ICP-OES ANALYSIS OF SELECTED HEAVY AND TRACE ELEMENTS IN DRINKING TAP AND SPRING WATER IN DURAME TOWN AND THE SURROUNDING AREAS

MSc. IN LASER PHYSICS

(SPECIALIZATION: LASER SPECTROSCOPY)

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THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS,

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ADVISOR'S APPROVAL SHEET

SCHOOL OF GRADUATE STUDIES

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This is to certify that the thesis entitled "Inductive coupled plasma-Optical emission spectroscopy (ICP-OES) analysis of selected heavy and trace elements in drinking tap and spring water in Durame city and the surrounding areas" 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 Tarekegn Tekle Ergeno ID No. GPPhysK/013/11 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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Name of the Advisor	Signature	Date

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We, the undersigned, members of the board of Examiners of the final open defense by Tarekegn Tekle Ergeno have read and evaluated his thesis entitled "Inductive coupled plasma-Optical emission spectroscopy (ICP-OES) analysis of selected heavy and trace elements in drinking tap and spring water in Durame city and 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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DECLARATION

I hereby declare that this M.Sc. thesis entitled, "Inductive coupled plasma-Optical emission spectroscopy (ICP-OES) analysis of selected heavy and trace elements in drinking tap and spring water in Durame city and the surrounding areas" 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.

Name: Tarekegn Tekle Ergeno

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This M.Sc. specialty or equivalent thesis has been submitted for examination with my approval as thesis advisor.

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

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List of Abbreviation

ICP-OES	Inductive Coupled Plasma Optical Emission Spectroscopy
WHO	World Health Organization
UNICF	United Nations International Children's Emergency Fund
ICP-MS	Inductive Coupled Plasma
Uv-Vis	Ultra violet Visible
FT-IR	Fourior Transform Infrared
HQ	Hazard Quotient
CDI	Chronic Daily Effect
RfD	Reference Dose
NAZ	Normal Absorption Zone
LOD	Limit of Detection
AAS	Atomic Absorption Spectroscopy
PH	Power of Hydrogen
EC	Electrical Conductivity
TDS	Total Dissolved Solids
EMR	Electromagnetic Radiation
EPA	Environmental Protection Agency

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ABSTRACT

This thesis presents an analysis of the concentrations of heavy metals and trace elements in drinking water from tap and spring sources in Durame city, Southern Ethiopia, using Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Water contamination by metals such as lead (Pb), cadmium (Cd), and iron (Fe) poses significant health risks, making it crucial to monitor these elements. Water samples from four sites were analyzed for physical parameters such as pH and electrical conductivity (EC), alongside concentrations of metals like arsenic (As), zinc (Zn), copper (Cu), chromium (Cr), and manganese (Mn). The results were compared with the World Health Organization (WHO) drinking water standards to assess potential health risks. The study found that while most metals, including Cu, Zn, and Cr, remained within permissible limits, levels of Cd, Pb, and Fe in some samples exceeded WHO guidelines. The high levels of these metals indicate potential contamination from industrial or agricultural activities in the area. Recommendations include implementing proper water treatment processes, strengthening local environmental regulations, and conducting regular water quality monitoring to ensure public health safety. This research provides important insights into the quality of drinking water in Durame and serves as a baseline for future studies on water safety and heavy metal contamination in the region.The results are validated in terms of precession, linearity and limit of detection.

Key Words: Drinking water, heavy and trace elements, Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Beer-Lambert's law.

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CHAPTER ONE

1. INTRODUCTION

1.1. Background information

One essential resource that has an impact on human life is water. Water that comes from two main natural sources is typically surface water (lakes, ponds, rivers, streams), and ground water (well water and bore holes). Worldwide, irrigation, domestic use, and industrial supply all depend heavily on water. However, urbanization, industrialization, and population growth are the main causes of groundwater contamination. It is difficult to clean up the contaminated ground water. Therefore, it's essential to preserve the ground water's quality. In general, metals like cobalt, zinc, manganese, copper, and iron are necessary, but high concentrations can have harmful effects on health. The presence of metal ions, such as Fe, Ni, and Pb, which are highly toxic and have an impact on the central nervous system, is essential to human life [35]. Water is obviously vital to the development of industry, agriculture, and other life-supporting industries and livelihoods. Because it is also necessary for every aspect of life, both the government and the public seek to guarantee that everyone has access to enough water, both in terms of quantity and quality (UNICEF/WHO, 2011) [56].

Source of the trace elements found in tap waters is the corrosion of household plumbing systems. Different factors such as pipe material and internal protective lining of the pipe are effective on the corrosion of pipe. The corrosion typically occurs over time and leads to release the elements into the water when water contacts with the metal coating [76]. Excessive intake of essential trace elements observed in portable water, especially cadmium, chromium, arsenic, and lead, has considerable biological toxicity and is dangerous to human health. Cadmium mainly accumulates in the human hepatic system and kidneys, disturbing estrogen secretion, and is also carcinogenic [67]. Chronic intakes of heavy metals have damaging effects on human beings and other animals. For example, Cr, Cu and Zn can cause non-carcinogenic hazardous such as neurologic involvement, headache and liver disease, when they exceed their safe threshold values. Acute and chronic arsenic exposure could also cause numerous human health problems. These included dermal, respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal,

neurological, developmental, reproductive, immunological, genotoxic, mutagenetic, and carcinogenic effects (such as liver cancer) [16, 17, 21].

Anthropogenic activities such as mining, industrial and agricultural activity also contribute to heavy metal pollution in the water body due to improper waste water management and run off from fertilizer. However, most of the heavy metals dissolved in surface water and ground water are usually removed during water treatment process [21].

Use the piping system of the water plant to distribute the treated water as tap water to consumers [25]. Therefore it is important to control water quality before allocating it to communities. One common technique that is used in the determination of water contaminants is by using spectroscopic techniques. Spectroscopy is a branch of science that studies the properties of matter through its interaction with electromagnetic radiation. Depending on the type of radiation used and the mater that it interacts there are different kinds of spectroscopic techniques such as atomic spectroscopy, UV-Vis spectroscopy, infrared spectroscopy, magnetic resonance spectroscopy, etc. In this study we have used inductively coupled plasma-optical emission spectroscopy (ICP-OES). ICP-OES is a multi-element technique that uses an extremely hot plasma source to excite atoms to the point where they emit wavelength specific photons of light, characteristic of each element. The number of photons produced is directly related to the concentration of that element in the sample. ICP-OES instrumentation comes in two configurations: radial and axial. The radial configuration uses a traditional vertical plasma source where the emitting light is viewed from the side (commonly known as side-on view). The axial configuration uses horizontal plasma, where the light is viewed directly down the center (commonly known as end-on view). The benefit of the axial design is that more photons are seen by the detector and as a result offers 5-10 times lower detection limits than the radial configuration. ICP-OES is capable of low parts per billion (ppb) detection limits. There is no question that ICP-OES is in a very healthy place, particularly for samples with high total dissolved solids that require good long-term stability and also when extremely high precision is required to monitor major analyze concentrations [45]

Health risk assessment can be performed through Hazard Quotient (HQ) in equation (1.1):

$$HQ = CDI/\mathrm{RfD} \quad \text{---------- 1.1}$$

Where CDI is chronic daily intake in mg/kg/day divided by reference dose (RfD) in mg/kg/day [38].

1.2. Statement of the problem

In my study area, activities such as industrial and agricultural activity might be contribute to heavy metal pollution in the water body due to poor wastewater management from industries (like the food and coffee processing industries) and extensive fertilizer runoff, industrial and agricultural activities in my study area may be a contributing factor to heavy metal pollution in the water body. The deterioration of the pipe work connecting the reservoir that holds the spring water from Mount Ambaricho, which is anterior from Durame town, is the cause of another contamination of drinking water. Drinking water is obtained from natural springs for 29% of the population in the study area and ground water (borehole) for 71% of the population. Spring water is found in two locations and there are five sources of ground water exist in Durame city. Due to the above reasons, the available drinking water in the area are prone to contamination by heavy metals. So in this MSc work, I investigate the presence and concentrations of heavy and trace metals in some drinking water sources in the study area mentioned above, using ICP-OES technique.

1.3. Objectives

1.3.1. General objective

The primary objective of this research is to measure the levels and concentrations of some chosen heavy metals and trace elements (As, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) in drinking tap and spring water in Durame, Southern Ethiopia by using ICP-OES.

1.3.2. Specific objectives

- To determine the kind and degree of concentration of trace elements in drinking water from taps and springs in Durame town and other nearby areas.
- To investigate the chemical characteristics of water, including its pH and EC levels.
- To contrast the pH, EC, and heavy and trace element concentrations with the WHO's allowable drinking water concentration limits.
- Evaluation of health risks.
- Examine the differences in heavy metal concentrations based on WHO guidelines.

1.4. Significance of Study

The importance of this study is to know the concentration of heavy metals and trace elements in drinking tap and spring water in Durame city and the surrounding areas. So knowing this result is used for treatment of drinking water in the town. The result of this study provides information to the consumers and the authorities about the condition of the drinking water in these areas. This study will also provide baseline information for other researchers who are interested to conduct in-depth research on the safety and chemical content of drinking water distributed to the area.

1.5. Limitations

Due to time and financial constraints only limited water samples and heavy metals were studied.

CHAPTER TWO

2. THEORETICAL BACKGROUND

2.1. Optical Spectroscopy

Optical spectroscopy is concerned with the measurement of the absorption, reflection and emission of light when it interacts with matter [38]. For more than 200 years optical spectroscopy has been utilized in various fields of science, industry and medicine, particularly in chemistry, biology, physics and astronomy. Optical spectroscopy is highly specific; each substance is discernible from all others by its spectral properties. [49]

2.1.1. Electromagnetic Radiation

In physics, electromagnetic radiation (EMR) consists of waves of the electromagnetic (EM) field, which propagate through space and carry momentum and electromagnetic radiant energy [22]. EM radiation exhibits both wave properties and particle properties at the same time. Wave characteristics are more apparent when EM radiation is measured over relatively large timescales and over large distances while particle characteristics are more evident when measuring small timescales and distances. [8]. A quantum theory of the interaction between electromagnetic radiation and matter such as electrons is described by the theory of quantum electrodynamics. Wave-particle duality is the concept in quantum mechanics that quantum entities exhibit particle or wave properties according to the experimental circumstances. Electromagnetic waves can be polarized, reflected, refracted, or diffracted, and can interfere with each other. [27]

a. Wave property of light

In homogeneous, isotropic media, electromagnetic radiation is a transverse wave [43]. Meaning that its oscillations are perpendicular to the direction of energy transfer and travel. It comes from the following equations:

$\Delta E = 0$ ---------- 2.1

$\Delta B = 0$ ---------- 2.2

Waves of the electromagnetic spectrum vary in size, from very long radio waves longer than a continent to very short gamma rays smaller than atom nuclei. Frequency is inversely proportional to wavelength, according to the equation:

$$v = f\lambda \quad \text{---------- 2.3}$$

where v is the speed of the wave (c in a vacuum or less in other media), f is the frequency and λ is the wavelength. As waves cross boundaries between different media, their speeds change but their frequencies remain constant.

A monochromatic electromagnetic wave can be characterized by its frequency or wavelength, its peak amplitude, its phase relative to some reference phase, its direction of propagation, and its polarization. The energy in electromagnetic waves is sometimes called radiant energy. [34]

b. Particle property of light

In 1900, Max Planck developed a new theory of black-body radiation that explained the observed spectrum. Planck's theory was based on the idea that black bodies emit light (and other electromagnetic radiation) only as discrete bundles or packets of energy. These packets were called quanta. In 1905, Albert Einstein proposed that light quanta be regarded as real particles. Later the particle of light was given the name photon, to correspond with other particles being described around this time, such as the electron and proton. A photon has an energy, E, proportional to its frequency, f, by

$$E = hf = \frac{hc}{\lambda} \quad \text{---------- 2.4}$$

Where $h = 6.626 \times 10^{-34}$ J·s is the Planck constant, λ is the wavelength and c is the speed of light. Equation number 2.4 is sometimes known as the Planck–Einstein equation [31]. In quantum theory (see first quantization) the energy of the photons is thus directly proportional to the frequency of the EMR wave [51].

As a photon is absorbed by an atom, it excites the atom, elevating an electron to a higher energy level (one that is on average farther from the nucleus). When an electron in an excited molecule or atom descends to a lower energy level, it emits a photon of light at a frequency corresponding to the energy difference. Since the energy levels of electrons in atoms are discrete, each element and each molecule emits and absorbs its own

characteristic frequencies. Immediate photon emission is called fluorescence, a type of photoluminescence. An example is visible light emitted from fluorescent paints, in response to ultraviolet. Many other fluorescent emissions are known in spectral bands other than visible light. Delayed emission is called phosphorescence. [12].

2.1.2. Interaction between light and matter

Light interacts with matter. When light encounters matter, a lot of things can happen. A few are particularly important to keep in mind when it comes to spectroscopy:

- Some light is **absorbed** and **transformed** into other forms of energy**.** Asphalt is black because it absorbs all colors of visible light very well. It heats up quickly in direct sun because a lot of that light is transformed into thermal energy (which is then emitted back out as invisible infrared light). Plants absorb mostly red and blue wavelengths of sunlight and turn them into chemical energy to live and grow.

- Light that is not absorbed by matter can be **reflected** off it. Snow is white because it reflects all colors of visible light extremely well. Grass is green because it reflects a lot of green wavelengths of sunlight.

- Light that is not absorbed or reflected by matter can be **transmitted** through it. Window glass is transparent, or "see-through," because it transmits all colors of visible light. Strawberry jell is red because it transmits red light and absorbs all other colors. [23]

Together, wave and particle effects fully explain the emission and absorption spectra of EM radiation. The matter-composition of the medium through which the light travels determines the nature of the absorption and emission spectrum. These bands correspond to the allowed energy levels in the atoms. Dark bands in the absorption spectrum are due to the atoms in an intervening medium between source and observer. The atoms absorb certain frequencies of the light between emitter and detector/eye, and then emit them in all directions. A dark band appears to the detector, due to the radiation scattered out of the light beam. For instance, dark bands in the light emitted by a distant star are due to the atoms in the star's atmosphere. A similar phenomenon occurs for emission, which is seen when an emitting gas glows due to excitation of the atoms from any mechanism, including heat. As electrons descend to lower energy levels, a spectrum is emitted that represents the

jumps between the energy levels of the electrons, but lines are seen because again emission happens only at particular energies after excitation. [3]

2.1.2.1. Atomic Spectra

We know that in an atom, electrons have discrete and specific energies. There are more energy states in an atom than there are electrons. When an electron transitions from one energy level to another, it emits light or photon with a specific wavelength. In any given set of conditions, the collection of all these specific wavelengths is what constitutes the atomic spectrum. Hence, atomic spectra are the spectra of atoms. Atomic spectra are defined as the spectrum of the electromagnetic radiation emitted or absorbed by an electron during transitions between different energy levels within an atom. [40]

Based on the type of interaction, spectroscopic techniques can be classified as absorption and emission spectroscopes. Absorption spectroscopy includes atomic absorption spectroscopy, Uv-Vis spectroscopy, FT-IR spectroscopy, etc. On the other hand, some examples of emission spectroscopes are atomic emission spectroscopy, ICP-OES, florescence spectroscopy, etc. In this research work ICP-OES is extensively used to determine and quantify heavy and trace metallic elements in drinking water. So we will discuss about the basic principles and instrumentations of ICP-OES in section 2.1 below.

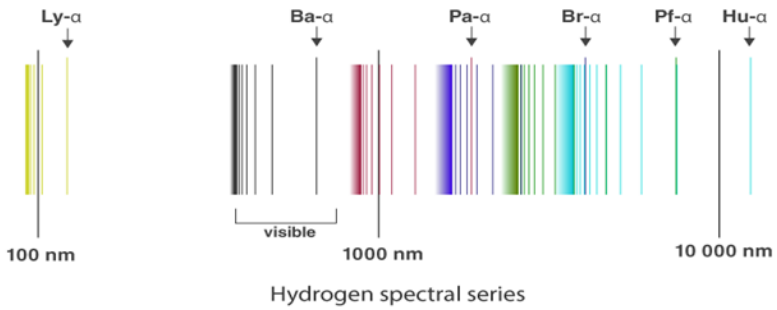


Figure 2.1: Spectral Series of Hydrogen Atom

2.2. Inductive coupled plasma optical emission spectroscopy (ICP-OES)

2.2.1. Theoretical Back Ground and Definition of ICP-OES

The ICP was developed for optical emission spectrometry (OES) by Wendt and Fassel at Iowa State University in the United States, and by Greenfield et al. at Albright & Wilson, Ltd. in the United Kingdom in the mid- 1960s [7]. The first commercially available ICP-OES instrument was introduced in 1974. The ICP is now not only the most popular source for OES but also an excellent ion source for mass spectrometry: inductively coupled plasma mass spectrometry (ICP-MS) [48]. ICP OES is a proven commercial success, and the future is still bright for ICP-based spectroscopic techniques.

On the basis of the spontaneous photon emission from excited atoms and ions in a radiofrequency discharge, ICP OES is a potent analytical instrument for identifying trace elements. Although solid samples must be extracted or acid-digested, liquid samples can be injected straight into the device. In order to maintain a temperature of about 10,000 K, the sample solution is transformed into an aerosol and sent into the plasma. After being released from their free state, the atoms are excited by additional collisional excitation. An element's origin can be determined by measuring the photons' wavelength. In comparison with other methods, ICP OES offers a higher atomization temperature, a more inert environment, and the capacity to provide simultaneous determinations for up to 70 elements [59]. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is a multielement technique that uses an extremely hot plasma source to excite atoms to the point where they emit wavelength specific photons of light, characteristic of each element. The number of photons produced is directly related to the concentration of that element in the sample. ICP-OES instrumentation comes in two configurations: radial and axial. The radial configuration uses a traditional vertical plasma source where the emitting light is viewed from the side (commonly known as side-on view). The axial configuration uses horizontal plasma, where the light is viewed directly down the center (commonly known as end-on view). The benefit of the axial design is that more photons are seen by the detector and as a result offers 5-10 times lower detection limits than the radial configuration. ICP-OES is capable of low parts per billion (ppb) detection limits. [46]

2.2.2. Characteristics of ICP-OES

The following is a list of some of the most beneficial characteristics of the argon ICP source:

- high temperature (6000–8000 K),
- high electron density (10^{14} –10^{16} cm^{-3}),
- appreciable degree of ionization for many elements,
- simultaneous multi-element capability (over 70 elements including P and S),
- low background emission and relatively low chemical interference,
- high stability leading to excellent accuracy and precision,
- excellent LODs for most elements (0.1–300 μg L^{-1}),*(33)*
- wide linear dynamic range (LDR) (four to six orders of magnitude),
- applicable to refractory elements, and
- cost-effective analyses.

Most routine applications of ICP OES use argon as the plasma gas. Mixed gas plasmas, however, have a number of intriguing uses and can even completely replace argon in order to increase analytical figures of merit. The addition of noble gases (H_2, N_2, O_2, He, and other halocarbon gases) to the auxiliary gas or emulization gas composition can enhance the thermal conductivity, electron number density, and temperature of the plasma. These changes can help atomize, ionize, and excite elements with high energies for ionization and excitation (e.g. F, Cl, Br, I, As, Se, P, and S), as well as make slurry analysis possible. Significantly more energetic conditions can be produced by adding even small amounts of He or O_2 to the plasma gas composition (5 percent), which may lead to fewer matrix effects. In comparison to traditional all-Ar plasma, temperatures and electron number densities are typically higher in an O_2-Ar plasma. By adding O_2 to the plasma, carbon deposition on the torch can be avoided for high-carbon matrices and organic solvent mixtures, and background emissions from the CN and C_2 bands can be minimized. Utilizing mixed-gas or alternative-gas plasmas has several disadvantages, including the need to modify the torch and/or other instrumentation components, the introduction of new potential interferences, and the increased operating costs related to utilizing various gases and mixtures. [1 ,15]

2.2.3. Components of ICP-OES

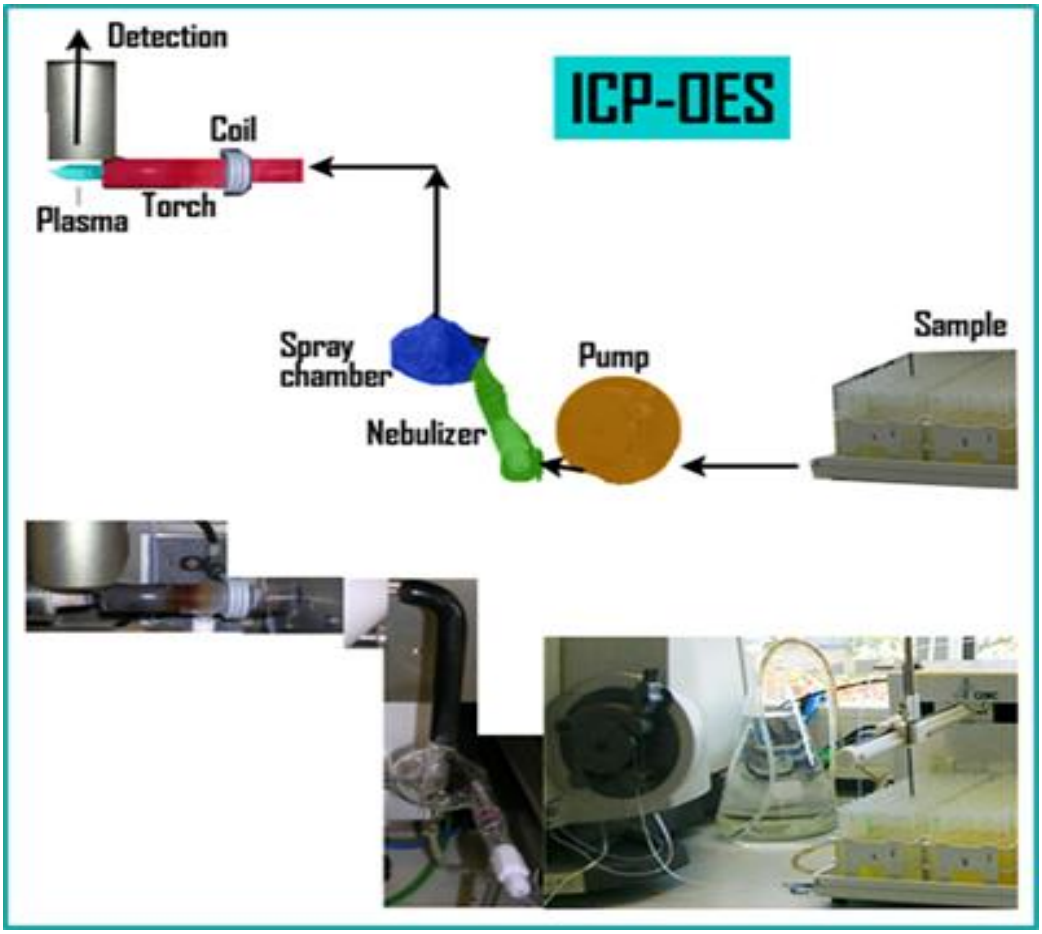


Figure 2.2: ICP-OES (Inductively coupled plasma - optical emission spectrometry) is a technique in which the composition of elements in (mostly water-dissolved) samples can be determined using plasma and a spectrometer. [42]

1. Sample Introduction in Plasma Spectrometry

A sample can be introduced as a gas, vapor, aerosol of fine droplets, or solid particles into the ICP's central channel using a sample introduction system (Stefánsson, 2007). The primary purpose of the sample introduction system is to introduce the greatest possible quantity of analytic plasma in the most appropriate form without affecting the emission signal that results from it or altering its stability (Griemand Sarojam, 2007). Liquid samples are typically used in plasma spectrometry due to their homogeneity, handle ability, and ability to create calibration standards. The sample introduction system's primary components can be summed up as follows: nebulizer, which creates an aerosol out of the liquid sample; aerosol and transfers it to the plasma through a spray chamber; a

system of desolation to lower the mass of solvent that reaches the plasma; an injector tube for the aerosol to be added to the plasma.

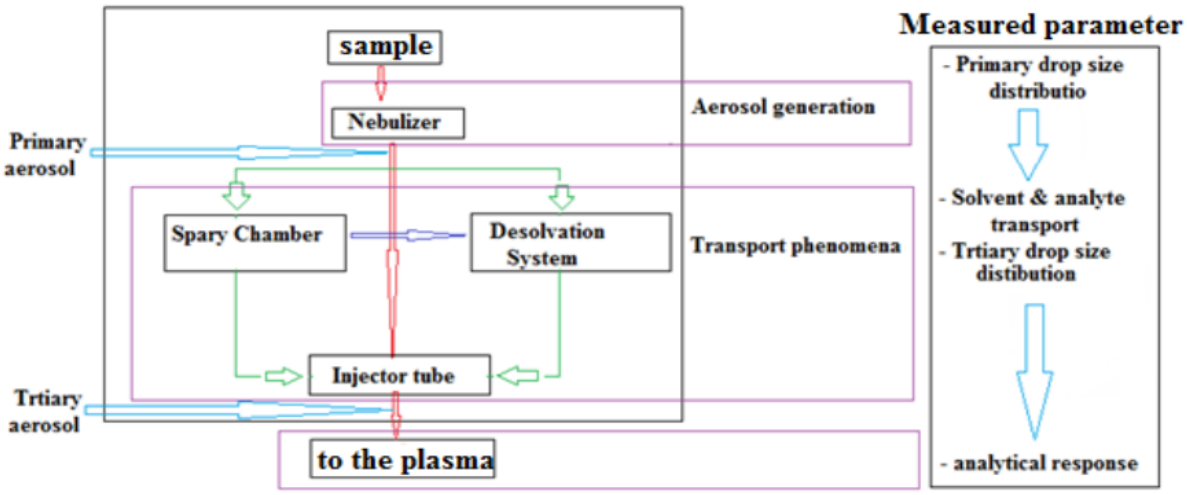


Figure 2.3:- Diagram illustrating the sample introduction system (EPA, 2013).

Peristaltic pumps: A peristaltic pump is a tiny pump that has numerous tiny rollers spinning at the same speed. Ensuring a steady flow rate of the liquid sample from its container to the nebulizer is the aim of the integrated peristaltic pump. By altering the speed of the rollers, the peristaltic pump additionally permits control over the sample uptake rate. Additionally, the pump enables the user to adjust for variations in the absorption rate brought about by the varying viscosities of the standards, blanks, and samples (Ronald and Wesley, 1988). Newton's second law is applied between two points on a streamline to obtain Bernoulli's equation. It states that

$$P_1 + \frac{1}{2}\rho V_1^2 + \gamma Z_1 = P_2 + \frac{1}{2}\rho V_2^2 + \gamma Z_2 \quad \text{----------} \quad 2.10$$

Where Z_1 and Z_2 are the heights or elevations of points 1 and 2 above some horizontal reference plane, P_1 and P_2, and V_1 and V_2 are the pressures and velocities at these same points, respectively; ρ is the gravitational constant; and is the fluid density. Using Bernoulli's equation for the peristaltic pump and spray, the following results can be obtained by dividing it by and calculating the atmospheric pressure (P_{atm}) for P_1

$$P_1 = P_2 + \frac{1}{2}\rho V_2^2 + \gamma Z_1 \quad \text{----------} \quad 2.11$$

Since, V_1 and Z_2 are equal to zero (*Jakmunee*, 1998).

Nebulizers: Nebulizers are devices that are used to transfer liquid samples from the plasma into an aerosol form. Nebulization is the process that is commonly used for the introduction of solution samples in ICP. A spray chamber filters out all of the droplets except those that are the proper size and velocity to be introduced into the plasma. The liquid is heaved into very small droplets by finely divided aerosol and argon gas, which simultaneously enters the nebulizer (WHO, 1996). Furthermore, the suitability, reasonable stability, and simplicity of use of the pneumatic nebulizer contribute to its continued popularity. Pneumatic nebulizers:

Three varieties are frequently used in ICP.

✓Concentric nebulizers have the benefits of excellent sensitivity and stability, but the small fragile fused silica holes are disposed to obstacle, especially when aspirating samples of high salt content.

✓Cross flow nebulizer, is designed to reduce the clogging problem in contrast to concentric nebulizers, it use a high-speed stream of argon perpendicular to the tip Of the sample capillary and broke sample solution into an aerosol with its Drawbacks include lower sensitivity and potential capillary misalignment.

✓Babington nebulizer that allows a film of the sample solution to flow over a Smooth surface having a small hole high-speed argon gas coming from the hole Shears the sheet of liquid into small droplets and the sample solution flows freely Over a small aperture, rather than passing through a fine capillary, resulting in a High tolerance to dissolved solids and the least susceptible to clogging of very Viscous liquid is its vital feature (*Ronald & Wesley*, 1988).

Spray chambers: During nebulization, a spray chamber is used to smooth out any peristaltic pump pulses and remove large droplets from the aerosol by gravity. In order to provide stability, particularly when organic solvents are involved, thermally stabilized spray chambers are occasionally used. Additionally, some ICP-OES spray chambers utilize external cooling to maintain the sample's thermal stability and reduce the amount of solvent that enters the plasma (WHO, 2011).

2. Source of Energy for ICP-OES

The ICP torch and its configurations: The plasma torch consists of three concentric tubes, which are typically made from quartz and they are the outer tube, middle tube, and sample

injector. The auxiliary gas is situated between the sample injector and the middle tube. The sample is transported from the nebulizer through the injector tube and into the ICP torch, which then directs the sample through the center of the plasma, in the form of a fine-droplet aerosol (WHO, 2011). When observing ICP emission, two fundamental torch configurations are used. It is possible to think of plasma as axial (end-on) or radial (side-on). Dual-view, a commercially available mode that combines the two fundamental modes, is the third viewing. Each viewing has advantages and disadvantages of its own.

Radial viewing: The NAZ plasma is viewed from its side, but this viewing restricts the NAZ observation volume, which in turn lessens the impact of possible background and spectral interferences.

Axial viewing: The plasma is rotated to a horizontal position and the NAZ of the ICP is observed from the end of the plasma and it provides, Better LODs than radial view and Better sensitivity.

Their short comings are: the increased potential for spectral interference, matrix -induced interferences, self-absorption.

Dual viewing: used for very complex sample matrices having a wide range of elemental concentrations, and lets the user to optimize the suitable configuration for the type of sample without the expense of two separate configurations (*Varner& Dvorak*, 2004).

Radio Frequency (RF) generator and Load Coil: It is a device that provides the power required for the generation and sustaining of the plasma discharge**.** Its function is to deliver power required to obtain and maintain the plasma, portions of which are as hot as 10,000°K. This power, typically ranging from about 700 to 1500 watts is transferred to the plasma gas through a load coil surrounding the top of the torch. The coils are made of copper tubing and are cooled by water during operation. Any variation in the load that is in the type of solution inserted in the plasma is compensated for by a modification in the coupling between the primary lines and the lines of the secondary circuit. The frequency is selected at 40.68MHz, which is a high frequency thus providing a weak background and excellent limits of detection (*WHO, Geneva*, 2009).

Interferences: Any chemical or physical process that dangerously distresses the measurement of the radiation of interest is called interference. Interferences in ICP may

start in the sample preparation phase and range to the plasma operating conditions. ICP and other methods of spectro-chemical analysis are typically subject to errors due to different types of interference:

Physical interference due to changes in viscosity of the solution, Chemical interference due to the generation of compounds that have low Atomization efficiency, Spectral interference due to the superposition of emission/ absorption lines, and Ionization interference which is a phenomenon shows a change in emission Intensity, causing the ionization equilibrium to shift, when coexisting elements include easily ionizable elements such as Na, K, Rb, and Cs.

Non-spectroscopic interferences are characterized by the physical properties of the sample (e.g. viscosity), matrix composition, instrumental setup and operating conditions. Generally, this results in greater intensity of neutral lines and reduced intensity of ionic lines (WHO, Geneva, 2009).

3. Emission Collector, Detector and Processor.

Focusing system: The wavelength-dispersive device or spectrometer's entrance slit receives the focus of the plasma emission radiations from the NAZ. For the instrument to be fully sensitive, ions must be collected using focusing optics, as scattered ions cannot be identified. By continuously exposing the charged ions to electric fields, ion focusing is accomplished. The ion optic system's secondary but equally crucial function is to keep particles, neutral species, and photons out of the mass spectrometer and detector. These species contribute to background levels and signal instability, which ultimately impair system performance (Clemens and Owners, 2009).

Diffraction grating: The diffraction grating, which is typically utilized with most contemporary instruments to split white light into a variety of wavelengths, is the central component of spectrometers. It is essentially a mirror (glass support) with many fixed parallel lines (between 1800 and 4320 lines/mm) covered in a photosensitive layer. When light hits such a grating, it is diffracted at an angle that varies according to the grating's density and wavelength (WHO, 1996).

$$d(sin\theta_i + sin\theta_r) = m\lambda \text{----------} \quad 2.13$$

Where Monochromatic beam incident on (blazed) diffraction grating at angle θ_i and diffracted at angle θ_r. The blaze spacing is d and m =0, 1... , m is called the diffraction order. Grating is combined Spectrometer that form the light in to well (*WHO*, 2003).

Wavelength Dispersion Device: In order to the measure several elements from the same sample the two commonly used devices in ICP are Polychromatic and Monochromatic.

Polychromatic is device with multiple exit slits and detectors in the same Spectrometer, each exit slit is aligned to an atomic or ionic emission line for a Specific element to allow simultaneous multi element analyses.

Monochromatic has only one exit slit and detector and used in multi element analyses by scanning rapidly, or slewing, from one emission line to another with sufficient speed rapid sequential multi element analyses are possible. Either by changing the angle of the diffraction grating by rotating it or by moving the detector in the exit plane of the monochromatic while leaving the grating in a fixed position. This means a sequential (monochromatic) device usually comprises an input slit controlled by computer through which the light emitted from the plasma enters; a collimating mirror which sends light to the grating; a grating used for light diffraction; and a mirror which transmits light to the output slit (*WHO*,1996).

2.2.4. Advantages of ICP-OES

i. Multi-element detection capability

One of the major advantages of ICP-OES is its ability to analyze multiple elements simultaneously. Thompson et al. (2014) conducted a comparative study of ICP-OES and Atomic Absorption Spectroscopy (AAS) for multi-element detection in water samples. Their review concluded that ICP-OES provided superior performance, especially for elements present in low concentrations, such as arsenic, cadmium, and chromium. The ability to analyze several elements in a single run has made ICP-OES the preferred choice for monitoring drinking water quality, particularly in regions affected by industrial pollution.

ii. Detection Limits and Sensitivity

A critical review by Smith and Helmers (2015) discussed the detection limits of ICP-OES, especially in the context of regulatory requirements for drinking water. The review highlighted that while ICP-OES offers ppb-level detection, certain ultra-trace elements, such as mercury and thallium, may require more sensitive techniques like Inductively Coupled Plasma Mass Spectrometry (ICP-MS). However, for most regulated metals like lead, copper, and zinc, ICP-OES detection limits are sufficient to meet the U.S. Environmental Protection Agency (EPA) and World Health Organization (WHO) standards. [41]

2.3. Determination of metal concentration using ICP-OES

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) has emerged as a powerful analytical technique for the determination of trace metals in environmental samples, particularly drinking water.

2.3.1. Beer-Lambert's law

Beer-Lambert law states that each equal thickness of light absorbing medium will absorb equal fraction of radiant energy. The law also states that the proportion of absorbed light is independent to the intensity of incident light. Lambert's law can be expressed by Equation 2.1 where I is the intensity of transmitted light, I_o is the intensity of incident light and T is the transmittance which can also expressed as percentage by multiplying T with 100.

$$\boldsymbol{T = \frac{I}{I_o}} \quad \text{----------} \quad \textbf{2.5}$$

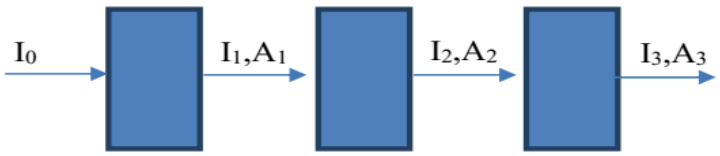
Beer's Law states that the total absorbance of a solution is equal to the sum of the absorbance of every individual element in the solutions. Thus, this makes the quantitative analysis possible to estimate the element present in the solutions. In addition, Beer's Law also states that absorbance is proportional to the thickness and concentration of the absorbing medium. Beer's Law can be expressed by Equation 2.6 where A is the absorbance, Ɛ is a proportional constant, b is the path length and ρ is the concentration of the sample.

$$\boldsymbol{A = \varepsilon b \rho} \quad \text{----------} \quad \textbf{2.6}$$

The combination of both laws is known as the Beer-Lambert Law which describes the relationship of both transmittance and absorbance. Equation 2.5 and Equation 2.6 show the relationship between transmittance and absorbance, where Ɛ is the extinction coefficient. Extinction includes all the light lost due to scattering, absorption and reflection by the particle in the sample (Owen, 2000; Hardesty and Attili, 2010). Figure 1 shows how Beer-Lambert Law works. [44]

$$T = e^{-\varepsilon b} \quad \text{----------} \quad \textbf{2.7}$$

$$A = log\left(\frac{1}{T}\right) = kb\rho \quad \text{----------} \quad \textbf{2.8}$$



Transmittance for each sample, $T = \frac{I_1}{I_0} = \frac{I_2}{I_1} = \frac{I_3}{I_2}$

Absorbance for each sample, $A = A_1 = A_2 = A_3$

Figure 2.4: shows how Beer-Lambert Law works

2.4. Heavy and trace elements contamination in drinking water

There are two types of heavy metal contamination in water, namely point sources and non-point sources. Surface water sources, including rivers, lakes, and ponds, can be polluted by effluent discharged from a point source via overflow or drainage. In non-point sources, heavy metal contaminants are carried into surface water sources by rainwater runoff (surface runoff) [9]. Insufficient water supplies and water treatment facilities, industrialization, agricultural activities, and natural factors are major causes of heavy metal contamination in water. Heavy metal contamination in water is caused by industries such as distilleries, tanneries, pulp and paper industries, textile industries, food industries, iron and steel industries, nuclear industries, etc. [20]

i. Heavy metals

There are about 40 heavy metals but the exact number depends on the definition used. Definitions are based on the density, atomic number or weight and/or toxicity. Heavy metals normally occur in nature and are essential to life but can become toxic through accumulation in organisms. Arsenic, cadmium, chromium, copper, nickel, lead and

mercury are the most common heavy metals which can pollute the environment. Mercury, lead and cadmium are of greatest concern because of their ability to travel long distances in the atmosphere.

Sources of heavy metals include mining, industrial production (foundries, smelters, oil refineries, petrochemical plants, pesticide production, chemical industry), untreated sewage sludge and diffuse sources such as metal piping, traffic and combustion by-products from coal-burning power stations. According to UNEP/GPA (2006), an increasingly serious global problem is the management of electronic waste (e-waste), particularly the disposal of used computers and mobile phones, which contain over 1 000 different materials, many of which are toxic to humans. [24, 39, 54]

ii. Trace elements

Trace metals are elements such as chromium, cobalt, copper, iron, magnesium, selenium, and zinc that normally occur at very low levels in the environment. Levels of trace metals in the environment increase when they are released from rocks. These releases can occur through natural processes or through human activities. Natural processes include breakdown of rocks, spreading of mid-ocean ridges, and volcanic activity. Natural sources of metals can be very important.

Human activities that release trace metals into the environment include mining, smelting, burning of coal, and wastewater disposal. The tar sands and diamond and metal mining can release trace metals into the surrounding environment. This often occurs when contaminated waste is not properly disposed of or when a lot of dust from the mine site blows around. For the most part, human contributions of trace metals to the environment have been approaching, or even exceeding, natural inputs. [60]

2.4.1. Standards of drinking water

Drinking water quality standards describes the quality parameters set for drinking water. Water may contain many harmful constituents, yet there are no universally recognized and accepted international standards for drinking water. Even where standards do exist, the permitted concentration of individual constituents may vary by as much as ten times from one set of standards to another. Many countries specify standards to be applied in their

own country In Europe, this includes the European Drinking Water Directive [44] and in the United States, the United States Environmental Protection Agency (EPA) establishes standards as required by the Safe Drinking Water Act. China adopted its own drinking water standard GB3838-2002 (Type II) enacted by Ministry of Environmental Protection in 2002 [28]. For countries without a legislative or administrative framework for such standards, the World Health Organization publishes guidelines on the standards that should be achieved. [29]

Drinking water quality standards are standards set to ensure the protection and safety of human health in regard to water consumption (NIS, 2007) [28]. The advancement in understanding the nature and effects of various contaminants in water has led to the establishment of regulatory bodies that set recommended (maximum allowable) limits for each water parameter, particularly for drinking water. The quality of water is assessed based on the concentration levels of these parameters (WHO, 2003) [29]. The quality of water is regarded as satisfactory when the concentration level of parameters investigated is less than the maximum allowable limits. These recommended standard limits are set based on their implication on human health. Excess of the recommended or allowable limits is a strong indication of health risk for consumers. World Health Organization (WHO) guideline is a backbone from which other regulatory bodies adopted their guideline (Peavy*et al.*, 1985).

i. Ranges of Standards: Drinking water standards include lists of parametric values, and also specify the sampling location, sampling methods, sampling frequency, analytical methods, and laboratory accreditation. For example, when comparing drinking water quality parameters in Kenya and Ethiopia with published guideline values (thresholds), scientists compared several standards: the Kenyan drinking water standard, Ethiopian standard, WHO health guideline, WHO Aesthetic guideline and the EAS (East African Standards) for natural potable water. Furthermore, the non-regulatory health-based screening levels (HBSLs) for cobalt, lithium, silver, strontium, and thallium published by the USGS and US EPA were also included in the analysis.[53]

ii. Parametric values: A parametric value in this context is most commonly the concentration of a substance, e.g. 30 mg/L of iron. Many countries not only specify parametric values that may have health impacts but also specify parametric values for a

range of constituents that by themselves are unlikely to have any impact on health. These include color, turbidity, pH, and the organ oleptic parameters (taste and odor).

2.4.2. Water quality parameters

Appropriate selection of quality parameters and representative physical and chemical analyses are necessary for the control of water quality. The study employed pipe water samples, and the frequency, quantity, and preservation of these samples were determined by analyzing quality parameters as well as the characteristics of the water samples. The main metrics used to assess the quality of drinking water are PH-value, EC, and chemical aspects of trace elements, according to the literature.

i. Total dissolved solids (TDS)

TDS is a measure of the dissolved combined content of all inorganic and organic substances present in a liquid in molecular, ionized, or micro-granular (colloidal sol) suspended form. TDS are often measured in parts per million (ppm). TDS in water can be measured using a digital meter [41]. Total dissolved solids are normally discussed only for freshwater systems, as salinity includes some of the ions constituting the definition of TDS. The principal application of TDS is in the study of water quality for streams, rivers, and lakes. Although TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects), it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants.

Primary sources for TDS in receiving waters are agricultural runoff and residential (urban) runoff, clay-rich mountain waters, leaching of soil contamination, and point source water pollution discharge from industrial or sewage treatment plants. The most common chemical constituents are calcium, phosphates, nitrates, sodium, potassium, and chloride, which are found in nutrient runoff, general storm water runoff and runoff from snowy climates where road de-icing salts are applied. The chemicals may be cations, anions, molecules or agglomerations on the order of one thousand or fewer molecules, so long as a soluble micro-granule is formed. More exotic and harmful elements of TDS are pesticides arising from surface runoff.

Total dissolved solids include both volatile and non-volatile solids. Volatile solids are ones that can easily go from a solid to a gaseous state. Non-volatile solids must be heated to a high temperature, typically 550 °C, in order to achieve this state change. Examples of non-volatile substances include salts and sugars. [7]

TDS [mg/L] = k_e × EC [µS/cm]---------- 2.9

The conversion factor k_e ranges from 0.5 to 0.8. Usually, **0.67** is used when the actual factor is unknown

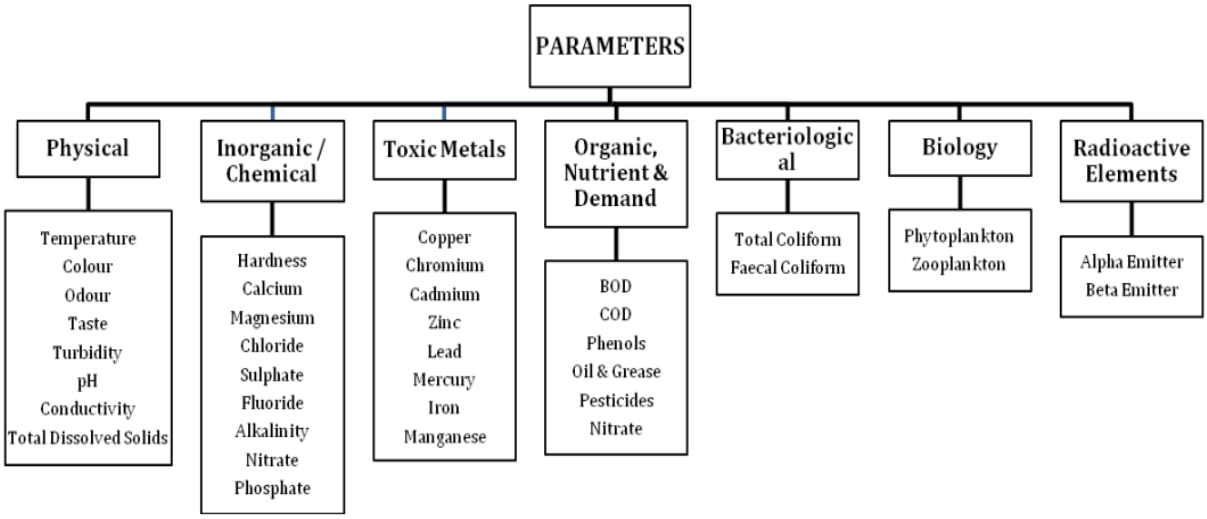


Figure 2.5: Parameters for water quality analysis [36]

2.5. Reviews of related literature

The presence of heavy metals in drinking water poses significant health risks, necessitating effective monitoring and assessment methodologies. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) has emerged as a powerful analytical technique for the determination of trace metals in environmental samples, particularly drinking water. This literature review synthesizes recent findings related to heavy metal contamination in drinking water and the application of ICP-OES in their analysis.

Wongsasuluk et al. (2014) conducted a comprehensive study on heavy metal contamination in drinking water sourced from shallow groundwater wells in an agricultural region of Thailand. Their findings revealed significant levels of heavy metals, raising

concerns regarding human health risks associated with long-term exposure. This study underscores the necessity for regular monitoring of drinking water quality, particularly in agricultural areas where pesticide and fertilizer runoff can contribute to metal contamination.

Similarly, Giri and Singh (2015) assessed the groundwater of the Subarnarekha River Basin in India, highlighting the health risks posed by metal contamination via drinking water pathways. Their research employed a combination of experimental and computational methods, paving the way for new strategies in trace contaminant analysis. The integration of computational modeling with empirical data can enhance predictive capabilities regarding contamination levels and their health implications.

In another study, Alidadi et al. (2019) evaluated health risks associated with arsenic and toxic heavy metal exposure in northeast Iran. Their assessment reinforced the critical need for health risk evaluations in regions with known contamination issues, indicating a widespread challenge across different geographical locations. [5 , 54 , 47 , 41]

Harrison et al. (2018) reviewed the health impacts of heavy metal contamination in drinking water and the role of ICP-OES in mitigating these risks. The study discussed ICP-OES's application in monitoring critical contaminants like lead, which has neurotoxic effects, particularly in children. The authors also examined ICP-OES's utility in detecting trace levels of arsenic and its role in preventing long-term health impacts such as cancer. They concluded that the high throughput and sensitivity of ICP-OES make it essential for routine health risk assessments in water systems. [30]

CHAPTER THREE

3. MATERIALS AND METHOD

3.1. The Study Area

Durame town is the administrative center of the Kembata Zone of the Central region of Ethiopia and has a latitude and longitude of (7°14′N37°53′E) with an elevation of 2101 meters above sea level.

3.2. Collection of samples

Four samples from Tap water have been collected from different stations throughout the city (Weta, Fulasa, Helelo and Ambaricho); which were frequently consumed by the citizen of Durame Town and around there were taken from 2024.

The contaminations of heavy metals and trace elements in (surface) water of four different water bodies (2 spring waters and 2 boreholes) in Durame town were analyzed.

Sampling techniques were designed to gather a small amount of material (water) that would accurately represent the sample being handled and be transportable to the analytical research laboratory. Equal amounts of water samples were collected in clean plastic bottles. Prior to collecting the samples, the bottles were thoroughly cleaned and then rinsed with tap water and distilled water. The water samples were collected in four individual plastics bottles of volume 300ml each. After acidification, water samples were kept in ice refrigerator and, Samples were carefully, and transport to Bishoftu Laboratory Horticoop Ethiopiafor the physical and chemical analysis based on the parameters set for this study.

The American Public Health Association (APHA), 22nd edition, and Indian Standard Methods IS: 3025 (Part I) provided standard sample collection protocols, procedures, and guidelines that were adhered to when collecting the samples. During the sample collection process, extra care was taken [62]. The samples were taken in plastic bottles from four distinct small water bodies (ponds) in Durame town (as shown in Figure). Each sample bottle was labeled clearly with a water resistant black ink, and additional pertinent information was noted. This sampling procedure was conducted in Jharkhand at the

conclusion of the monsoon (viz. after September 2021 in the middle. As soon as the collected water samples arrived at the laboratory, they were filtered using a vacuum-type filtration apparatus. Using a 0.45 µm membrane filter, the water samples were filtered.[36]

Figure 3.1: Collecting drinking water sample from one of the sample site (left) and the lab center for physical and chemical characterization of water samples (right).

3.3. Sample Preparation Procedure

i. Procedure for pH measurements in water

Testing materials were used in various procedures to determine the pH value of water (Clemens and Owners, 2009). Put a clean glass beaker with a stirring bar and thermometer in it with the water sample inside. The pH is then measured while stirring at a rate that will avoid splashing and the loss or addition of basic or acidic gases through atmospheric exchange. The water sample is measured portion by portion until the next portion differs by no more than 0.05 pH units.

ii. Procedure of water sample preparation for chemical analysis

Testing materials were used in various procedures to measure the drinking water sample preparation (WHO, 2008). Following meticulous filtering of the collected samples through Whitman filter papers to remove impurities and solid particles from the liquid, 5 milliliters of the sample were filled in the pipette then into volumetric flasks that had

been previously (before) treated. A milliliter of concentrated HNO_3 was added, along with two or three drops of 30% H_2O_2. Placing the vial in a 50 ml baker makes it easier to handle and less likely to tip over when it is placed on a hot, flat dish. However, it is important to ensure that the vial is dry and free of moisture to prevent spills or spitting of the sample. Remove the vial from the heated flat dish, add one milliliter of concentrated HNO_3, two or three drops of 30% H_2O_2, and heat until the mixture is dry (free of moisture). Continue until a translucent residue (that is, one that can be seen through a miniature fiber optic spectrometer that uses a small tungsten halogen lamp as a partial light source) is left. If needed, gently dissolve the residue. After that, add 4 milliliters of water, swirl to fully (much) combine, and store in the fridge.

3.4. Experimental Measurement

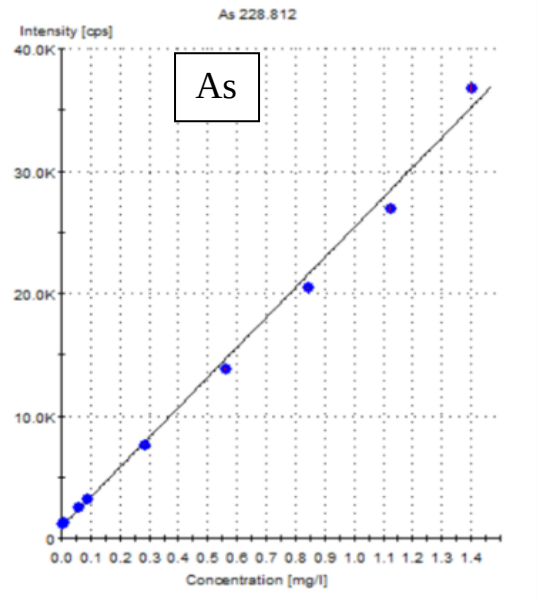
After the probe's reading was submerged in the beaker containing the sample, it was discovered that the water was tested directly using a pH probe from a multi-meter. A small portion of the sample and distilled water were used to rinse the probe. The conductivity of the water was measured using a conductivity probe multi-meter by submerging it in the beaker containing the sample, and a reading in terms of mS/cm was obtained from the display. By following these procedures, the chemical parameters can be determined using ICP-OES. By mixing water with argon gas at a high flow rate in a nebulizer, which is powered by a peristaltic pump, a fine aerosol is created using the water. When a fine droplet of water enters the plasma, it goes through three stages: desolation, vaporization, and atomization. The spray chamber uses gravity to remove large aerosols, and only aerosols of fine droplet are introduced to the central part of the ICP-OES, which was initialized and allowed to achieve thermal equilibrium over 30min. A prior to departing from the plasma and reaching the subsequent apparatus, the atoms were extracted and ionized using the energy that was available in the ICP. The operating parameters of the ICP were regulated by software, promoting the atoms to their respective excited states within the wave length range of 175 nm and 777 nm. Both of them then relaxed to the ground by emitting characteristic photons whose energies were determined by the quantized energy level structure of the atoms or ions. The ICP uses a lens or concave to collect some of the photons it emits.

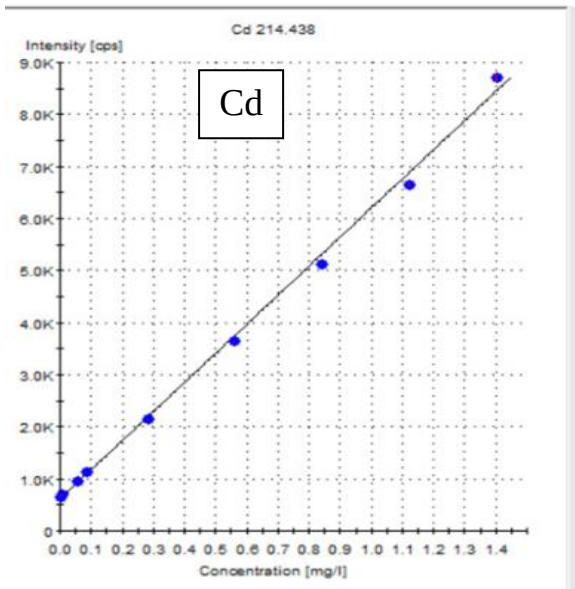
CHAPTER FOUR

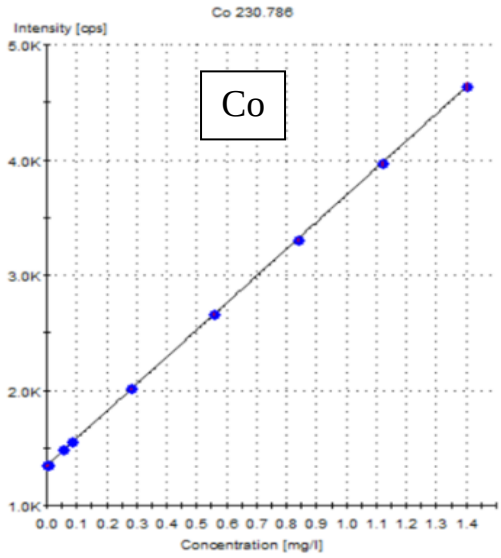
4. RUSLTS AND DISCUSSION

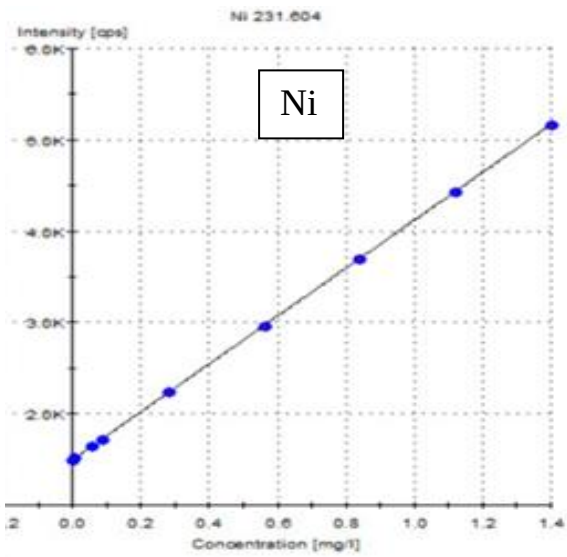
4.1. Calibration curves

To quantify the amount of elements present in the drinking water samples, calibration curves (intensity versus concentration curves) are made for all elements that are investigated in this research work. The calibration curves are made by preparing a serious of known concentrations of each element and measure the intensity of each concentration. These calibration curves are used to determine the concentrations of these elements from the water samples collected from the sampling site where the concentration of the elements are unknown.









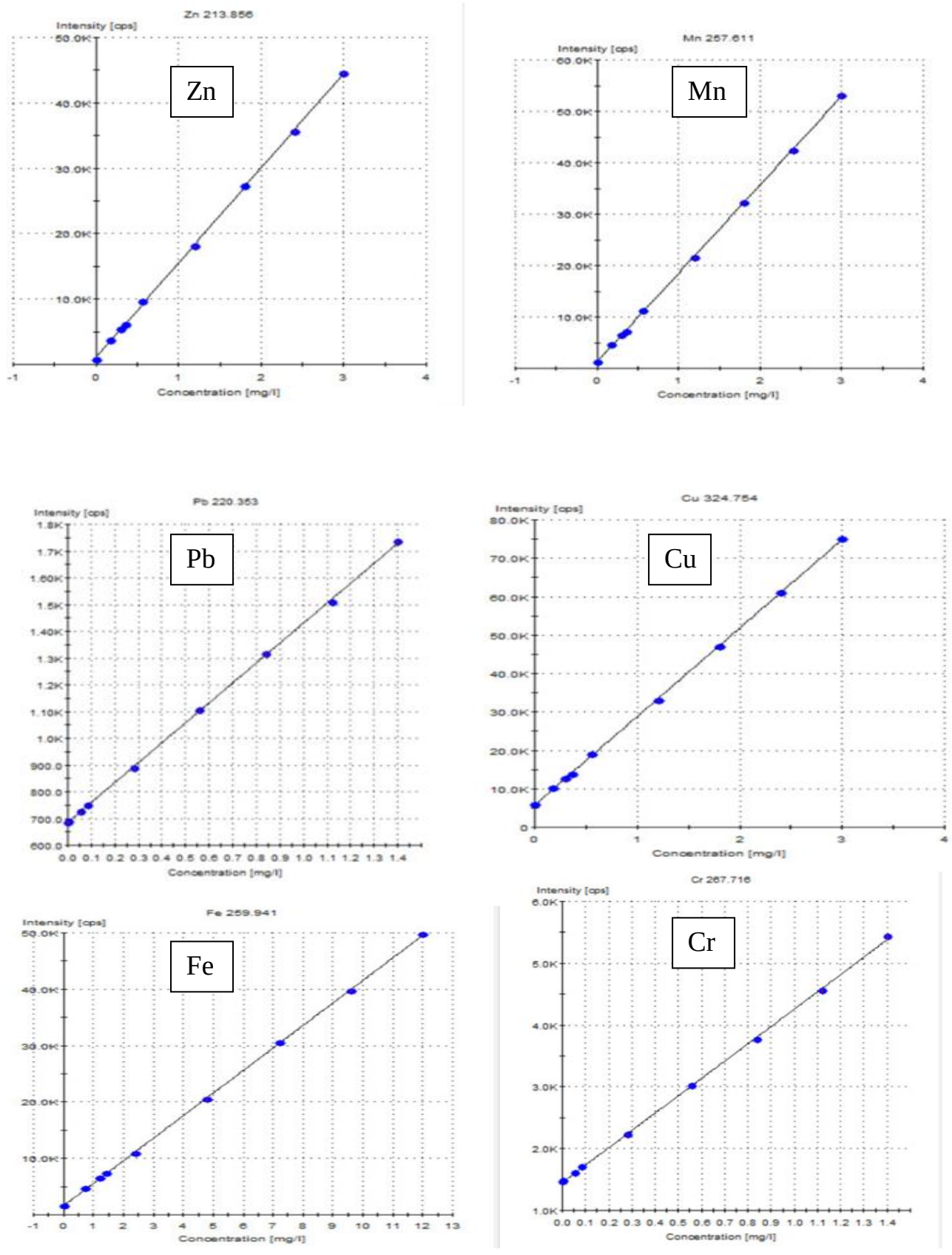


Figure 4.1: Concentration versus intensity graphs for the different elements investigated in this work

4.2. Determination of concentration and physical parameters (PH and EC) in drinking water samples

4.2.1. Physical parameters

The physical parameters such as, EC and PH, measured from collected water samples from different place of Durame town using ICP-OES are presented in the table 4.1.

Table 4.1: Physical parameter concentrations (pH and EC) for five sampling points are shown.

Sources	**Bore hole**		**Spring water**		**WHO**
Lab code	24HWA 1358	24HWA 1359	24HWA 1360	24HWA 1361	
Parameters	**Weta**	**Fulasa**	**Helelo**	**Ambaricho**	
pH	7.58	7.10	5.92	6.37	Minimum 6.6 Maximum 7.8
EC(µS/cm)	310	160	390	50	297 – 570
TDS (mg/L)	207.7	107.2	261.3	33.5	

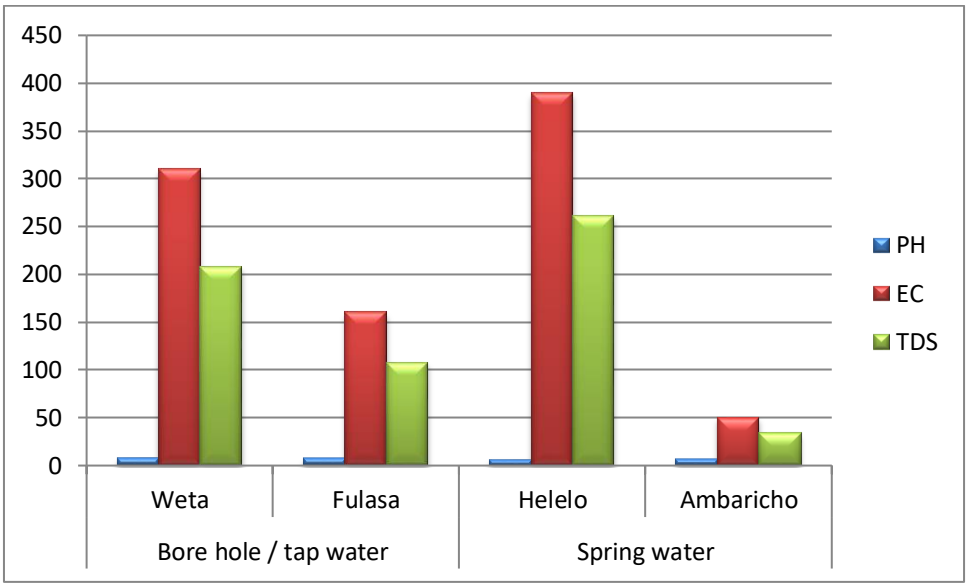


Figure 4.2: PH, EC and TDS variation across sampling points

Water contamination is a common problem in towns, even with notable efforts made in recent decades to provide clean drinking water. This is because the concentration of contaminants in drinking water can lead to health problems. To ascertain the impact of drinking pipe water drawn from various locations within the town on quality was the motivation behind the current study. The mean value was 6.74 and 228 μs/cm for PH and EC respectively. In the present study, the mean pH value varied from 6.6 to 7.8 and was within the permissible limit set by water standard of WHO [21]. So in my study the pH value of water samples for Weta site and Fulasa site are within the permissible limit of WHO standard. But the pH values of Helelo site and Ambaricho site were recorded below the permissible limit set by WHO. Water pollution can be detected when the value of EC is high (Xianhong, et al., 2021). EC of the tap water was fluctuated between 297 to 570μs/cm, whereas in this study it ranged as per normal range 297 to 570μs/cm for Weta site & Helelo site and less than 297μs/cm for Fulasa site and Ambaricho site (Table 4.1). This implies the value obtained for EC was found to be within allowable limits of WHO standards that it has no contamination effect in four sites while PH value obtained by the experiment was 6.74 which were in between the limit of it set by WHO. It may not be important to evaluate the concentration of parameters in the samples to report possible contamination that would be representing health hazard.

4.2.2. Concentrations of heavy and trace elements

Using ICP-OES spectroscopy the emission intensity at different wavelengths that corresponds to the emission wave length of each element under investigation are measured from the water samples collected from the sample sites. These intensities are shown below in Table 4.2.

Table 4.2: The characteristic wavelength and the mean values of intensities of heavy metals and trace elements.

Metals		As	Pb	Zn	Cd	Cu	Ni	Co	Fe	Mn	Cr
Unit		Cps	Cps	Cps	Cps	Cps	Cps	Cps	Cps	Cps	Cps
Wave length (nm)		430.01	220.35	213.86	214.44	324.75	231.60	230.79	259.94	257.61	267.72
Weta	Intensity	1182.54	677.404	2513.93	556.935	7156.62	1469.08	1315.5	2045.65	1182.85	1446.38
	Stdv	0.61612	3.72559	18.2728	178.935	20.173	9.98353	2.10229	95.7068	10.705	9.47792
Fulasa	Intensity	1168.16	671.148	22771	651.989	7207.37	1459.74	1298.82	2035.48	1190.42	1424.2
	Stdv	15.0112	11.1564	334.147	7.88243	24.2753	10.3353	11.9177	12.7401	7.3887	2.72335
Helelo	Intensity	1177.09	671.776	1779.62	664.777	6938.01	1455.98	1311.98	3179.57	1354.18	1436.07
	Stdv	11.6966	5.17756	40.763	6.86204	24.77	4.18243	8.93197	64.8993	10.7206	7.48213
Ambarich o	Intensity	1174.72	663.708	2373.01	662.237	7178.74	1455.84	1306.93	3994.31	1456.1	1435.92
	Stdv	3.32856	4.10021	25.4889	5.81361	22.4856	2.41711	8.88793	56.6452	12.6703	1.37413

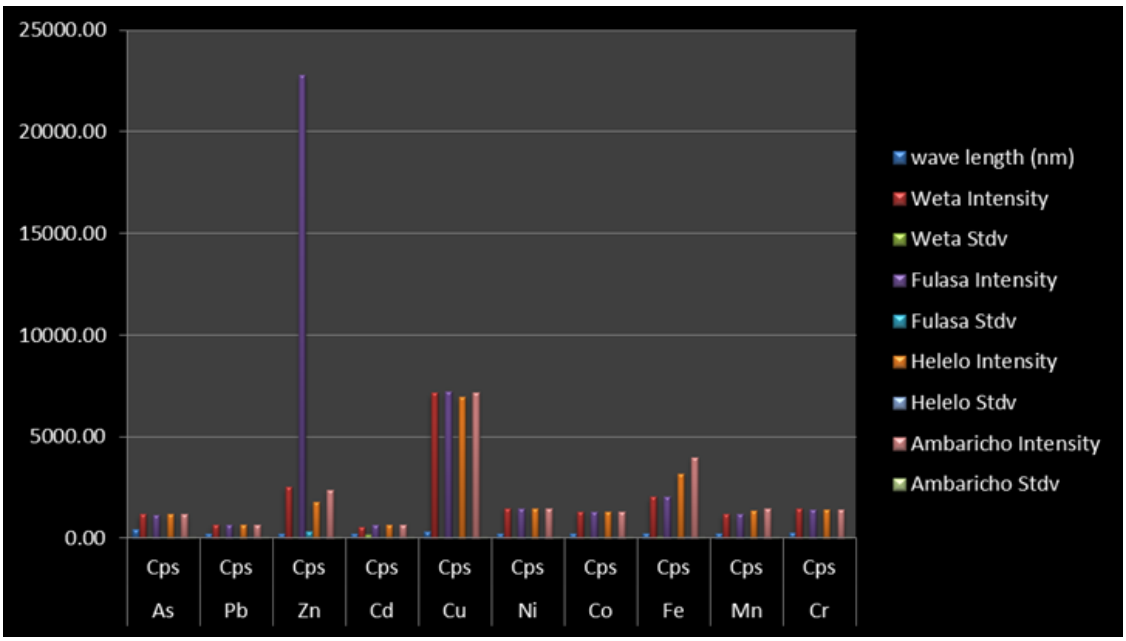


Figure 4.3: The characteristic wavelength and the intensity emitted by elements across the sample points.

Then these intensity values are converted to the corresponding concentrations by using the equations generated from the calibration curves. The resulted concentration values are shown in the following table, Table 4.3.

Table 4.3. Concentrations (mg/L) of heavy metals and trace elements (As, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) in drinking tap and spring water.

Heavy metals	Bore hole		Spring water		WHO
	Wota	Fulasa	Helelo	Ambaricho	
As	< 0.001	< 0.001	< 0.001	< 0.001	0.01
Pb	0.067	0.063	0.063	0.057	0.01
Zn	0.072	0.963	0.039	0.065	**NGL
Cd	0.015	0.015	0.016	0.016	0.003
Cu	0.036	0.037	0.06	0.036	1
Ni	< 0.003	< 0.003	< 0.003	< 0.003	0.07
Co	< 0.020	< 0.020	< 0.020	0.02	NM
Fe	0.084	0.099	0.291	0.428	***NGL
Mn	0.003	0.001	0.013	0.021	0.4
Cr	0.006	< 0.007	< 0.007	< 0.007	0.05

NM = Not mentioned,**NGL= No Guideline, because it occurs in drinking-water at concentrations well below those at which toxic effects may occur, The permissible limit for Zn in water according to WHO criteria is 5 mg/L.*** NGL=No Guideline, because it is not of health concern at concentrations normally observed in drinking water, but may affect the acceptability of water at concentration above 0.3mg/L [61].

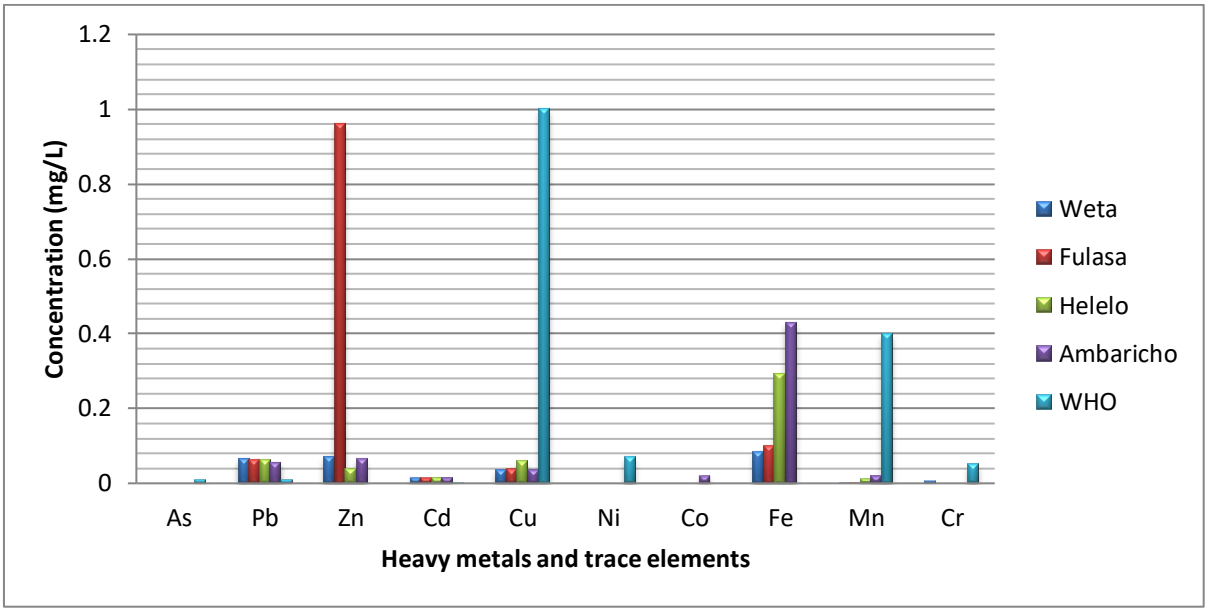


Figure 4.4: The concentration of heavy metals and trace elements variation across sampling points

Four samples were taken from different places of Durame town. When we were studying the concentration of heavy metals and trace elements in each of samples in the laboratory we tested and took the values three times for each of them on lab report as shown Appendix 1.

The following are some of the heavy and trace metals studied in this work and their characteristic properties and toxicity / health risk.

Arsenic is naturally occurring element. It is odorless and tasteless. The maximum acceptable concentration of arsenic in drinking water recommended by the World Health Organization is 0.001mg/L [6]. In my study none of the sample are exceeds the WHO standard.

Cadmium is the one most commonly found metal. It found with zinc, carbonate and sulfide ore. One source is ingestion of grown foodstuffs, especially grain and leafy vegetables, which readily absorb cadmium from the soil. The cadmium may occur in groundwater naturally or as a contaminant from sewage sludge, fertilizers, polluted groundwater or mining and industrial effluents [14].Increase of Cd may be changes the pH of the water. Cadmium can be present in groundwater from a wide variety of sources in the environment and from industry. In my present study all samples are exceeding the WHO standards.

Chromium is one of the heavy metal present in nature but it occurs in only in combined state. In our present study in whole sample it is under limits of WHO standards.

Copper is common heavy metal found in environment and spread through the natural phenomenon it is widely used in industries and agriculture. It is trace essential element for human health. In my study none of the sample are exceeds the WHO standard.

Iron is naturally occurring metal in nature in the form of magnetite hematite etc. It enters into water in the extraction of metal from its ore. It also enter into the water aluminum waste products which are contains iron are discharged into water. Iron content in the body exceeds and stored in liver, pancreas, and heart, damage these organs. In my present study a sample from Ambaricho site the concentration of Fe exceeds the max concentration of 0.3mg/L.

Lead is a toxic metal which occurs naturally in the environment. It is used in many products found in and around homes. But the concentration of lead may be increases due to human activities, it enter into environment through the exhaust of cars. It enters into water through the corrosion of pipes. Small amounts of lead it causes many health problems, especially in the case children below six-year-old are most risk. Lead can cause disruption of the biosynthesis of hemoglobin, rise in blood pressure kidney damage etc [18]. In my present study all the samples are exceeds the max concentration according to WHO standard.

Manganese is one of the most abundant metals in earth crust it present in the form of oxides and hydroxides. It is one of the common essential trace element and toxic. The statement about manganese forming deposits in pipes and causing issues with water quality is well-supported by research in water treatment and infrastructure. Manganese is known for precipitating as manganese oxides in water distribution systems, which can lead to the formation of black particles, affecting both the taste and appearance of water [19]. In my study none of the sample are exceeds the WHO standard.

Nickel is one of the essential heavy metal present in the earth crust. It is found in sand stone and slate, element accumulates in sediments of biological cycles. In my present study none of the sample are exceeds WHO standard.

Zinc is an essential trace metal. It enters into water on locations where zinc ore are found. It is used treatment and prevention of zinc deficiency and its consequences, including stunted growth and acute diarrhea in children, and slow wound healing. Zinc leaks from zinc pipes and rain pipes, consequential to circulation of carbon rich water. Increase concentration zinc may be causes the toxicity leading to stomach aches and vomiting colics, fevers and diarrhea [50]. In my present study none of the sample are exceeds WHO standard.

Cobalt is an essential element for the growth of many marine algal species. Cobalt has also been shown to enhance growth of some plants at low concentrations. In higher concentrations, cobalt is toxic to humans and to terrestrial and aquatic animals and plants. To protect freshwater aquatic life from acute toxic effects of cobalt, it is recommended that the interim maximum concentration of total cobalt should not exceed 0.11mg/L [26]. In my present study none of the sample are exceeds WHO standard.

As we see on the figures at the characteristic peak wavelength of Cu the intensity emitted is the highest value from those metals across the samples except sample-II. This means that the numbers of photons emitted at a given wavelength are much more that from the rest of heavy metals. In sample-II, Zn has the highest emission intensity recorded from the rest of samples. In the contrary Cd in each of samples the intensity emitted is very low.

In the study the concentration of heavy metals as WHO standard the concentration of Cu is 1mg/L and according to the lab report recorded values in each of samples were near to the permissible limit WHO standard. This indicates that the greater the concentration of an element, the more intense the light emission recorded. Zn also in sample-II is highly concentrated that's why more intense light emission takes place. So we can conclude that more light intensity emitted by metals are highly concentrated across the samples.

4.3. Health Risk Assessment

Health risk assessment involves evaluating the potential adverse health effects due to exposure to hazardous substances, such as heavy metals, found in drinking water. In this study, water samples were collected from various sources in Durame city and analyzed for heavy metals including lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), iron (Fe), and others. The health risk assessment was conducted by comparing the measured concentrations of these metals to the World Health Organization (WHO) permissible limits and calculating the Hazard Quotient (HQ) for each metal.

4.3.1. Exposure Assessment

Exposure assessment evaluates the extent to which individuals in Durame city might be exposed to heavy metals through drinking water. The concentration of heavy metals in water samples was determined using Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The metals that exceeded the WHO permissible limits were lead, cadmium, and iron. The chronic daily intake (CDI) of these metals can be calculated using the following formula:

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad \text{----------} \quad 4.1$$

Where:

- **C** = concentration of the contaminant in water (mg/L),
- **IR** = ingestion rate (L/day), typically 2 L/day for adults,
- **EF** = exposure frequency (days/year), typically 365 days/year,
- **ED** = exposure duration (years), typically 30 years,
- **BW** = body weight (kg), typically 70 kg for adults,
- **AT** = averaging time (days), usually 365 days/year × exposure duration.

4.3.2. Toxicity Assessment

The toxicity assessment evaluates the adverse health effects associated with exposure to hazardous metals. Each metal has a reference dose (RfD), which represents the maximum acceptable oral dose of the substance without significant risk of adverse health effects. The toxicity values for metals commonly found in water are as follows:

- **Lead (Pb):** 0.0014 mg/kg/day
- **Cadmium (Cd):** 0.0005 mg/kg/day
- **Copper (Cu):** 0.04 mg/kg/day
- **Zinc (Zn):** 0.3 mg/kg/day
- **Iron (Fe):** 0.7 mg/kg/day

4.3.3. Risk Characterization

Risk characterization combines the results of the exposure and toxicity assessments to estimate the potential health risks. The Hazard Quotient (HQ) is calculated as the ratio of the estimated exposure (CDI) to the reference dose (RfD):

$$HQ = \frac{CDI}{RfD} \text{----------} \quad 4.2$$

- **HQ < 1**: Indicates no significant risk of adverse health effects.
- **HQ > 1**: Suggests potential for adverse health effects.

The overall health risk is quantified by calculating the Hazard Index (HI), which is the sum of the HQs for all metals:

$$HI = HQ_{Pb} + HQ_{Cd} + HQ_{Cu} + HQ_{Zn} + HQ_{Fe} \quad \text{---------- 4.3}$$

If the **HI** exceeds 1, it indicates a potential for adverse non-carcinogenic health effects from the combined exposure to multiple metals. Results of Risk Assessment:

- **Lead (Pb):** All samples exceeded the WHO permissible limit of 0.01 mg/L, with concentrations ranging from 0.057 to 0.067 mg/L. Lead exposure is especially harmful to children, causing developmental issues, cognitive deficits, and nervous system damage. The HQ for lead in all samples was above 1, indicating significant health risks.
- **Cadmium (Cd):** Cadmium concentrations also exceeded the WHO standard of 0.003 mg/L in all samples, with values ranging from 0.015 to 0.016 mg/L. Cadmium is known to cause kidney damage and bone demineralization over long-term exposure. The HQ for cadmium was significantly higher than 1, indicating a high risk of adverse health effects.
- **Iron (Fe):** In some samples, iron concentrations were above the WHO guideline of 0.3 mg/L, with values up to 0.428 mg/L. While iron is essential for human health, excessive levels can lead to organ damage. The HQ for iron in these samples suggested a moderate risk, especially for individuals with prolonged exposure.
- **Copper (Cu) and Zinc (Zn):** Copper and zinc concentrations were within the WHO permissible limits, with HQ values below 1, indicating no significant health risks from these metals.

The overall Risk the combined Hazard Index (HI) for lead, cadmium, and iron in all samples exceeded 1, which suggests that residents consuming water from these sources are at risk of adverse health effects, particularly from lead and cadmium. The high levels of lead and cadmium in drinking water could lead to significant health problems, including cognitive impairment in children, kidney dysfunction, and increased risk of cardiovascular disease.

In conclusion the health risk assessment indicates that the levels of lead and cadmium in drinking water in Durame city pose a substantial health risk to the population. Immediate action is required to reduce exposure to these toxic metals. Implementing water treatment

systems to remove lead and cadmium, regular monitoring of water quality, and raising public awareness are essential measures to mitigate these health risks.

4.4. Validation of Experimental Result

Since data of experimental result concerning concentration of heavy metals and trace elements expressed in detail at APPENDIX 1. The experimental results are validated in terms of precision, linearity and limit of detection.

i. Precision

Precision is determined by a statistical method called a standard deviation. Standard deviation is how much, on average, measurements differ from each other. High standard deviations indicate low precision, low standard deviations indicate high precision. As we see each measurements the standard deviation were put around 0.001 , 0.002 and 0.004. But some of heavy metals like Fe at Weta site, Pb at Fulasa site, Zn at Fulasa site and Fe at Helelo site were recorded as 0.014, 0.009, 0.015 and 0.011 respectively. Therefore, in all cases the values of standard deviation were much less than that of mean values for each of heavy metals and trace elements. So in my recorded values for each of experimental data almost all were precise values even if as I mentioned before about Fe, Pb and Zn.

ii. Linearity

In a linear calibration curve, there is a value called the calibration coefficient, denoted by 'r,' which measures the strength and the direction of association between two variables. The correlation coefficient value ranges from −1 to +1.A value of +1 indicates a perfect positive linear correlation, −1 denotes a perfect negative correlation, and 0 implies no correlation between the two variables. A positive correlation value establishes that as one variable increases, the other increases, and vice versa. On the contrary, a negative correlation value indicates that as one variable increases, the other variable decreases, and vice versa. Squaring the correlation coefficient results in the coefficient of determination, denoted by 'r^2' or 'R^2'. This value ranges from 0 to 1. A value closer to 1, such as 0.999, indicates an excellent fit, whereas a value close to 0 indicates a poor fit. Therefore my experimental data expressed in calibration curve in detail at APPENDIX 2, 3, 4and in Figure 4.1 for each of heavy metals and trace elements and expressed below in Table 4.4.

Table 4.4: The linearity of experimental data from each of calibration curves.

Metals	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Correlation coefficient (R^2)	0.9976	0.9988	0.9999	0.9998	0.9999	0.9999	0.9999	0.9999	0.9992	0.9998

iii. Limit of detection (LOD)

The limit of detection (LOD) can be calculated using various methods. One common approach is to determine LOD as three times the standard deviation of the instrument response for the blank, divided by the calibration curve slope, as per the International Union of Pure and Applied Chemistry (IUPAC) guidelines.

$$LOD = 3 \times \left(\frac{Standard\,deviation\,of\,the\,blank\,measurements}{Slope\,of\,the\,calibration\,curve}\right) \quad \text{---------- 4.5}$$

Table 4.5: The limit of detection comparing with mean value of the concentration of heavy metals and trace elements

Heavy metals	**Bore hole / tap water**				**Spring water**			
	Wota		**Fulasa**		**Helelo**		**Ambaricho**	
	LOD	**Mean**	**LOD**	**Mean**	**LOD**	**Mean**	**LOD**	**Mean**
As		< 0.001		< 0.001		< 0.001		< 0.001
Pb	0.0027	0.067	0.0016	0.063	0.0165	0.063	0.0124	0.057
Zn	0.0002	0.072	0.0031	0.963	0.0004	0.039	0.0002	0.065
Cd	0.0005	0.015	0.0016	0.015	0.0005	0.016	0.0005	0.016
Cu	0.0000	0.036	0.0001	0.037	0.0001	0.06	0.0000	0.036
Ni		< 0.003		< 0.003		< 0.003		< 0.003
Co		< 0.020		< 0.020		< 0.020		<0.020
Fe	0.0105	0.084	0.0015	0.099	0.0083	0.291	0.0075	0.428
Mn	0.0002	0.003	0.0000	0.001	0.0002	0.013	0.0002	0.021
Cr	0.0022	0.006	< 0.007	< 0.007		< 0.007		< 0.007

As we see from the data given in the table 4.5 all LOD values are less than the corresponding mean values of heavy metals and trace elements. So we can check or conclude our results are acceptable.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

This study focused on evaluating the concentrations of heavy metals and trace elements in drinking water from Durame city and surrounding areas, using Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The water sample collected was tested the concentration for heavy metal and trace elements (As, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) and physical parameters such as temperature, pH, EC and TDS of the ground water and spring water.

Pipe drinking and spring water of Durame town shows nearly acceptable value for EC and pH has a different value at different sampling places but the average value is acceptable value in terms of WHO for water quality guide lines value.

The study highlights that while most trace elements like Cu, Zn, and Cr remain within acceptable limits set by the World Health Organization (WHO) standards for drinking water, while some of trace elements and heavy metals (Cd and Pb in all sampling sites, Fe in Ambaricho site) exceed the WHO permissible limit. The exceedance of WHO permissible limits for Cd, Pb, and Fe in the water samples indicates potential contamination from industrial, agricultural, or urban sources. The excessive levels of cadmium and lead are of particular concern due to their significant health risks, including toxicity to the kidneys, nervous system, and cardiovascular system. Iron, in some samples, was also detected at levels higher than the WHO guidelines, though its health risks are typically associated with longer-term exposure and may not be immediately apparent.

The presence of these heavy metals may pose health risks to local populations if the water is used for drinking, agriculture, or other domestic purposes.

In general, consuming water with above of permissible limit value could cause serious health problem. Those water sources that do not conform to National Standard will result in public health problem in long time exposure. Therefore, the local water authority shall strengthen local water quality monitoring and control system as well as risk assessment and management mechanisms.

Key Findings:

- **Cadmium (Cd):** All samples had concentrations above the WHO permissible limit. Chronic exposure to cadmium is known to cause severe health effects, including kidney damage, bone demineralization, and it is a recognized carcinogen.
- **Lead (Pb):** Lead levels in all samples exceeded the WHO guidelines. Lead is highly toxic, particularly to children, affecting cognitive development and causing long-term neurological damage. For adults, lead can contribute to high blood pressure and kidney damage.
- **Iron (Fe):** While iron is an essential nutrient, excessive levels, as found in sample IV, can lead to organ damage, particularly in the liver and pancreas. High iron levels also impact water's taste and aesthetic qualities.

Water Quality Parameters:

- **pH:** The pH levels of the water samples varied, with some falling below the permissible range for safe drinking water. Water with a pH outside of the acceptable range can corrode pipes, leading to the leaching of metals such as lead and copper into the water supply.
- **Electrical Conductivity (EC) and TDS:** Both EC and TDS were within the WHO limits in all samples. These measures are important indicators of the overall salinity and ionic content of water and can be related to the presence of dissolved solids, including salts and metals.

The results indicate a clear need for intervention to mitigate the health risks associated with contaminated drinking water in Durame city. The high levels of toxic metals like cadmium and lead suggest that the water sources are either contaminated due to industrial activities, agricultural runoff, or deteriorating infrastructure, such as corroded pipes. These findings underscore the importance of routine water quality testing and the implementation of proper water treatment techniques to ensure public safety.

Health Implications: Prolonged exposure to water contaminated with heavy metals can lead to serious health issues, particularly for vulnerable populations such as children, pregnant women, and the elderly. Cadmium exposure, for instance, can lead to skeletal damage and kidney failure over time. Lead exposure, even at low levels, can cause

developmental delays in children, lower IQ scores, and behavioral problems. Immediate action is needed to address these contamination levels to prevent long-term health consequences in the community.

5.2. Recommendation

Provide suggestions for any possible future research avenues, such as expanding the analysis's metal range or raising the ICP-OES technique's sensitivity for trace element detection. In order to reduce the health hazards associated with the high concentrations of Cd, Pb, and Fe in water samples, a multifaceted strategy that includes prompt treatment, source control, ongoing monitoring, and public education is necessary. The long-term sustainability of water resources can be maintained while protecting public health by addressing contamination at both the source and user levels.

Therefore, the recommends of this study:-

- **Implement appropriate water treatment technologies:** Introduce or enhance water treatment systems to remove heavy metals from the affected water sources. Technologies such as activated carbon filters, reverse osmosis, and ion exchange systems are effective in removing heavy metals like Cd and Pb.
- **Regular maintenance of treatment systems:** Ensure that water treatment facilities are regularly maintained to maintain their efficiency in removing contaminants.
- **Strengthen environmental regulations:** Advocate for the implementation of stricter environmental regulations to limit the release of heavy metals into the environment.
- **Sustainable agricultural practices:** Promote the use of eco-friendly and sustainable farming practices that reduce the need for heavy metal-containing fertilizers and pesticides.
- **Public Awareness and Education:** Educating the local population about the risks associated with heavy metal contamination in drinking water is essential. This includes promoting safe water consumption practices and the importance of using properly treated water for drinking and cooking.
- Further studies, has to be performed for further analysis of physico -chemical and Trace metal analysis in other Pipe water found of Durame town.

In conclusion, while some of the water sources in Durame city meet the required standards for safe drinking water, the presence of hazardous metals such as cadmium, lead, and iron in several samples is alarming. Immediate actions are necessary to improve water

treatment processes and to reduce environmental pollution to protect public health and ensure a sustainable and safe water supply for the future.

REFERENCES

1. A. Fisher, S.J. Hill, (2007). Alternative and Mixed Gas Plasmas, in *Inductively Coupled Plasma Spectrometry and its Applications*, eds. S.J. Hill, Blackwell Publishing Ltd, Oxford, 226–250.
2. Ab Razak NH, Praveena SM, Aris AZ, Hashim Z.,(2015). Drinking water studies: a review on heavy metal, application of biomarker and health risk assessment (a special focus in Malaysia). *Journal of epidemiology and global health*. 5(4):297–310.
3. Albert KhGilmutdinov, (1999). Atomic Absorption, Theory. Kazan State University, Russia, pp 33–42, volume 1, Elsevier Ltd.
4. Alidadi, H.., Sany, S. B. Tavakoly., et.al (2019). Health risk assessments of arsenic and toxic heavy metal exposure in drinking water in northeast Iran. Environmental Health and Preventive Medicine, P. 24..http://doi.org/10.1186/s12199-019-0812-x
5. Asfaram, Arash., et.al (2016). Biosorption of Zn2+, Ni2+ and Co2+ from water samples onto Yarrowialipolytica ISF7 using a response surface methodology, and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). RSC Advances, 6 , 23599-23610. http://doi.org/10.1039/C5RA27170C
6. Bonkoungou IJ, Damanka S, Sanou I, Tiendrébéogo F, Coulibaly SO, Bon F, Haukka K, Traoré AS, Barro N, Armah GE. (2011). Genotype Diversity of Group A Rotavirus Strains in Children with Acute Diarrhea in Urban Burkina Faso, 2008–2010 Journal of Medical Virology 83, 1485–1490
7. C.B. Boss, K.J. Fredeen, (1997). *Concept, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry*, 2nd edition, Perkin-Elmer, Norwalk.
8. Carmichael, H. J., (2007). "Einstein and the Photoelectric Effect" (PDF). Quantum Optics Theory Group, University of Auckland. http://www.qo.phy.auckland.ac.nz/talks/photoelectric.pdf.
9. Chowdhary P., Bharagava R.N., Mishra S., Khan N., (2019). Role of Industries in Water Scarcity and Its Adverse Effects on Environment and Human Health. *Environ. Concerns Sustain. Dev.* 2029:235–256.
10. Giri, S., & Singh, A. (2015). Human health risk assessment via drinking water pathway due to metal contamination in the groundwater of Subarnarekha River

Basin, India. Environmental Monitoring and Assessment, 187, 1-14 .http://doi.org/10.1007/s10661-015-4265-4

11. Griem, H.R. Plasma Spectroscopy. McGraw Hill, New York, (1964).
12. Haneef, Deena T. Kochunni, Jazir. (2017) "7 Differences between Fluorescence and Phosphorescence". http://www.majordifferences.com/2016/11/7-differences-between-fluorescence-and-Phosphorescence.html ,
13. Harrison, D., et al. (2018). *Health Impacts of Heavy Metal Contamination in Drinking Water: Role of ICP-OES.* Toxicology Reports.
14. HoungK.H .&D .Y . Lee (1998). Comparisons of linear and nonlinear Langmuir and Freundlich curve-f it in the study of Cu, Cd and Pb adsorption on Taiwan soils, J. Soil Sci., 163 (2), 115- 121.
15. J.R. Chirinos, K. Kahen, S.E. O'Brien, A. Montaser,(2002). 'Mixed-gas Inductively Coupled Plasma Atomic Emission Spectrometry Using a Direct Injection High Efficiency Nebulizer', *Anal. Bioanal. Chem.*, 372(1), 128–135.
16. Kamani H, Mahvi A, Seyedsalehi M, Jaafari J, Hoseini M, Safari G, et al. (2017). Contamination and ecological risk assessment of heavy metals in street dust of Tehran, Iran. Int J Environ Sci Technol.;14(12):2675–82.
17. Kamani H, Mirzaei N, Ghaderpoori M, Bazrafshan E, Rezaei S, Mahvi AH. (2018). Concentration and ecological risk of heavy metal in street dusts of Eslamshahr, Iran. Human and ecological risk assessment: an international journal;24(4):961–70.
18. Lantzy R.J. Mackenzie F.T. (1979). Atmospheric trace metals: global cycles and assessment of man's impact, Geochim. Cosmochim. Acta, 43: 511- 525.
19. Lemly, A.D., (2002). Selenium assessment in aquatic ecosystems—a guide for hazard evaluation and water quality criteria: New York, Springer-Verlag, 3
20. Lin L., Yang H., Xu X. Effects of Water Pollution on Human Health and Disease Heterogeneity: A Review. *Front. Environ. Sci.* 2022;10:880246. doi: 10.3389/fenvs.2022.880246.
21. Liu X, Song Q, Tang Y, Li W, Xu J, Wu J, et al. Human health risk assessment of heavy metals in soil–vegetable system: a multimedium analysis. Sci Total Environ. 2013;463:530–40.
22. Mattsson MO, Simkó M. Emerging medical applications based on non-ionizing electromagnetic fields from 0 Hz to 10 THz. Med Devices (Auckl). 2019 Sep

12;12:347-368. doi: 10.2147/MDER.S214152. PMID: 31565000; PMCID: PMC6746309.

23. Mohd Ali, M., Hashim, N., Bejo, S. K. and Shamsudin, R. (2017). Optical parameters in food and agricultural processing, International Food Research Journal 24(3): 908-914
24. Morel, F. M. M. and N. M. Price. 2003. The Biogeochemical Cycles of Trace Metals in the Oceans. Science. 300(5621):944-947. DOI: 10.1126/science.1083545.
25. N. H. Ab Razak, S. M. Praveena, A. Z. Aris, and Z. Hashim, 2015. "Drinking water studies: A review on heavy metal, application of biomarker and health risk assessment (a special focus in Malaysia)," *Journal of Epidemiology and Global Health*, vol. 5, no. 4, pp. 297-310.
26. N.K. NagpalPh.D, et al. (2004). TECHNICAL REPORT - WATER QUALITY GUIDELINES FOR COBALT, Water, Air and Climate Change Branch Ministry of Water, Land and Air Protection PO Box 9341 STN PROV GOVT Victoria BC V8W 9M1
27. National Aeronautics and Space Administration, Science Mission Directorate. (2010). Wave Behaviors. Retrieved *[insert date - e.g. August 10, 2016]*, from NASA Science website: http://science.nasa.gov/ems/03_behaviors
28. NIS (2007) "Nigerian Standard for Drinking Water Quality"ICS 13.060.20.
29. Nowicki, Saskia; Birhanu, Behailu; et.al (2023). "Water chemistry poses health risks as reliance on groundwater increases: A systematic review of hydrogeochemistry research from Ethiopia and Kenya". Science of the Total Environment. 904: 166929. *doi*:*10.1016/j.scitotenv.2023.166929*. *PMID* *37689199*.
30. P. Botes, (December, 2003). "Investigation of mobility of trace elements in river sediments using Table of Content," .
31. Paul M. S. Monk (2004). *Physical Chemistry*. John Wiley and Sons. p. 435. ISBN 978-0-471-49180-4.
32. Peavy, H. S., Rowe, D. R., &Tchobanoglaus, G. (1985). Environmental Engineering. International Edition, McGraw-Hill BookCo. Singapore. pp 12 – 56.
33. Physicochemical analysis of the bottled drinking water available in the Dhaka City of Bangladesh. *Journal of materials and environmental science*, *8*(6), 2076–2083.

34. Purcell and Morin, Harvard University. (2013). Electricity and Magnetism, 820p (3rd ed.). Cambridge University Press, New York. *ISBN 978-1-107-01402-2. p 430*

35. RavisankarTadiboyinaa , and Prasada Rao Ptsrkb, 2016.Trace Analysis of Heavy Metals in Ground Waters of Vijayawada Industrial Area INTERNATIONAL JOURNAL OF ENVIRONMENTAL & SCIENCE EDUCATION, VOL. 11, NO. 10, 3215-3229.
36. Ritabrata Roy, 2019. An Introduction to Water Quality Analysis Vol. 06: International Research Journal of Engineering and Technology (IRJET), e-ISSN: 2395-0056, p-ISSN: 2395-0072.
37. Ronald L. M, Wesley L. B, and Noman E. P. Specific Conductance Theoretical Considerations and Application to Analytical Quality Control. *Geological Survey Water Supplypaper 2311, US, (1988)*
38. S. Muhammad, M. T. Shah, and S. Khan, 2011. "Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan," *Microchemical Journal*, vol. 98, no. 2, pp. 334-343.
39. Schind1ler, D. W. 2010. Tar sands need solid science. Nature. 468:499-501. 43
40. Semat, Henry and Katz, Robert, (1958). "Physics, Chapter 42: Optical Spectra and Atomic Structure" Robert Katz Publications. : https://digitalcommons.unl.edu/physicskatz/. University of Nebraska – Lincoln.
41. Smith, J., &Helmers, P. (2015). *Detection Limits of ICP-OES for Heavy Metals in Drinking Water*. Environmental Science & Technology.
42. SPECTRO Analytical Instruments GmbH, (2024), https://www.spectro.com/icp-oes
43. Stratton, Julius Adams (1941). "Chapter V Plane waves in unbounded, isotropic media". *Electromagnetic Theory*. McGraw-Hill Book Company, New York, NY. ISBN 978-0-470-13153-4.
44. TAN CHUN HO, (2015). DETERMINATION OF Pb(II), Cu(II) AND Ni(II) IN WATER BY DIRECT MEASUREMENT USING UV/VIS SPECTROPHOTOMETER, p.9, University SainsMalaysia.
45. Thomas R. (2015). Determining elemental impurities in pharmaceutical materials: How to choose the right technique. *Spectroscopy*.30(3),https://www.spectroscopyonline.com/view/determining

elemental-impurities-pharmaceuticalmaterials-how-choose-right-technique. Published 2015. Accessed September 17, 2021.

46. Thomas R. (Published 2015. Accessed September 17, 2021). Determining elemental impurities in pharmaceutical materials: How to choose the right technique. *Spectroscopy*. 2015;30(3), https://www.spectroscopyonline.com/view/determining-elemental-impuritiespharmaceuticalmaterials-how-choose-right-technique. Published 2015. Accessed September 17, 2021.
47. Thompson, M., et al. (2014). *Comparative Study of ICP-OES and AAS for Multi-Element Detection in Water Samples.* Journal of Analytical Atomic Spectrometry.
48. V.A. Fassel,(1986). 'Analytical Inductively Coupled Plasma Spectroscopies—Past, Present, and Future', *Fresenius Z. Anal. Chem.*, 324(6), 511–518.
49. W. Schmidt, , (2005). Optical Spectroscopy in Chemistry and Life Sciences, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN 3-527-29911-4.
50. Wang, J.S., Huang, P.M., Liaw, W.K., and Hammer, U.T., (1991). Kinetics of the desorption of mercury from selected freshwater sediments as influenced bychloride, Water, Air, and Soil Pollution, 56, 533-542
51. Weinberg, S. *(1995).* The Quantum Theory of Fields. *Vol. 1.* Cambridge University Press. *pp.* 15–17. ISBN 978-0-521-55001-7.
52. WHO (2003): "Manual of Basic Technique for a Health labouratory" World Health Organization, 2nd edition, Geneva.
53. WHO 2008, Guidelines for drinking water quality, World Health Organization, Geneva.
54. Wongsasuluk, Pokkate., et.al (2014). Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in UbonRatchathani province, Thailand. Environmental Geochemistry and Health, 36, 169-182.http://doi.org/10.1007/s10653-013-9537-8
55. World Health Organization (WHO). (2003). *Guidelines for Drinking-water Quality* (3rd ed.). WHO Press.
56. World Health Organization, in drinking-water, Background document for preparation of WHO Guidelines for drinking-water quality WHO, Geneva, (2011).
57. World Health Organization, pH in drinking water, Background document for preparation of *WHO Guidelines for drinking-water quality, WHO, Geneva* (1996).

58. World Health Organization, Potassium in drinking water, Background document for
preparation of *WHO Guidelines for drinking-water quality WHO, Geneva, (2009).*
59. XiandengHou and Bradley T. Jones, Encyclopedia of Analytical Chemistry, (2000). John Wiley & Sons, Ltd
60. Yang L., Zhang M., Wei J., Qi J. 2022. Pollution Load Estimation and Control Countermeasures of Zhangze Reservoir. *Front. Environ. Sci.*;10:874124. doi: 10.3389/fenvs.2022.874124.

APPENDIXS

Appendix 1

Horticoop Ethiopia (Horticulture) PLC

Soil, Water and Plant Analysis Laboratory

Laboratory Test Report

Test Overview

Customer: Tarekegn Tekle

Tel: +251 911 55 54 00

Hawassa,

Country: Ethiopia

Information about sample			
Sampled By	Client	Order Number	HEON/24 - 201
Report Date	August 24, 2024	Received date	August 16, 2024
Location	Hawassa		

Lab Code	Description	Concentration	As	Pb	B	Zn	Cd	Hg	Cu	Ni	Co	Fe	Mn	Cr	Se
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
24HWA 1358	Weta	Conc.1	< 0.001	0.067	0.023	0.071	0.016	0.023	0.035	< 0.003	< 0.020	0.069	0.001	0.008	0.004
		Conc.2	< 0.001	0.068	0.020	0.071	0.015	0.019	0.036	< 0.003	< 0.020	0.088	0.001	0.005	0.006
		Conc.3	< 0.001	0.065	0.021	0.073	0.015	0.016	0.036	< 0.003	< 0.020	0.095	0.008	0.006	0.004
		Mean	< 0.001	0.066	0.021	0.072	0.015	0.019	0.036	< 0.003	< 0.020	0.084	0.003	0.006	0.005
		Stdv	-	0.002	0.001	0.001	0.001	0.003	0.000			0.014	0.004	0.002	0.001
24HWA 1359	Fulasa	Conc.1	< 0.001	0.073	0.018	0.950	0.015	0.018	0.037	< 0.003	< 0.020	0.101	0.002	< 0.007	< 0.012
		Conc.2	< 0.001	0.057	0.017	0.962	0.016	0.026	0.036	< 0.003	< 0.020	0.097	0.001	< 0.007	< 0.012
		Conc.3	< 0.001	0.059	0.017	0.979	0.014	0.024	0.037	< 0.003	< 0.020	0.100	0.001	< 0.007	< 0.012
		Mean	< 0.001	0.063	0.017	0.963	0.015	0.023	0.037	< 0.003	< 0.020	0.099	0.001	< 0.007	< 0.012
		Stdv	-	0.009	0.001	0.015	0.001	0.004	0.001	-	-	0.002	0.000	-	-
24HWA 1360	Helelo	Conc.1	< 0.001	0.064	0.031	0.041	0.016	0.007	0.059	< 0.003	< 0.020	0.279	0.013	< 0.007	< 0.012
		Conc.2	< 0.001	0.059	0.031	0.039	0.016	0.006	0.061	< 0.003	< 0.020	0.301	0.014	< 0.007	< 0.012
		Conc.3	< 0.001	0.067	0.029	0.038	0.017	0.009	0.061	< 0.003	< 0.020	0.293	0.013	< 0.007	< 0.012
		Mean	< 0.001	0.063	0.030	0.039	0.016	0.007	0.060	< 0.003	< 0.020	0.291	0.013	< 0.007	< 0.012
		Stdv	-	0.004	0.001	0.002	0.001	0.002	0.001	-	-	0.011	0.001	-	-
24HWA 1361	Ambaricho	Conc.1	< 0.001	0.060	0.009	0.064	0.017	0.001	0.036	< 0.003	< 0.020	0.418	0.021	< 0.007	< 0.012
		Conc.2	< 0.001	0.054	0.008	0.066	0.015	0.001	0.036	< 0.003	< 0.020	0.437	0.022	< 0.007	< 0.012
		Conc.3	< 0.001	0.056	0.007	0.066	0.016	0.001	0.036	< 0.003	< 0.020	0.428	0.020	< 0.007	< 0.012
		Mean	< 0.001	0.057	0.008	0.065	0.016	0.001	0.036	< 0.003	< 0.020	0.428	0.021	< 0.007	< 0.012
		Stdv	-	0.003	0.001	0.001	0.001	0.000	0.000	-	-	0.010	0.001	-	-

Analytical Methods	
Parameter	Applied Standard
Fe, Mn,Cu, Zn, B, As, Pb, Hg, Co, Ni, Cr and Cd	Wet digestion + ICP-OES determination

Zufan Girkidan — Lab Head

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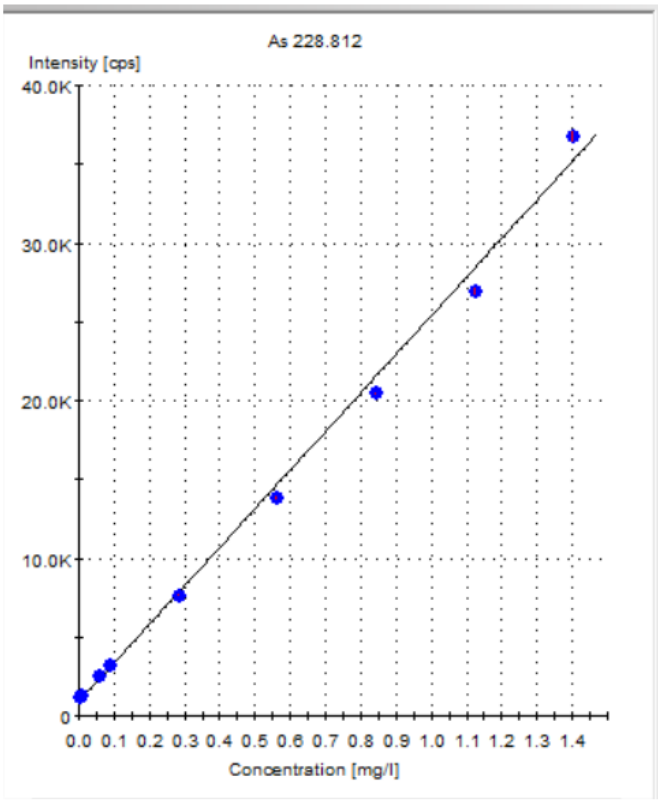
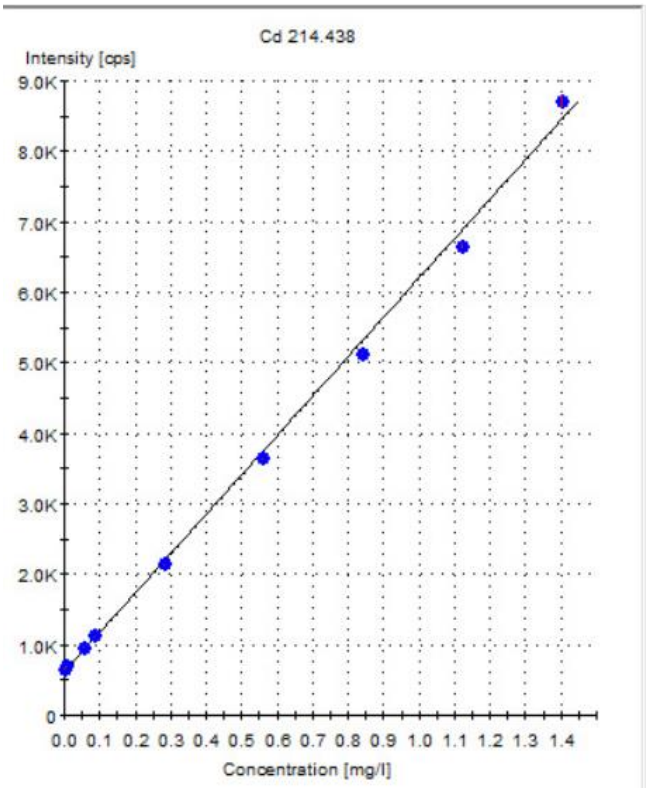
Appendix 2



Coef. A0:	-0.03627
Coef. A1:	4.0827e-005
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.000565 mg/l - 1.68 mg/l
Line Info:	
BEC:	0.0475 mg/l
DL:	0.000565 mg/l
Std.Error:	0.0389 mg/l
Corr.Coef.:	0.997614
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.0005646	[mg/l]	Lock
Conc. Min:	0.0005646	[mg/l]	Lock
Conc. Max:	1.68	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock

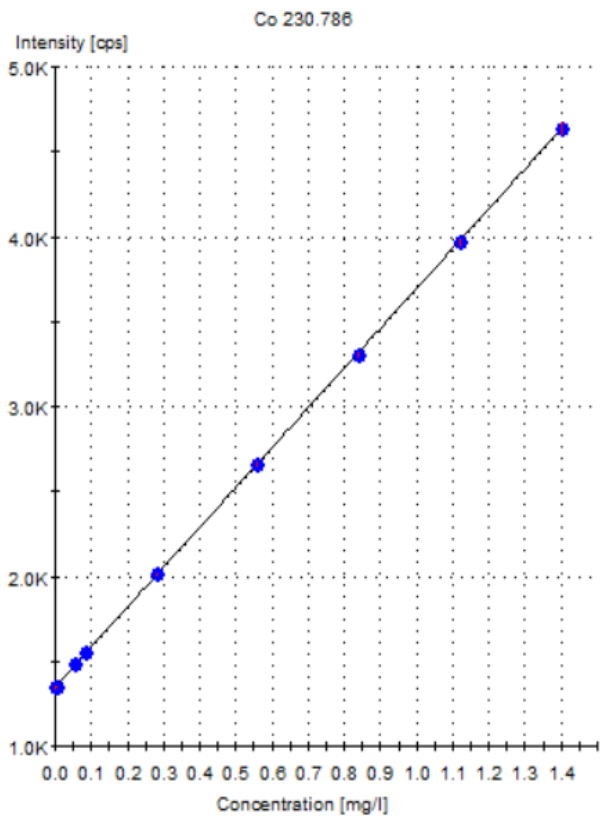


Coef. A0:	-0.10972
Coef. A1:	0.00017888
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.00253 mg/l - 1.68 mg/l
Line Info:	
BEC:	0.116 mg/l
DL:	0.00253 mg/l
Std.Error:	0.0273 mg/l
Corr.Coef.:	0.998827
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.002526	[mg/l]	Lock
Conc. Min:	0.002526	[mg/l]	Lock
Conc. Max:	1.68	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock

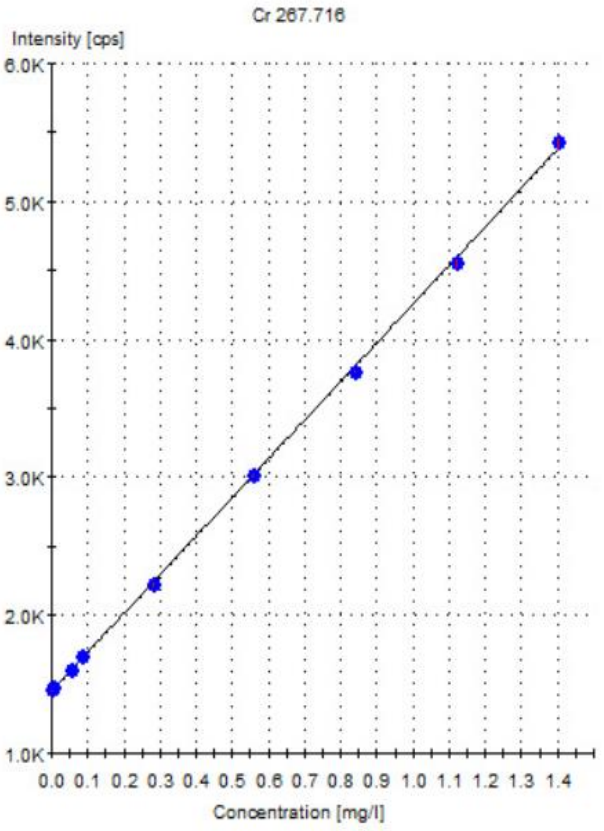
Appendix 3



Coef. A0:	-0.57591
Coef. A1:	0.00042649
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.015 mg/l - 1.68 mg/l
Line Info:	
BEC:	0.575 mg/l
DL:	0.015 mg/l
Std.Error:	0.00383 mg/l
Corr.Coef.:	0.999977
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.01499	[mg/l]	Lock
Conc. Min:	0.01499	[mg/l]	Lock
Conc. Max:	1.68	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock

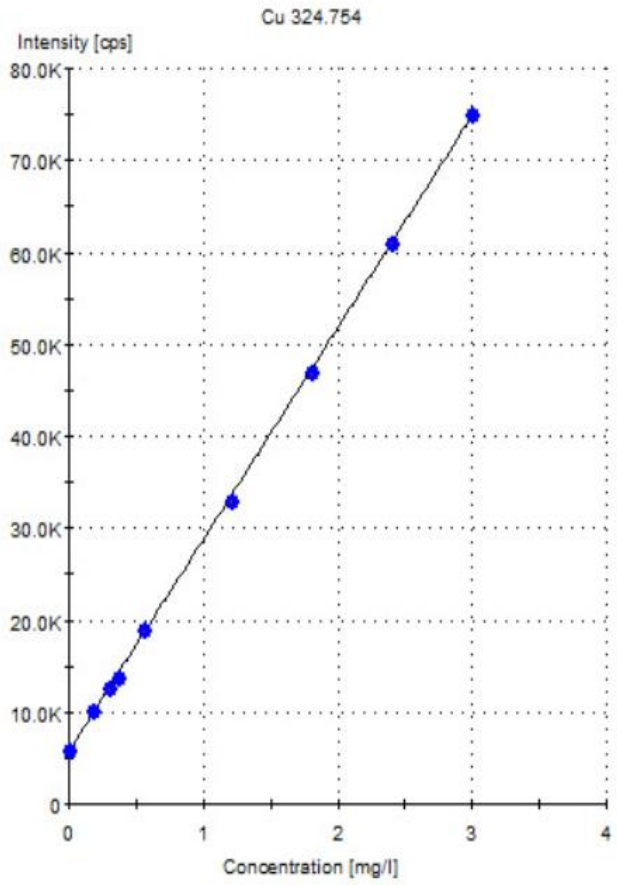


Coef. A0:	-0.5173
Coef. A1:	0.00035649
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.00726 mg/l - 1.68 mg/l
Line Info:	
BEC:	0.516 mg/l
DL:	0.00726 mg/l
Std.Error:	0.0101 mg/l
Corr.Coef.:	0.99984
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.007255	[mg/l]	Lock
Conc. Min:	0.007255	[mg/l]	Lock
Conc. Max:	1.68	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock

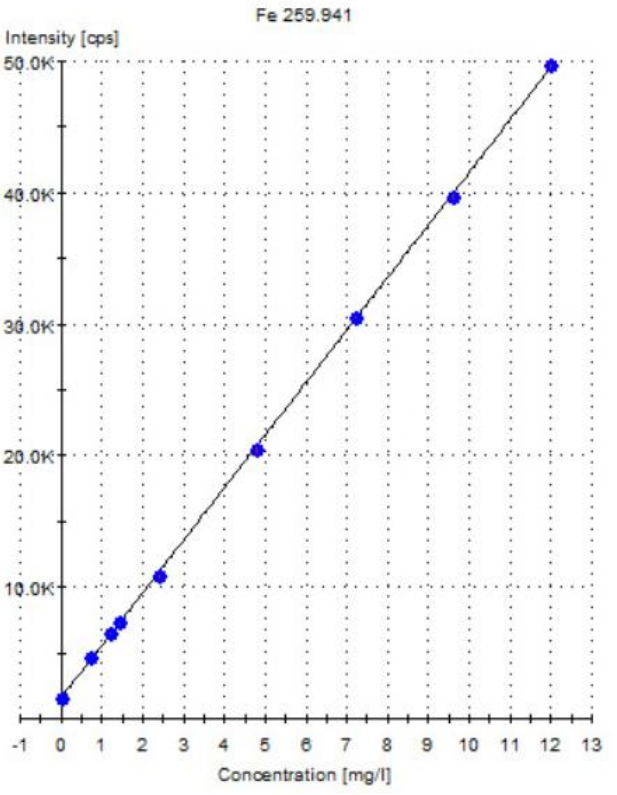
Appendix 4



Coef. A0:	-0.25046
Coef. A1:	4.3445e-005
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.00128 mg/l - 3.6 mg/l
Line Info:	
BEC:	0.257 mg/l
DL:	0.00128 mg/l
Std.Error:	0.0115 mg/l
Corr.Coef.:	0.99995
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.001276	[mg/l]	Lock
Conc. Min:	0.001276	[mg/l]	Lock
Conc. Max:	3.6	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock

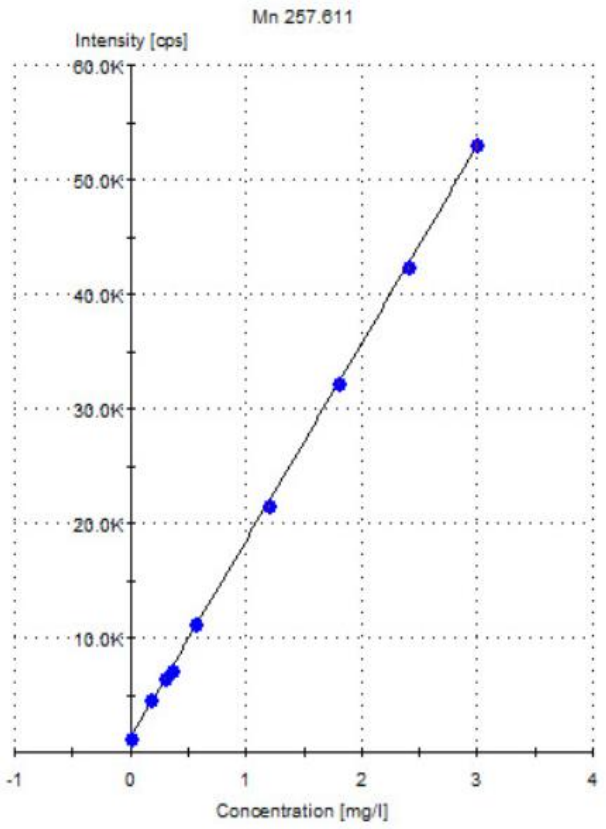


Coef. A0:	-0.39076
Coef. A1:	0.00025009
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.0056 mg/l - 14.4 mg/l
Line Info:	
BEC:	0.374 mg/l
DL:	0.0056 mg/l
Std.Error:	0.0555 mg/l
Corr.Coef.:	0.999928
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.005598	[mg/l]	Lock
Conc. Min:	0.005598	[mg/l]	Lock
Conc. Max:	14.4	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock

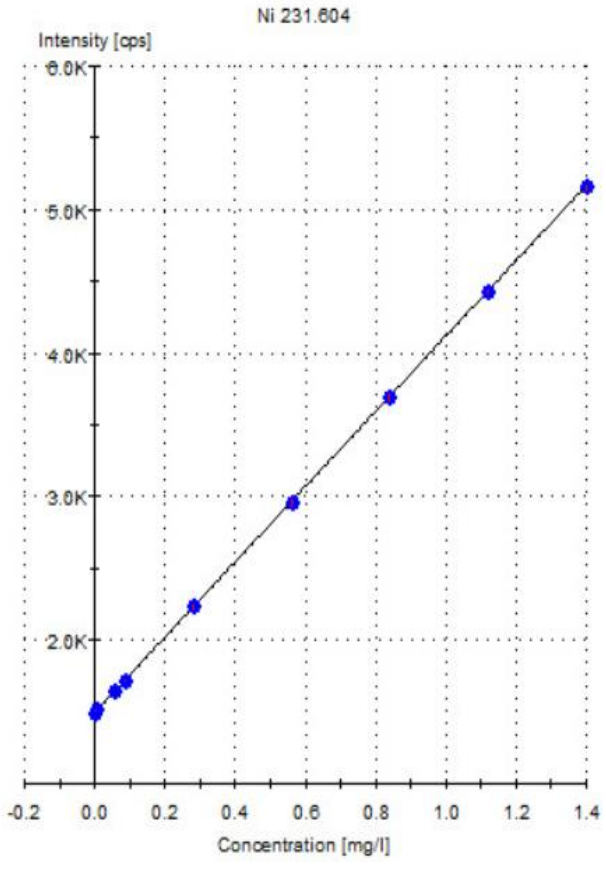
Appendix 4



Coef. A0:	-0.07107
Coef. A1:	5.8062e-005
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.000489 mg/l - 3.6 mg/l
Line Info:	
BEC:	0.0659 mg/l
DL:	0.000489 mg/l
Std.Error:	0.0145 mg/l
Corr.Coef.:	0.999922
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.0004894	[mg/l]	☑ Lock
Conc. Min:	0.0004894	[mg/l]	☐ Lock
Conc. Max:	3.6	[mg/l]	☐ Lock

Dist. Ele.	Type	Factor	Use	Lock

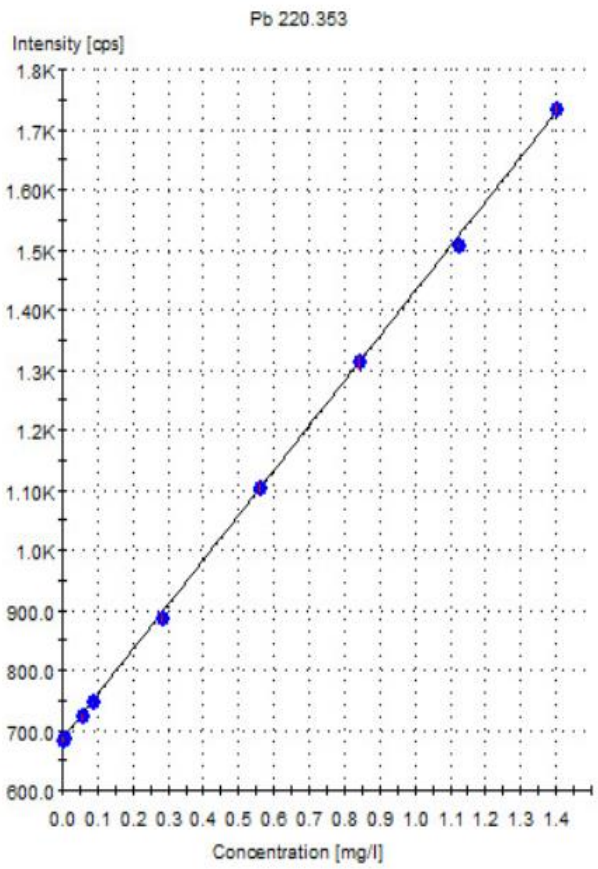


Coef. A0:	-0.57017
Coef. A1:	0.00038121
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.00333 mg/l - 1.68 mg/l
Line Info:	
BEC:	0.571 mg/l
DL:	0.00333 mg/l
Std.Error:	0.00205 mg/l
Corr.Coef.:	0.999997
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.003327	[mg/l]	☐ Lock
Conc. Min:	0.003327	[mg/l]	☐ Lock
Conc. Max:	1.68	[mg/l]	☐ Lock

Dist. Ele.	Type	Factor	Use	Lock

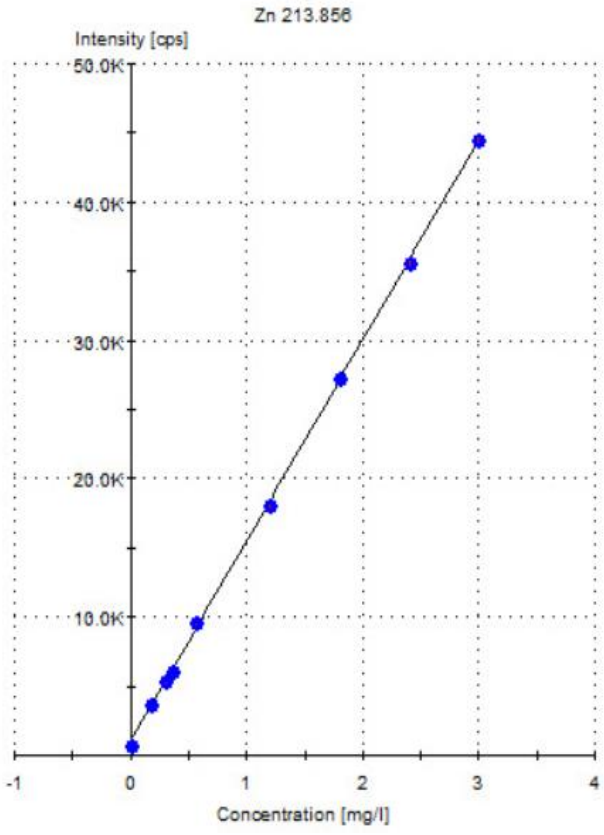
Appendix 5



Coef. A0:	-0.91929
Coef. A1:	0.0013418
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.0204 mg/l - 1.68 mg/l
Line Info:	
BEC:	0.914 mg/l
DL:	0.0204 mg/l
Std.Error:	0.00758 mg/l
Corr.Coef.:	0.99992
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.02042	[mg/l]	Lock
Conc. Min:	0.02042	[mg/l]	Lock
Conc. Max:	1.68	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock



Coef. A0:	-0.066754
Coef. A1:	6.8891e-005
Coef. A2:	--
Coef. A3:	--
Matr.Corr.:	No
Matrix Conc.:	--
Line Range:	0.00162 mg/l - 3.6 mg/l
Line Info:	
BEC:	0.0501 mg/l
DL:	0.00162 mg/l
Std.Error:	0.0176 mg/l
Corr.Coef.:	0.999884
Dist.Factor:	Factors defined in Conc/Conc

Detection Limit:	0.001621	[mg/l]	Lock
Conc. Min:	0.001621	[mg/l]	Lock
Conc. Max:	3.6	[mg/l]	Lock

Dist. Ele.	Type	Factor	Use	Lock