standards were diluted with deionizer water [36] to obtain four working standards of each metal. After shaking and homogenizing the solutions, the selected metals were analyzed after the instrumental operating conditions were optimized for maximum signal intensity of the instrument. Calibration curves for Cr, Cu ,Mn, Ni, and Pb were obtained by using suitable standard solutions prepared from stock solutions.

# CHAPTER FOUR

# 4 RESULT AND DISCUSSION

## 4.1 Result

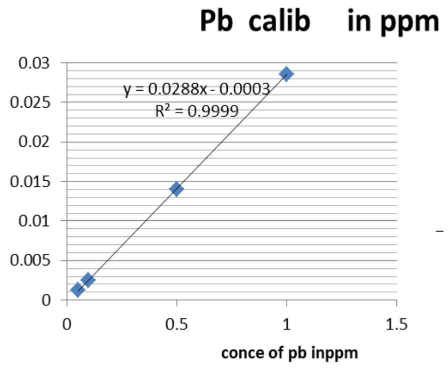
### 4.1.1. Calibration curve

Determination of trace metals concentration was done by using FAAS (BUCK SCIENTIFIC MODEL 210VGP). Intermediate standard solutions (10 mg/L) of metals of interest were prepared from the 1000 mg/L standard stock solutions. These solutions were diluted to the desired concentrations to calibrate the instrument (A 10 ppm) multi-element solution containing Cr, Cu, Mn, Ni and Pb, was utilized to prepare elemental calibration solutions). This multi-element solution was diluted with 2% nitric acid to obtain working standards for each metal of interest).These intermediate standards were diluted with de ionized water to obtain four working standards of each metal. After shaking and homogenizing the solutions, the selected metals were analyzed after the instrumental operating conditions were optimized for maximum signal intensity of the instrument. Calibration curves for Cr, Cu , Mn, Ni, and Pb were obtained by using suitable standard solutions prepared from stock solutions. Calibration curves for each selected metal was set to ensure the accuracy of the instrument and to confirm that the results of determination were true and reliable.

Calibrations curves were determined by measuring the absorbance of the different concentrations of heavy metals from stock solutions at a fixed wave length determined from Figure 4.1 below. The calibrations curves obtained are as shown below in both sample types. The absorbance and concentrations shows a good linear relationships with $R^2$(0.994 – 0.9999) and. The concentrations versus absorbance calibration curve is given by $Y$= a$x$+b which is equivalently $Y$=Absorbance and a=concentration therefore, Absorbance = concentration $\cdot x$+b.

**Table 4.1**Instrumental calibration

| Pb(ppm) | Absorbance |
|---|---|
| 0.05 | 0.001269 |
| 0.1 | 0.002518 |
| 0.5 | 0.01401 |
| 1 | 0.028568 |



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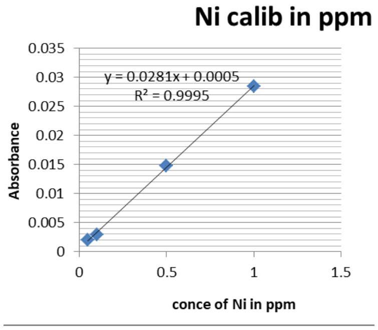
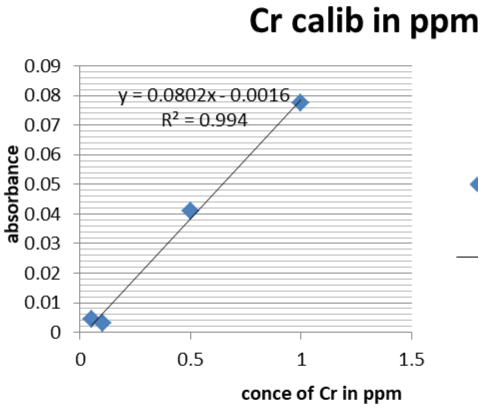
| Ni (ppm) | Absorbance |
|---|---|
| 0.05 | 0.002051 |
| 0.1 | 0.002971 |
| 0.5 | 0.01481 |
| 1 | 0.02848 |



| Cr (ppm) | Absorbance |
|---|---|
| 0.05 | 0.004285 |
| 0.1 | 0.002969 |
| 0.5 | 0.040921 |
| 1 | 0.077514 |



| Cu (ppm) | Absorbance |
|---|---|
| 0.01 | 0.001447 |
| 0.05 | 0.009421 |
| 1 | 0.088724 |
| 2 | 0.184248 |

| Mn(ppm) | Absorbance |
|---|---|
| 0.03 | 0.001895 |
| 0.1 | 0.010773 |
| 0.3 | 0.033067 |
| 0.5 | 0.054568 |

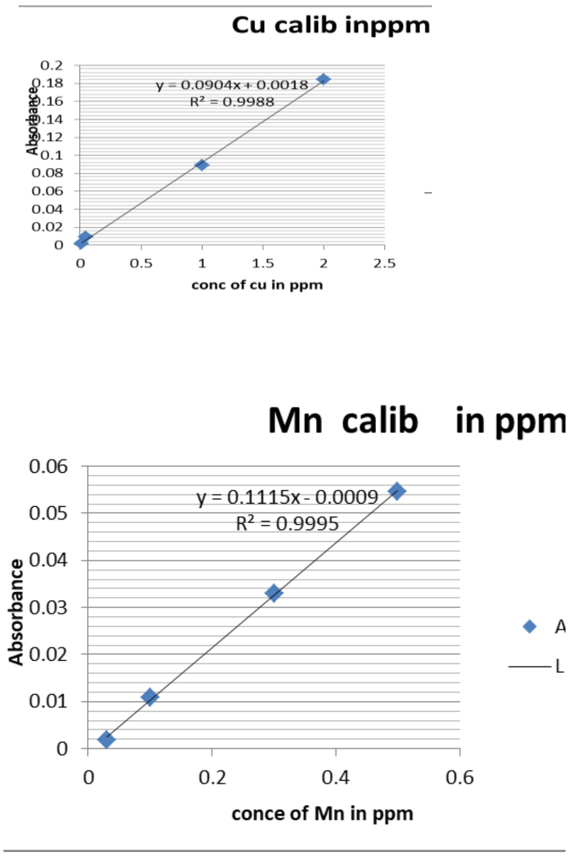


**Figure 4.1.**Concentration versus absorbance calibration curve

### 4.1.2 Heavy metals concentrations in coatings of scratch mobile recharge cards and scratch lottery cards

The concentrations of heavy metals Cu, Pb, Cr, Ni and, Mn in mobile phone recharge cards and lottery cards of two sample types (mobile and lottery cards) coating materials were scratched using a scraper into a special plastic tube. The coatings were acid digested for the heavy metals concentrations by Flame Atomic Absorption Spectrophotometer (FAAS) technique.

The heavy metals concentrations (in part per million ppm) were: Cu (0.954ppm, 1.07ppm), Pb (0.085ppm,0.071ppm),Mn (0.084ppm, 0.055ppm), Cr (0.073ppm, 0.060 ppm), and Ni (0.051ppm, 0.0413 ppm) for both samples types of mobile and lottery cards respectively. For both the coatings analyzed,( Cu ) elements had the highest concentration whereas (Ni) metal had the lowest concentration.

The FAAS results of the heavy metals concentrations in coatings of scratch mobile recharge cards and scratch lottery cards were shown in Table (4.2and4.3) and Figure (4.3). Amounts of Elements (Cu, Pb, Mn, Cr and Ni ) articulated in part per million (ppm). The bar chart shows that copper( Cu ) metal has the largest concentration in both mobile and lottery cards and The next concentrated element is also lead ( Pb) in both mobile card and lottery cards While nickel (Ni) element has the smallest concentration in both sample cards but Manganese (Mn) and Chromium(Cr) elements are respectively next to lead (Pb) for both cards .

The study discovered that the results for both cards were very related and it seems that the sample types builds the use of material with same essential work on their respective scratch cards. Also, the level concentration of the metals were found to be in the descending order of Cu, Pb, Mn, Cr ,Ni respectively for two Samples types. Very high (Cu) concentrations are recorded in both mobile and lottery cards. As we see from table 4.2and figure 4. 3 below the concentrations of heavy metals copper (Cu) in lottery card is higher than mobile cards where as for the rest heavy metals such as Lead (Pb) Manganese (Mn ) Chromium( Cr ) and Nickel ( Ni) the concentrations of heavy metals are higher in mobile card than lottery cards. the distributions concentrations of the heavy metals were also found in the order of decreasing its concentrations Cu, Pb, Mn, Cr, Ni for both mobile and lottery card respectively. Currently, there is no locate standard either close by or worldwide for heavy metal concentration in recharge cards coatings; it is therefore difficult to determine if the values obtained in this study particularly from the FAAS results are too high or too low.

Depending on the review of literatures, the acceptable set standards were (0.05, 0.5 , 0.1 , 1) for heavy metals Cu, Pb , Mn, Cr , Ni for both types of samples The levels of Copper (Cu) obtained from the analysis were ( 0.953ppm) for mobile cards and (1.067ppm) for lottery cards), this shows that the values of ( Cu) obtained was below the acceptable values in mobile cards (and lottery cards (10mg/l).Copper manifests at low concentrations and exposure to copper compound dirt can cause dermatitis, discoloring of the skin, irritation of the nose and throat, while continual exposure can cause brain damage.

Copper (Cu) was vital work in animal metabolism but excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death Nickel (Ni) values obtained were ( 0.051ppm) in mobile card and ( 0.0413ppm) in lottery cards and it's below the suggested value and Nickel (Ni) above its serious level might bring about grave lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis Ni is also known as a human carcinogen

The concentrations of Chromium (Cr) were (0.073ppm) in mobile card and (0.060ppm) in lottery cards these levels were below the acceptable limit value (0.05mg/l). Dermal exposures to chromium have been associated with skin rashes, kidney and liver damage, lung problems even death..

**Table4.2Concentrations of heavy metals in samples**

| Sample type | Pb(ppm) n=3 | Ni(ppm)n=3 | Mn (ppm) n=3 | Cr(ppm) n=3 | Cu (ppm) n=3 |
|---|---|---|---|---|---|
| **Mobil card** | 0.088 | 0.051 | 0.085 | 0.075 | 0.951 |
| | 0.085 | 0.049 | 0.081 | 0.071 | 0.953 |
| | 0.081 | 0.053 | 0.086 | 0.073 | 0.957 |
| **Lottery** | 0.072 | 0.042 | 0.057 | 0.061 | 1.06 |
| | 0.069 | 0.043 | 0.055 | 0.063 | 1.09 |
| | 0.073 | 0.039 | 0.053 | 0.059 | 1.05 |

Variance and standard deviation of heavy metals concentrations in coatings of scratch mobile recharge cards and lottery cards are as follows

Mean ($\bar{x}$) =x/n

Standard deviation (σ ) = $\sqrt{\frac{\sum(x-\bar{x})}{n}}$

Variance = $\sigma^2$

Where $\boldsymbol{\Sigma}$ is sum, σ is the standard deviation, $\boldsymbol{x}$ is the value, $\boldsymbol{\chi}$ is the mean and $\boldsymbol{n}$ is the total number

**Table.4.3 Concentrations of heavy metals in samples cards(average value)**

| **Sample type** | **Pb** | | **Ni** | | **Mn** | | **Cr** | | **Cu** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (Av) | **SD** | (Av) | **SD** | (Av) | **SD** | (Av) | **SD** | (Av) | **SD** |
| Mobile | 0.0846 | 0.0035 | 0.051 | 0.0020 | 0.084 | 0.0026 | 0.073 | 0.0020 | 0.953 | 0.0031 |
| Lottery | 0.071 | 0.0021 | 0.0413 | 0.0021 | 0.055 | 0.0020 | 0.060 | 0.0020 | 1.067 | 0.0208 |

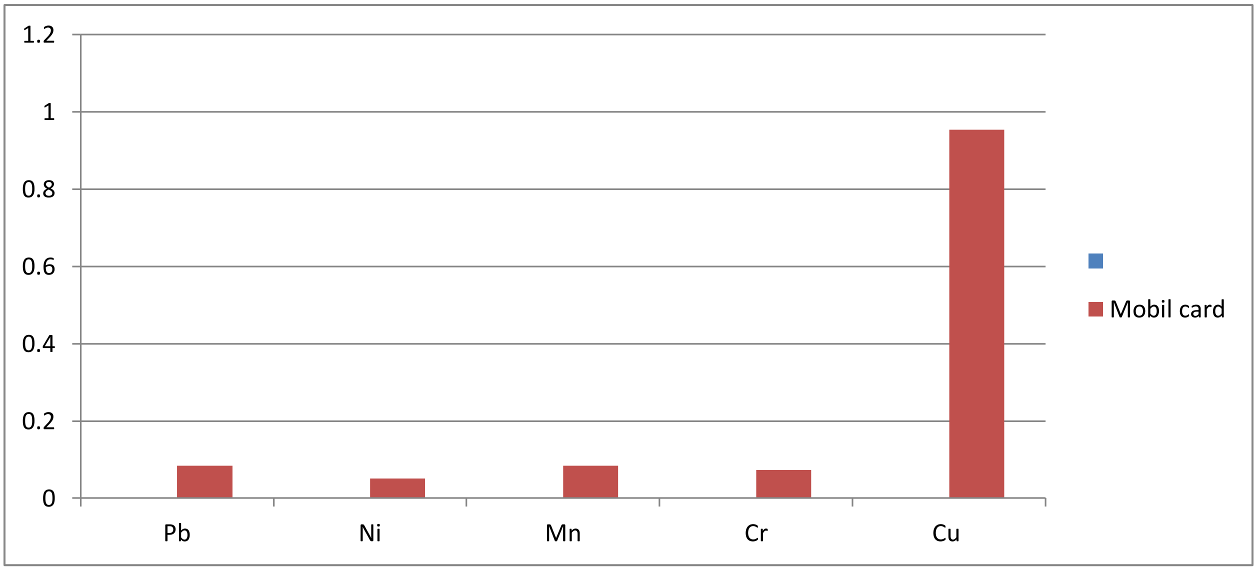


**Figure 4.2 Heavy Metal Concentration by ppm for mobile cards**

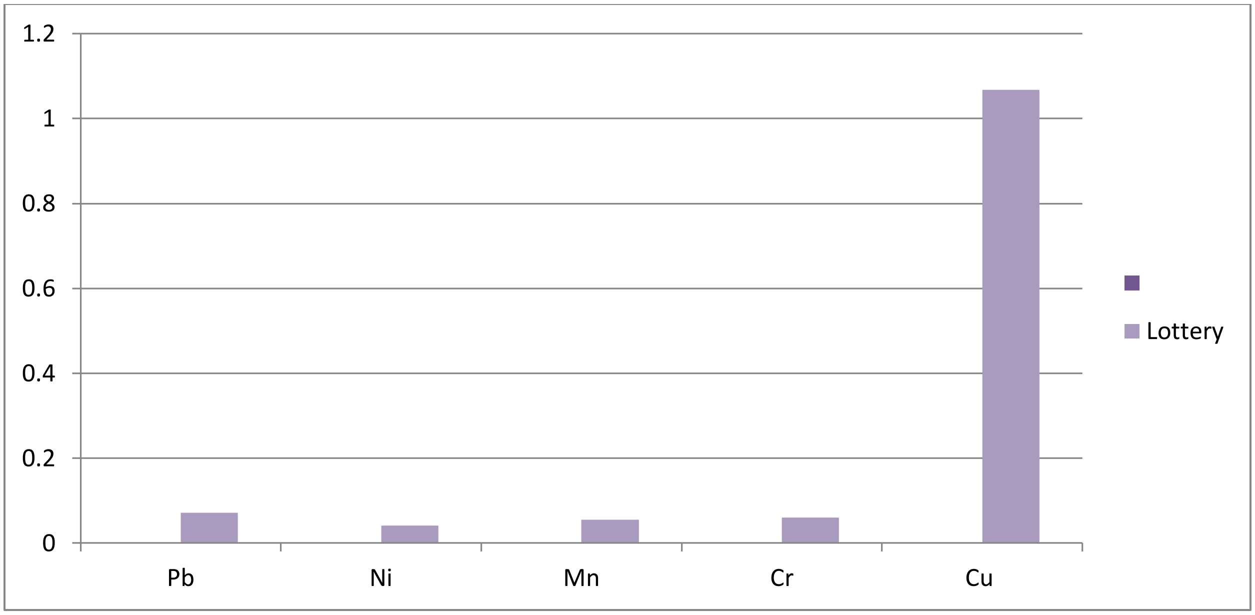


**Figure 4.3**Heavy Metal Concentration by ppm for scratch lottery cards**.**

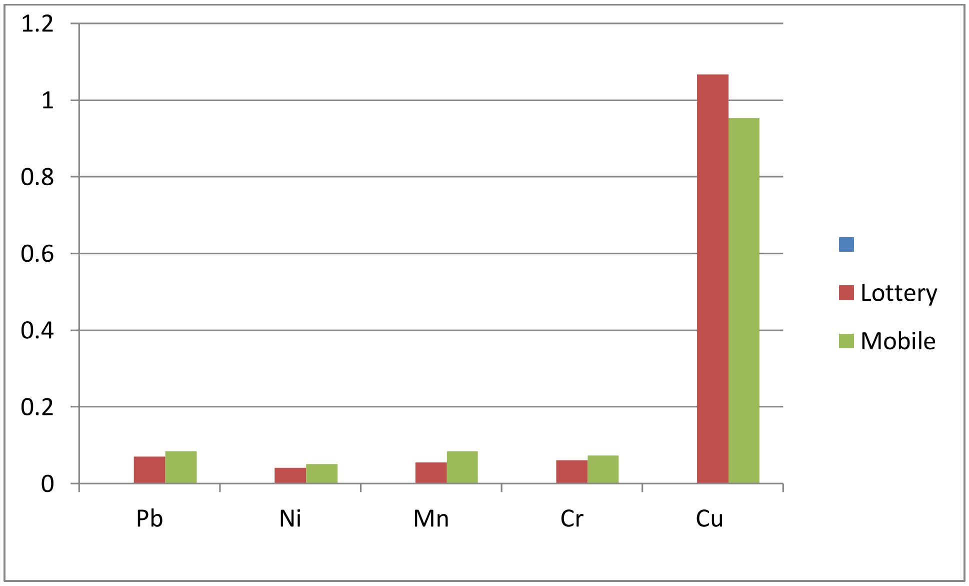


**Figure 4.4**Heavy Metals concentrations by ppm for both mobile and lottery

## 4.2 Validation of experimental result

The parameters to be checked for method of validation;

*Precision method;* is the degree of agreement among individual test results of the concentration of heavy metals in coatings of mobile recharge and lottery scratch cards when the system is applied repetitively. The analytical precision of the method was assessed from the reproducibility determinations of different heavy metals concentrations of mobile recharge cards and lottery cards and a relative standard deviation of absorbance. We can determine the precision from the variance or the standard deviation of the results. The standard deviation value calculated and shown in Table 4.3 for both cards shown and our method is in good precision.

*Linearity method;* is determining the stock solution of heavy metals concentrations in coatings of scratch mobile recharge cards and scratch lottery cards using the in the black at five different heavy metals concentrations by constructing calibration curve Five different concentrations of heavy metals from 10µg/ml to 1000µg/ml were analyzed according to experimental conditions. Then the calibration curve was recognized according to the data obtained and the concentrations of heavy metals in standard solutions. The results show a good linear relationship and the different concentrations of heavy metals concentrations in scratch mobile recharge cards and lottery scratch card in (ppm) was also analyzed according to experimental condition.

The calibration curve was established according to the obtained result and the concentration of heavy metals in coatings of scratch mobile recharge cards and lottery cards in standard solution and $R^2$(0.994 – 0.9999) and therefore the results show a good linear relationship $y$ = a$x$+ b *Where y is absorbance and x is the concentrations.*

Here are the concentrations to absorbance calibrations curve for the heavy metals indicated.

Cr. Cu Ni
$y= 0.080x+0.001$ $y=0.090x+0.001$ $y=0.028x+0.00$
$R^2=0.0998$ $R^2=0.999$
$R^2= 0.994$.

Pb Mn

$y=0.028x +0,00$ $y=0.111x+0.00$

$R^2=0.0999$ $R^2=0.999$

Where ***a*** is the slope of regression line and ***b*** is the intercept of *y*.

*Limit of detection (LOD);* is defined as the lowest concentrations that can be calculated from calibration curve recognized the limit of detections for the above heavy metals are as follows

LOD= $3\frac{\boldsymbol{\sigma}}{s} =$ Pb $= 0.375,$ Cr $= 0.025,$ Cu = $0.0102$, Ni= $0.021$ Mn = 0.069 for scratching mobile cards

LOD= $3\frac{\boldsymbol{\sigma}}{s} = =$ Pb $= 0.224$ , Cr $= 0.075,$ Cu = $0.69$, Ni=0.225 Mn= $0.054$ for scratching lottery cards

Where σ is standard deviation and ***s*** is slope of linearity calibration curve.

### 4.3 Conclusions

The presence and levels of heavy metals, such as Cu, Pb, Mn, Cr as well as Ni in mobile phone recharge cards and lottery cards were identified.

The bar chart shows that copper ( Cu ) metal has the largest concentration in both mobile and lottery cards and The next concentrated element is also lead ( Pb) in both mobile card and lottery cards, while nickel (Ni) element has the smallest concentration in both sample cards but Manganese (Mn) and Chromium(Cr) elements are respectively next to lead (Pb) for both cards.

Calibrations curves were determined by measuring the absorbance of the different concentrations of heavy metals from stock solutions at a fixed wave length determined from Figure 4.1 below. The calibrations curves obtained are as shown below in both sample types. The absorbance and concentrations shows a good linear relationships with $R^2$(0.994 – 0.9999) .

The Flame atomic absorption spectroscopy (FAAS) results of the heavy metals concentrations in coatings of scratch mobile recharge cards and scratch lottery cards were shown in Table (4.2and4.3) and Figure(4.3)and the level of heavy metals such as Cu, Pb , Mn, Cr , Ni in both types of samples are obtained from the analysis were Cu ( 0.953ppm) for mobile cards and (1.067ppm) for lottery cards), this shows that the values of ( Cu) obtained was below the acceptable values in mobile cards and lottery cards to the heavy metals scratch recharge cards contain high levels of Copper (Cu) metals which go beyond the recommended limits, however levels of Mn, Pb, Cr, and Ni elements were within the acceptable values. These heavy metals may be toxic if ingested at higher or lower concentrations.

Finally, higher concentrations of heavy metals were found in mobile cards samples than lottery cards samples with the exception of copper (Cu) metal as compared with lottery card samples.

## 4.4Recommendations

Having fingernails to scratch off the heavy metals is not a protected practice. Rather cutting edge or any particular scraper should be used as an alternative.

More attentions should be taken not to pollute our foods with the material to stay away from ingestion of the substance.

Caution statements regarding to this opaque thin film coat should be clearly written on every recharge card and lottery cards by all stake holders.

Independently from this, using the printed numbers to top up the mobile phone account or online system should be optimistic since this does not present metal discovery hazard and is commercial.

Additional studies can be approved out to assessed another elements such as, Mo, Ti , Zn, Ca and Al also another radioactive isotopes that guide to support cancer and related ailments as well as some non-metal elements which may be poisonous if ingested at a high concentration.

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# APPENDICES


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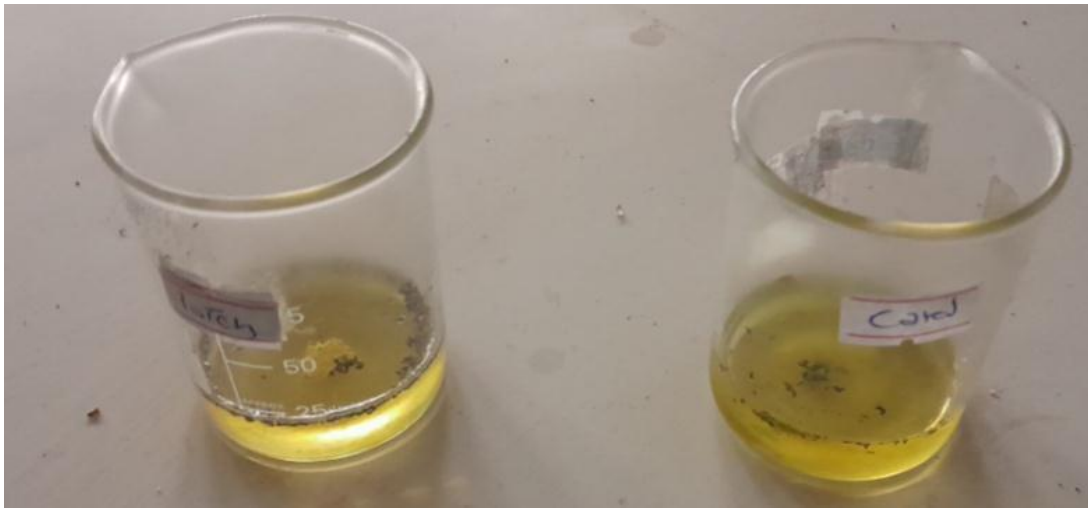
1502118189887
10000301000508


National Lottery
150,000
Win Up to 150,000 Br.!
Scratch The Lucky and Playing Numbers Then Match any of The Lucky Numbers to any of the Playing Numbers, win the prize Shown for that Number
PRIZE
VOID IF REMOVED
LOTTERY
BINGO
CALLER'S CARD


5
50
25
Cold


MC
L


VWR