# EFFECTS OF MINERAL ACIDS ON ABSORPTION SIGNALS OF METAL ANALYTES IN WATER BY ATOMIC ABSORPTION SPECTROSCOPY

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## DECLARATION AND RECOMMENDATION

### DECLARATION

I declare that this research is my original work and to the best of my knowledge has not been presented for any degree in any other university.

**SIGNED**…..……..Date……...……

**J. B. M. TANA**

### RECOMMENDATION

I declare that this work has been done under our supervision and is submitted with our approval.

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## DEDICATION

To my parents Mr. and Mrs. Musungu and my lovely wife Susan. Your love and support has significantly contributed to what i am today.

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## ABSTRACT

A major requirement in flame spectroscopic methods is that the sample be introduced into the excitation source in form of an aqueous solution. Unfortunately, many materials of interest such as soils, animal tissues, plants, petroleum products and minerals are not directly soluble in water and extensive preliminary treatment is often required to obtain a solution of the analyte in a form ready for atomization. On the other hand, some samples contain both organic and inorganic matrices, which require digestion prior to instrumental analysis. This requires careful consideration of digestion reagents. In this project, the effects of mineral acids on absorption signals of metal analytes in water by atomic absorption spectroscopy were studied. This was done with respect to variations in metal concentration and acid concentration with the aim of determining the most suitable acid for digestion purposes and the most effective acid concentration for trace metal analysis by Atomic Absorption Spectroscopy (AAS). Different concentrations of metal analytes of manganese, iron, copper, zinc and lead were digested with different concentrations of nitric, hydrochloric and perchloric acids and analyzed using the Atomic Absorption Spectrophotometer. In this analysis, water samples from River Njoro (a fresh water system) and Lake Nakuru (a highly alkaline water system) were used to confirm the applicability of the results obtained. In the standards, lake Nakuru and River Njoro water samples, it was realized that perchloric and nitric acids had equal but higher peak enhancing effects as compared to hydrochloric acid on the absorption signals of all metal analytes except for iron in Lake Nakuru water sample and copper in both Lake Nakuru and River Njoro water samples. The most effective concentration for digestion purposes was at 10 % v/v for all acids. It was therefore concluded that acids have varied peak enhancing effects on absorption signals of metal analytes in water. This variation is dependent on the concentration and nature of the acid with the more oxidizing acids having greater peak enhancing effects than the less oxidizing acids. For effective determination of Mn, Fe, Pb and Zn metal analytes in River Njoro and Lake Nakuru water samples more reliable results would be obtained when 10 % v/v nitric or perchloric acids are used for digestion purposes. While for effective determination of Cu in Lake Nakuru and River Njoro water samples, more reliable results would be obtained when 10 % perchloric, nitric or hydrochloric acids are used for analysis.

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# CHAPTER ONE

# INTRODUCTION

Driven by the dynamics of economic growth and development, by rapid advances in science and technology and by their own increasing requirements, modern societies have been introducing an even greater number and quantity of pollutants into the environment. The air we breathe, the water we drink, the food we eat and in general, the physical environment has thus come to contain constituents and properties harmful to our health. Often, the effects of these are insidious and hence are not directly perceived by those affected. They may take years or even generations to become manifest (Castro *et al*, 1997). Although these effects tend to be more serious and complex in highly industrialized societies, they are also of serious and urgent concern in developing countries. These countries are experiencing rapid and uneven development that all too often has not been coupled with adequate sensitivity and concern for threats to the environment with the ability of the society to find necessary resources to mount appropriate remedial and preventive actions.

The most affected natural resources are water bodies, which require special attention in pollution control programmes due to their important role in waste management (Nickson. *et al*. 2001). Almost all pollutants no matter where they originate end up in water bodies, either through rains from atmospheric sources or as leaches from underground or surface dumping sites (Danielsson *et al*, 1999; Jung, 2001; Armienta *et al*, 2001; Ongley *et al*, 2001). This makes water pollution control an important function especially because water is one of the most basic essentials in life. It could even be argued that life is aquatic since water is both essential and the most abundant substance in the protoplasm. However, we mainly speak of an aquatic habitat as one in which water is mainly an external as well as an internal medium (Marshall, 2002). Water occupies about three quarters of the earth's surface (Alloways and Ayres, 1997). Fresh water however occupies a relatively small portion as compared to marine and terrestrial habitats, but their importance to man is far greater than the area due to the following reasons.

Fresh water bodies are the most convenient and cheapest sources of water for domestic and industrial use. Even though three quarters of the earth's surface is covered by water, most of this water is saline water, which would be very expensive to desalinate for effective domestic and industrial use. Fresh water components are the limiting factors in the hydrological cycle (Gray, 1996). These water components are limiting since most of the water ends up in soils,

lake, oceans or in other water bodies thus being contaminated. On the other hand, it may be difficult to quantify the safety of water without analysing it since most water contaminants are not visible even under a microscope while some contaminants may have long-term adverse effects to animals and human beings. These factors emphasize the need for efficient management of fresh water resources to ensure that they do not become a limiting factor to man.

In coming up with efficient and effective management programmes of water bodies, we need to use standard methods of analysis that will take into consideration the many parameters that occur in water samples just before instrumental analysis. One of the most important factors to consider in using a standard method especially for analysis of inorganic substances such as heavy metals is the pre-treatment procedures involved. These procedures are mainly used in digesting samples prior to analysis by AAS (Skoog and West, 1996). Oxidation with liquid reagents (such as mineral acids) is the most common method used in digestion procedures. The study of the effects of these acids on the sample is therefore of main concern to determine the most appropriate reagent for analysis of a given element since different methods require different types of acids example nitric, hydrochloric or sulphuric acid or a mixture of them and different amounts are recommended (APHA, 1992). The peak enhancement effects of these must therefore be different upon the sample analyte.

This study is needful since little work has been done to determine the enhancement effects of mineral acids on absorption signals of metal analytes in natural water systems despite their wide use in sample digestion. Its findings are therefore going to contribute immensely in improving standard methods of water analysis.

### 1.1 Statement of the Problem

Mineral acids constitute a group of reagents that are mainly used in digesting water samples, soils, sediments, plants and animal tissues for trace metal analysis. The choice of the most effective acid or acid mixture is a major problem since acids may have varied peak enhancing effects on absorption signals of metal analytes in water (Skoog and West, 1996; Haines and Fiefield, 2000). This calls for a study of effects of mineral acids on the absorption signals of metal analytes in natural waters to determine the most effective acid and the most appropriate concentration for digestion purposes.

### 1.2 Main objective

The main objective of this study is to determine the peak enhancement effects of mineral acids on absorption signals of metal analytes in water. The following are the specific objectives.

#### 1.2.1 Specific objectives

- To determine the most suitable acid between nitric, perchloric and hydrochloric acid for digestion purposes in the analysis of Cu, Fe, Mn, Pb, and Zn.
- To determine the most suitable concentration of hydrochloric, nitric and perchloric acid in the determination of Zn, Fe, Mn, Pb and Cu by AAS.
- To determine differences if any in analysis of fresh water from River Njoro and alkaline water from Lake Nakuru.

### 1.3 Hypotheses

- Mineral acids have no varied effects on the absorption signals of metal analytes in water.
- This lack of variation does not depend on the concentration or the nature of the acid used.
- The more oxidizing acids have a low enhancing effect on the absorption signal of metal analytes in water than the less oxidizing acids.
- There is no difference in the analysis of fresh and alkaline water samples from River Njoro and Lake Nakuru respectively.

### 1.4 Justification

Many times the determination of heavy metals (via spectrophotometric methods) requires the sample to be digested prior to instrumental analysis (Skoog and West, 1996; Miraslov, 1999). However, it is not always clear which acids or concentrations of acids are most suitable for analysis of the metal analyte in question. A study of the metal analytes under different acid conditions is therefore necessary to determine the most effective acid for digesting the sample before instrumental analysis by AAS. These metals were selected for analysis since they constitute some of the most abundant elements in natural water systems and thus may pose the greatest risks if their concentrations exceed the maximum permissible limits.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Heavy Metals

Heavy metals is a general collective term applying to a group of metals and metalloids with atomic densities greater than 6 gm $cm^{-3}$ (Alloways and Ayres, 1997). This definition applies to elements such as Cu, Hg, Ni, Pb and Zn, which are commonly associated with pollution problems (Tam and Yao, 1999). Unlike most organic pollutants such as organohalides, heavy metals occur naturally in rock and ore minerals and so there is a range of normal background concentrations of these elements in soils, sediments, water and living organisms (Leblanc *et. al,* 2000*)*. Pollution gives rise to high concentrations of the metal relative to the normal background levels (Manroy *et. al,* 2004). Therefore, presence of the metal is insufficient evidence of pollution. The relative concentration is all-important to help in policy formulation for pollution control.

Apart from aerosols in the atmosphere and direct effluent discharge into waters, the concentration of heavy metals available to terrestrial, aquatic and marine organisms and their bioavailability is determined by the solubilization and release of metals from rock forming minerals and the adsorption and precipitation reactions, which occur in soils and sediments (Van Den Berg *et al*, 1999).

The extent to which metals are adsorbed, depends on the properties of the metal concerned (valence, radius, degree of hydration and coordination with oxygen), the physico-chemical environment (pH and redox status), the nature of the adsorbent such as (permanent and pH dependent charges, complex-forming ligands), other metals present and their concentrations and the presence of soluble ligands in the surrounding fluids (Alloway, 1995). Although heavy metals differ widely in their chemical properties, they are used widely in electronics, machines, and aircraft as well as high-tech applications. Consequently, they tend to reach the environment from a vast array of anthropogenic sources as well as natural geochemical processes (Marques *et. al.* 2001; Kagwanja and Omoga, 1999). Some of the oldest cases of environmental pollution in the world were caused by heavy metal uses such as Cu, Hg and Pb mining, smelting and utilization by ancient civilizations such as Romans and Phoenicians (Leblanc *et al,* 2000).

## 2.2 Biochemical Properties of Heavy Metals

Some heavy metal elements are required by most living organisms in small but critical concentrations for normal health growth referred to as micronutrients or essential trace elements. Those elements which are essential or whose deficiency causes disease under normal living conditions include Cu, Mn, Fe and Zn for both plants and animals. Other metals such as Cu, Cr, Se and iodine for animals; boron and molybdenum for plants (Marshall, 2002; Lee *et al*, 2001; Davis *et al*, 2003). Most of the micronutrients are essential for being constituents of enzymes and other important proteins involved in key metabolic pathways. Hence, a deficient supply of the micronutrient results in a shortage of the enzyme leading to metabolic dysfunction, which may cause death.

Elements with no known biochemical functions are called non-essential elements, sometimes also referred (incorrectly) as toxic elements. These include; As, Cd, Hg, Pb, Sb, Ti and V. They cause toxicity at concentrations, which exceed the tolerance of the organism but do not cause deficient disorders at low concentrations like micronutrients (Fernandez-Turriel *et al*, 2001). At the biochemical level, the toxic effects caused by excess concentrations of these metals include; competition for sites with essential metabolites, replacement of essential ions, reactions with Sulphur Hydryl (-SH) groups, damage to the cell membrane and reactions to phosphate group of Adenosine Diphosphate (ADP) and Adenosine Triphosphate (ATP) (Alloway and Ayres, 1997).

Organisms have homeostatic mechanisms which enable them tolerate small fluctuations in the supply of most elements but prolonged excesses eventually exceed the capacity of the homeostatic system to cope and toxicity occurs, which if severe can cause the death of the organism. An example of homeostasis in animals and the control of the excess concentrations of metals is the formation of the metallothionein proteins containing the -SH group which binds certain metals such as Cd and Zn and enables them to be excreted without causing biochemical dysfunction. In plants, similar compounds called phytochelatins carry out the same function binding divalent metals such as Cd into a physiologically inactive form (Alloway and Ayres, 1997).

## 2.3 Heavy Metals

### Fe

Iron is the fourth most abundant element in the earths crust. Its greatest use is for structural compounds such as iron and steel, but it is also used for making dyes and abrasives. It is an essential micronutrient in trace quantities for most organisms but ingestion of excessive amounts may result in inhibition of activities of many enzymes. The amount produced must be very large because only a small portion of all iron ingested is absorbed from the gastro-intestinal tract. Inhalation of iron dust can cause benign pneumoconiosis and enhance harmful effects of sulphur dioxide and various carcinogens (Greenwood and Earnshaw, 2001). Many streams are poisoned by high levels of iron in acid mine drainage. Pyrite (iron sulphide) is often found in close association with coal deposits. Upon exposure to moisture and atmospheric oxygen, the ferrous iron is oxidised to the ferric state. A reaction that is frequently accelerated by the bacteria of the *thiobacillus-ferrobacillus* group. The ferric iron can then react with sulphide in the presence of water to produce a yellow flocculent mass of ferric hydroxide (Davis *et al*, 2003). Besides being acidic, water affected in this way becomes deficient in oxygen. Such poisoning of streams is reckoned as one of the main causes of fish kills in areas where iron is mined. Although particularly associated with mining, streams running through iron-laden strata may be contaminated.

### Mn

Manganese is one of the most abundant transition elements. Its abundance in the earths crust is estimated to be about 0.09 percent. Most commonly, it is found as *pyrolusite* ($MnO_2$). Manganese is concentrated in the so-called manganese modules found on the ocean floor. These contain a high proportion of manganese present as $MnO_2$. The metal is used mainly in alloys. Manganese imparts hardness to steel when used in concentrations of up to 13% by weight. Pure Manganese is a hard brittle metal with a reddish colour. It melts at $1244^{O}C$ and boils at $2120^{O}C$; the pure metal has a density of $7.47gcm^{-3}$. Biologically, it is an essential micronutrient for most organisms. However, in excessive amounts, it affects animals adversely causing crumps, tremors and hallucinations, manganic pneumonia and renal degeneration (Marshall, 2002).

**Pb**

Lead is widely distributed naturally but the greatest risks from it normally arise from emissions to the environment associated with human use of the metal and its derivatives. Fumes and dust come from the smelting of lead, from the manufacture of insecticides, paints, pottery glazes and storage batteries, and from gasoline containing lead additives. Sewage sludge may contain very high levels of lead and its use as a fertilizer may contaminate soils (Arnason and Fletcher, 2002). High levels may occur in urban air as a result of the high traffic density and associated emission of lead from gasoline additives.

Lead affects microoganisms by retarding the heterotrophic breakdown of organic matter. Little is known regarding the harmfulness of lead to plants, where it tends to be localised in the root system. Animals may take in lead by inhalation or ingestion. Only tetraethyl lead can be adsorbed through the skin. Absorption is very slow but excretion is even slower so that lead tends to accumulate. Most of the lead is taken up by red blood cells and circulated throughout the body where it may concentrate initially in the liver and kidneys (Marshall, 2002). Thereafter, it may be redistributed to the bones, teeth and brain. In the bones, lead is immobilized and does not contribute to immediate toxicity but is a potential hazard since it may be mobilized during feverish illnesses, as a result of cortisone treatment, and in old age.

Anaemia is the first symptom of chronic lead poisoning in animals because lead interferes with the synthesis of haem. This is associated with abdominal symptoms, which may include nausea, vomiting and abdominal pain. More serious is the degeneration of tissue in the central nervous system (CNS), which is also observed in children (Marshall, 2002).

**Cu**

Copper is one of the most abundant trace metals. It is widely used in its metallic state, either in the pure form or in alloys. For almost all organisms, it is an essential micronutrient. It may occur in very high concentrations in water, sediments and biota in some localised areas as a result of mining activities, intensive use of copper pellets in pig rearing, or from the application of copper fungicides (Alloway, 1995). There is no evidence of food chain magnification and most toxic effects are due to immediate exposure to the element (Alloways and Ayres, 1997). All organisms are harmed by excess concentrations, which may be as low as 0.5 parts per million (ppm) for algae (Marshall, 2002). Most fish are killed by a few ppm. In higher animals, brain damage is a characteristic feature of copper poisoning.

**Zn**

Zinc makes up 0.004% of the earth's crust. Its most important use is as a protective coating of other metals, particularly in galvanizing iron and steel. It is an essential micronutrient and is regarded as one of the less hazardous elements, though its toxicity may be enhanced by the presence of arsenic, lead, cadmium and antimony, as impurities (White, 2003). Toxic effects can result from inhalation of fumes from galvanizing baths. Zinc fever is characterised by chills, fever and nausea. Removal from the fumes leads to complete recovery. Zinc chloride fumes have sometimes caused fatal oedema of the lungs (Marshall, 2002). Zinc or galvanised containers are not recommended for food storage but are acceptable for drinking water. This is because acidic food can dissolve enough zinc from the container to cause poisoning.

## 2.4 Common Sample Preparation Methods

A limitation of flame spectroscopic methods is the requirement that the sample be introduced into the excitation source in form of an aqueous solution (Skoog and West, 1996). Unfortunately, many materials of interest such as soils, animal tissues, plants, minerals and petroleum products among others are not directly soluble in common solvents and therefore extensive preliminary treatment is required to obtain a solution of the analyte in a form ready for atomization. The digestion and solution steps are often time consuming and may introduce more errors than the spectroscopic measurement itself. Digestion of refractory materials usually requires rigorous treatment of the sample at high temperatures (L'vov, 2005). The reagents used in digesting a sample may introduce some chemical interference where the analyte of interest may be present as an impurity. Unless considerable care is taken in trace analysis, reagents may be a larger source of the element of interest (Haines and Fiefield, 2000). This can lead to serious errors even with blank corrections.

Some common methods used for digesting samples for AAS analysis include; wet digestion methods such as treatment with hot mineral acids, oxidation with sulphuric, nitric, perchloric and hydrochloric acid and dry oxidation methods i.e. combustion in an oxygen bomb or other container (to avoid loss of analyte), ashing at high temperatures and high temperature fusion with reagents such as boric oxide, sodium carbonate, sodium peroxide or potassium pyrosulphate (L'vov, 2005).

A major advantage of electro thermal atomization is that some materials can be atomised directly thus avoiding the solution step. Liquid samples such as blood, petroleum products and organic solvents can be pipetted directly into the furnace for ashing and atomization (Skoog and West, 1996).

### 2.5 Sample Digestion Procedures used in AAS Analysis

Trace elements in natural water samples are predominantly bound to organic matrices (White, 2003). In order to characterise these compounds using AAS, they must be separated from their biological and environmental matrices. This means that organic matter must be destroyed through sample digestion. Digestion therefore assists in breaking down matrices and thereby enabling the metal analytes to be in soluble form for effective analysis. If the digestion media is very effective in the solubilization of metal analytes in water, then realistic results of the analytes's concentration in the water sample will be found. If not, wrong results will be found leading to errors.

#### 2.5.1 Wet Digestion (Acid Oxidation) Methods

Mineral acids have often been used in wet digestion processes to reduce interferences by organic matter and to convert metals associated with particulates to a form (usually the free metal) that can be determined by spectroscopic techniques such as AAS (Gaspar *et al*, 2004). In determining total extractable metals in a given sample, it is needful to use the most effective digestion method in order to provide complete and consistent recovery which is compatible with the analytical method and metal being analyzed (APHA, 1992).

The methods written in standard books of water and wastewater analysis (APHA, 1992) mainly employ the use of nitric acid in the digestion of a great variety of samples. This acid is usually used in digestion of easily oxidized samples. In the case of partially oxidisable organic matter $HNO_3$–$H_2SO_4$ and $HNO_3$-HCl acid mixtures are employed. For difficult to oxidize organic matter $HNO_3$ -$HClO_4$ acid mixture is usually employed (APHA, 1992). These acid mixtures are used in specified ratios for effective digestion procedures (Singh and Kashem, 1999). Unfortunately, no literature has been cited in analytical chemistry books and journals as to how these mineral acids affect the absorption signals of metal analytes in water even though it is known that acid digestion techniques generally yield separable precision for most sample types that are digested by the technique (Pinta, 1982; APHA, 1992).

Even though these mixed acid digestion procedures have been effective in sample digestion, there is a great possibility that when used, many interfering elements may be added since acids may contain some of the elements under study (Skoog and West, 1996). It is therefore needful to minimize the volume of the acid used in the digestion process.

### 2.6 Water

Procurement and preservation of water samples for AAS analysis is a critical procedure since the manner in which the sample is treated can greatly affect the results of the analysis. Ideally, the measurement of the trace analyte concentration should take place insitu although this is not possible. Alternatively, the samples should be analysed as soon as possible after collection, since trace inorganics can be lost during sample storage. This can be through adsorption onto container walls or incorporation into microoganisms (bacteria, algae etc) (Manroy *et al*, 2004). Minimization of this loss requires careful consideration of the type of container used, decantation procedures and preservatives (if any) added. Plastic, Teflon and quartz containers are the least susceptible to adsorption (Skoog and West, 1996). Common preservatives, which can be added to water samples, include; mineral acids, NaOH and $HgCl_2$ (L'vov, 2005). Refrigeration or freezing of the sample also minimizes loss as well as chemical change. Alloways and Ayres, (1997) described the various forms in which trace metals may be present in water. The categories include dissolved metals, suspended metals, total metals, extractable metals and organometallics. They added that the chemical or physical form of these metals in water is often of interest since the form in which a particular element is present, will greatly influences its toxic effects. The chemical state of chromium affects its toxicity example $Cr^{+6}$ is more carcinogenic than $Cr^{+3}$.

### 2.7 Principle of AAS

The procedure is based on flame absorption rather than on flame emission and depends upon the fact that metal atoms absorb strongly at discrete characteristic wavelengths, which coincide with the emission spectral line of a particular metal (White, 2003). The liquid sample is atomized in a standard or modified flame photometer burner. A hollow cathode lamp (HCL) precedes the atomizer; it emits the spectrum of the metal used to make the cathode. This beam transverses the flame and is focused on the entrance slit of a monochrometer, which is set to read the intensity of the chosen spectral line. Light with this wavelength is absorbed by the atoms of the metal in the flame and the degree of absorption is a function of the concentration of the metal in the sample (Skoog and West, 1996).

### 2.7.1 Trace Metal Monitoring by AAS

AAS is one of the most widely used techniques for the analysis of inorganic pollutants. The primary reasons for its extensive use are; its simplicity of operation, speed, high sensitivity and versatility, relative freedom from interference and low cost. Over 60 metals and metalloids are amenable to AAS analysis at concentration levels ranging from milligrams to femtograms per millilitre depending on the element, atomizer and conditions employed (Gump *et al*, 2002). The most significant limitation of AAS is the lack of simultaneous multi-element analysis capability. Nearly all analysis is for a single element at a time although various instruments permit analysis of 2 to 6 elements simultaneously under microprocessor control. Thus, AAS is most widely suited for analysis where trace metal concentrations are desired with high accuracy and precision.

The most commonly used atom reservoir in AAS is the flame, either air-acetylene ($2400^{o}K$) or nitrous oxide-acetylene ($3200^{o}K$) for more refractory elements. In all convectional flame atom sources, the sample is introduced into the flame by nebulizing the sample solution thereby producing a dispersion of small droplets. These droplets are then dried and the resulting solid decomposed, vaporised and reduced into free atoms by the flame. The efficiency of atom formation is then a complex function of numerous interrelated steps. The size of the nebulised droplets and their distribution clearly affects desolvation rates. The composition of the dried solid particles can significantly affect decomposition rates. The electron density of the flame, flame composition and flame gas velocity (residue time) affect all processes involved (White, 2003; L'vov, 2005). Given the number of processes required and the relatively short analyte residence time in the absorption region of most flames (in the order of 10 ms) the overall efficiency of atom production is low. In the discrete cycle of non-flame atomizers, several reactions (desolvation, decomposition etc.), which occur simultaneously i.e. over rather broad zones in a flame, are separated in time using a non-flame atomizer. This allows time and temperature optimisation for each step and presumably improves atomization efficiencies (Skoog and West, 1996).

### 2.8 Types of Flames in AAS

The most popular flames are air-$C_2H_2$ flame and $N_2O$-$C_2H_2$**.** The nitrous oxide-acetylene flame provides higher atomization efficiencies as seen in table **2.1**. Thus better detection limits for refractory elements such as Si, Al, Sc, Ti, V, Zr and rare earths. The hotter and more reducing $N_2O$-$C_2H_2$ flame minimizes interference effects. The burner control unit is

designed for convenient and safe burner operations. Flow controllers with flow meters; allow the adjustment of the fuel-oxidant ratio, which is critical for some elements. The burning velocities listed in table **2.1** are critical flame parameters. Flames achieve stability only within a certain region of gas flow rate. If gas velocities do not exceed the burning velocities, the flame propagates inside the burner, resulting into a flashback condition (L'vov, 2005). The gas flow rates and burning velocities should be optimized for effective analysis. At higher flow rates, the flame continues to burn and blows off the burner.

**Table 2.1: Properties of flames employed in AAS**

| **Fuel-oxidant** | | **Combustion reaction** | **Theoretical-stoichiometric temperature (K)** | **Maximum burning velocity (cm $s^{-1}$)** |
|---|---|---|---|---|
| 1 | $C_3H_8$-Air | $C_3H_8+5O_2+20N_2 \longrightarrow 3CO_2+4H_2O + 20N_2$ | 2267 | 39-43 |
| 2 | $H_2$-Air | $2H_2+O_2+4N_2 \longrightarrow 2H_2O+4N_2$ | 2380 | 300-440 |
| 3 | $C_2H_2$-Air | $C_2H_2+O_2+4N_2 \longrightarrow 2CO+H_2+4N_2$ | 2540 | 158-266 |
| 4 | $H_2$-$O_2$ | $2H_2+O_2 \longrightarrow 2H_2O$ | 3080 | 400-1400 |
| 5 | $C_3H_8$-$O_2$ | $C_3H_8+5O_2 \longrightarrow 3CO+4H_2O$ | 3094 | 370-390 |
| 6 | $C_2H_2$-$N_2O$ | $C_2H_2+5N_2O \longrightarrow 2CO_2+H_2O+5N_2$ | 3150 | 285 |
| 7 | $C_2H_2$-$O_2$ | $C_2H_2+O_2 \longrightarrow 2CO+H_2$ | 3342 | 1100-2480 |

Source: L'vov, 2005

## 2.9 Previous Work in this area

Pinta (1982) studied the mechanisms of atomization in a complex medium where he related absorbance variation as a function of heating temperature in an aqueous and concentrated acid medium. He noted that two identical absorbances are not necessarily obtained in the same sequence of reaction since absorbance may be influenced by excess amounts of acids modifying the chemical equilibrium and by the nature of the salt in solution. He also observed that the sequence of reactions leading to atomization can be modified by the qualitative and quantitative nature of the matrix. For cadmium, he concluded that its atomization in an absorbing medium occurs via the oxide when nitric acid is used and via the chloride when hydrochloric acid is used. He also observed that the excesses of the corresponding acid did not modify the decomposition and atomization temperatures and consequently concluded that acids influence the atomization mechanism much more by their qualitative nature than by their concentration. For chromium, he observed that the presence of

1 % $H_2SO_4$ in chromium solution produced a 10 % enhancement in absorbance and attributed this to the fact that the matrix interactions were either negligible or depressed.

Pinta's (1982) work shows that mineral acids have varied peak enhancing effects on metal analytes in water. It is therefore needful to apply these studies not only in aqueous and concentrated acid mediums but also in fresh water and saline water bodies. This will help improve the existing methods of water analysis.

Muiva, (2002), in an unpublished report determined the effects of mineral acids on absorption signals of standards of lead, cadmium, copper and zinc by AAS and made the following observations. That the effects of mineral acids on the absorption signals of these metal analytes at different concentrations depend on; their chemical nature, the solubilities of their respective salts, possible contribution of nebulization efficiency and matrix effect on the atomization process. For all acids, he observed that the general trend was that there existed an initial relatively large increase in absorbance on going from a neutral to an acidic solution (at low acid concentration) with the exception of lead in sulphuric acid at high concentrations. He further concluded that for measurement of low concentrations of Pb, Cd, Cu and Zn, more reliable results would be obtained in 0-10 % HCl acid solutions. The most suitable nitric acid and sulphuric acid concentration for the determination of these elements are 10 % and 5 % respectively. He further observed that sulphuric acid was not necessarily suitable for determining lead when the acid concentration was greater than 5 %. Perchloric acid was found to be the best acid in the determination of Pb, Cd, Cu and Zn at low concentrations particularly at 10 % v/v. He therefore concluded that the most efficient and effective digestion procedures for the determination of Zn, Cu, Pb and Cd are best done in 10 % v/v perchloric acid. While Muiva conducted simulation studies using standard solutions, this study was concerned with both simulations and the applicability of these results in natural water bodies. Lake Nakuru and River Njoro water samples were used to ascertain the enhancement effects of mineral acids on metal analytes in natural water. The use of samples from the two water bodies was mainly done to determine the differences if any in the analysis of fresh River Njoro water and alkaline water from Lake Nakuru. Analysis was carried out under similar conditions as those used in simulation studies. In this case, only the acid concentration was varied between 0 to 50 % v/v.

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Reagents

- Distilled water
- Hydrochloric acid (Analar grade)
- Nitric acid (Analar grade)
- Perchloric acid (Analar grade)

The mineral acids used were bought in 2.5 litres capacity from Sigma-Aldrich chemicals. Water was distilled from Egerton University chemistry laboratories.

- Lead standard solution
- Copper standard solution
- Iron standard solution
- Manganese standard solution
- Zinc standard solution

The standard solutions used were bought in 500 mL capacity each containing 1000 ppm of the analyte of interest. These were supplied from Sigma-Aldrich chemicals limited.

## 3.2 Equipment and Glassware

A manual operated Thermo Jarrell Ash S11 AA/AE Spectrophotometer double beam instrument was used for this work. All the parameters for analysis of each metal were optimized in accordance to the manufacturer's specifications. Each element was analyzed using its own lamp. All the glassware used for analysis were pyrex make with the indicated confidence limits.

- Eighteen (100±0.1) mL volumetric flasks
- Three plastic wash bottles
- Six (100±0.05) mL beakers
- Six (400±0.05) mL beakers
- One each of (10±0.2) mL and (50±0.2) mL measuring cylinder
- Six (25±0.1) mL Pipettes and pipette fillers
- 144 plastic sample bottles

All the glassware were cleaned using 25% chromic acid in order to minimize any forms of interferences from spurious absorbance values resulting from impurities.

### 3.3 Preparation of standard solutions from stock solutions

From the 1000-ppm zinc stock solution, consecutive dilutions were made to make 400 mL each of 0.1, 0.4, 1, 2, 5 and 10-ppm standard solutions. One hundred and twenty (120 mL) millilitres of the 0.1-ppm standard solution were equally distributed in six sample bottles. This was repeated for 0.4, 1, 2, 5 and 10-ppm concentrations and for Fe, Cu, and Mn. For lead, the respective dilutions made from its stock solution were in concentrations of 0.1, 0.4 and 2-ppm since it occurs in trace quantities in water. However, its (lead) procedure was repeated as above.

### 3.4 Preparation of different acid concentrations

Percent acid/water (% v/v) concentrations were made by adding 10, 20, 30, 40 and 50 mL of concentrated analar HCl acid in five 100 mL volumetric flasks. This was done using the pipettes. Distilled water was added to the 100 mL mark in each of the five flasks to obtain the desired concentrations (10, 20, 30, 40 and 50 % v/v). This procedure was repeated with $HNO_3$ and $HClO_4$ acids in different containers. Sulphuric acid was not used in this project since it forms sulphates with metal ions, which are not soluble in water.

### 3.5 Sampling of Lake Nakuru and River Njoro water

Four water samples were collected from River Njoro and Lake Nakuru through the grab sampling method. This was done using a sampling stick, which was used from the shoreline to scoop water from the middle of the River into a 200 mL plastic container tied at the end of the sampling stick. This procedure was done 100 meters along the river down stream from the point of the first sample. This was repeated for Lake Nakuru where the samples were taken from two positions 100 meters apart. Samples were collected beneath the surface of water and stored in plastic containers. The sample bottles were covered with aluminium foil and placed in a fridge to prevent metabolic processes of microoganisms, which might have caused changes in the sample (L'vov, 2005).

### 3.6 Digestion of standard samples

The standard samples were digested by adding 2 mL of each acid concentration (0, 10, 20, 30, 40 and 50 % v/v) to 0.1-ppm of Fe. This was repeated for 0.4, 1, 2, 5 and 10-ppm Fe concentrations. The digested standards were left for thirty minutes before being analyzed through AAS. This procedure was repeated under $HNO_3$ and $HClO_4$ acid media and for different concentrations of Mn, Pb Cu and Zn standards.

### 3.7 Digestion of Lake Nakuru and River Njoro water samples

One hundred and twenty (120 mL) millilitres of River Njoro water sample were equally distributed in six sample bottles using 10 mL measuring cylinders. Two millilitres (2 mL) of different concentrations of HCl acid (0, 10, 20, 30, 40 and 50 % v/v) were added to each of the six samples and left still for 30 minutes before Atomic Absorption Spectrophotometric analysis. This procedure was repeated under $HNO_3$ and $HClO_4$ acid media and for Lake Nakuru water sample.

### 3.8 AAS instrumental calibration and analysis of the standards, Lake Nakuru and River Njoro water samples

The manual operated thermal Jarrel AAS machine was calibrated for each metal analyte under study. This was done after careful trials of analysis to determine the exact parameters where absorption of the respective metals was highest. The Lake Nakuru and River Njoro water samples were analyzed under the same parameters as those of the standards as seen in table **3.1** below. Acetylene ($C_2H_2$) was used as fuel and air as the oxidant to provide a lean fuel, which has less fuel than oxidant. Its flame was regulated to a blue colour with a burner height of between 5-10 mm. For lead, manganese, zinc and iron, the most effective analysis was done with the burner height at 5 mm. For copper, it was at 8 mm. The samples were analyzed via Atomic Absorption Spectrophotometer after being left still for thirty minutes upon addition of different concentration of acids. At least three absorbance readings were recorded in order to determine the most accurate value. Results obtained were analyzed using the Statistical Analysis System (SAS, 2004) at 0.05 level of significance ($\alpha$ =0.05). This was done to determine the most effective acid and acid concentration, for enhancement of AAS absorption signals of metal analytes in water.

**Table 3.1: AAS instrumental parameters for analysis of metal analyte**

| **Metal analyte** | **Pb** | **Mn** | **Zn** | **Cu** | **Fe** |
|---|---|---|---|---|---|
| **Wave length (nm)** | **217** | **279.5** | **213.9** | **324.7** | **248.3** |
| **Burner height (mm)** | **5** | **5** | **5** | **8** | **5** |
| **Slit width (mm)** | **1.0** | **1.0** | **1.0** | **1.0** | **0.3** |
| **Voltage (v)** | **0.6** | **0.6** | **0.7** | **0.8** | **0.3** |
| **Current (Amp)** | **5** | **5** | **3** | **8** | **8** |
| **Linear range (ppm)** | **15** | **3** | **0.4** | **4** | **5** |
| **Limit of detection (mg/mL)** | **0.1** | **0.02** | **0.008** | **0.03** | **0.04** |

# CHAPTER FOUR
# RESULTS AND DISCUSSION

## 4.1 Results

The Atomic Absorption Spectrophotometric instrumental analysis for the standards was done for each metal analyte concentration under digestion of different concentrations of the three acids ($HClO_4$, $HNO_3$ and HCl). Example, analysis of 0.1-ppm of Fe was done under 0, 10, 20, 30, 40 and 50 % v/v HCl acid, then repeated under $HNO_3$ and $HClO_4$ acids. This procedure was repeated for Fe in 0.4, 1, 2, 5 and 10-ppm in different concentrations of the three acids and results recorded. In the River Njoro and Lake Nakuru water samples, AAS analysis was done for Pb, Mn, Zn, Fe and Cu after digesting each water sample successively with HCl, $HNO_3$ and $HClO_4$ acids. The atomic absorption spectrophotometer gave out digital readings, which were recorded manually. To determine whether there were any significant differences in these results, a statistical analysis was done at $\alpha = 0.05$ level of significance using the SAS, 2004 program. Below is a report of the observations and findings.

## 4.2 Results on enhancement effect of acid concentration on absorption signals of metal analytes in the standards

Table **4.1** shows digital absorption signals recorded during the analysis of different metal analyte concentrations of Cu in different concentrations of HCl acid as a digestion medium. To observe the trends of absorbance relative to acid concentration, figures **4.1** and **4.2** have been used to illustrate this.

**Table 4.1. Absorption signals of Cu using different concentrations of HCl medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | **0** | **10** | **20** | **30** | **40** | **50** |
| **0.1 ppm** | 0.00200± 0.00047 | 0.00400± 0.00037 | 0.00300± 0.00036 | 0.00300± 0.00039 | 0.00200± 0.00041 | 0.00100± 0.00051 |
| **0.4** | 0.00100± 0.00049 | 0.01300± 0.00310 | 0.01100± 0.00259 | 0.01100± 0.00261 | 0.00900± 0.00249 | 0.00800± 0.00184 |
| **1** | 0.02900± 0.00464 | 0.03200± 0.00512 | 0.03100± 0.00507 | 0.02800± 0.00454 | 0.02700± 0.00378 | 0.02300± 0.00322 |
| **2** | 0.05900± 0.00790 | 0.06700± 0.00871 | 0.06300± 0.08190 | 0.06000± 0.00840 | 0.05700± 0.00798 | 0.05300± 0.00689 |
| **5** | 0.17000± 0.02210 | 0.17400± 0.02264 | 0.17200± 0.02236 | 0.17000± 0.02208 | 0.16800± 0.02184 | 0.16300± 0.02119 |
| **10** | 0.30100± 0.03913 | 0.31000± 0.04030 | 0.30600± 0.03978 | 0.30200± 0.03926 | 0.29900± 0.03887 | 0.29700± 0.03861 |

The main observation for all metal analyte concentrations and acid media is that there exists an initial relatively large increase in absorbance on going from a neutral to an acidic solution at low acid concentration (10 % v/v). As the percent acid concentration (% v/v) is further increased, the absorbance of metal analytes decrease gradually. Figure **4.1** and **4.2** show the absorption trends of different concentrations of HCl acids on 0.1, 0.4, 1, 2, 5 and 10-ppm copper standards. From these figures, we notice that as the acid concentration is increased from 0 to 10 % v/v, absorbance increases drastically to its highest value. Further increase in acid concentration results into gradual decrease in absorbance with the lowest absorbance value at 50 % v/v acid concentration. This was observed for all metal analyte concentrations (0.1, 0.4, 1, 2, 5 and 10 ppm) under different acid concentrations (0, 10, 20, 30, 40 and 50 % v/v) of the three digestion media. This indicates that higher concentrations of acid have peak de-enhancing effects on absorption signals of metal analytes in water. This is perhaps due to presence of interfearants from the digestion media (acids) whose effects are pronounced with increase in acid concentration.

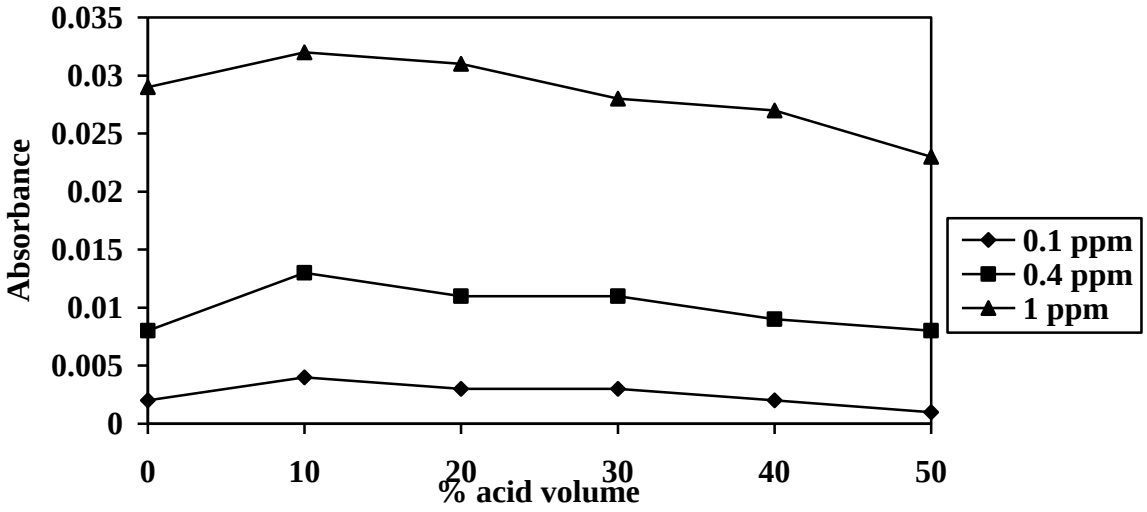


**Fig 4.1. Absorption trends of different concentrations of HCl acid on 0.1, 0.4 and 1 ppm Cu standards**

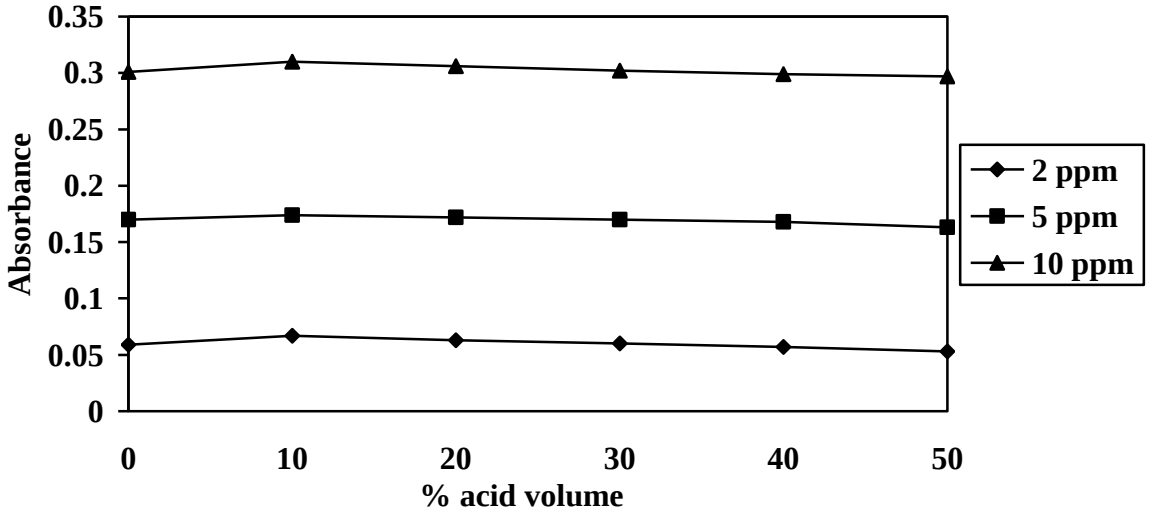


**Fig 4.2. Absorption trends of different concentrations of HCl acid on 2, 5 and 10 ppm Cu standards**

Graphs illustrating a similar trend for different concentrations of other metal analytes are in appendix **8.** From figures, **4.1** and **4.2** above, it is also important to note that enhanced absorption signals imply high sensitivity. Since sensitivity is given by the ratio between change in absorbance and change in concentration (**S**=Δ**A**/Δ**C**). Where Δ**A** is change in absorbance and Δ**C** is change in concentration. This implies that the higher the change in absorbance, the higher the sensitivity and vice versa. A comparison of figures **4.1** and **4.2** for hydrochloric acid with figures **4.3** and **4.4** for nitric acid and figures **4.5** and **4.6** for perchloric acid reveals that the highest sensitivity at the **0.1**-**0.4**-ppm concentration level was observed when perchloric acid was used as a digestion medium. Sensitivity in this case was calculated using change in absorbance between the two concentration levels (**0.1**-ppm and **0.4**-ppm) for HCl, $HNO_3$ and $HClO_4$ acids as shown below.

Sensitivity $_{HCl}$ = (0.013-0.004)/0.4-0.1= 0.03

Sensitivity $_{HNO_3}$= (0.015-0.007)/0.4-0.1= 0.02

Sensitivity $_{HClO_4}$= (0.019-0.008)/0.4-0.1= 0.036

These calculations were done using the digital absorbance results at the ten percent acid concentration (10 % v/v) of the three acids in the analysis of copper. Since at this concentration, the highest absorbance was observed upon addition of the digestion media. See figures **4.3, 4.4, 4.5** and **4.6** in the adjacent pages. This shows that an effective digestion medium enhances the sensitivity of the AAS analytical method for trace metal analysis.

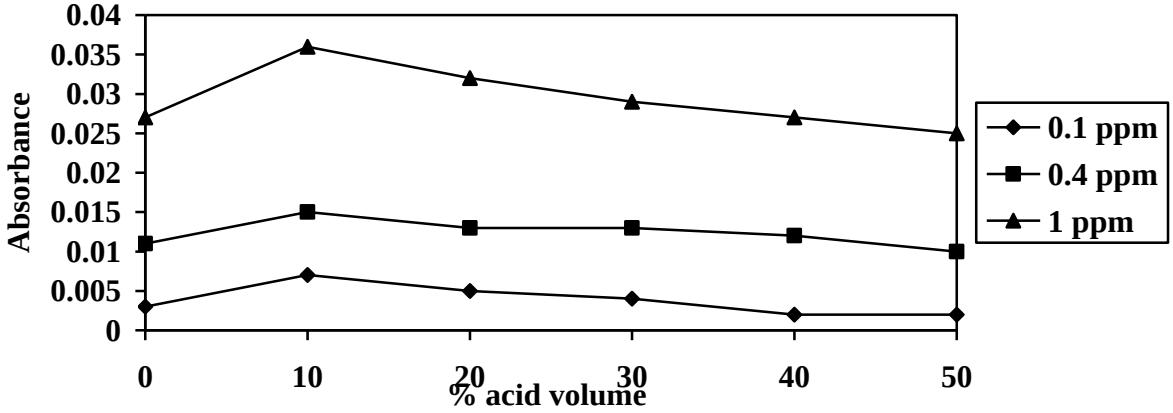


**Fig 4.3. Absorption trends of different concentrations of Nitric acid on 0.1, 0.4 and 1 ppm Cu standards**

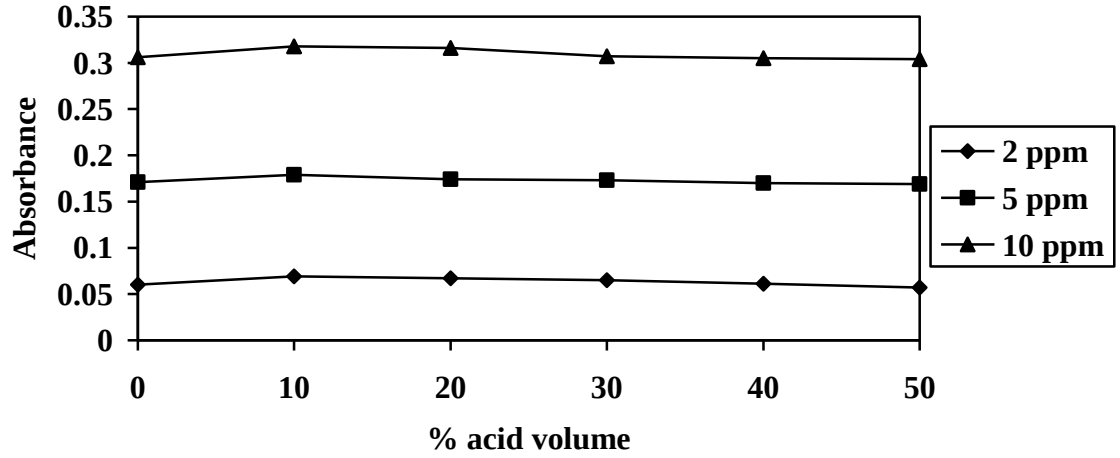


**Fig 4.4. Absorption trends of different concentrations of Nitric acid on 2, 5 and 10 ppm Cu standards**

The digital absorbance data that was used to draw figures **4.3** and **4.4** is shown in appendix 1 table 1, while that used to draw figures **4.4** and **4.5** is shown in appendix 1 table 2. At the lower concentration levels (0.1, 0.4 and 1-ppm), the peak enhancing effect from a non-acidic to an acidic solution (at 10 % v/v) is very high for all the acids (HCl, $HNO_3$ and $HClO_4$) as seen in figures **4.1**, **4.3** and **4.5** but tends to level at higher metal analyte concentrations (figures **4.**2, **4.4** and **4.6**). This implies that the acid with the highest peak enhancing effect is the best suited for analysis of minute concentrations of metal analytes in water through the AAS method.

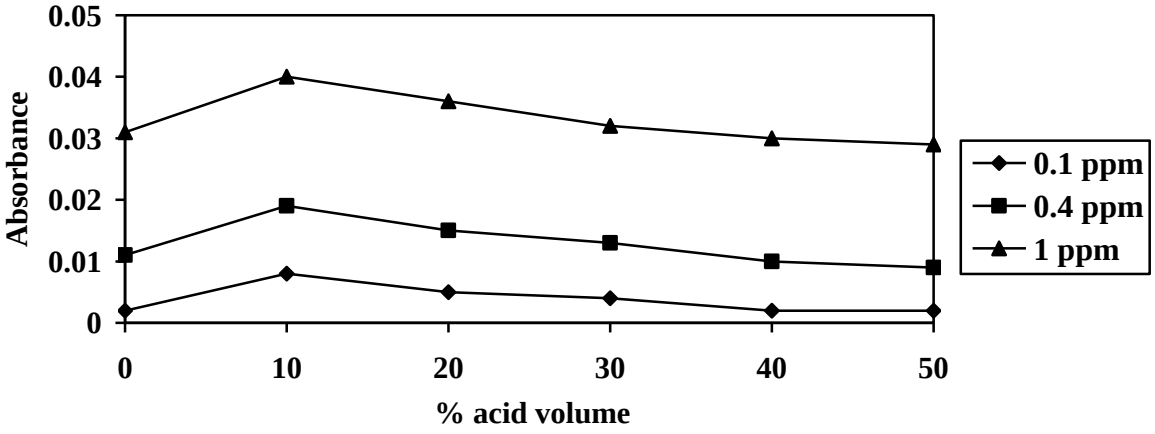


**Fig 4.5. Absorption trends of different concentrations of perchloric acid on 0.1, 0.4 and 1 ppm Cu standards**

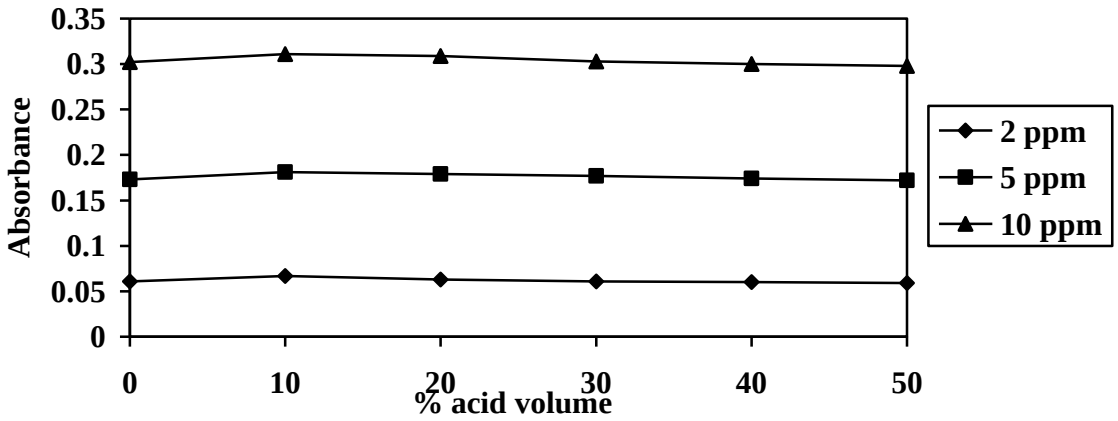


**Fig 4.6. Absorption trends of different concentrations of perchloric acid on 2, 5 and 10 ppm Cu standards**

### 4.3 Statistical analysis on enhancement effect of acids on absorption signals of metal analytes in the standards.

The statistical analysis of standards revealed that $HClO_4$ and $HNO_3$ acids had equal but higher peak enhancing effects than HCl acid in the analysis of all metal analytes at the 0.1-ppm concentration (as seen in table **4.2** below). The two acids had duncan ratings of a in the analysis of Mn, Zn, Cu, Pb and Fe while HCl acid has a duncans rating of b which shows that they are more effective as digestion media as compared to HCl acid. This table as with other statistical tables (**4.2-4.7, 4.10 and 4.11**) reveals the statistical analysis of the effectiveness of the three acids as digestion media on different concentrations of metal analytes. The subscript alphabetical letters a, b and c indicate the duncans rating of the effectiveness of the three acids with the most effective having letter a, the second having letter b and the least effective

letter c. Absorbance means of the three acids are also given. Means followed or rated by the same letter are not significantly different. The M.S.E row is an abbreviation for Means Square Error. This value is used to calculate the standard error (S.E). This is done by dividing M.S.E by the number of means in this case three and obtaining the square root of the result. The standard error (S.E) is then used to calculate the Least Square Range ($L.S.R_p$). Where $_p$ indicates the number of means, being compared the least being two. The $L.S.R_p$ is calculated by multiplying the Standard Error (S.E) by the Significant Standardized Range (S.S.R), which is obtained from statistical tables in the f test. In this case, we obtain S.S.R from f-test at error degrees of freedom (d.f) 2 since d.f = n-1. Our n in this case is three since we are comparing three means. Comparisons are then made using the calculated $L.S.R_p$. If the observed difference between the two or three means is greater than the $L.S.R_p$, then we conclude that the pair of means are significantly different. If not, they are not significantly different and will be rated with the same letter.

**Table 4.2. Effects of acids on 0.1 ppm standard concentrations of metal analytes**

| Acid | Metal | | | | |
|---|---|---|---|---|---|
| | **Mn** | **Zn** | **Cu** | **Pb** | **Fe** |
| **$HClO_4$** | $0.0058966_a$ | $0.0132669_a$ | $0.0038333_a$ | $0.0042667_a$ | $0.006833_a$ |
| **$HNO_3$** | $0.0063333_a$ | $0.0138333_a$ | $0.0038333_a$ | $0.0045000_a$ | $0.006667_a$ |
| **HCl** | $0.0051667_b$ | $0.011000_b$ | $0.0025000_b$ | $0.0036667_b$ | $0.004167_b$ |
| **M.S.E** | 0.50310 | 0.36431 | 0.58793 | 0.37682 | 0.42531 |

Means followed by the same letter are not significantly different

In the 0.4-ppm concentration, the two acids ($HClO_4$ and $HNO_3$) had equal but greater peak enhancing effects than HCl acid in the analysis of Mn, Pb, Zn and Fe. For Cu at 0.4-ppm concentration, all the three acids were equally effective with duncan ratings a. (Table **4.3** below).

**Table 4.3. Effects of acids on 0.4 ppm standard concentrations of metal analytes**

| Acid | Metal | | | | |
|---|---|---|---|---|---|
| | **Mn** | **Zn** | **Cu** | **Pb** | **Fe** |
| **$HClO_4$** | $0.0075000_a$ | $0.044667_a$ | $0.0123333_a$ | $0.0060000_a$ | $0.0095000_a$ |
| **$HNO_3$** | $0.0075000_a$ | $0.044333_a$ | $0.0123333_a$ | $0.0060000_a$ | $0.0086667_a$ |
| **HCl** | $0.0063333_b$ | $0.043000_b$ | $0.0105000_a$ | $0.0053000_b$ | $0.0060000_b$ |
| **M.S.E** | 0.3768 | 0.44721 | 0.34334 | 0.49063 | 0.27100 |

Means followed by the same letter are not significantly different

At the 1.0-ppm metal analyte concentration, we had $HClO_4$ and $HNO_3$ acids being equally but more effective than HCl acid in the analysis of Mn, Cu and Fe. Perchloric acid was however, the most effective followed by $HNO_3$ and HCl acid in the analysis of Zn at the 1.0-ppm metal analyte concentration as seen in table **4.4** below. This clearly shows that the peak enhancing effect of acids is perhaps determined by the nature of an acid since the more oxidizing acids ($HNO_3$ and $HClO_4$) seem to have higher peak enhancing effects than the lesser oxidizing acid (HCl).

**Table 4.4. Effects of acids on 1.0 ppm standard concentrations of metal analytes**

| Acid | Metal | | | |
|---|---|---|---|---|
| | **Mn** | **Zn** | **Cu** | **Fe** |
| **$HClO_4$** | $0.0033500_a$ | $0.0788333_a$ | $0.0330000_a$ | $0.0181906_a$ |
| **$HNO_3$** | $0.0333333_a$ | $0.0761667_b$ | $0.0323333_a$ | $0.0186667_a$ |
| **HCl** | $0.0318333_b$ | $0.0716667_c$ | $0.0283333_b$ | $0.0156667_b$ |
| **M.S.E** | 0.25701 | 0.37431 | 0.28761 | 0.324893 |

Means followed by the same letter are not significantly different

At the 2-ppm metal analyte concentration, $HClO_4$ and $HNO_3$ acids were equally but more effective as compared to HCl acid in the analysis of Mn and Fe. Perchloric acid was the most effective in the analysis of Pb, Cu and Zn followed by $HNO_3$ and HCl acids in this order (table **4.5** below). Also, an indication that the nature of an acid may influence the enhancement of absorption signals of metal analytes in water.

**Table 4.5. Effects of acids on 2.0 ppm standard concentrations of metal analytes**

| Acid | Metal | | | | |
|---|---|---|---|---|---|
| | **Mn** | **Zn** | **Cu** | **Pb** | **Fe** |
| **$HClO_4$** | $0.0638333_a$ | $0.1440000_a$ | $0.0631667_a$ | $0.0281667_a$ | $0.0421667_a$ |
| **$HNO_3$** | $0.0631667_a$ | $0.1400000_b$ | $0.0618333_{ab}$ | $0.0263333_b$ | $0.0403333_a$ |
| **HCl** | $0.0613333_b$ | $0.1375000_c$ | $0.0600000_b$ | $0.025000_c$ | $0.0378333_b$ |
| **M.S.E** | 0.32110 | 0.31911 | 0.33607 | 0.36001 | 0.38887 |

Means followed by the same letter are not significantly different

At the 5-ppm metal analyte concentration, we had $HClO_4$ acid being the most effective in the digestion of Mn, Cu and Fe with a duncan rating a, followed by $HNO_3$ and HCl acids with duncan ratings of b and c respectively. Nitric acid was more effective in the analysis of Zn followed by $HClO_4$ and HCl acids in this order. These observations clearly indicate that the two acids $HClO_4$ and $HNO_3$ have higher peak enhancing effects as compared to HCl acid. This may be attributed to their nature since they are more oxidizing than HCl acid. This may be the reason why they are more effective as digestion media as compared to HCl acid. (table **4.6** below).

**Table 4.6. Effects of acids on 5.0 ppm standard concentrations of metal analytes**

| Acid | Metal | | | |
|---|---|---|---|---|
| | **Mn** | **Zn** | **Cu** | **Fe** |
| **$HClO_4$** | $0.1595000_a$ | $0.362283_b$ | $0.1760000_a$ | $0.0930000_a$ |
| **$HNO_3$** | $0.1548333_b$ | $0.367500_a$ | $0.1726667_b$ | $0.0891667_b$ |
| **HCl** | $0.1496667_c$ | $0.358938_c$ | $0.1695000_c$ | $0.0860000_c$ |
| **M.S.E** | 0.2617 | 0.6554 | 0.29078 | 0.321109 |

Means followed by the same letter are not significantly different

At the 10-ppm metal analyte concentration, $HClO_4$ acid was the most effective in the analysis of Fe followed by $HNO_3$ then HCl acid in this order. The two acids ($HNO_3$ and $HClO_4$) were equally but more effective in the analysis of Cu as compared to HCl acid. Nitric acid was more effective in the analysis of Mn and Zn followed by $HClO_4$ then HCl acid as seen in table **4.7**. These observations are a pointer to the fact that the nature of an acid may influence the peak enhancement process during digestion with the more oxidizing acids such as $HClO_4$ and $HNO_3$ having greater peak enhancing effects that the less oxidizing acid (HCl).

**Table 4.7. Effects of acids on 10.0 ppm standard concentrations of metal analytes**

| Acid | Metal | | | |
|---|---|---|---|---|
| | **Mn** | **Zn** | **Cu** | **Fe** |
| **$HClO_4$** | $0.304667_b$ | $0.5498333_{ab}$ | $0.3088916_a$ | $0.170333_a$ |
| **$HNO_3$** | $0.314333_a$ | $0.557167_a$ | $0.3093333_a$ | $0.166000_b$ |
| **HCl** | $0.298333_c$ | $0.549000_b$ | $0.3028333_b$ | $0.157000_c$ |
| **M.S.E** | 0.56085 | 0.0013944 | 0.2844 | 0.4568 |

Means followed by the same letter are not significantly different

**4.4 Results from River Njoro and Lake Nakuru water samples.**

In both River Njoro and Lake Nakuru water samples, we observed a relatively large increase in absorbance when going from a neutral to an acidic solution at 10 % v/v. This was seen in the analysis of Pb, Fe, Zn, Mn and Cu. Figures **4.7** and **4.8**. Show absorption trends of different concentrations of hydrochloric, nitric and perchloric acids on Mn in River Njoro and Lake Nakuru water samples respectively.

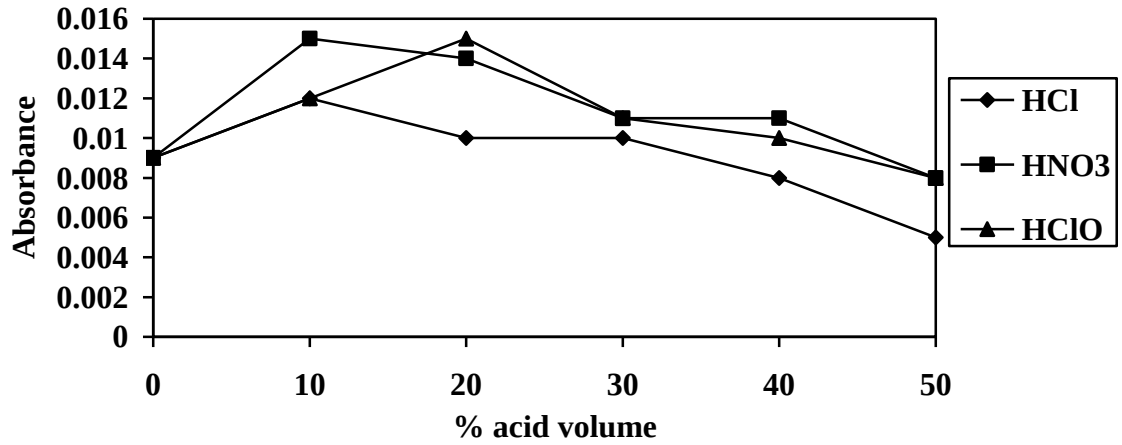


**Fig 4.7. Absorption trends of different concentrations of hydrochloric, nitric and perchloric acids on Mn in River Njoro water sample**

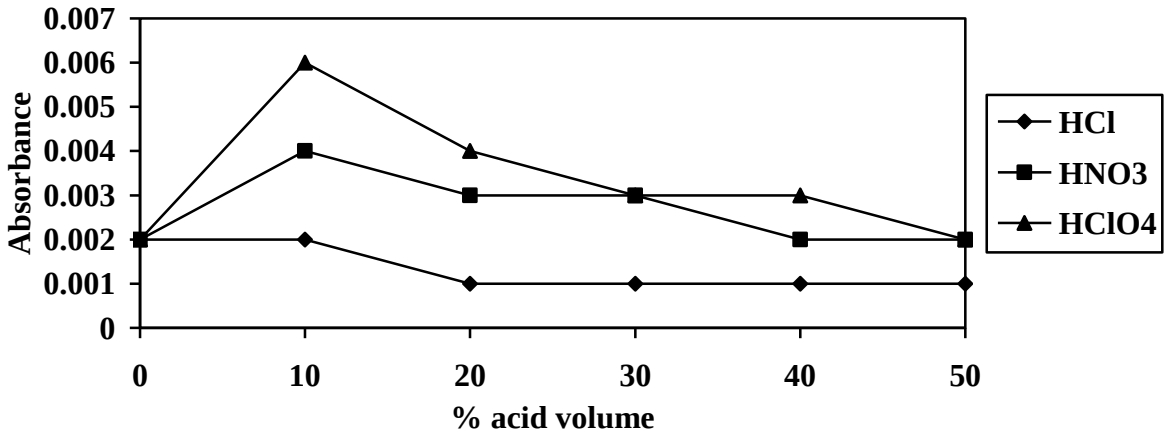


**Fig 4.8. Absorption trends of different concentrations of hydrochloric, nitric and perchloric acids on Mn in Lake Nakuru water sample**

These figures were drawn from the manually recorded digital absorption signals of manganese from tables **4.8** and **4.9** below during the AAS analysis of this metal analyte in River Njoro and Lake Nakuru water samples. The absorbance values are means of three readings that were taken for each analysis.

**Table 4.8. Absorption signals of Mn in River Njoro sample under different acid media**

| **Acids** | **% acid volume** | | | | | |
|---|---|---|---|---|---|---|
| | **0** | **10** | **20** | **30** | **40** | **50** |
| **HCl** | 0.00900± 0.00101 | 0.01200± 0.00140 | 0.01000± 0.00117 | 0.01000± 0.00116 | 0.00800± 0.00094 | 0.00500± 0.00058 |
| **$HNO_3$** | 0.00900± 0.00105 | 0.01500± 0.00176 | 0.01400± 0.00164 | 0.01100± 0.00128 | 0.01100± 0.00127 | 0.00800± 0.00093 |
| **$HClO_4$** | 0.00900± 0.00106 | 0.01200± 0.00141 | 0.01500± 0.00175 | 0.01100± 0.00126 | 0.01000± 0.00109 | 0.00800± 0.00091 |

**Table 4.9. Absorption signals of Mn in Lake Nakuru sample under different acid media**

| **Acids** | **% acid volume** | | | | | |
|---|---|---|---|---|---|---|
| | **0** | **10** | **20** | **30** | **40** | **50** |
| **HCl** | 0.00200± 0.00006 | 0.00200± 0.00005 | 0.00100± 0.00003 | 0.00100± 0.00003 | 0.00100± 0.00003 | 0.00100± 0.00002 |
| **$HNO_3$** | 0.00200± 0.00006 | 0.00400± 0.00012 | 0.00300± 0.00011 | 0.00300± 0.00010 | 0.00200± 0.00007 | 0.00200± 0.00004 |
| **$HClO_4$** | 0.00200± 0.00006 | 0.00600± 0.00018 | 0.00400± 0.00013 | 0.00300± 0.00009 | 0.00300± 0.00008 | 0.00200± 0.00005 |

From figures (**4.7** and **4.8**), we note that subsequent increase in acid concentration had a peak de-enhancing effect perhaps due to presence of interfearants in the acids. Since digestion,

media are used to solubilize the metal analytes in a sample by releasing them from matrices, the higher the concentration of a digestion medium, the lesser the solubilization effect. This is because when in high concentrations, the digestion media will largely exists in molecular as opposed to aqueous form within the water sample. This observation was also seen for all metal analytes in the three acid media for both River Njoro and Lake Nakuru water samples. In both water samples, perchloric acid had the highest peak enhancing effect followed by nitric then hydrochloric acid as seen in figures **4.7** and **4.8**. This may be attributed to its oxidising nature as an acid

### 4.5 Effectiveness of nitric, perchloric and hydrochloric acids as digestion media in River Njoro water sample

Statistical analysis of the acids revealed that the most effective digestion media for analysis of Mn in River Njoro water sample were $HNO_3$ and $HClO_4$ acids, which according to table **4.10** were equally but significantly different as compared to HCl acid. This may be due to the nature of the two acids as digestion media since the two are more oxidizing as compared to HCl acid.

**Table 4.10. Means of absorbance of different acid media used in digestion of water samples from River Njoro**

| Acid | Metal | | | | |
|---|---|---|---|---|---|
| | **Mn** | **Pb** | **Fe** | **Zn** | **Cu** |
| **$HClO_4$** | $0.0108333_a$ | $0.0221667_a$ | $0.0278333_a$ | $0.0198333_a$ | $0.0013333_a$ |
| **$HNO_3$** | $0.0113333_a$ | $0.0221667_a$ | $0.0278333_a$ | $0.017333_b$ | $0.0011667_a$ |
| **HCl** | $0.0099972_b$ | $0.019667_b$ | $0.0257773_b$ | $0.016333_b$ | $0.0011667_a$ |
| **M.S.E** | 0.611555394 | 0.862747549 | 0.655489638 | 0.795822425 | 0.360882067 |

Means followed by the same letter are not significantly different

This observation was also seen in the analysis of Pb and Fe in which the two acids were equally effective ($HNO_3$ and $HClO_4$) but their effectiveness was significantly different as compared to that of HCl acid. Table **4.10** above.

$HClO_4$ acid was the most effective digestion medium in the analysis of Zn in River Njoro water sample. The effectiveness of $HNO_3$ and HCl acids was not significantly different from one another since the two had duncan ratings of b as seen in table **4.10** above.

For Cu in River Njoro water sample, the effectiveness of the three acids was not significantly different (Table **4.10**) perhaps due to the occurrence of this metal analyte in minute concentrations in this water body. Very low concentrations of metal analytes may not be significant enough to show the effectiveness of an acid as a digestion media especially when the limit of detection of the metal analyte under study is low. The limit of detection for copper metal using the thermo Jarrel AAS is 0.03 mg/mL.

### 4.6 Effectiveness of nitric, perchloric and hydrochloric acids as digestion media in Lake Nakuru water sample

For the Lake Nakuru water sample, the SAS, 2004 statistical analysis revealed that the most effective acids for digestion of Mn were $HClO_4$ and $HNO_3$ with duncan ratings of a. The effectiveness of the two was however significantly different from that of HCl which had a rating b as seen in table **4.11** below.

**Table 4.11. Means of absorbance of different acid media used in digestion of water samples from Lake Nakuru**

| Acid | Metal | | | | |
|---|---|---|---|---|---|
| | **Mn** | **Pb** | **Fe** | **Zn** | **Cu** |
| **$HClO_4$** | $0.0033333_a$ | $0.0280000_a$ | $0.0096667_a$ | $0.0116667_a$ | $0.016667_a$ |
| **$HNO_3$** | $0.0025000_a$ | $0.0286667_a$ | $0.0093333_a$ | $0.00111667_a$ | $0.016667_a$ |
| **HCl** | $0.0013333_b$ | $0.025667_b$ | $0.0091667_a$ | $0.00106333_b$ | $0.013333_a$ |
| **M.S.E** | 0.36491758 | 0.602494813 | 0.92303846 | 1.13856635 | 0.72018516 |

Means followed by the same letter are not significantly different

A similar observation was seen for Pb and Zn in this water sample. The effectiveness of $HClO_4$ and $HNO_3$ acids were not significantly different with duncan ratings a. Their effectiveness was however significantly different from that of HCl acid which had a rating b. See table **4.11** above. This observation may be attributed to the nature of the two acids ($HClO_4$ and $HNO_3$) since they are more oxidizing as compared to hydrochloric acid.

The effectiveness of the three acids was not significantly different in the analysis of Cu and Fe in this water body since they all had duncan ratings a. This observation may have been due to the occurrence of this metal analyte in minute concentrations in this water body. See table **4.11** above.

### 4.7 Conclusions

From the observations made on the analysed data (tables **4.2** to **4.7, 4.10, 4.11** and figures **4.1** to **4.8**), the following conclusions stand merit;

a. Mineral acids have varied enhancement effects on the absorption signals of metal analytes in natural waters. This variation depends on acid concentration and the nature of the acid with the more oxidizing acids (such as $HNO_3$ and $HClO_4$) having greater peak enhancing effects than the less oxidizing acids (such as HCl).

b. The most suitable concentration for digestion was at 10 % v/v acid concentration. Higher concentrations of acid have peak de-enhancing effects on absorption signals of metal analytes in water. This observation was true for standards, River Njoro and Lake Nakuru water samples**.**

c. There were no significant differences between Lake Nakuru and River Njoro water samples. Since in both samples, the more oxidizing acids ($HNO_3$ and $HClO_4$) had greater peak enhancing effects than the less oxidizing acid (HCl) for all metal analytes except Cu in both water samples and Fe in Lake Nakuru water sample.

d. For measurement of Pb, Zn, Mn, Cu and Fe, in the standards, River Njoro and Lake Nakuru water samples, more reliable results can be obtained in 10 % v/v nitric or perchloric acid solutions. The most effective concentration for digestion procedures in the analysis of Zn, Cu, Pb, Mn and Fe will best be done in 10 % v/v perchloric or nitric acids.

From the above conclusions, it should be noted that acids influence the atomization mechanism not only by their qualitative nature (Pinta, 1982) but also by their concentrations. The more oxidising acids have higher peak enhancing effects compared to the less oxidizing acids. Since acids may contain analytes of interest, whose effects are pronounced in high concentrations (L'vov, 2005), digestion should be done at an optimum concentration for effective analysis. It should also be noted that even though perchloric acid was found to have greater peak enhancing effects, it is not recommended for use since it reacts explosively with organic matter in the presence of heat. The most preferable would therefore be nitric acid.

## 4.8 Recommendations

- In the determination of the enhancement effects of mineral acids on metal analytes in water, heat should be applied in order to reduce the effect of interfearants when analysing natural water samples. In doing this, it should be noted that the use of perchloric acid will be disadvantaged since this acid reacts explosively with organic matter in the presence of heat.

- This study should be carried out with high precision instruments such as inductively coupled plasma in order to effectively determine the peak enhancement effects of minute concentrations of metal analytes such as Pb, Cu and others not used in this study.

- Since most digestion procedures employ the use of mixtures of digestion reagents (such as $HNO_3$-$HClO_4$ acids), and whose prescription is given in ratios, studies should be carried out to determine the most effective concentration to be used for digestion purposes to enhance the discovery of the most effective wet digestion procedures for metal analyte analysis in water.

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## APPENDICES

**Appendix 1**

**Appendix 1. T1. Absorption signals of Cu using different concentrations of $HNO_3$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00300± 0.00033 | 0.00700± 0.00077 | 0.00500± 0.00051 | 0.00400± 0.00046 | 0.00200± 0.00027 | 0.00200± 0.00025 |
| 0.4 | 0.01100± 0.00251 | 0.01500± 0.00360 | 0.01300± 0.00310 | 0.01300± 0.00295 | 0.01200± 0.00278 | 0.01000± 0.00170 |
| 1 | 0.02700± 0.00297 | 0.03600± 0.00396 | 0.03200± 0.00349 | 0.02900± 0.00344 | 0.02700± 0.00356 | 0.02500± 0.00357 |
| 2 | 0.06000± 0.00660 | 0.06900± 0.00610 | 0.06700± 0.00630 | 0.06500± 0.00600 | 0.06100± 0.00671 | 0.05700± 0.00627 |
| 5 | 0.17100± 0.01881 | 0.17900± 0.01611 | 0.17400± 0.01566 | 0.17300± 0.01557 | 0.17000± 0.01530 | 0.16900± 0.01521 |
| 10 | 0.30600± 0.02754 | 0.31800± 0.02862 | 0.31600± 0.02528 | 0.30700± 0.02456 | 0.30500± 0.02745 | 0.30400± 0.02736 |

**Appendix 1. T2. Absorption signals of Cu using different concentrations of $HClO_4$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00200± 0.00004 | 0.00800± 0.00024 | 0.00500± 0.00015 | 0.00400± 0.00012 | 0.00200± 0.00006 | 0.00200± 0.00004 |
| 0.4 | 0.01100± 0.00055 | 0.01900± 0.00095 | 0.01500± 0.00072 | 0.01300± 0.00065 | 0.01000± 0.00050 | 0.00900± 0.00063 |
| 1 | 0.03100± 0.00248 | 0.04000± 0.00320 | 0.03600± 0.00288 | 0.03200± 0.00244 | 0.03000± 0.00210 | 0.02900± 0.00203 |
| 2 | 0.06100± 0.00488 | 0.06700± 0.00536 | 0.06300± 0.00531 | 0.06100± 0.00488 | 0.06000± 0.00480 | 0.05900± 0.00472 |
| 5 | 0.17300± 0.01384 | 0.18100± 0.01267 | 0.17900± 0.01432 | 0.17700± 0.01416 | 0.17400± 0.01378 | 0.17200± 0.01346 |
| 10 | 0.30200± 0.02416 | 0.31100± 0.009333 | 0.30900± 0.00909 | 0.30300± 0.00897 | 0.30000± 0.00900 | 0.29800± 0.00596 |

**Appendix 2**

**Appendix 2. T1. Absorption signals of Fe using different concentrations of HCl medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00200± 0.00003 | 0.00800± 0.00019 | 0.00500± 0.00011 | 0.00500± 0.00010 | 0.00300± 0.000013 | 0.00200± 0.00011 |
| 0.4 | 0.00500± 0.00009 | 0.01100± 0.00017 | 0.00800± 0.00016 | 0.00500± 0.00008 | 0.00400± 0.00012 | 0.00300± 0.00011 |
| 1 | 0.01500± 0.00060 | 0.01900± 0.00076 | 0.01700± 0.00068 | 0.01500± 0.00061 | 0.01300± 0.00052 | 0.01200± 0.00048 |
| 2 | 0.03700± 0.00148 | 0.04100± 0.00164 | 0.04000± 0.00160 | 0.03800± 0.00152 | 0.03600± 0.00144 | 0.03500± 0.00140 |
| 5 | 0.08700± 0.00348 | 0.08900± 0.00445 | 0.08800± 0.00352 | 0.08700± 0.00261 | 0.08500± 0.00255 | 0.0800± 0.00320 |
| 10 | 0.15800± 0.00632 | 0.16500± 0.00495 | 0.16000± 0.00601 | 0.15600± 0.00468 | 0.15200± 0.00456 | 0.15100± 0.00453 |

**Appendix 2. T2. Absorption signals of Fe using different concentrations of $HNO_3$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00300± 0.00009 | 0.01200± 0.00071 | 0.00900± 0.00036 | 0.00800± 0.00031 | 0.00500± 0.00028 | 0.00300± 0.00012 |
| 0.4 | 0.00600± 0.00018 | 0.01500± 0.00045 | 0.01200± 0.00036 | 0.00900± 0.00027 | 0.00600± 0.000018 | 0.00400± 0.00013 |
| 1 | 0.01700± 0.00051 | 0.02500± 0.00118 | 0.02300± 0.00115 | 0.01800± 0.00072 | 0.01500± 0.00060 | 0.01400± 0.00056 |
| 2 | 0.03900± 0.00195 | 0.04700± 0.00235 | 0.04600± 0.00240 | 0.04100± 0.00164 | 0.03600± 0.00144 | 0.03300± 0.00139 |
| 5 | 0.08700± 0.00435 | 0.09500± 0.00380 | 0.09200± 0.00552 | 0.09000± 0.00430 | 0.08600± 0.0516 | 0.08500± 0.00501 |
| 10 | 0.16300± 0.00978 | 0.17100± 0.00684 | 0.17000± 0.000681 | 0.16700± 0.00671 | 0.16400± 0.00632 | 0.16100± 0.00449 |

**Appendix 2. T3. Absorption signals of Fe using different concentrations of $HClO_4$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00200± 0.00001 | 0.01600± 0.00080 | 0.01100± 0.00055 | 0.00700± 0.00003 | 0.00300± 0.00002 | 0.00200± 0.00004 |
| 0.4 | 0.00600± 0.00030 | 0.01800± 0.00090 | 0.01200± 0.00060 | 0.00900± 0.00043 | 0.00700± 0.00035 | 0.00500± 0.00020 |
| 1 | 0.01300± 0.00051 | 0.02100± 0.00105 | 0.01800± 0.00070 | 0.01700± 0.00070 | 0.01600± 0.00040 | 0.01200± 0.00050 |
| 2 | 0.04100± 0.00205 | 0.04700± 0.00235 | 0.04500± 0.00229 | 0.04300± 0.00231 | 0.04000± 0.00200 | 0.03700± 0.00185 |
| 5 | 0.09300± 0.00462 | 0.09900± 0.00491 | 0.09400± 0.00470 | 0.09300± 0.00465 | 0.09000± 0.00452 | 0.08900± 0.00413 |
| 10 | 0.16900± 0.00831 | 0.17400± 0.00870 | 0.17200± 0.00851 | 0.17100± 0.00810 | 0.17000± 0.00760 | 0.16700± 0.00835 |

**Appendix 3**

**Appendix 3. T1. Absorption signals of Mn using different concentrations of HCl medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00400± 0.00002 | 0.00700± 0.00021 | 0.00600± 0.00009 | 0.00500± 0.00018 | 0.00400± 0.00012 | 0.00300± 0.00011 |
| 0.4 | 0.00600± 0.00017 | 0.00800± 0.00023 | 0.00700± 0.00006 | 0.00600± 0.00018 | 0.00500± 0.00015 | 0.00400± 0.00010 |
| 1 | 0.03100± 0.00155 | 0.03500± 0.00140 | 0.03300± 0.00110 | 0.03200± 0.00090 | 0.03100± 0.00130 | 0.02800± 0.00120 |
| 2 | 0.06000± 0.00300 | 0.06500± 0.00260 | 0.06300± 0.00210 | 0.06300± 0.00211 | 0.06000± 0.00180 | 0.05700± 0.00292 |
| 5 | 0.14900± 0.00447 | 0.15300± 0.00459 | 0.15200± 0.00603 | 0.15000± 0.00450 | 0.14800± 0.00441 | 0.14600± 0.00292 |
| 10 | 0.29800± 0.00831 | 0.30900± 0.00827 | 0.30200± 0.00799 | 0.29600± 0.00781 | 0.29400± 0.00789 | 0.29100± 0.00780 |

**Appendix 3. T2. Absorption signals of Mn using different concentrations of $HNO_3$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00500± 0.00025 | 0.00900± 0.00028 | 0.00800± 0.00021 | 0.00800± 0.00020 | 0.00500± 0.00010 | 0.00300± 0.00006 |
| 0.4 | 0.00800± 0.00094 | 0.01000± 0.00117 | 0.00900± 0.00104 | 0.00700± 0.00081 | 0.00600± 0.00017 | 0.00500± 0.00058 |
| 1 | 0.03200± 0.00371 | 0.03600± 0.00423 | 0.03500± 0.00410 | 0.03400± 0.00397 | 0.03200± 0.00374 | 0.03100± 0.00120 |
| 2 | 0.06000± 0.00703 | 0.06800± 0.00797 | 0.06500± 0.00762 | 0.06300± 0.00737 | 0.06200± 0.00725 | 0.06100± 0.00715 |
| 5 | 0.15300± 0.01793 | 0.1600± 0.01872 | 0.15900± 0.01863 | 0.15500± 0.01816 | 0.15200± 0.01781 | 0.15000± 0.01758 |
| 10 | 0.31100± 0.03645 | 0.31900± 0.03715 | 0.31600± 0.03704 | 0.31600± 0.03703 | 0.31500± 0.03692 | 0.30900± 0.03621 |

**Appendix 3. T3. Absorption signals of Mn using different concentrations of $HClO_4$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00400± 0.00043 | 0.00900± 0.00103 | 0.00800± 0.00081 | 0.00700± 0.00079 | 0.00500± 0.00056 | 0.00300± 0.00036 |
| 0.4 | 0.00700± 0.00079 | 0.01000± 0.00116 | 0.00900± 0.00104 | 0.00800± 0.00079 | 0.00600± 0.00017 | 0.00500± 0.00015 |
| 1 | 0.03400± 0.00398 | 0.03600± 0.00422 | 0.03300± 0.00387 | 0.03200± 0.00375 | 0.03200± 0.00372 | 0.03000± 0.00352 |
| 2 | 0.06100± 0.00715 | 0.06900± 0.00808 | 0.06700± 0.00785 | 0.06500± 0.000762 | 0.06200± 0.00722 | 0.05900± 0.00695 |
| 5 | 0.15800± 0.01852 | 0.16400± 0.01922 | 0.16300± 0.01910 | 0.16100± 0.01886 | 0.15700± 0.01840 | 0.15300± 0.01793 |
| 10 | 0.30200± 0.03539 | 0.31300± 0.03668 | 0.31000± 0.03633 | 0.30500± 0.03575 | 0.30100± 0.03527 | 0.29700± 0.03481 |

**Appendix 4**

**Appendix 4. T1. Absorption signals of Zn using different concentrations of HCl medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00800± 0.00093 | 0.01400± 0.00164 | 0.01300± 0.00152 | 0.01100± 0.00129 | 0.00800± 0.00094 | 0.00600± 0.00070 |
| 0.4 | 0.04100± 0.00481 | 0.04500± 0.00527 | 0.04400± 0.00515 | 0.04200± 0.00492 | 0.04200± 0.00490 | 0.04000± 0.00468 |
| 1 | 0.07300± 0.00856 | 0.07900± 0.00926 | 0.07200± 0.00844 | 0.07000± 0.00820 | 0.06900± 0.00808 | 0.06700± 0.00785 |
| 2 | 0.13800± 0.01617 | 0.14200± 0.01664 | 0.14000± 0.01640 | 0.13700± 0.01605 | 0.13500± 0.01582 | 0.13300± 0.01558 |
| 5 | 0.35800± 0.04195 | 0.36300± 0.04254 | 0.36200± 0.04243 | 0.36100± 0.04231 | 0.35700± 0.04184 | 0.35500± 0.04161 |
| 10 | 0.53600± 0.06282 | 0.56000± 0.06563 | 0.55700± 0.06528 | 0.55300± 0.06481 | 0.55000± 0.06446 | 0.54300± 0.06364 |

**Appendix 4. T2. Absorption signals of Zn using different concentrations of $HClO_4$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00900± 0.00103 | 0.02100± 0.00246 | 0.01900± 0.00223 | 0.01500± 0.00176 | 0.01100± 0.00128 | 0.00800± 0.00091 |
| 0.4 | 0.04600± 0.00539 | 0.05000± 0.00583 | 0.04700± 0.00551 | 0.04300± 0.00501 | 0.04000± 0.00468 | 0.04000± 0.00461 |
| 1 | 0.07500± 0.00879 | 0.08100± 0.00949 | 0.08000± 0.00938 | 0.07700± 0.00902 | 0.07300± 0.00855 | 0.07100± 0.00832 |
| 2 | 0.14100± 0.01652 | 0.15300± 0.01792 | 0.14700± 0.01723 | 0.14300± 0.01676 | 0.14100± 0.01652 | 0.13900± 0.01629 |
| 5 | 0.36100± 0.04231 | 0.37800± 0.04430 | 0.37300± 0.04372 | 0.36900± 0.04324 | 0.36400± 0.04266 | 0.36000± 0.04219 |
| 10 | 0.54400± 0.06375 | 0.58100± 0.06809 | 0.56900± 0.06668 | 0.55300± 0.06480 | 0.54900± 0.06434 | 0.54700± 0.06411 |

**Appendix 4. T3. Absorption signals of Zn using different concentrations of $HClO_4$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.01000± 0.00117 | 0.01700± 0.00199 | 0.01600± 0.00187 | 0.01300± 0.00152 | 0.00700± 0.00081 | 0.00600± 0.00017 |
| 0.4 | 0.04100± 0.00481 | 0.05000± 0.00584 | 0.04800± 0.00563 | 0.04500± 0.00527 | 0.04300± 0.00504 | 0.04100± 0.00480 |
| 1 | 0.07600± 0.00891 | 0.08500± 0.00996 | 0.08200± 0.00961 | 0.08000± 0.00938 | 0.07700± 0.00902 | 0.07300± 0.00855 |
| 2 | 0.13800± 0.01617 | 0.14600± 0.01711 | 0.14300± 0.01676 | 0.14000± 0.01641 | 0.13700± 0.01605 | 0.13600± 0.01594 |
| 5 | 0.36500± 0.04278 | 0.36900± 0.04325 | 0.36400± 0.04266 | 0.36200± 0.04243 | 0.36000± 0.04219 | 0.65700± 0.04184 |
| 10 | 0.54700± 0.06410 | 0.55800± 0.06539 | 0.55100± 0.06458 | 0.54800± 0.06423 | 0.54700± 0.06411 | 0.54300± 0.06363 |

**Appendix 5**

**Appendix 5. T1. Absorption signals of Pb using different concentrations of HCl medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00200± 0.00023 | 0.00600± 0.00072 | 0.00400± 0.00043 | 0.00300± 0.00035 | 0.00300± 0.00030 | 0.00200± 0.00019 |
| 0.4 | 0.00500± 0.00058 | 0.00800± 0.00093 | 0.00700± 0.00080 | 0.00600± 0.00073 | 0.00500± 0.00057 | 0.00300± 0.00035 |
| 2 | 0.02500± 0.00293 | 0.02800± 0.00327 | 0.02800± 0.00321 | 0.02700± 0.00314 | 0.02600± 0.00303 | 0.02400± 0.00281 |

**Appendix 5. T2. Absorption signals of Pb using different concentrations of $HNO_3$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00300± 0.00035 | 0.00800± 0.00091 | 0.00600± 0.00069 | 0.00500± 0.00058 | 0.00300± 0.00030 | 0.00200± 0.00023 |
| 0.4 | 0.00600± 0.00071 | 0.01000± 0.00030 | 0.00700± 0.00082 | 0.00500± 0.00057 | 0.00500± 0.002051 | 0.00400± 0.00041 |
| 2 | 0.02800± 0.00321 | 0.03000± 0.00352 | 0.02900± 0.00331 | 0.02700± 0.00311 | 0.02600± 0.00301 | 0.02500± 0.00290 |

**Appendix 5. T3. Absorption signals of Pb using different concentrations of $HClO_4$ medium in different metal analyte concentrations**

| Metal concentration | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| 0.1 ppm | 0.00200± 0.00023 | 0.00600± 0.00068 | 0.00500± 0.00058 | 0.00400± 0.00046 | 0.00300± 0.00031 | 0.00200± 0.00021 |
| 0.4 | 0.00400± 0.000043 | 0.00900± 0.00104 | 0.00700± 0.00081 | 0.00500± 0.00051 | 0.00500± 0.00050 | 0.00400± 0.00043 |
| 2 | 0.02700± 0.00310 | 0.02900± 0.00339 | 0.02700± 0.00313 | 0.02600± 0.00304 | 0.02500± 0.00291 | 0.02400± 0.00281 |

**Appendix 6**

**Appendix 6. T1. Absorption signals of Pb in River Njoro waters under different acid media**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.00200± 0.00020 | 0.02200± 0.00251 | 0.02000± 0.00229 | 0.02000± 0.00228 | 0.01900± 0.00221 | 0.01700± 0.00115 |
| $HNO_3$ | 0.00200± 0.00023 | 0.02800± 0.00327 | 0.02500± 0.00291 | 0.02300± 0.00261 | 0.02100± 0.00241 | 0.01600± 0.00182 |
| $HClO_4$ | 0.00200± 0.00022 | 0.02100± 0.00240 | 0.02000± 0.00234 | 0.01800± 0.00211 | 0.01600± 0.00183 | 0.01500± 0.00173 |

**Appendix 6. T2. Absorption signals of Zn in River Njoro waters under different acid media**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.01900± 0.00219 | 0.02000± 0.00230 | 0.01800± 0.00220 | 0.01400± 0.00161 | 0.01300± 0.00152 | 0.01100± 0.00127 |
| $HNO_3$ | 0.01900± 0.00223 | 0.02100± 0.00246 | 0.01800± 0.00211 | 0.01700± 0.00116 | 0.01700± 0.00115 | 0.01300± 0.00150 |
| $HClO_4$ | 0.01900± 0.00221 | 0.02300± 0.00263 | 0.02200± 0.00257 | 0.02000± 0.00231 | 0.01800± 0.00210 | 0.01700± 0.00115 |

**Appendix 6. T3. Absorption signals of Cu in River Njoro waters under different acid media**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.00100± 0.00012 | 0.00200± 0.00023 | 0.00100± 0.00005 | 0.00100± 0.00004 | 0.00000± 0.00000 | 0.00000± 0.00000 |
| $HNO_3$ | 0.00100± 0.00011 | 0.00200± 0.00021 | 0.00200± 0.00022 | 0.00100± 0.00020 | 0.00100± 0.00011 | 0.00100± 0.00009 |
| $HClO_4$ | 0.00100± 0.00010 | 0.00200± 0.00020 | 0.00200± 0.00019 | 0.00100± 0.00021 | 0.00100± 0.00011 | 0.00100± 0.00010 |

**Appendix 6. T4. Absorption signals of Fe in River Njoro waters under different acid media**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.02900± 0.00334 | 0.03000± 0.00352 | 0.02800± 0.00329 | 0.02500± 0.00293 | 0.02400± 0.00281 | 0.02300± 0.00269 |
| $HNO_3$ | 0.02900± 0.00338 | 0.03200± 0.00353 | 0.02900± 0.00337 | 0.02700± 0.00316 | 0.02600± 0.00305 | 0.02400± 0.00282 |
| $HClO_4$ | 0.02900± 0.00337 | 0.03100± 0.00350 | 0.03000± 0.00349 | 0.02800± 0.00328 | 0.02400± 0.00280 | 0.02100± 0.00246 |

**Appendix 7**

**Appendix 7. T1. Absorption signals of Pb in Lake Nakuru waters under different acid media**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.02900± 0.00087 | 0.03000± 0.00091 | 0.02700± 0.00081 | 0.02600± 0.00078 | 0.02400± 0.00072 | 0.02300± 0.00068 |
| $HNO_3$ | 0.02900± 0.00081 | 0.03200± 0.00084 | 0.03000± 0.00090 | 0.02800± 0.00083 | 0.02600± 0.00076 | 0.02700± 0.00080 |
| $HClO_4$ | 0.02900± 0.00077 | 0.03300± 0.00096 | 0.02900± 0.00086 | 0.02700± 0.00079 | 0.02600± 0.00071 | 0.02400± 0.00075 |

**Appendix 7. T2. Absorption signals of Fe in Lake Nakuru waters under different acid media**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.01000± 0.00030 | 0.01000± 0.00027 | 0.00900± 0.00022 | 0.00900± 0.00024 | 0.00800± 0.00021 | 0.00700± 0.00021 |
| $HNO_3$ | 0.01000± 0.00027 | 0.01200± 0.00031 | 0.01000± 0.00028 | 0.00900± 0.00022 | 0.00900± 0.00020 | 0.00800± 0.00017 |
| $HClO_4$ | 0.01000± 0.00029 | 0.01100± 0.00030 | 0.01000± 0.00025 | 0.00900± 0.00023 | 0.00900± 0.00021 | 0.00700± 0.00019 |

**Appendix 7. T3. Absorption signals of Zn in Lake Nakuru waters under different acid**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.01100± 0.00021 | 0.01200± 0.00025 | 0.01100± 0.00021 | 0.01100± 0.00019 | 0.00800± 0.00019 | 0.00600± 0.00013 |
| $HNO_3$ | 0.01100± 0.00020 | 0.01400± 0.00024 | 0.01200± 0.00023 | 0.01100± 0.00023 | 0.01000± 0.00020 | 0.00900± 0.00017 |
| $HClO_4$ | 0.01100± 0.00022 | 0.01500± 0.00024 | 0.01300± 0.00020 | 0.01200± 0.00022 | 0.01100± 0.00018 | 0.00800± 0.00015 |

**Appendix 7. T4. Absorption signals of Cu in Lake Nakuru waters under different acid**

| Acids | % acid volume | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 40 | 50 |
| HCl | 0.00200± 0.00006 | 0.00200± 0.00007 | 0.00100± 0.00003 | 0.00100± 0.00003 | 0.00100± 0.00002 | 0.00100± 0.00002 |
| $HNO_3$ | 0.00200± 0.00005 | 0.00300± 0.00006 | 0.00200± 0.00004 | 0.00100± 0.00004 | 0.00100± 0.00003 | 0.00100± 0.00001 |
| $HClO_4$ | 0.00200± 0.00005 | 0.00300± 0.00007 | 0.00200± 0.00004 | 0.00200± 0.00003 | 0.00100± 0.00003 | 0.00100± 0.00001 |

## Appendix8

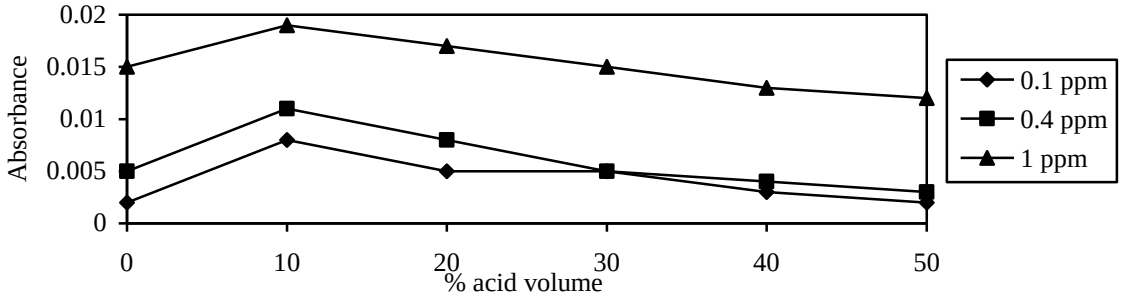



Fig 1. Peak enhancement effects of different concentrations of hydrochloric acid on 0.1, 0.4 and 1 ppm Fe standards

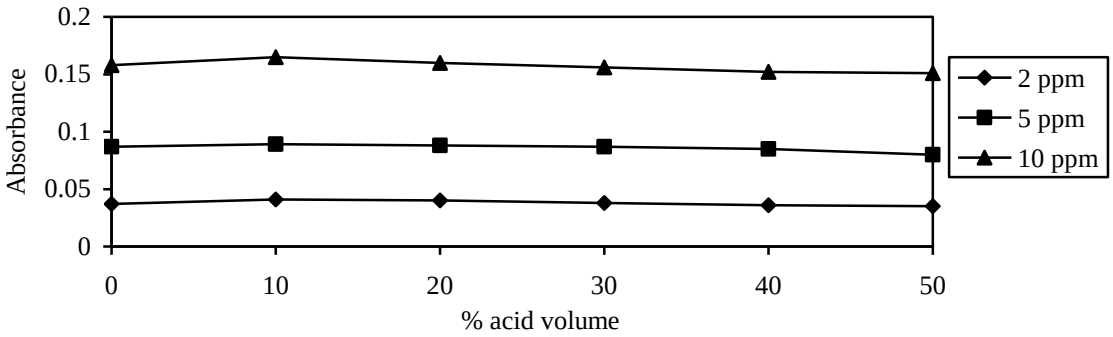



Fig 2. Peak enhancement effects of different concentrations of hydrochloric acid on 2, 5 and 10 ppm Fe standards

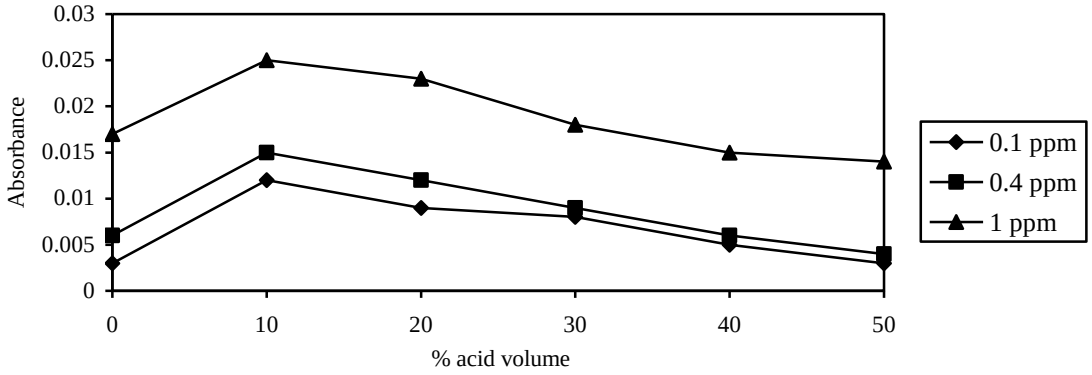



Fig 3. Peak enhancement effects of different concentrations of nitric acid on 0.1, 0.4 and 1 ppm Fe standards

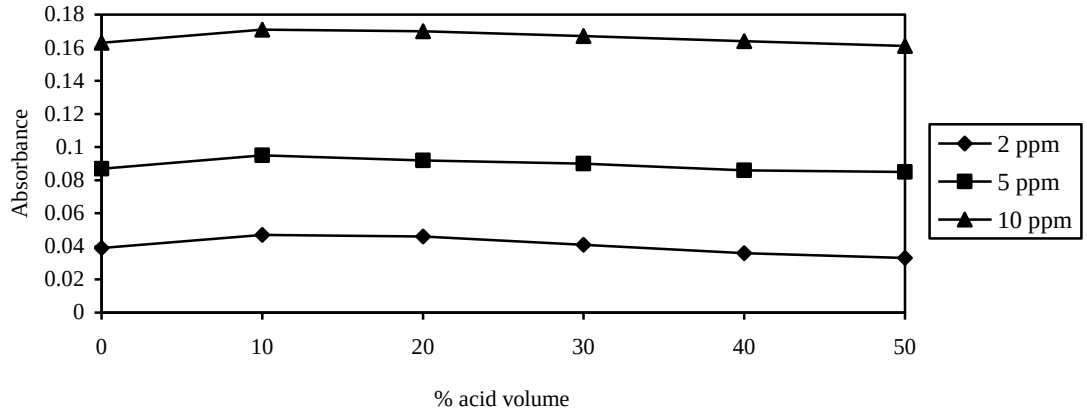



Fig 4. Peak enhancement effects of different concentrations of nitric acid on 2, 5 and 10 ppm Fe standards

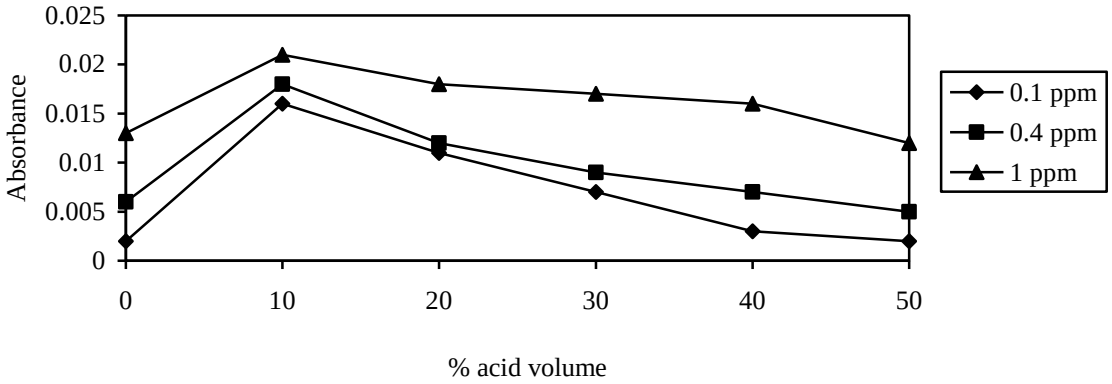



Fig 5. Peak enhancement effects of different concentrations of perchloric acid on 0.1, 0.4 and 1 ppm Fe standards

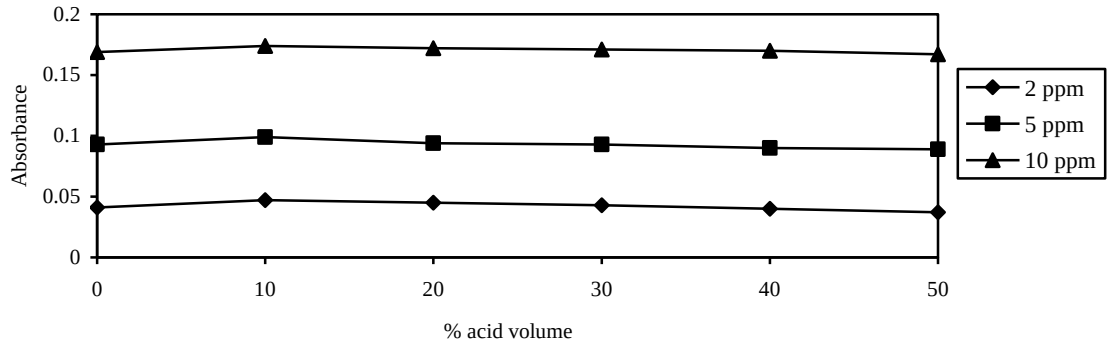



Fig 6. Peak enhancement effects of different concentrations of perchloric acid on 2, 5 and 10 ppm Fe standards

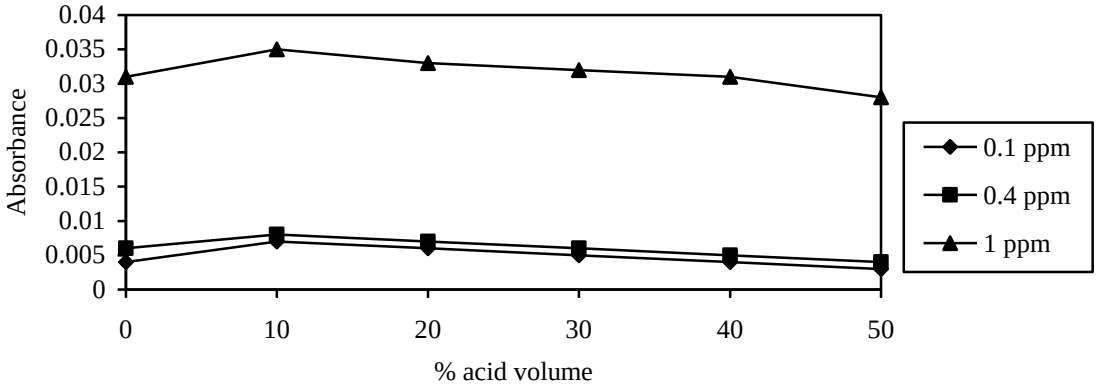



Fig 7. Peak enhancement effects of different concentrations of hydrochloric acid on 0.1, 0.4 and 1 ppm Mn standards

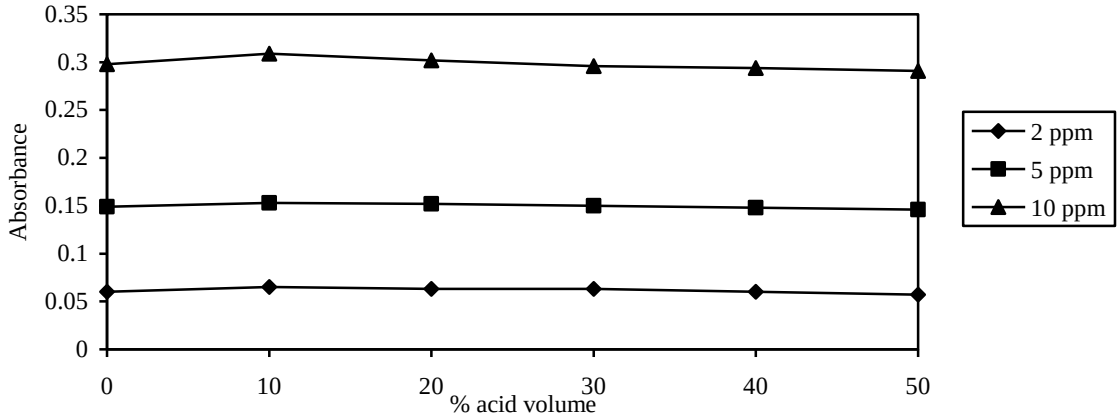



Fig 8. Peak enhancement effects of different concentrations of hydrochloric acid on 2, 5 and 10 ppm Mn standards

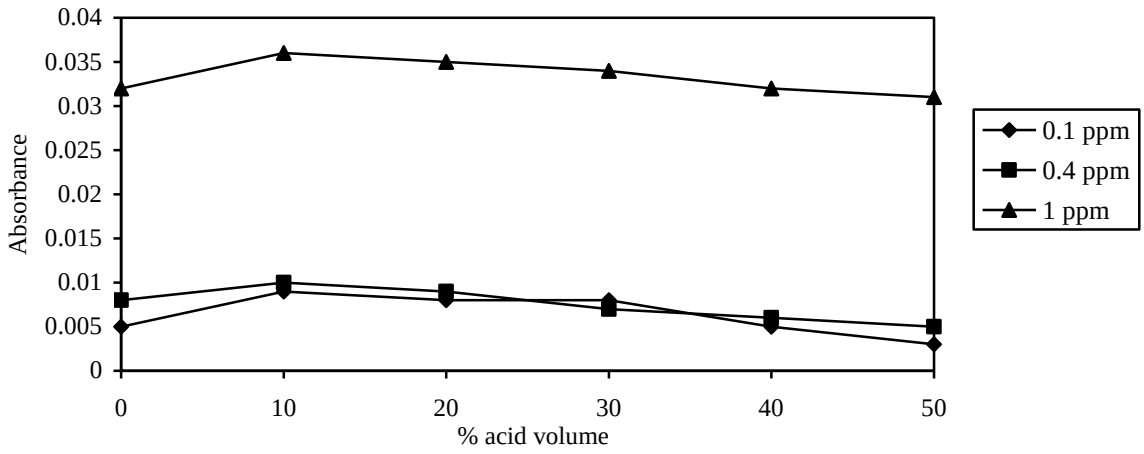



Fig 9. Peak enhancement effects of different concentrations of nitric acid on 0.1, 0.4 and 1 ppm Mn standards

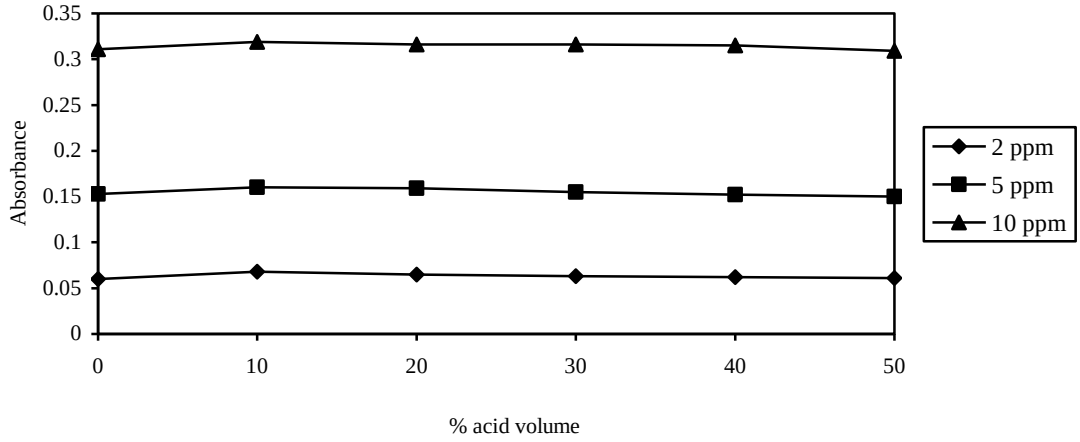



Fig 10. Peak enhancement effects of different concentrations of nitric acid on 2, 5 and 10 ppm Mn standards

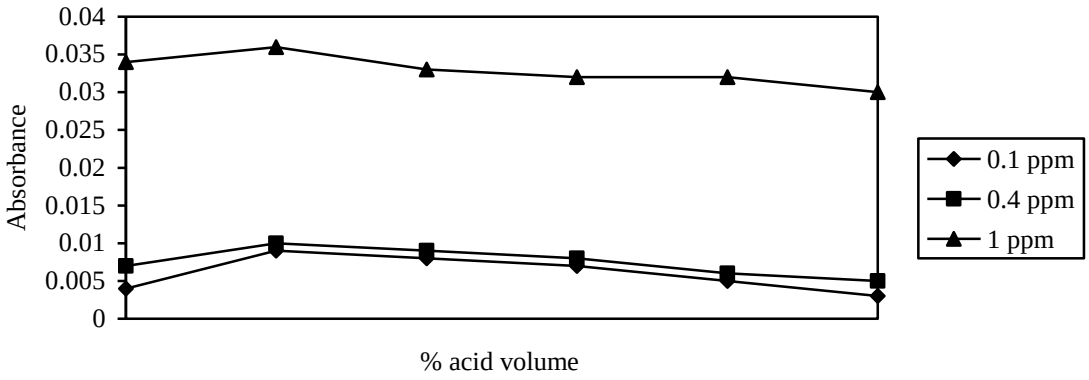



Fig 11. Peak enhancement effects of different concentrations of perchloric acid on 0.1, 0.4 and 1 ppm Mn standards

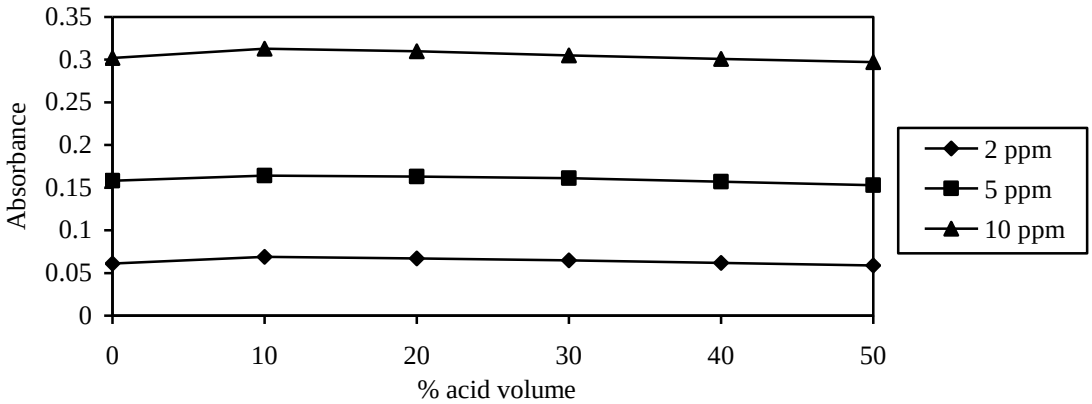



Fig 12. Peak enhancement effects of different concentrations of perchloric acid on 2, 5 and 10 ppm Mn standards

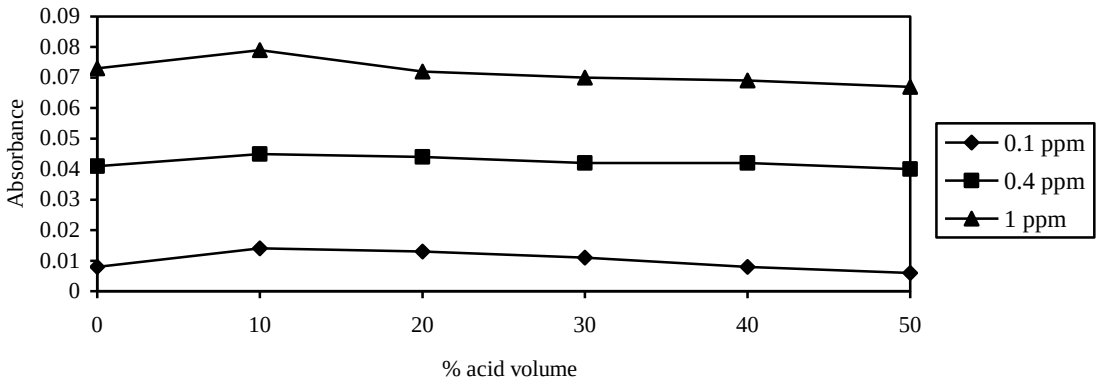



Fig 13. Peak enhancement effects of different concentrations of hydrochloric acid on 0.1, 0.4 and 1 ppm Zn standards

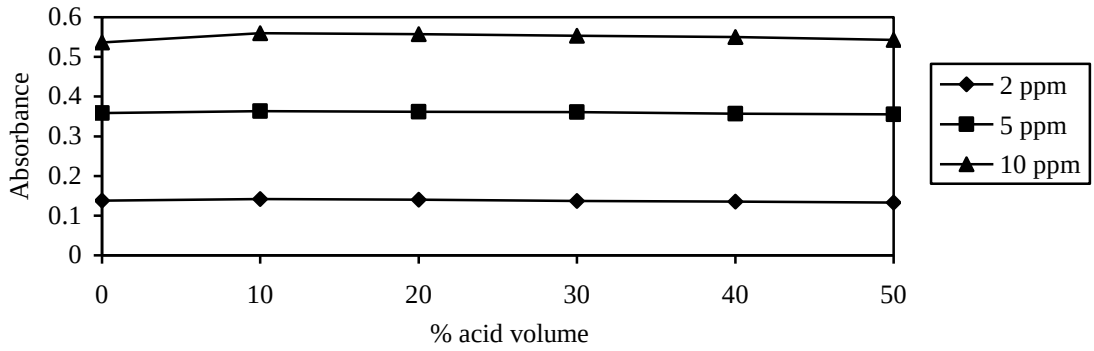



Fig 14. Peak enhancement effects of different concentrations of hydrochloric acid on 2, 5 and 10 ppm Zn standards

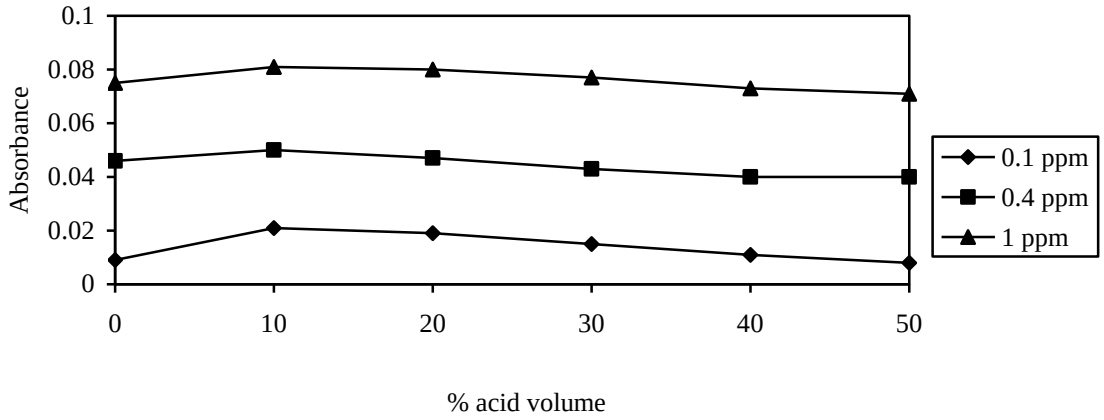



Fig 15. Peak enhancement effects of different concentrations of nitric acid on 0.1, 0.4 and 1 ppm Zn standards

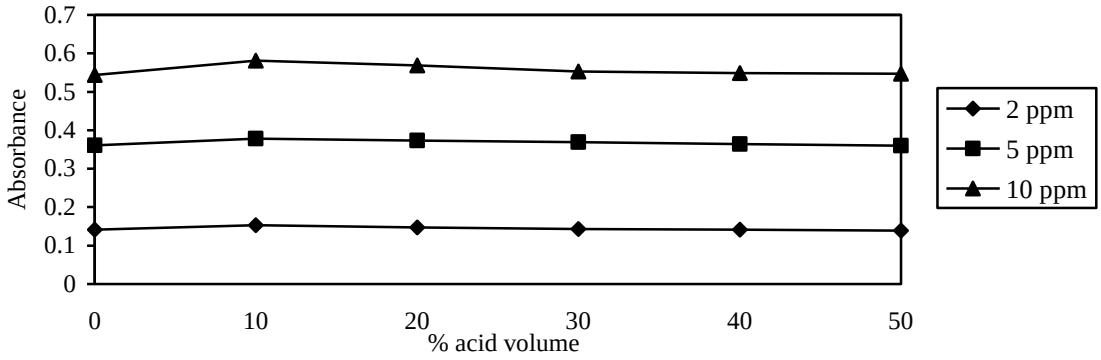



Fig 16. Peak enhancement effects of different concentrations of nitric acid on 2, 5 and 10 ppm Zn standards

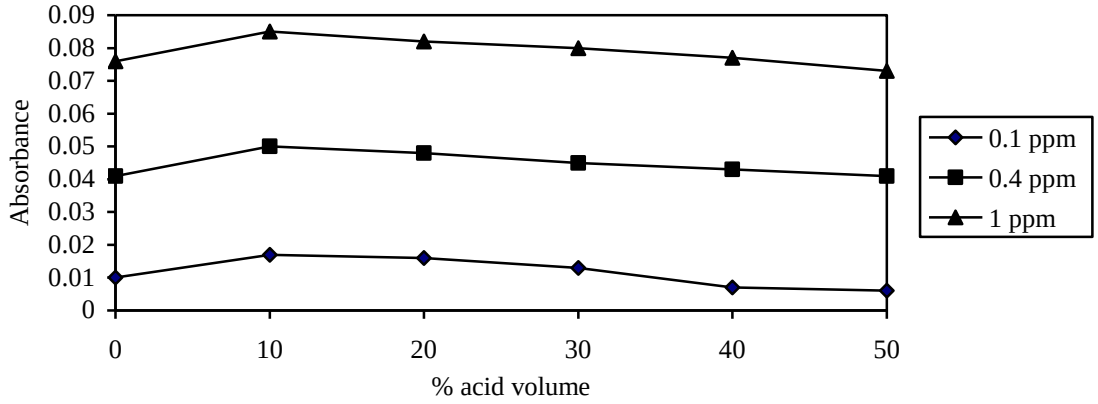



Fig 17. Peak enhancement effects of different concentrations of perchloric acid on 0.1, 0.4 and 1 ppm Zn standards

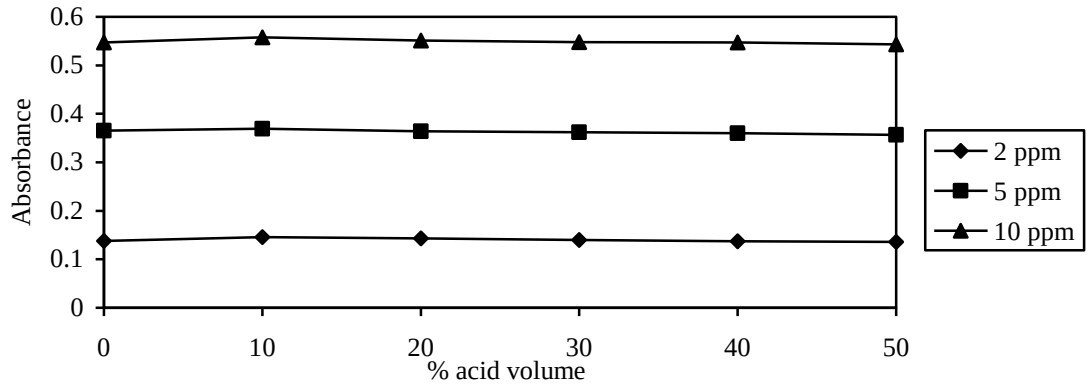



Fig 18. Peak enhancement effects of different concentrations of perchloric acid on 2, 5 and 10 ppm Zn standards

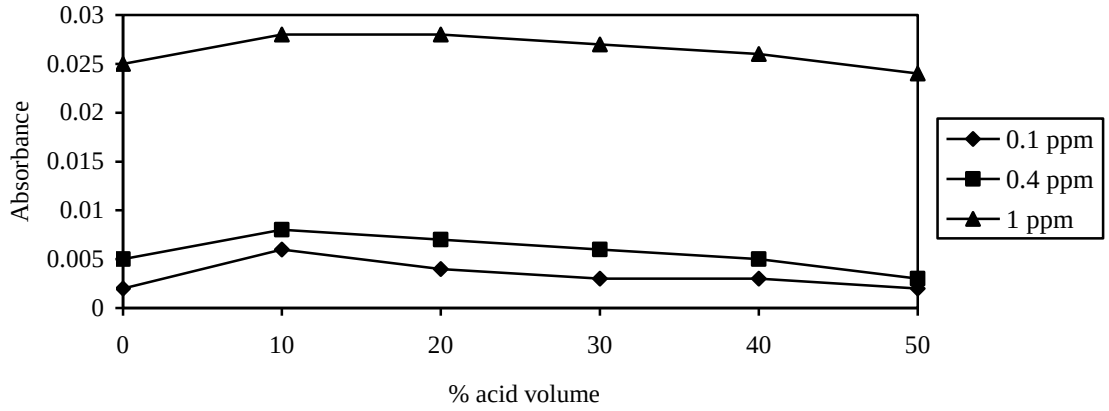



Fig 19. Peak enhancement effects of different concentrations of hydrochloric acid on 0.1, 0.4 and 2 ppm Pb standards

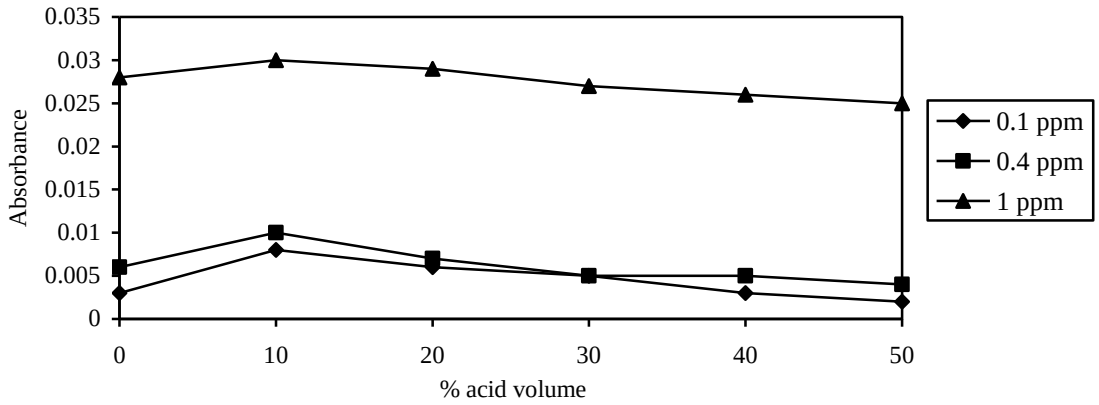



Fig 20. Peak enhancement effects of different concentrations of nitric acid on 0.1, 0.4 and 2 ppm Pb standards

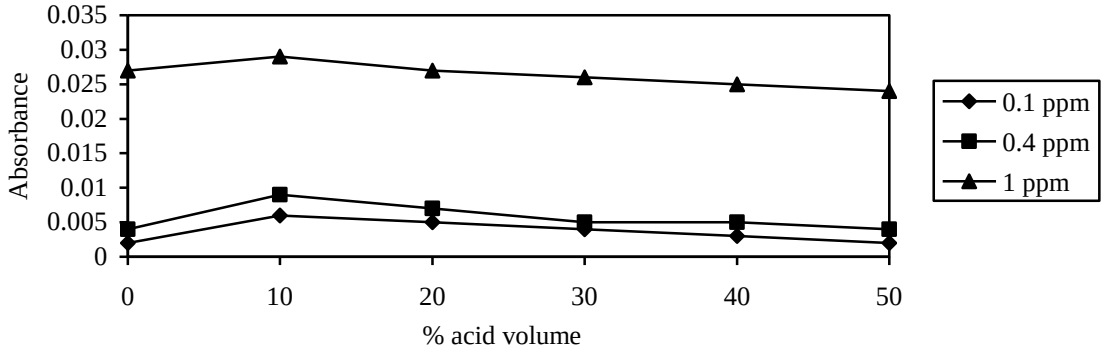



Fig 21. Peak enhancement effects of different concentrations of perchloric acid on 0.1, 0.4 and 1 ppm Pb standards

**Appendix 9 (a)**

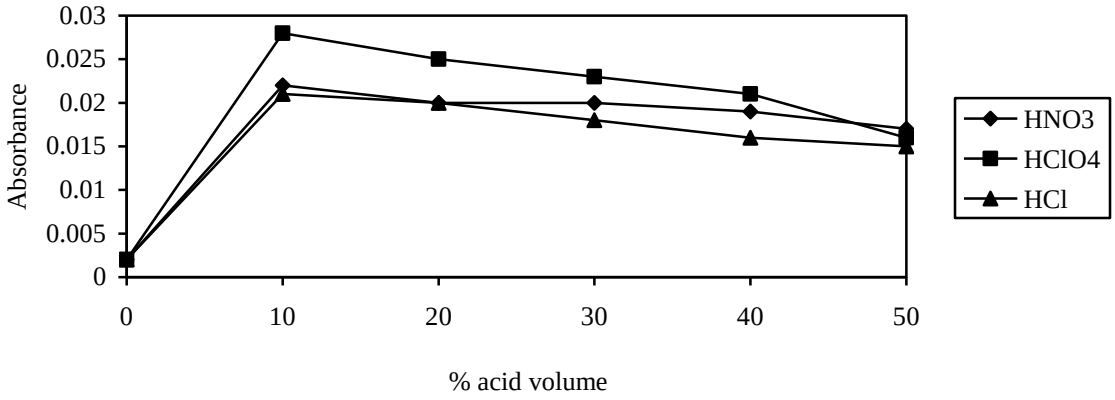



Fig 1. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Pb in River Njoro water sample

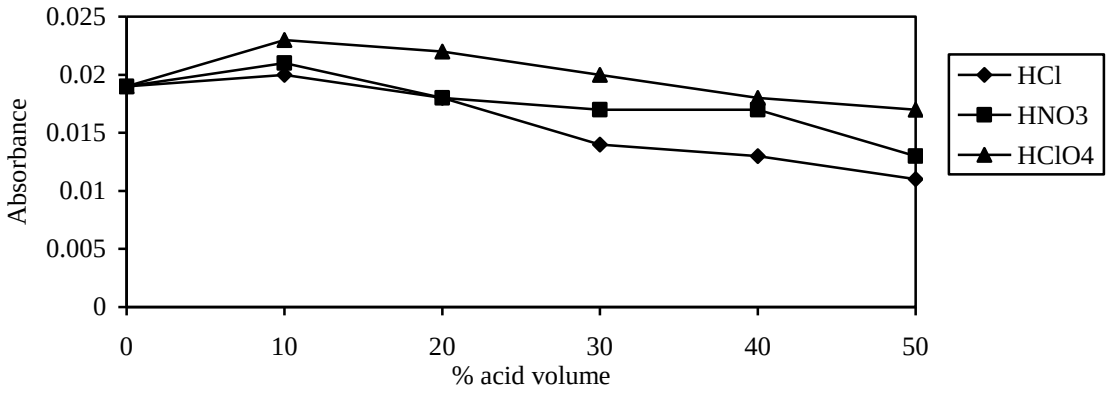



Fig 2. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Zn in River Njoro water sample

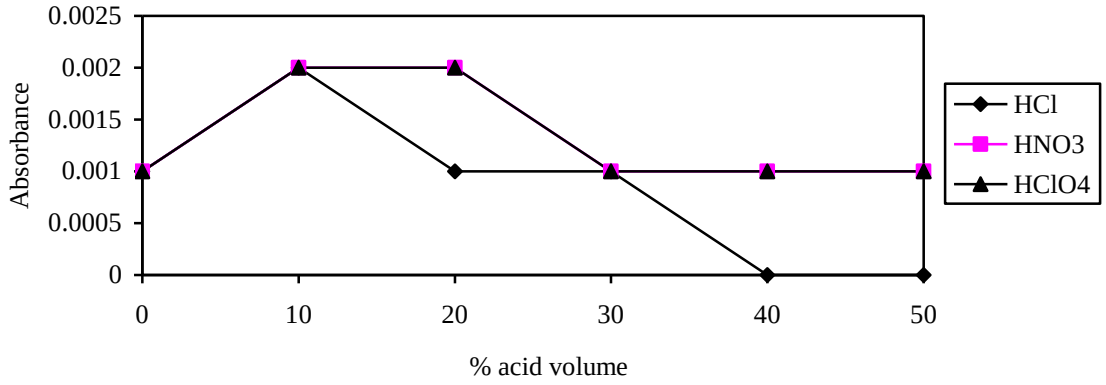



Fig 3. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Cu in River Njoro water sample

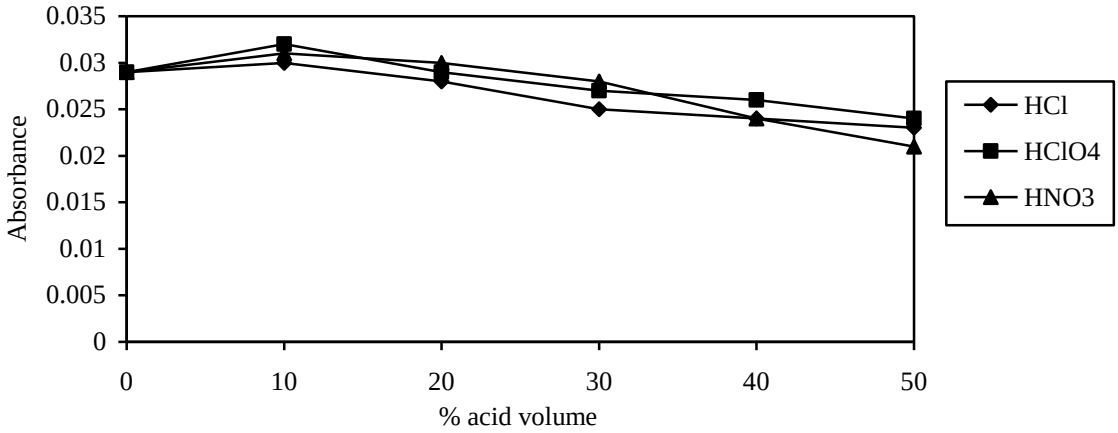



Fig 4. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Fe in River Njoro water sample

## Appendix 9 (b)

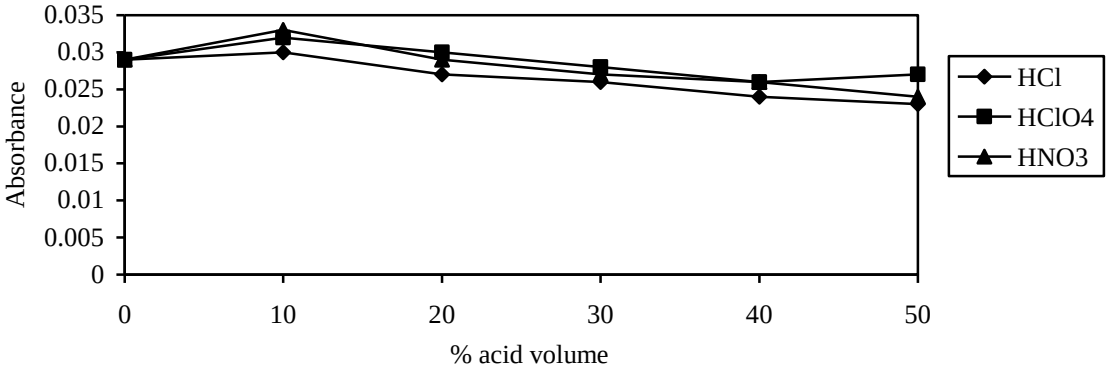



Fig 1. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Pb in Lake Nakuru water sample

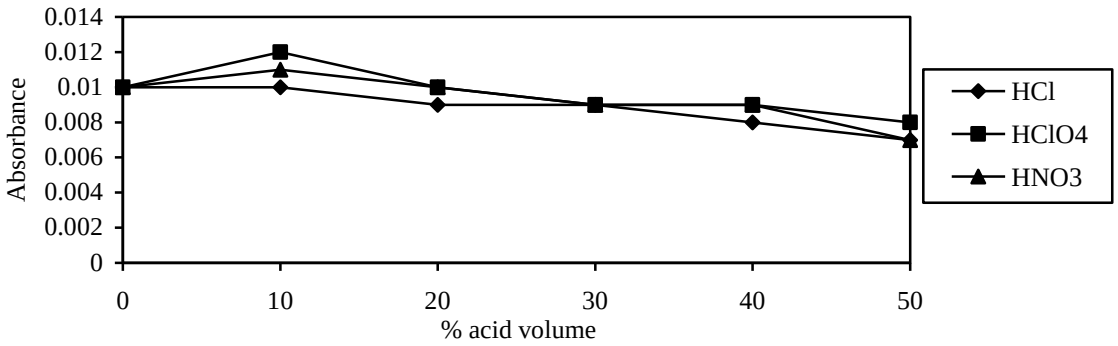
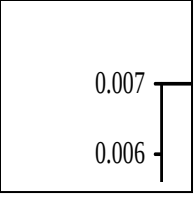



Fig 2. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Fe in Lake Nakuru water sample



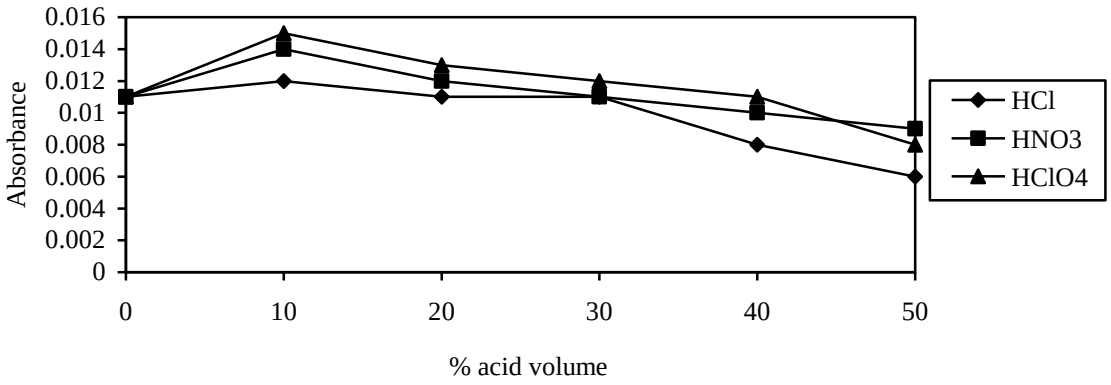




Fig 3. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Zn in Lake Nakuru water sample

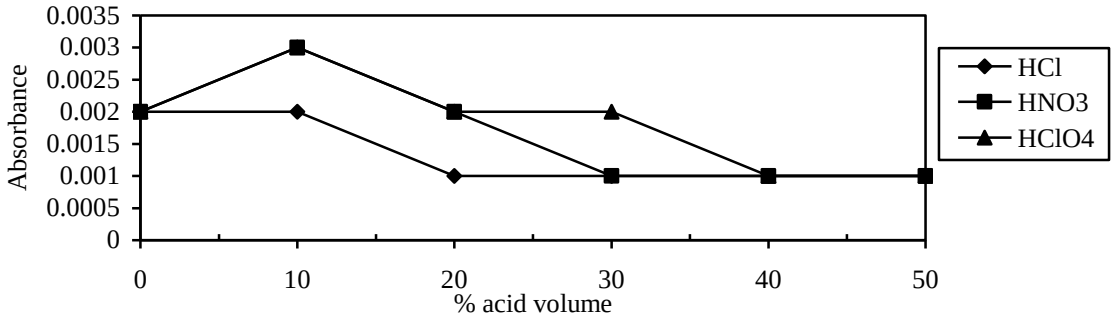



Fig 4. Peak enhancement effects of different concentrations of hydrochloric, nitric and perchloric acids on Cu in Lake Nakuru water sample