

INVESTIGATION OF LEVELS OF SOME HEAVY METAL
PRESENTS IN LIVESTIKE'S WATER AND RAW MILK IN EAST GUJI
ZONE, ETHIOPIA USING ATOMIC ABSORPTION SPECTROSCOPY



MSC IN LASER SPECTROSCOPY

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HAWASSAUNIVERSITY, HAWASSA, ETHIOPIA

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**THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS, COLLEGE OF
NATURAL AND COMPUTATIONAL SCIENCE, SCHOOL OF GRADUATE
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SCHOOL OF GRADUATE STUDIES
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This is to certify that the thesis entitled “investigation of levels of some heavy metal presents in livestock’s water and raw milk in east Guji zone, Ethiopia using atomic absorption” submitted in partial fulfillments of the requirements for the Degree of Master of Science with specialization in Laser Spectroscopy, the Graduate Program of the Department of Physics, and has been carried out by Debele Nedi ID No. GPPhysK/008/10 under my supervision. Therefore, I recommended that the student has fulfilled the requirements and hence hereby can submit the thesis to the department.

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We, the undersigned, members of the board of Examiners of the final open defense by Debele Nedi have read and evaluated his thesis entitled “Atomic absorption spectroscopic of heavy metal contents of raw milk and water consumed in Ethiopia the surrounding areas”, and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirements of the degree of M.Sc. in Laser Physics.

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I hereby declare that this M.Sc. thesis entitled, “investigation of levels of some heavy metal presents in livestock’s water and raw milk in east Guji zone, Ethiopia using atomic absorption anion is my original work and has not been presented a Degree/Diploma in any other university, and all courses of material used for this thesis have been duly acknowledged.

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LIST OF ABBREVIATION

AAS.....	Atomic Absorption Spectroscopy'
PPM	Part per million
EMR.....	Electromagnetic Radiation
I_0	intensity of the incoming beam
I	intensity of the transmitted beam
l	absorbing path length
C	Concentration of Absorbing Species.
A	Absorbance
T	Transmittance
WHO.....	World health organization
Cu.....	Copper
Pb.....	Lead
Cr.....	Chromium
Ni.....	Nickel
Co.....	Cobalt
MDL.....	Method Detection Limit
IDL.....	Instrumental Detection Limit

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ABSTRACT

In this work heavy metal concentration in raw cow milk and live stock water in east Guji Zone were studied using FAAS. The Raw Cow's milk and water were collected from six farms of Liben bulb, Liben, mugayo, Goro Dola Daraara, Goro Dola Haraqalo and, Wadera Lagu, Wadera Calo site Guji zone, Ethiopia and HNO₃ was used in the optimal microwave digestion process to break down the milk and water samples. The heavy metal contents obtained using FAAS show slight different among six samples in cow milk and water. The concentration of Pb, Ni, Co, Cr and Cu were determined by using AAS. Pb, Ni, Co, Cr, and Cu were found in every sample of milk and water. The concentration of Pb, Ni, Co, Cr and Cu, 0.046 - 0.084 mg\L , 0.17 - 0.245, 0.0035 -0.097mg\L, 0.045 - 0.104 mg and 0.161 -0.473 mg\Lin milk and WHO of the above elements 0.04, 0.07, 0.05),0.05,2.0)in cow milk and the concentration of Pb ,Ni,Cr,Cu andCu,0.034-0.084mg\L,0.134-0.344,0.034-0.295,0.045-0.104and0.026-0.094in water and The WHO above element, 0.01, 0.02, 2.0, 0.05, and 0.05 in water. The concentration Cu and Ni are more than Co, Cr, and Pb in both milk and water, concentrations are generally the lowest in milk and water.

Keywords Cow milk, water, Heavy metal, AAS, Beer-Lambert 'slaw

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Milk is a nutrient rich food that constitutes fundamental component of human diet, produced by mammary glands of mammals [1]. The nutritional components in milk are energy, water, carbohydrate, fat, protein, milk flavor, vitamins, minerals and minor biological proteins and enzymes. Cows are still considered most important among species in milk production with a contribution of 580.5 million kg (83.3%) of 696.6 million kg globally according to FAO 2010 [2]. Milk is also good source of calcium, phosphorus, potassium, vitamin ,riboflavin, vitamin A, vitamin B-12 and niacin and a good source of protein [3]. However, chemical hazards and contaminants which are risk factors for dairy products can as well be contained in milk and dairy products [4]. Therefore, its contamination, among other compounds, by heavy metals, can represent a serious public health problem due to different disorders that these cause to consumers, particularly in children and milk is very important component of human diets that are mainly consumed by children and adults especially elderly people around the whole world [5]. The interest in these elements is increasing due to the available reports of relationships heavy metals status in food and drinking water and the prevalent oxidative diseases in living beings. Lead, Cadmium, Chromium, Nickel, Arsenic and Mercury are the most common toxic metals of concern according to WHO reported. [6]. Heavy metals are among the most dangerous contaminants in the environment, though many of those, under suitable conditions, play the role of bio elements necessary for correct functioning of the human body, e.g. zinc, iron, copper and selenium [7]. So far, no biological role has been

demonstrated that could be played by mercury, cadmium, arsenic and lead, and they are considered to be substances totally alien to the human organism and harmful, even at very low concentrations. It has been determined that the presence of heavy metals in milk is basically due to the fact that they are ingested by cows through water and fodder that are contaminated by different sources, such as industrial waste that is indiscriminately dumped into the environment, mining activities, pesticide residues used in agriculture, water released from urban areas and in certain regions, by natural processes such as volcanic activity, where fine particles are emitted into the air that can reach irrigation water, soil and forages, becoming a risk factor that causes contamination. its contamination could have a huge effect on the milk quality. This amount of water is controlled by the amount of lactose synthesized by the secretor cells of the mammary gland [8] Ethiopia holds the largest livestock population in Africa [9,10]. The total cattle production for the country is estimated to be 52.13 million and the total annual national milk production comes from about 10 million milking cows and is estimated 3.2 billion liter [10]. Despite the essential benefits of consuming milk, the contamination of milk from moderate agricultural practices, industrial pollutants in the environment, animal feeds and use of sewage sludge in Agriculture is increasing and therefore requires urgent attention because of the risk this contamination poses especially to the health of the consumers .The determination of heavy metals can be performed by several instrumental techniques [11, 12] but the most common ones are spectroscopic techniques. Spectroscopy is a branch of science that studies the properties of matter through its interaction with electromagnetic interaction. From quantum mechanical perspective, electromagnetic radiation is a source of quanta of energy and matter has discreet energy levels. The science of spectroscopy examines an atom's or molecule's when interacting with specific wavelengths of electromagnetic energy. The absorption or emission spectra produced by spectroscopic methods give us a variety of

useful details, including the kinds and concentrations of elements, the sorts of functional groups, and the types of bonds that are present in a sample. [13]. The light wavelength that certain element specifically absorbs or emitted is used in technique. They line up with the energy required to transfers electron from one energy level to other energy [14]. Heavy metal contamination should not be present in the feed or drinking water. Management of livestock farms, including cleaning of cages, personnel, and equipment, must ensure hygienic conditions and adhere to regulations for food safety. Grass and concentrate are typically fed to dairy animals. The content of milk and general clean lines determine its quality. On the other hand, eating tainted food such as milk can result in food-borne illnesses (FBDs). In particular, consuming raw or unpasteurized milk and milk products contaminated with microorganisms might expose humans to infections [15]. AAS is an analytical technique used to determine the concentration of metal atoms/ions in different environmental samples. Metals make up 75% of Earth's chemical elements. In some cases metal content in a material is desirable, but it can also be contaminants (poisonous). Therefore measuring metal content is critical for many different applications. AAS finds wide application in different fields such as environmental pollution control, pharmaceuticals, agriculture and copes, mining, food and beverage, and forensic investigation [16]. When concentration, essential metals more than WHO heavy metal can't be essential, because toxicity to living organism [17] . The popularity of AAS can be attributed to its selectivity, simplicity, and convenience in use. The radiations from the monochromatic a received by detectors which convert them to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes. The atoms then absorb radiations of characteristic wavelengths from an external source which is usually a hollow cathode lamp [18] The amounts of metal in uncontaminated milk is minute ,but their contents may be significant altered as metal that may be contaminate from different cattle

feeds and environments such as Pb, Co, Cr, Ni and Cu [19]. AAS has been widely used by different researchers for the analysis of heavy metallic element concentrations in raw milk for the sake of quality control. Currently, metals present in milk powder is much below 50 mg/kg can be referred as trace metals [20]. The ash of cow's milk contains some major elements such as calcium, phosphorus and magnesium, in addition to potassium, sodium and chlorine and a wide range of trace elements including zinc, copper, iron, manganese and iodine. Thus cow's milk is an important source of protein, minerals and vitamins in the human diet [21]. Milk is addressed as an ideal food. It is also considered as an excellent source of Calcium (Ca), fewer amount of Zinc (Zn), and a very small content of Copper (Cu) and Iron (Fe) [10]. Milk and dairy products become contaminated with heavy metals either through contamination of the original cow's milk, which may be due to exposure of lactating cow to environmental pollution or consumption of contaminated feed stuffs and water [22]. The primary cause of this heavy metal contamination in the food chain is environmental pollution. Two potentially dangerous Elements that have caused a great deal of anxiety are lead and cadmium [23]. Cadmium and lead are among the heavy metals that have caused the most concern in terms of adverse effects on human health [24]. They are readily transferred through food chains and are not known to serve any essential biological function [25, 26]. For instance; Ca and Pb have the serious effects on the kidney and nervous system respectively [27, 28]. As a result, the regular absorption of small amounts of certain elements, such as lead, may cause serious effects on the health of growing children, including retardation of mental development such as reading and learning disabilities as well as deficiencies in concentration, adverse fact son kidney function, blood chemistry and the cardiovascular system, as well as hearing degradation [29, 30]. Cobalt (Co) is also toxic metal at higher concentrations which is released into the environment. They originated from dumping industrial wastes in the rivers, as well as due

to application of phosphate fertilizers [31].The acid digestion procedures are the most popular sample pre-treatment techniques for elemental determination in biological and environmental samples, and acid digestion induced by microwave energy is a well-established method [32].Due to the growing environmental pollution it is necessary to determine and monitor the levels of heavy metals in milk, because they can significantly influence human health [33, 34] . The determination of heavy metals can be performed by several instrumental techniques including photometric chromatography, ion chromatography, FAAS, inductively coupled plasma optical emission spectrometry, potentiometric stripping, capillary zone electrophoresis, 3 differential pulse anodic stripping voltammeters, mid IR spectrometry, particle induced X-ray emission and complex metric titration [35].

1.2 .Statement of the Problem

Milk is widely considered as one of the world's most valuable protein food.

Milk products are very important human nutrient since their consumption has increased in recent years [36].In the study area east Guji zone from wadera, Liben, and Goro Doola woreda rural area the society consumes high amount of the unprocessed cow's milk in their everyday diet, but the quality of the milk has not been assessed yet depending on the presence of essential and nonessential elements [37] .The Aim of this study is to determine the mean concentrations of heavy metals including Pb, Co,, Cr Ni ,and Cu, water and milk in east Guji zone from wadera woreda and Goro Dola woreda and Liben woreda. Therefore, considering the numerous complications and the possible presence of these metals in milk is necessary to pay major attention to the presence of heavy metals in milk and its products as a high-consumption group in the society, which is the main objective of the thesis work.

1.3 Objective of the Study

1.3.1 General objective

- The general objective of this study is to investigate the level of some heavy metal presents in livestock water and raw cow milk in east Guji zone, Ethiopia by using atomic absorption spectroscopy technique.

1.3.2. Specific Objective

- To determine the concentration of some heavy metals present in cattel drinking water and raw milk in three woreda of east Guji zone.
- Study the relation between the qualities of water used for cattle drink with the cow milk To compare the results with the permissible limit values established by guidelines of different international and national organization

1.4. Scope of the study

This study's objectives were to prepare standard solutions of water and cow milk. Use a spectrometer to quantify the absorbance of the various concentrations prepared above from the various intensities measured at the corresponding wave lengths where maximal absorbance occurs. Plot a calibration curve (concentration vs. absorbance) using water and milk cow data. Use AAS is spectrometer to measure the absorbance of water and milk derived from different sources. Verify the experimental method's linearity, accuracy, relative standard deviation, and detection.

1.5. Limitation of the study

Only five heavy metals, lead (Pb), cobalt (Co), copper (Cu), nickel (Ni), and chromium (Cr) were taken into consideration in this study due to budgetary and scheduling limitations. The five cow's Milk and water that are now for sale in the markets were the focus of attention. Restriction on the instrument's time consuming capabilities.

1.6. Significance of the study

The significance of this study is:

- Give evidence to the authorities for further improvement of the milk and water quality.
- It helps to know the people the quality milk at the area and used to recommend the people living around the study area after determination of metal in the milk. Therefore, it is essential to determine the level of heavy metals in cow's milk so that the warning signals, wherever required, can be given to the society.
- It is very important to educate the society about the harmful effect of contaminated milk products with heavy metals once they are present in concentrations greater than the acceptable total residual level, it may be difficult to reduce them to an acceptable level during processing.

CHAPTER TWO

2. THEORY

2.1. Spectroscopy

The study of how matter absorbs and emits light and other radiation, as well as how these processes rely on the wavelength of the radiation is known as spectroscopy. The scientific field of spectroscopy examines how electromagnetic radiation interacts with matter, such as atoms and molecules [38]. An atom or molecule will change its energy levels as a result of the interaction between electromagnetic radiation and matter. Thus, knowledge of the nature of electromagnetic radiation and the interactions between atoms and molecules is required to comprehend these interactions. Spectrophotometers, spectrographs, or spectral analysis are terms used to describe spectral measurement instruments. The Steps of spectral analysis are the first step in most laboratory spectroscopic analyses. Next, a light source from any desired range of the light spectrum is selected, and the light passes through the sample and into a dispersion array (a diffraction grating instrument) before being caught by a photo diode. When used for astronomy, the telescope .In Absorption spectroscopy, the sample's compounds are excited by the electromagnetic radiation provided by a light source. Their molecules absorb energy from the electromagnetic radiation, become excited, and jump from a low energy ground state to a higher energy state of excitation. A detector, usually a photodiode, on the opposite side of the sample records the sample's absorption of wavelengths, and determines the extent of their absorption. The spectrum of a sample's absorbed wavelengths is known as its absorption spectrum, and the quantity of light absorbed by a sample is its absorbance.

2.1.1. Electromagnetic Radiation

The flow of electrically charged particles through vacuum or matter, or oscillating electric and magnetic disturbance, is two sources of electromagnetic radiation. Consider light as a wave to better characterize several properties of electromagnetic radiation, such as its diffraction, reflection, and refraction. Other properties like absorption, emission, and scattering are more correctly portrayed when light is also thought of as particle. [39].The disturbance results from the combined wave moving perpendicular to both the electric and magnetic oscillating fields. The electromagnetic and electric waves have certain properties, such as Amplitude, wavelength, and frequency. In a vacuum, all electromagnetic waves move at precisely the same speed $c = 3 \times 10^8$ m/s. Electromagnetic radiation (EMR) is made-up of electromagnetic radiant energy and waves of the electromagnetic field that travel through space. The electromagnetic spectrum is made-up of various types of radiation, such as radio waves, microwaves, infrared, visible light, ultraviolet, X-rays, and gamma rays. The primary application of spectroscopy is the study of atom and molecular structures.

2.2.2. Interaction of EM Radiation with Matter

Charged particles interact with matter through electromagnetic waves, causing the substance to vibrate. Depending on the characteristics of the materials, this contact may cause the electromagnetic wave to be absorbed, transmitted, reflected, or refracted.

Absorption is a process where an atom in lower level absorbs a photon of frequency and moves to an upper levels. Absorption of electromagnetic radiation is consider as a process that shows how a matter can take up a photon's energy and transform electromagnetic energy into internal energy of the absorber.

Emission is the processing which a quantum mechanical system (such as molecule, an

atom or a subatomic particle) transits from to man excited energy state to lower energy state(e.g. its ground state) and in the form of photon. An atom can have different energy levels; the lowest energy level is the most stable state of an atom is the ground state (E_1) to move to the excited level (E_2), a higher energy level when it receives enough thermal or light (photon) energy.

Scattering is one of principle forms of photon interaction and it occur due to the interaction of the photon with free electrons loosely bound valence shell electrons.

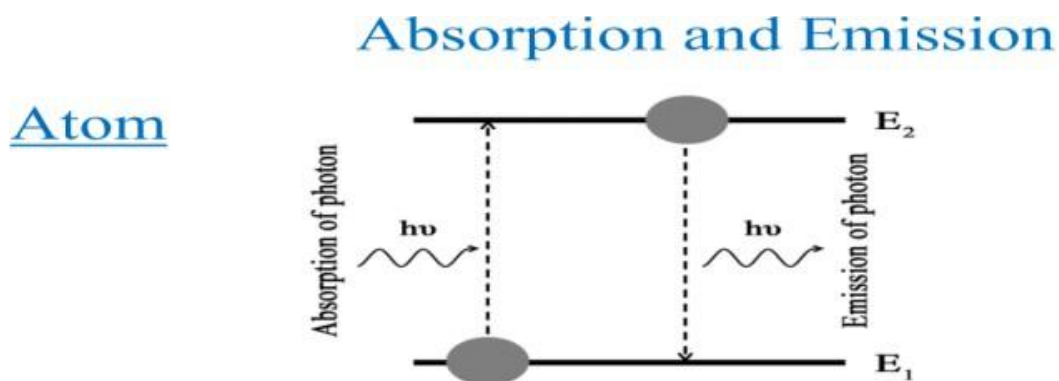
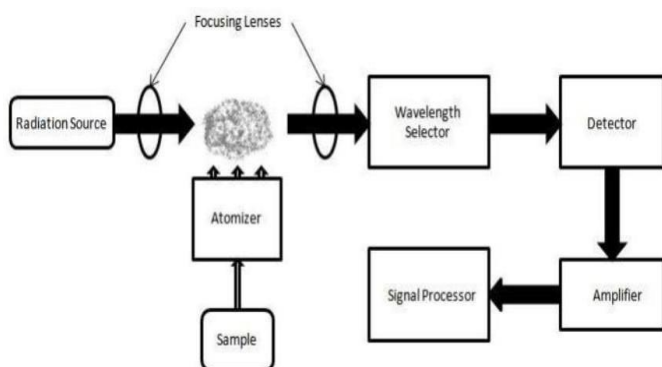


Figure 2.1.InteractionEMRbyabsorptionand emission

2.2. Atomic Absorption Spectrometry (AAS)

AAS is an analytical method based on the absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by gaseous atoms resulting in changes in electronic structure.

AAS is an analytical technique used to determine the concentration of metal atoms\ions in a sample. It's is uses the principle that atom can absorb light at a specific, unique wavelength. The amount of light that absorbed at this wavelength is directly proportional to the concentration of the absorbing ions or atoms. The radiations from the monochromatic a received by detectors which convert them to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes. The atoms then absorb radiations of characteristic wavelengths from an external source. The atoms of lead, nickel,



zinc, and cadmium absorb radiations of wavelengths of 283.9nm, 232.0 nm, 213.9 nm, and 228.8 nm respectively from an external source which is usually a hollow cathode lamp [40]. They are different kinds of Spectroscopy such as; atomic Spectroscopy, Uv-Vis Spectroscopy, infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance spectroscopy, etc.

Figure 2.2.Schematic FAAS Diagram Equipment's

2.2.2. Components of AAS .Spectroscopy

1.The Radiation Source(Hollow cathode lamp)

There are two types of radiation sources: line and continuous sources. A continuum source emits radiation over a broad range of wavelengths, with a relatively smooth variation in intensity. A line source, on the other hand emit radiation at selected wavelength To achieve the highest level of sensitivity in measuring this narrow absorption of light, a line source that emits the precise wavelengths that an atom may absorb must be used. The HCL is a line source or radiation source that is used to elevate the energy level of the target metal's electrons and produce a steady, powerful output. In atomic absorption spectroscopy the one kind of discharge lamp utilized as a light source is a hollow cathode lamp. In AAS the radiation source is a line source and the common source is the hallow cathode lamp (HCL). Hallow cathode lamp (HCL) AAS lamps utilize the hollow cathode

effect to generate light at wave length for the elements of interest. Hollow cathode is used as a spectra line source for atomic Absorption (AA) Instruments.

2. Atomizers

The process of breaking down particles into individual atoms is known as atomization. The analytic is heated to a high temperature in a flame or graphite furnace to achieve this. It is best to maximize the fraction of free analytic atoms in the atomizer compared to those in the sample solution [41].

3. Wavelength Selector

Monochromatic: This is a very important part in an AAS spectrometer. It is used to separate out all of the thousands of lines. Monochromators is used to select the specific wave length of light which is absorbed by the sample and to exclude other wave length. Wavelength selector is instruments component that either select or transmits a narrow band of wavelength emanating from abroad band optical source transmits one or more line from discrete wavelength. The two general types of wavelength selector used to provide narrow band of radiation are filters and Monochromators. Monochromators have the advantage that the output wavelength can be varied continuously over a considerable spectral range. Filters operate by absorbing all but a restricted band of radiation from a continuous source. In addition to absorption measurements, narrow bandwidths increase the likelihood of adherence to Beer's law. No selector is capable of Producing radiation of a single wavelength. Instead, the output of such a device is a range of contiguous wavelengths called a band.

4. Light Detectors

Today, the detector technology employed in all atomic absorption spectrometers is the photomultiplier. The detectors calculate the intensity ratio between the source and the chosen line that is isolated by a Monochromators. The automatic internal amplification of photomultipliers is one of their benefits. Detector is transforms the light energy to electrical energy. There are two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference.

2.2.2. Working Principle of Atomic Absorption Spectroscopy

AAS is analytical technical used to determine how much of certain elements are in sample. AAS is uses the Principle that atoms can absorb light at a specific, unique wavelength. When specific wave length of light is provide the energy (light) absorbed by atom. If the light of a specific wavelength is passed through a flame containing that atom, electron present in different energy levels, knows as orbital's, absorb a certain wavelength and excite to higher energy levels .The extents of absorption is directly proportional to the number of ground-state atoms in the flame. The ground state is more stable than the excite state and electro spontaneously return back to the ground state .it emits the same amounts of radiant energy is called fluorescence. The relationship between the quality of ground state atoms presents in flame and the degree of absorption is directly proportional. The steps involved in the analysis are given below.

- Conversion of sample in to solution form.
- Preparation of blank solution

- Preparation of series of standard solutions.
 - Setup instruments parameters.
 - Measure the absorbance of standard solution
 - Plot Calibration curve(concentration vs. absorbance)
 - Measure the absorbance of the sample solution.
- Unknown concentration of the elements is calculated from calibration curve which uses the principle of Beer-Lambert law.

2.2.3. Beer-Lambert's Law

Beer-Bouguer's law, often known as Beer-Lambert's law, or just Beer's law, is the name given to the linear relationship between the concentration and absorbance of electromagnetic radiation. Written as follows is the generic Beer-Lamberts law:

$$A = \alpha_{\lambda} b c \dots\dots\dots 2.1$$

Where A the measured absorbance α_{λ} is a wavelength – dependent absorptive coefficients b is the path –length and c is the analyze concentration .when working in concentration units of modality, the Beer-lamberts' law are written as

$$A = \epsilon_{\lambda} b c \dots\dots\dots 2.2$$

Where ϵ is the wavelength-dependent molar absorptive coefficient with units of the $M^{-1}cm^{-1}$ wavelength subscript is often dropped with the understanding that a value of is for a specific wavelength. If multiple species that absorb light at a given. The fractional change in light intensity $\left(\frac{dI}{I} = \alpha dx\right)$. Where $\alpha = \epsilon c$

Then, the absorbance or optical density A, is given by $A = -\ln\left(\frac{I_t}{I_0}\right) = \epsilon cl$



Figure 2.3. The cell containing a solution through which a monochromatic beam of light passes and is partially absorbed by the solution. Where I_0 is the intensity of the incident beam and I_t is the intensity of the transmitted beam.

l is the absorbing path length, c is the concentration of the absorbing species. Absorbance (A) and Transmittance (T) can be defined in terms of I_0 and I_t

$$T = P/P_0 \text{ or symbolize as } T = I_t/I_0 \dots\dots\dots 2.3$$

Where P or I_t is the power (Intensity) of light after it passes through the sample and I_0 is the initial light power (intensity). This is simply a measure of how many photons pass through the sample without being absorbed. This is then related to the

$$\text{absorbance by: } I_t = I_0 \times 10^{-\epsilon cl} \quad 2.4$$

Where, ϵ is the molar absorptivity (formerly known as the molar extinction coefficient), l is path length and c is the concentration of the absorbing species. Putting this equation together with that connecting absorbance and light intensity gives the familiar expression called Beer-Lambert Law: Thus, the magnitude of the Absorbance will depend directly on the concentration (c) of the absorbing species, the Path Length (l) of the light through the cell and the ability of the species to absorb radiation at the given wavelength, the extinction coefficient (ϵ). These quantities are related to the absorbance via the Beer-Lambert Law:

$$A = \epsilon c l \dots\dots\dots(2.5)$$

Note that: The Absorbance is directly proportional to each factor [42].

2.2. Literature Review

This section reviews a few studies conducted by various researchers that used the atomic absorption spectroscopy technique to determine the presence of heavy metals in raw milk and drinking water from cows. Any metallic element that is dangerous or poisonous at low concentrations and has a comparatively high density is referred to as a heavy metal.[43]. Heavy Metals are a general collective term, which applies to the group of metals and metalloids with atomic density 5 times or more high than water [44]. The elements that are classified as heavy metals are arsenic (As), copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), silver (Ag), chromium (Cr), iron (Fe), and platinum (Pt). Living organisms require trace elements such as zinc and copper, even at low concentrations (less than 10 mg/L) daily. But at high concentrations (>10 mg/L), they turn hazardous. The majority of these metals, which are simple cationic forms and can be discharged from industry, are Cd, Cu, Ni, Hg, As, Ag, Cr, and Fe.

Tasaw Belete et al studied the concentrations of Cr, Mn, Ni, Zn, Cd, and Pb in fresh cow milk in the Bore studied the concentration zone of Ethiopia. HNO₃ and H₂O₂ were used in the optimized microwave digestion process to break down the milk samples. Not every milk sample used in the study contained the metals Co, Ni, Cd, and Pb. In the milk samples from the four study sites, the values of Cr, Mn, Cu, and Zn were 0.845–0.895, 0.411–0.441, 0.087–0.122, and 5.003–6.218 µg/mL, respectively. The mean concentrations of Mn and Cr in the milk samples from the four farms do not significantly differ from one another, but the mean concentration of Zn does. The measured heavy metal concentrations were similar to some of the values reported in. [45]. Samuel Bekele et al

investigated the concentrations of ten heavy metals (Cr, Ni, Cu, Zn, As, Cd, Pb, Fe, Co and Mn) in domestically produced cow milk from Hawassa Industrial Zone (HIZ), Ethiopia and assesses the associated human health risks from milk consumption. Estimated Daily Intake (EDI), Target Hazard Quotients (THQ), Hazard Index (HI) and Target Cancer Risk (TCR) were used as indices to evaluate potential human health risks from milk consumption. Average concentrations of metals in milk from Industrial (IZ) and Non-industrial Zone (NIZ) decreased in the order Zn>Fe>Mn>Cu>Cr>Ni>Pb>As>Co>Cd and Zn>Fe>Mn>Cu>Cr>As>Ni>Pb>Co>Cd, respectively. Mean concentrations of Zn (5093.33 ± 223.49 $\mu\text{g kg}^{-1}$), Fe (592.0 ± 63.19 $\mu\text{g kg}^{-1}$) and Cu (77.78 ± 13.94 $\mu\text{g kg}^{-1}$) in milk from IZ as well as Zn (3953.33 ± 63.15 $\mu\text{g kg}^{-1}$) and Cu (63.0 ± 9.78 $\mu\text{g kg}^{-1}$) in milk from NIZ were above the maximum tolerance limits proposed by International Dairy Federations. From the results of human health risk assessments, it was concluded that effects of all heavy metal may affect human health as indicated by the elevated HI. Effluents from industries in HIZ are assumed to be the main sources of the heavy metals. Therefore, awareness creation of farmers and policy interventions with respect to waste disposal are recommended to protect the health of the ecosystem and the public [46]. Mike Odongo studied the levels of Pb, Cr, and Cd in raw bovine milk produced within Oyam District by using Atomic Absorption Spectroscopy. All the three metals were detectable in all samples and their concentrations were in the order of Cr > Pb > Cd. Finally, human health risk associated with drinking the milk was identified using Target Health Quotient (THQ) Measure and found that Lead, Cadmium and Chromium in milk is safe in terms of poisoning for consumption by humans. With regards to presence of heavy metals in raw bovine milk, then Necessity of vigorous regular national monitoring of milk contamination as well as quality of safe animal feed as main source of contamination should be emphasized. The Target Hazard Quotient (THQ) of all heavy metals analyzed

(Pb, Cr and Cd) in milk samples were found to be less than 1. Hence it would be inferred that it's safe to drink the milk from this area [47]. Amha Teklu et al studied the concentration of heavy metals in cow's milk that was collected from the districts of Butajirra and Meskan in south central Ethiopia. One hundred ninety-three healthy and nursing cows provided fresh cows' milk. HNO₃ and H₂O₂ were used in the optimized microwave digestion process to break down the samples. Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb), and Zinc (Zn) were analyzed using AAS, and Calcium (Ca), Magnesium (Mg), Potassium (K), and Sodium (Na) were analyzed using MP-AES. Ni was not found in the milk samples out of all the elements that were evaluated. In the milk samples under study, the following ranges of concentrations were found: 0.0 – 0.03, 0.0– 0.4, 0.03 – 1.1, 0.0 – 1.9, 0.0 – 0.7, 0.0 – 12.3, 0.0 – 8.2, 380.1 – 532.4, 159.6 – 397.9, 1114.2– 1685.8, and 495.9 – 1298.3 respectively [48].

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Description of the Study Area

The study was carried out in Guji Zones of Ethiopia. Three woreda such as Wadera, Goro Dola, and Liben woreda are selected.

- In Wadera woreda: Calo and Lagu kebeles
- In Goro Dola woreda: Dararaa and Haraqalo kebeles
- In Liben woreda: Bulbuli and Mugayo kebeles

The detailed description of the study areas are presented on the maps Indicated in Figure 3.1. Guji is located 555 km south of Addis Ababa. This location is a potential area for agricultural production of maize. The district is predominantly rural district and the weather condition is Desert area. In Guji zone five woreda, include above woreda are called pastoralist.

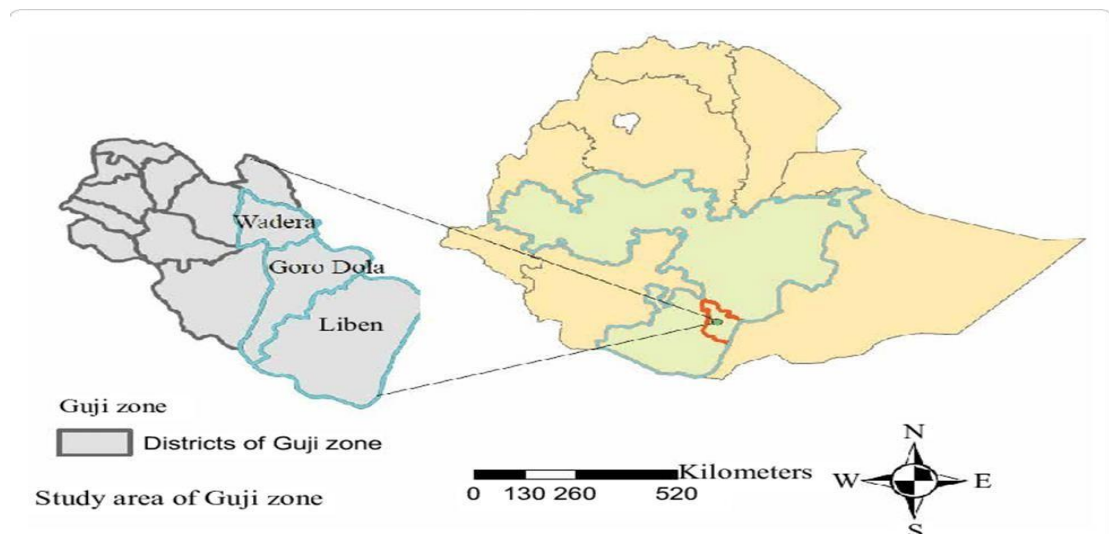


Figure 1.1. Study area of Guji zone

3.1. Sample Collection

Milk samples were collected from random Guji zone. Total of 6 raw milk samples and 6 water sample were collected fresh from selected cows during morning milking taking 50 ml per sample. Samples were collected in sterile plastic bottles and kept in iced box at 4°C. The samples were then transported to lab Purposive sampling method was used to select three kebeles from wadera, Goro Dola and Liben districts Purposive sampling method was used to select two kebeles from wadera, lagu and calo and two kebeles from Goro Dola ,Daraara and haraqalo and 2 kebele Liben districts bulbuli,and mugayo with significant dairy farms and background information from previous studies on the presence of the heavy metals of interest in water which increases the likelihood of finding the elements of interest in cow's milk .the sampling bottles were soaked in 30% nitric acid and raised with deionizer water before collection of raw milk in order to avoid possible contamination. The udder of each cow washed with distilled water before milking



Figure 3.2. Sample collected from cattle's drink water and cow milk from different sampling area.

3.3. Chemicals and Reagents

The chemicals used in this study are: HNO₃, deionizer water and stock standard solutions

of Cr, Co, Ni, Cu, and Pb. Nitric acid was used for cleaning glassware and digesting milk samples throughout this work. Stock standard solutions of Cr, Co, Ni, Cu, and Pb having concentration 1000 mg/L in 2% HNO₃ were purchased from Buck Scientific Puro-Graphictm (USA.)

3.4. Apparatus and Instrumentation

The following apparatus were used: Volumetric flasks, measuring cylinders, pipettes, micropipettes, flame atomic absorption spectrophotometer, filter paper Whitman (No. 42). Determination of trace metals concentration was done by using FAAS (BUCK SCIENTIFIC MODEL 210VGP).

3.5. Milk Sample Digestion and Preparation for Analysis

FAAS Exactly 1.000g of milk samples were taken from each of the homogenized plastic bottles and transferred to digestion round bottom flask to which 2.5mL of 69-72% concentrated HNO₃ and Optimized wet digestion procedure was employed for mineralization of the milk samples to obtain a clear solution. Collected milk samples were subjected to optimum wet digestion. To the milk samples, 6 ml of freshly prepared 4:2 (2:1, v/v) mixture of concentrated HNO₃ was added. Each mixture was then heated on a heating digester for 90 min by setting the temperature at 180°C. Six milliliters of recently made 4:2 (2:1, v/v) concentrated HNO₃ mixture were added to the milk samples.[49]. Six reagent blank samples were prepared for the analysis of the milk samples. All the digested samples were stored in a refrigerator until analysis. All samples were digested in triplicates. The digests were analyzed for the selected metals by using FAAS

3.6. Water Sample Digestion and Preparation for Analysis

The mixture (water and nitric acid) was then filtered using Whitman filter paper no.42 in 50 ml volumetric flask dilates to the label mark with deionizer water. The mixture was cooked on a hot plate for one hour at 95 °C until no brown smells were present and the volume dropped to 10 cm³. 5 ml of analytical grade nitric acid was added to 50 ml of water that had been measured and placed in blanks were processed as pre-test samples for background correction, and each was examined by FAAS for the necessary metal.

Tables 3; 1 Instrumental working Conditions of 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
Co	240.7	0.2	4.5	3.106	0.050

Table3.2 Method and instrumental detection limits

Heavy metal	MDL(mg/Kg)	IDL(mg/L)
Pb	0.106	0.040
Cr	0.061	0.040
Ni	0.153	0.020
Co	0.051	0.050
Cu	0.14	0.005

Method detection limit,"or" MDL,"means the minimum measured concentration of

a substance that can be reported with 99% confidence that the measured concentration is distinguished from method blank results.

$$\mathbf{MDL=3\sigma,}$$

M, =Method, D,=detection , L =limit , σ =standard deviation, I= Instrument

The method detection limit of the studied heavy metal suggested that the method of detection limit of each element is above the detection limit. Therefore sensitive analytical method is good for all studied heavy metals.

CHAPTER FOUR

4. RESULTS AND DISCUION

4.1. Calibration of the Instrument

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 Co, Cu, Ni ,Pb and Cr,).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 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 Co, Cu, Cr , Pb and Ni 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. The quality of results obtained for heavy metal analysis using FAAS are seriously affected by the calibration and standard solution the data qualities obtained from the inductively atomic Absorption Spectroscopy for metals analyses are highly affected by the calibration and standard solutions. The calibration graphs and determination of regression coefficient of each of the elements were determined by plotting working standards concentrations versus their intensities. The determination of regression coefficient (R_2) shows that there was a good relationship between Concentration and intensity of each metal as presented in Figure below

Table 4.1. The absorbance and concentration data that are used to plot the calibration curve.

Cr (ppm)	Absorbance	Ni (ppm)	Absorbance	Pb (ppm)	Absorbance
0.05	0.004285	0.05	0.001552	0.05	0.001268
0.5	0.03792	0.1	0.002797	0.1	0.002618
1	0.075514	0.5	0.012798	0.5	0.014801
2	0.1541	1	0.02648	1	0.30247

Co (ppm)	Absorbance	Cu (ppm)	Absorbance
0.05	0.00138	0.01	0.001547
0.5	0.023458	0.05	0.009521
1	0.043329	0.5	0.090724
2	0.086107	1	0.174248

concentration for Lead(ppm)

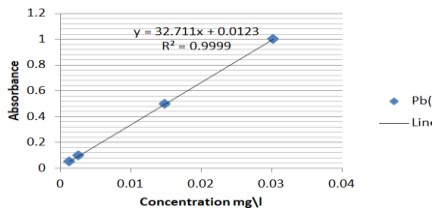


Figure a

Ni (ppm)

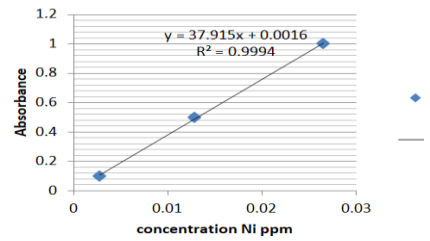


Figure b

calibration oc Cu

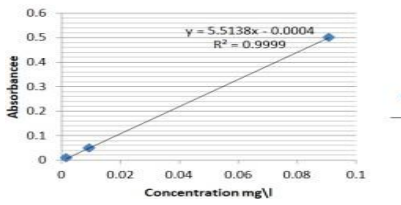


Figure d

calibration Co

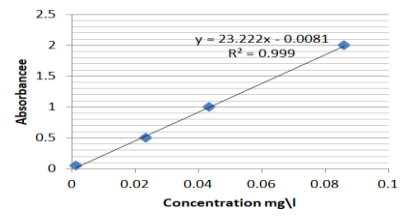


Figure c

calibration of Cr

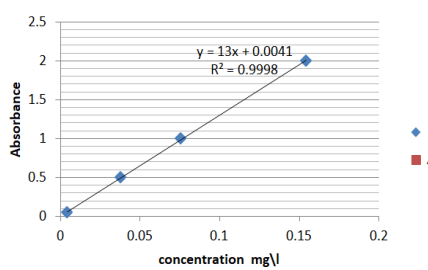


Figure e

Figure 4.1. Concentration vs. absorbance calibration curves for different metals .Figure a, b, c, d, And e represents calibration curves for Pb, Ni, Cu, Co, and Cr respectively.

Table 4.2. The Regression equation and correlation coefficients of the different metals determined from the calibration curve.

no	Meta	Concentration	correlation	Regeration
.	L	standard in(mg\l)	coefficient R ²	Equation
1	Pb	0.05 ,0.1, 0.5, 1	0.9999	Y=32.711x+0.0123
2	Cr	0.05,0.5,1,2	0.9998	y=13x+0.0041
3	Ni	0.05,0.1,0.5,1	0.9994	y=37.1915 X+0.0016
4	Co	0.05,0.5,1,2	0.9999	Y=23.222 X+0.0081
5	Cu	0.01,0.05,0.5,1	0.9999	Y=5.5138X-0.0004

4.2. Mean Concentration of Metals in Cow Milk

Average metal concentrations in the fresh cow milk from the three farms of woreda we represented.

Table 4.3. Mean Concentration of Metals in Milk.

Metal	Liben mugayo	Liben Bulbul	Goro Dola Daraara	Goro Dola haragalo	Wadera lagu	Wadera calo
Pb	0.046±0.0016	0.063±0.0016	0.084±0.00126	0.055±0.0016	0.045±0.0013	0.074.±0.0017
Co	0.097±0.0216	0.0044±0.0025	0.065±0.0016	0.075±0.0025	0.057±0.0021	0.0035±0.0021
Cr	0.074±0.0017	0.057±0.0017	0.064±0.002	0.093±0.0021	0.085±0.0017	0.047+0.0017
Ni	0.245±0.0017	0.203±0. 0021	0.245±0.00048	0.17±0.0029	0.226±0.0021	0.126±0.0025
Cu	0.32±0.0017	0.229±0.0016	0.247±0.0013	0.473±0.0024	0.161±0.0016	0.145±0.0016

From the detected elements, the highest mean concentration was obtained for Cu and the lowest was for Co among all the sampling farms of Guji zone. The Mean concentrations of heavy metals detected in the milk samples can be arranged in the order of Cu > Ni > Cr > Pb > Co

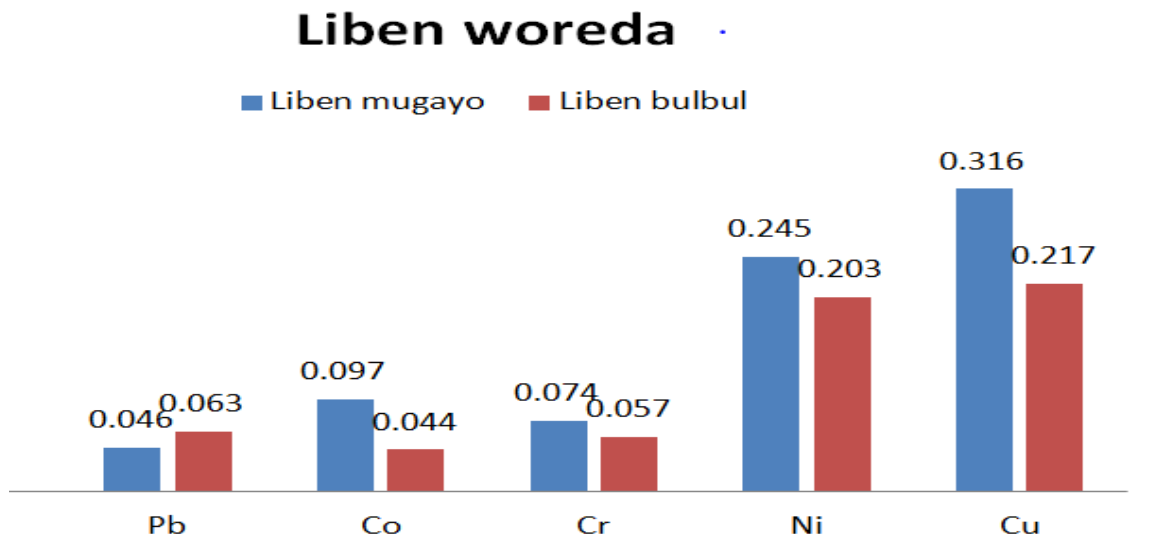


Figure 4.2. Concentrations of heavy metals in cow milk from Liben woreda

The level of Cu in cow's milk sample in Liben woreda site was higher than Ni, Cr, Co and Pb. The concentration of five heavy metal in the milk samples of two sites was found to follow in decreasing order of Cu > Ni > Co > Cr > Pb. The levels Pb lower than Ni, Cr, and Cu and Cr and. five heavy metal could be detected.

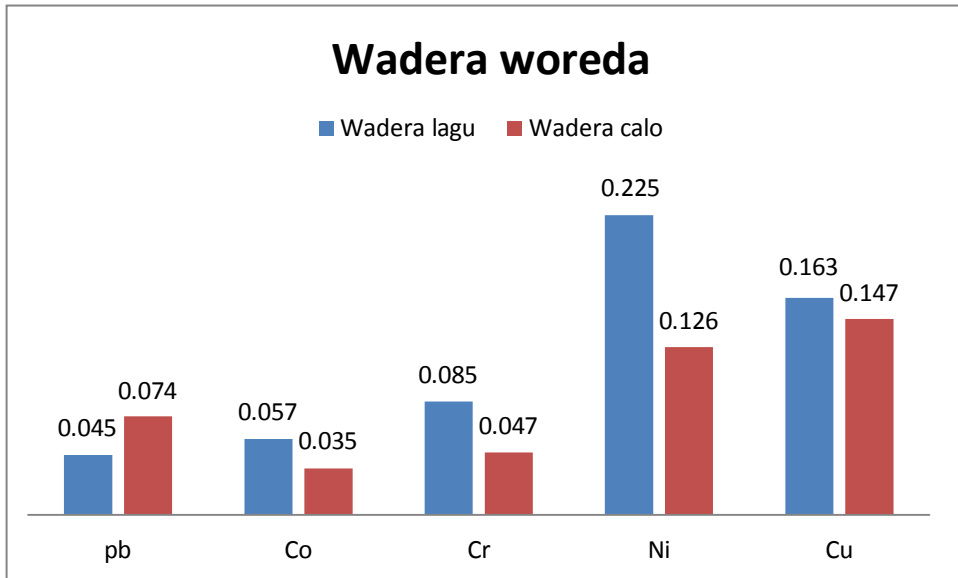


Figure 4.3. Concentrations of heavy metals in cow milk from Wadera woreda

The level of Cu in cow's milk sample in Wadera woreda site was higher than Ni, Cr, Cu and Pb. The concentration of in the milk samples of two sites was found to follow in decreasing order of Ni > Cu > Cr > Pb > Co. Co the lower than Ni, Cr, Cu and Pb and. five heavy metal could be detect.

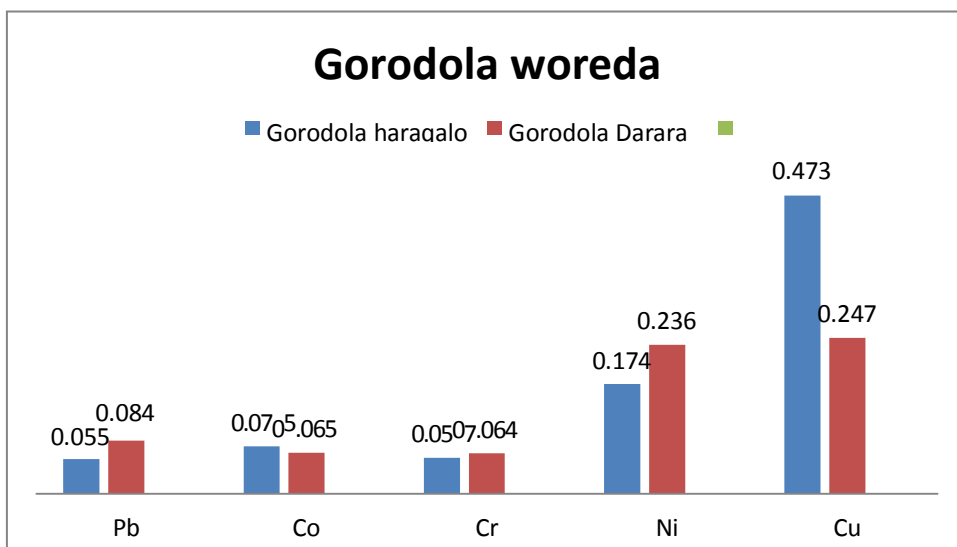


Figure 4.4. Concentration s of heavy metals in cow milk from Gorodola

The level of Ni in cow's milk sample in Goro Dola site was higher than N, Cr,Co and Pb .The concentration of in the milk samples of two sites was found to follow in decreasing order of Cu>Ni>Co>Pb>Cr,Co the lower than Ni,Cr,Cu and Pb and. five heavy metal could be detect.

4.3. Mean Concentration of Metals in water

Table4.4.MeanConcentration of Metals in water

Metal	Study Sites mean concentration standard					
	Liben mugayo	Liben bulbul	Darara Goro Dola	Haragalo Goro Dola	wadera lagu	Wadera Calo
Pb	0.045±0.0017	0.038±0.00216	0.034±0.0016	0.094±0.0017	0.045±0.0017	0.084±0.0017
Co	0.055±0.0017	0.065±0.0013	0.094±0.0017	0.057±0.0029	0.026±0.002	0.084±0.0016
Cr	0.048±0.0025	0.095±0.0021	0.045±0.0029	0.064±0.0023	0.104±0.002	0.066±0.0025
Ni	0.215±0.0017	0.174±0.0025	0.135±0.002	0.154±0.0025	0.206±0.0021	0.344±0.00216
Cu	0.085±0.0016	0.144±0.0026	0.034±0.0025	0.295±0.002	0.053±0.0039	0.125±0.0016

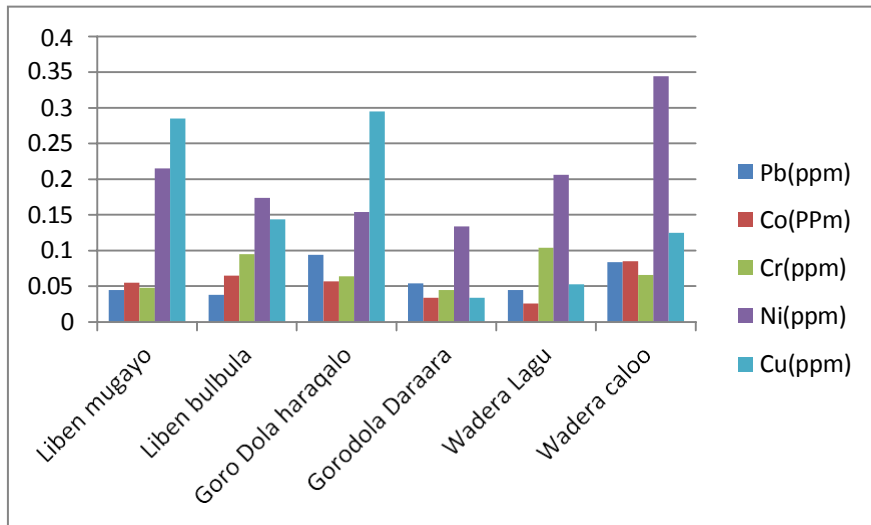


Figure 4.6. Concentration of mean water

Cu highest Mean Concentration in water and Cobalt is the lower mean concentration in water. The order of concentration from the highest to the lowest is: $Cu > Ni > Cr > Pb > Co$

Different heavy metals in cattle's drink water from various sample locations

In Liben Woreda the concentrations of heavy metals in the decreasing order of: $Cu > Ni > Cr > Co > Pb$

In Goro Co Dola the concentrations of heavy metals in the decreasing order of:

$Cu > Ni > Pb > Cr > Co$

In Wadera the concentrations of heavy metals in the decreasing order of:

$Ni > Cu > Cr > Pb > Co$

The level of Cu and Ni in water sample in three woreda site was higher than Cr, Co and Pb. The water sample of six sites was found to follow in decreasing order of

$Cu = Gorodola\ haraqalo > Liben\ mugayo\ Liben\ Bulbul\ wadera\ calo > Liben\ mugayo\ wadera\ lagu\ calo\ Goro\ Dola\ Daraara$

In General Ni was higher in wader Calo than other sample sites and Co, Cr and Pb are lowers than other sample site.

4.4. Validation of Experimental Results

4.4.1. Linearity method

Linearity is the measure of the strength of the degree of correlation between the instrument response (absorbance) and the known concentration of metal. This strength can be determined from the correlation/Regeration coefficient R^2 . In this work, the regression values obtained from different metals have values between 0.9994 and 0.9999 which suggests a good correlation between absorbance and concentration.

4.4.2. Precessions

The precession of an analytical procedure describes the closeness among series of measurements. It s usually expressed as variance, standard deviation .it is usually expressed as Variance, standard or percent's standard deviation of expressed set of measurements. The precision of the results determined in this work also described by the standard deviation. The precision of the measurements can be determined by examining the standard deviation (SD) value associated with each mean concentration.

Precision for milk

1. Chromine(Cr). $\pm 0.0017\text{mg/L}, \pm 0.0017\text{mg/L}, \pm 0.002\text{mg/L}, \pm 0.0021\text{mg/L},$
 $\pm 0.0017\text{mg/L},$
 $\pm 0.0017\text{mg/L},$
2. Lead(Pb). $\pm 0.0016\text{mg/L}, \pm 0.0016\text{mg/L}, \pm 0.00126\text{mg/L}, \pm 0.0016\text{mg/L}, \pm 0.0013\text{mg/}$
 L, \pm
 $0.0017\text{mg/L},$

3. Cobalt(Co). $\pm 0.0216\text{mg/L}$, $\pm 0.00216\text{mg/L}$, $\pm 0.0025\text{mg/L}$, $\pm 0.0016\text{mg/L}$, $\pm 0.0025\text{mg/L}$,

$\pm 0.0021\text{mg/L}$, 4. Copper

(Cu): $\pm 0.0017\text{mg/L}$, $\pm 0.0016(\text{mg/L})$, $\pm 0.0013\text{mg/L}$ $\pm 0.0024\text{mg/L}$, $\pm 0.006\text{mg/L}$,
 $\pm 0.0016\text{mg/L}$

5. Nickel(Ni). $\pm 0.0017\text{mg/L}$, $\pm 0.0021\text{mg/L}$, $\pm 0.0048\text{mg/L}$, $\pm 0.0029\text{mg/L}$,
 $\pm 0.0021\text{mg/L}$,

$\pm 0.0025\text{mg/L}$

Precision for water.

1. Lead(Pb). $\pm 0.0017\text{mg/L}$, $\pm 0.00216\text{mg/L}$, $\pm 0.0016\text{mg/L}$, $\pm 0.0017\text{mg/L}$, $\pm 0.0017\text{mg/L}$,
 $\pm 0.0017\text{mg/L}$

2. Cobalt(Co). $\pm 0.0017\text{mg/L}$, $\pm 0.0013\text{mg/L}$, $\pm 0.0017\text{mg/L}$, $\pm 0.0029\text{mg/L}$, $\pm 0.002\text{mg/L}$,
 $\pm 0.0016\text{mg/L}$

3. Chromine(Cr). $\pm 0.0025\text{mg/L}$, $\pm 0.0021\text{mg/L}$, $\pm 0.0029\text{mg/L}$, $\pm 0.0023\text{mg/L}$, $\pm 0.002\text{mg/L}$,

$\pm 0.0025\text{mg/L}$,

Nicle(Ni). $\pm 0.0017\text{mg/L}$, $\pm 0.0025\text{mg/L}$, $\pm 0.002\text{mg/L}$, $\pm 0.0025\text{mg/L}$, $\pm 0.0021\text{mg/L}$,
 $\pm 0.00216\text{mg/L}$

5. Copper(Cu). $\pm 0.0016\text{mg/L}$, $\pm 0.0026\text{mg/L}$, $\pm 0.0025\text{mg/L}$, $\pm 0.002\text{mg/L}$, $\pm 0.0039\text{mg/L}$,
 $\pm 0.0016\text{mg/L}$

4.4.3. Limit of detection (LOD)

The limit of detection (LOD) is taken as the lowest concentration of the analyte in the sample that can be detected, but not necessarily quantified, under the stated conditions of the test. LOD is calculated as [50]:

$LOD=3\sigma$, where σ is the standard deviation, D, detection, L, Limit

To determine the LOD, I use statistical calculations such as mean, variance, and standard deviation of the concentration values of water and milk

Table 4.5. Statically analysis of cow milk.

Metal Name	Mean	Variance	Standard deviation	LOD
Pb	0.06	0.00000225	0.0015	0.0045
Co	0.062	0.000001	0.001	0.003
Cr	0.07	0.00000225	0.0015	0.0045
Ni	0.203	0.000004	0.002	0.006
Cu	0.26	0.00000289	0.0017	0.0051

Table 4.6. Statistical analysis of water

Metal name	Mean	Variance	Standard deviation	LOD
Pb	0.057	0.000986	0.0314	0.0942
Co	0.063	0.00012544	0.0112	0.0336
Cr	0.07	0.00020449	0.0143	0.0033
Ni	0.204	0.0001552516	0.01246	0.003738
Cu	0.245	0.00020164	0.0142	0.00426

$$\text{Mean} = \frac{x}{n}, \quad \sigma = \sqrt{\frac{\sum(x-\chi)^2}{n}}$$

Standard deviation $\sigma = \sqrt{\text{variance}}$ Where \sum is sum, σ is the standard deviation, x is the value, χ is the mean and n is the total number.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATION

5.1. Conclusion

The main objective of this study was to determine the concentration of heavy metal in raw cow milk and water in Guji zone Oromo regional of Ethiopia. Six sampling sites of this woreda were purposely selected. The samples collected from the six different sample sites were composited for each site. Atomic Absorption spectrometer was used to assess the level of metals in cow milk. The heavy metals such as Pb, Co, Cr, Ni and Cu detected in the cow milk and water site even though they were reported in the cow milk and watering several studies. The heavy metals such as Pb, Co, Cr, Ni and Cu were detected in milk samples and water of Liben, Goro Dola, and Wadera woreda. And the concentrations were found Pb, Co, Cr, Ni and Cu in the range of: 0.06 ± 0.0015 , 0.062 ± 0.001 , 0.07 ± 0.0015 , 0.203 ± 0.002 and 0.26 ± 0.0017 mg/L respectively in the milk samples of a five sites under study. From the detected heavy metals, the highest mean concentration was found for Cu (0.26 ± 0.0017 mg/L) and lowest was for Co (0.049 ± 0.0015 mg/L) and the heavy metal detect in water samples of Liben, Goro Dola and Wadera Concentration Pb 0.057 ± 0.0026 , Co 0.064 ± 0.0019 , Cr 0.07 ± 0.0065 , Ni 0.205 ± 0.00216 , Cu 0.123 ± 0.0023 . Which mean that, Cu > Ni > Cr > Pb > Co concentration of milk in three woreda. The concentration heavy metal detect in water samples of three woreda Liben Woreda, Cu > Ni > Cr > Co > Pb, Goro Dola, Cu > Ni > Pb > Cr > Co Wadera, Ni > Cu > Cr > Pb > Co. The results concentration of milk and water direct proportional each heavy metal. And therefore concentration of milk cow dependent the concentration water.

The Pb levels obtained in the milk cow range between 0.046 mg\ and 0.084 mg\ L and

these values are above the maximum limit set by WHO(0.04).The Ni levels obtain in the milk cow range between 0.17 mg\L and 0.245mg\L above the maximum limit set by WHO (0.07 mg\L). the Co levels obtain in the milk range between0.0035 and 0.097mg\L below the maximum limit set by WHO (0.05).The Cr levels obtain in the milk cow range between 0.045 and 0.104 mg\L .below the maximum limit set by WHO (0.05) mg\L. The Cu levels obtain in the milk cow range between 0.161 and 0.473 below the maximum limit set by WHO (2.0) work mg\L.

The Pb levels obtained in water range between 0.034 and 0.084 mg\L and these values are below the maximum limit set by(0.01).The Ni levels obtained in water range between 0.134and 0.344 these values area above maximum limit set by WHO (0.02).The Cu levels obtained in water range between 0.034 and 0.295 below the maximum limit set by WHO (2.0).The Cr levels obtained in water range between 0.045 and 0.104 below the maximum limit set by WHO (0.05).The Co levels obtained in water range between 0.026 and 0.094 below the maximum limit set by WHO(0.05). In this study, the concentration of heavy metals in milk from cows and water samples from three separate woreda is determined. Milk and water are tested using atomic absorption spectroscopy and Comparing the metal concentrations detected in this study to some of the reported levels in the literature, it was discovered that they were comparable..

5.2. Recommendation

This study was the first to the area on the determination of heavy metal in raw cow milk and water so, future studies should focus on the determination of other heavy metal and study water deeply. Based on the finding and conciliation investigation heavy metal in milk and water above, the following Recommendation is forwarded.

- Researchers in the field of health science are advised to begin more evaluations and provide additional details about pure water or high-quality milk. Heavy metal levels in milk and water should be monitored.
- Research should concentrate on the water in all three woreda since the concentration of milk cow depends on the content of water.

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APPENDICS

Appendics.1



Figure Sample collect from three Woreda in Guji

Appendices2



Figure2.FAAS (BUCKSCIENTIFICMODEL210).



Figure3.Sampleonhotplate Figure4: Sample taken to Figure5 Screen

DisplayFigure7.

During

experimental

laboratory room for measuring each sample

