AN INVESTIGATION OF MINERALS IN THE WATER AND SOURCE ROCKS OF RURII SPRING IN MERU COUNTY, KENYA: A POSSIBLE POTENTIAL ECONOMIC OUTLET

BY

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DECLARATION

This is my original work and has not been presented for academic award in any university.

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DEDICATION

I gladly dedicate this work to my beloved father the late Mungai Mwenja, who enabled me to acquire my Bachelor's degree in Chemistry and Biochemistry at Kenyatta University in 1996.

ACKNOWLEDGEMENT

ABSTRACT

This study dealt with the investigation of minerals in the water and surrounding rocks of Rurii spring which is located in Meru County, Kenya. The spring is well known for discharging highly carbonated and salty water for many years, but no research has been done previously with regard to this phenomenon. The sampling was done twice during the dry and rainy seasons, in the months of September and November 2012, respectively. Ten samples or replicates of the mineral water, rocks and sediments were collected and analysed in each case. The mineral content and other quality parameters of the water were determined. Rock and sediment samples around the spring were analysed for the major oxides (SiO_2, Na_2O, K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, MnO and TiO_2). The analytical methods used were AAS, XRF, UV/VIS and Titrimetry. The mineral water was found to be very rich in free CO_2 and HCO_3^-, with almost two to three litres of carbon dioxide per litre of mineral water at room temperature. The CO_2 most likely originates from the earth's crust and rises through a volcanic vent to the surface where it gets mixed with the water to form H_2CO_3. Sodium level was 1043 ± 35.0 mg/l and 954.4 ± 20.3 mg/l, while chloride was 950.9 ± 13.1 mg/l and 853.6 ± 10.0 mg/l, during the dry and rainy periods, respectively. This was extremely high and contributed to the salty taste in the water. In general, the water had a very high level of mineral content which was responsible for the large TDS (5056.7 ± 51.2 mg/l and 4923.1 ± 40.7 mg/l) as well as very high electrical conductivity (6014.0 ± 41.0 mg/l and 5986.0 ± 40.0 mg/l), in dry and rainy seasons, respectively. The overall mineral analysis of the water, rocks and sediments revealed abundance of dolomite, $CaMg(CO_3)_2$ and feldspar, $(K,Na,Ca)Al_2Si_2O_8$, containing rocks in the studied area. There was no remarkable difference between the results obtained for the dry and rainy seasons.

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ABBREVIATIONS AND ACRONYMS

A   Absorbance

AAS   Atomic Absorption Spectrophotometer

APHA   American Public Health Association

AWWA   American Water Workers Association

CDTA   1, 2-cyclohexanediaminetetraacetic acid

COD   Chemical Oxygen Demand

CPRG   Chlorophenol red-β-D-galactopyranoside

CWTL   Central Water Testing Laboratories

DE   Diatomaceous Earth

EC   Electrical Conductivity

EDLs   Electrodeless Discharge Lamp

EDTA   Ethylenediamminetetraacetic acid

EDXRF   Energy Dispersive X-Ray Fluorescence

GPS   Global Positioning System

I   Transmitted light

I_o Intensity of Incident Light

ICP   Inductively Coupled Plasma

KEBS   Kenya Bureau of Standards

KHP   Potassium Hydrogen Phthalate

KNBS   Kenya National Bureau of Statistics

LOI   Loss On Ignition

MPN   Most Probable Number

MUG   4-Methyl-umbelliferyl-β-D-glucuronide

NED   N-(-1-naphthyl)-ethylenediamine dihydrochloride

NIST	National Institute of Standards and Technology
NTUs	Nephelometric Turbidity Units
ONPG	Ortho-nitrophenyl- β-D-galactopyranoside
Plc	Public Limited Company
p.s.i	Pounds Per Square Inch
SEM	Scanning Electron Microscopy
SPSS	Statistical Package for Social Sciences
STI	Science Technology and Innovation
TCM	Tata Chemicals Magadi
TCU	True Colour Units
TDS	Total Dissolved Solids
TEM	Transmission Electron Microscopy
TH	Total Hardness
TISAB	Total Ionic Strength Adjustment Buffer
TON	Threshold Order Number
TSS	Total Suspended Solids
UV-VIS	Ultraviolet-Visible
WDXRF	Wavelength Dispersive X-Ray Fluorescence
WHO	World Health Organisation
WRMA	Water Resources Management Authority
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

CHAPTER ONE

INTRODUCTION

1.1   Background Information

A single groundwater sample may be representative of its source for many years. Water is universal and an excellent solvent because it dissolves more substances than any other liquid. This means that as water passes through the ground it takes along minerals. All groundwater contain salts carried in solution. The types and concentration of salts depend on water movement, rock types or geology and human activities in a given area (Rono, 2008).

In a geologically active environment like Rift Valley, groundwater frequently has higher salt content. Higher temperatures increase solubility of many compounds in water which explains the high level of salinity. Water that comes from a natural spring and contains minerals is called mineral water (Murigi, 2004). The most abundant cationic constituents in groundwater are the more soluble alkali elements (Na^+, K^+) and the alkaline earth elements (Ca^{2+}, Mg^{2+}), while the most common anions are bicarbonate (HCO_3^-), Chloride (Cl^-) and Sulphate (SO_4^{2-}). However, other less common (trace) cations and anions are dissolved in small quantities. The quality of water is also greatly influenced by human activities such as disposal of domestic, urban, industrial and agricultural wastes (Ngugi, 2009).

Rurii Spring in Meru County has been known to discharge water rich in carbon dioxide and mineral salts for a long time. However, there is no evidence so far of any other scientific research that has been done on the spring to investigate the minerals that occur there. Carbon dioxide is most probably discharged naturally from the earth's crust since the area has numerous volcanic hills.

CO_2-rich springs have been reported from all over the world. The occurrence of these springs is related to major faults and volcanoes. In South Korea, many CO_2-springs are found in Mesozoic granitoids and the surrounding rocks. The CO_2-rich water can be classified into three chemical water

types; Ca-HCO$_3$ water, Ca(Na)-HCO$_3$ water, and Na-HCO$_3$ water. Most of the soda waters show a high CO$_2$ concentration (P$_{CO2}$ 0.12 atm to 5.21 atm), a slightly acid pH (4.8-6.76), and high ion concentration. CO$_2$-rich cold springs occur near the active volcanoes at Wudalianchi, North East China. The springs are rich in CO$_2$, with HCO$_3^-$ as the predominant anion and have elevated contents of total dissolved solids >1000 mg/l (Chan Ho, *et al.*, 2005).

A study of CO$_2$-rich (up to 3000 mg/l), mineral (up to 460 meq/l) and cold (2 ^{0}C – 9 ^{0}C) springs of the lower Engadine region in the Swiss Alps, indicate the existence of Ca-HCO$_3$ water, Na-HCO$_3$, Cl$^-$ water and NaMgHCO$_3$, SO$_4^{2-}$ water (Pierre, *et al.*, 1988). By the close of the 19th Century, CO$_2$ gas was found in free state in many of Saratoga Springs in New Yolk. The springs discharge carbonated mineral water along Saratoga fault which is bottled and sold commercially (Zink, 1993). The CO$_2$ in mineral springs may be derived from a variety of sources, including liberation of CO$_2$ by metamorphic processes, magmatic degassing, oxidation of organic matter, and interaction of water with sedimentary carbonate rocks. The origin of the CO$_2$ gas can be determined by isotopic analysis of ^{13}C, which indicates the presence of mantle derived CO$_2$ gas (-8 < δ ^{13}C% < -3), or CO$_2$ derived from biogenic activity in the soil (-22 < δ ^{13}C% < -25), it may also be the result of metamorphic devolatilization (δ ^{13}C% > 2) (Mao, *et al.*, 2009).

In Kenya, CO$_2$-rich mineral springs occur at Mount Margaret in Kedong Valley, Lake Magadi, Esageri near Eldama Ravine and Kireita near Uplands (Bulbois and Walsh, 2007). The Rurii spring is within Meru-Isiolo area which lies in the South-Eastern quarter of degree sheet 36 (Kenya) and is bounded by the latitudes 0° and 0° 30' N and by longitudes 37° 30' and 38° E. It is approximately 35 KM East of Meru Town in Igarii location, Tigania East District, Meru County, Kenya. The place is semi-arid and sparsely populated. The spring is in a valley at the floor of Nyambene range on the southern end, adjacent to Thuguri and Panga hills. There is a marshy ground at a short distance from the spring and sand is mined from the nearby Thiti River. The exact GPS location for Rurii spring is 0° 01' 47.88" N, 37° 53' 22.96" E, and elevation of 2,943 ft. above sea level (Figure 1).

RURII SPRING

Figure 1: Geological map of the Meru-Isiolo area

Source: Ministry of Mining (2012).

A mineral deposit is a rock or mineral that is of economic value and which can be worked profitably (Rutley, 1988). Deposits containing valuable elements are called ore deposits. An ore is a mixture of the valuable mineral (s); termed the ore mineral and the accompanying, unwanted minerals termed as the gaunge while the metal content of an ore is its tenor.

Kenya is blessed with a vast array of buried mineral wealth whose proper exploitation would greatly transform the economy. Data from the Kenya National Bureau of Statistics, KNBS (2012), shows that the country earned Kshs 18.173 billion from export of minerals in 2011 compared to Kshs 14.996 billion in 2010, representing 21.2 percent increase in total earnings from the sector (Table 1.2). However, analysts estimate the total industry's potential to be in excess of Kshs 100 billion if proper mining laws are enacted and implemented. Tables 1.1 and 1.2 shows mineral production and sales in Kenya from 2007-2011, respectively.

Table 1.1: Mineral production in Kenya, 2007-2011.

Mineral	unit	2007	2008	2009	2010	2011*
Soda ash	Tonnes	386,578	502,846	404,904	473,689	499,052
Salt (crude and refined)	Tonnes	11,596	24,345	24,125	6,194	24,639
Fluorspar	Tonnes	85,115	130,100	5,500	40,750	95,051
Soda crushed raw	Tonnes	843,043	865,788	948,076	959,160	1,054,236
Corondum (ruby)	Kgs	4800	4,950	5,575	5,450	6,240
Carbon dioxide	Tonnes	11,028	22,030	15,711	16,345	16,275
Diatomite	Tonnes	201	72	231	224	713
Garnets (green)	Kgs	815	821	965	1,075	1,205
Gypsum**	Tonnes	5,000	5,000	5,345	5,500	6,520
Vermiculite	Tonnes	300	320	315	395	515
Gold (Unwrought)	Kgs	3,023	340	1,055	2,355	1,636
Gemstones	Tonnes	9	21	39	168	310

Source: Kenya National Bureau of Statistics (2013).

*Provisional

**Excluding Gypsum used for cement

Table 1.2: Mineral sales value (Kshs Million), 2007-2011.

Mineral	2007	2008	2009	2010	2011*
Soda ash	4,769.5	8,881.7	6,085.4	6,980.0	7,354.0
Salt (crude and refined)	58.1	139.2	154.7	35.3	140.3
Fluorspar	995.5	1,949.2	122.5	789.0	3,984.4
Soda crushed raw	430.4	442.0	484.0	467.0	495.5
Corondum (ruby)	47.0	47.5	57.5	55.7	66.5
Carbon dioxide	78.6	117.9	84.0	98.0	105.0
Diatomite	8.9	3.5	14.0	9.0	15.0
Garnets (green)	26.4	27.2	29.3	30.5	35.5
Gypsum**	5.0	5.2	5.3	5.4	6.0
Vermiculite	78.0	78.5	79.0	83.0	88.5
Gold (Unwrought)	3,922.9	592.9	2,284.0	6,217.0	5,651.0
Gemstones	111.0	178.6	141.3	226.0	231.0
Total	**12,538.7**	**14,471.4**	**11,550.0**	**14,995.9**	**18,172.7**

Source: Kenya National Bureau of Statistics (2013).

*Provisional

**Excluding Gypsum used for cement

1.2   Problem Statement

The Rurii mineral spring is characterised by discharge of highly carbonated and salty water throughout all seasons which is consumed by the local community and also fed to the livestock. The water has a mixture of bitter and salty taste. It is said to provide relief for heart-burn and other indigestion problems, which depicts its anti-acid properties perhaps due to the presence of CO_3^{2-} and HCO_3^- ions (Hersi, 2003). Most of the water evaporates as it flows away from the spring leaving behind white salt deposits on the ground (Appendix VI). The main purpose of this study was to report the occurrence and hydrochemistry of the mineral-rich Rurii spring which has not been done previously. The study was based on the premise that the discharge of carbonated mineral water from these rocks is an indication of appreciable mineral deposits underneath or around the area. The minerals can be exploited commercially and boost efforts to turn-round our economy in tandem with the Kenya Vision 2030.

1.2 Hypothesis

There are appreciable minerals present in the water and neighbouring rocks of Rurii spring found in Meru County, Kenya. However, adequate explorations and studies have not been done in the past to determine their economic potential for further resource exploitation.

1.3 Overall Objective

To undertake a thorough investigation of the minerals present in the water and source rocks of Rurii spring and evaluate their economic value.

1.4 Specific Objectives

i. To carry out qualitative and quantitative analysis of the minerals present in the water and surrounding rocks of Rurii spring, thus establish their identity and economic significance.

ii. To determine the extent of water quality of Rurii mineral spring in order to ascertain its suitability for human consumption.

iii. To evaluate the overall commercial feasibility of the minerals found in the water and source rocks of Rurii spring for possible industrial exploitation.

1.6 Justification

One of the key pillars of Kenya Vision 2030 is Science, Technology and Innovation (STI), which is aimed at accelerating Kenya to acquire a medium income and industrialized status by the year 2030. In this study, the researcher applied analytical chemistry to explore for valuable minerals from the water and source rocks of Rurii spring in Meru County, Kenya. These minerals could be utilized in the production of mineral water, cement, salt licks for livestock, fertilizers, laboratory chemicals, pharmaceutical products, carbonated drinks, dry ice for refrigeration, fire extinguishers or put into other relevant uses. In addition, the minerals can be exported and earn more foreign exchange to run our economy. Moreover, the spring can be developed into a modern Spa Park.

CHAPTER TWO

LITERATURE REVIEW

2.1   Introduction

This chapter gives an overview of the vital minerals of Kenya, CO_2-rich Springs of Saratoga, CO_2 mining in Kenya, previous geological study of Meru-Isiolo area, water quality parameters, types of rocks and minerals, and the theory of analytical techniques.

2.2   The Principal Minerals of Kenya

Most parts of the country are represented in the precious resource map with far-flung and largely under-developed areas like Turkana and Garissa possessing proven deposits of mineral resources. Sources at the Ministry of Energy intimate that the discovery of oil and natural gas in Isiolo, Kwale, Lamu and Turkana is imminent (Figure 2.1). Some of the important minerals are described below.

2.2.1 Gold

This is a soft yellow precious metal which occurs in native form or as an alloy with copper and silver. It is widely used in jewellery. The purity of gold may be expressed either in fineness or in carats. Pure or fine gold is said to be 1,000 fines or 24 carats. Native gold 989 fines have been found but as a rule it ranges from 850 to 950 fines (McHugh, 1988). Most counties to the west of Rift Valley fall under an expansive Gold Belt that stretches from Kakamega to Kuria. These include areas such as Nandi, Siaya, Kakamega, Vihiga, Migori, Trans-Mara, Turkana, Kuria and Bondo. In most of these areas inefficient mining methods, especially along river beds have been going on for decades. Most of these efforts are, however, exploited by middlemen who purchase the gold far below nominal prices and end up making great profits in the international market (Ministry of Mining, 2012).
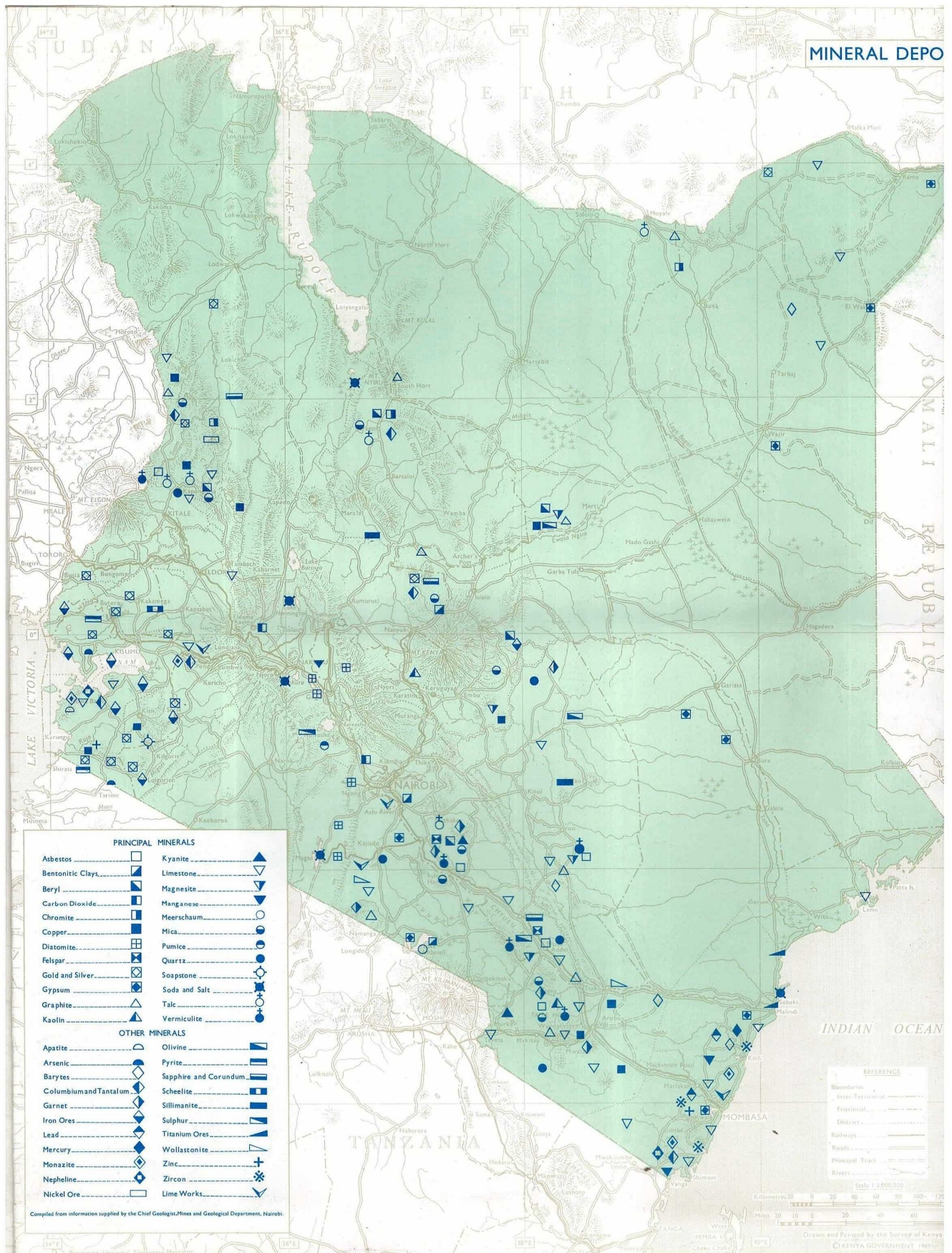
Figure 2.1: Distribution of the principal minerals of Kenya
Source: Ministry of Mining (2012).

2.2.2 Coal

Coal is a mineral of fossilized carbon composed primarily of carbon along with variable quantities of hydrogen, oxygen, nitrogen and sulphur. Coal forms when dead plant matter is converted to peat, which in turn is converted into lignite, then sub-bituminous coal, then into bituminous coal and finally anthracite. This involves biological and geological processes that take place over a long period (Taylor, *et al*, 2009). It is mainly used as a fossil fuel for production of electricity and/ or heat and also greatly utilized in smelting of metals. Only a few years ago, a 500 square kilometer region cutting through Kitui and Mutito called the Mui Basin was declared one of the Africa's most coal-rich areas. Already, a Chinese firm Fenxi Mining Company have set base in Kitui, ready to extract the mineral whose quality has been passed as high (Walsh and Bubois, 2012).

2.2.3 Iron Ore

Iron ores are rocks and minerals from which metallic iron can be economically extracted (Gordon, 1996). The major ores of iron are magnetite Fe_3O_4 (72.4% Fe), hematite Fe_2O_3 (70.0% Fe), and limonite $Fe_2O_3.2H_2O$ (59.9% Fe). Iron ore is used in the manufacture of steel products and significant deposits have been discovered in Taita Taveta, Kitui, Meru, Kilifi and Samia. In Taita Taveta district, extraction of the mineral has already commenced, while a local industrialist has declared intension to mine in the Mutomo area of Kitui.

2.2.4 Soda Ash

Soda ash is one of Kenya's most important exports, mined predominantly in the lake Magadi area of Kajiado in form of $Na_2CO_3.NaHCO_3.H_2O$ (Trona). But the potential to multiply that, according to the Government is massive. The mining is done by Tata Chemicals Magadi (TCM) previously known as Magadi Soda Company. TCM has built deep socio-economic connections with the local community through education, health and employment initiatives. Soda Ash is used in the

manufacture of glass, salt, preservatives, soap, water softeners and dyes among many other applications (Hill, 1964).

2.2.5 Titanium

The main titanium ores are ilmenite (FeOTiO$_2$) and rutile (TiO$_2$). Aircrafts, space ships and missiles bodies are built with alloys of titanium for corrosion resistance and tensile strength at low weight. Most of titanium extracts are used in the production of titanium oxide which is a white powder used as a base pigment in manufacture of paper, paint and plastics among other products (Cornelis, *et al*, 1995). Body piercing equipment are made with titanium as it is rust proof while hip joints, ball joints and other human body internal bone interventions are done with titanium. Dental implants are also done in titanium (Wilberg, 2001). In 2011, Tiomin Mining Company Limited (now known as Base Titanium Limited) started extracting titanium from sand dunes in Kwale District. There are significant deposits of titanium in Malindi and Lamu as well.

2.2.6 Vermiculite

This mineral is a hydrated magnesium-aluminium-iron silicate and a member of mica family. It may vary in colour from golden yellow to brown or even black. It is a strange mineral made famous by its expansion or exfoliation properties. Vermiculite can expand up to 30 times its original size when heated. Thereafter it becomes odourless and fire-proof, making it useful material for insulation (William, 1999). In its original form, it is used in the manufacture of brake pads and other industrial applications mostly as a compound. It is found in large quantities in Makueni and Machakos Counties and also inside the Tsavo National Park (Walsh and Bubois, 2012).

2.2.7 Fluorspar

Found in abundance in Kerio Valley, this is one mineral whose immense value has never been capitalized. Fluorspar or fluorite (CaF$_2$) is an industrial mineral largely used in the manufacture of Portland cement, lenses for microscopes, fluorescent bulbs and for smelting. The mineral also has

aesthetic uses as ornaments are curved out of it (Watson, 1979). Fluorite is a major source of hydrogen fluoride (Equation 2.1). HF is liberated from the mineral by the action of concentrated sulphuric acid. The resulting HF is converted into fluorine, fluorocarbons, and diverse fluoride substances (Ford, 1994).

$$CaF_2(s) + H_2SO_4 (l) \rightarrow CaSO_4(s) + 2HF (g) \hspace{4cm} 2.1$$

2.2.8 Carbon Dioxide

This mineral is used in the carbonation of beverages and is found in plenty in the Kireita area of Kiambu County and Esageri in Baringo District. Carbacid and East Africa Breweries Limited are the main extractors of the mineral, but there is enough for export, although the capacity is not completely developed for that (Walsh and Bubois, 2012).

2.2.9 Manganese

Mostly used in the manufacture of steel, bleaches, metallurgical and chemical applications. The major ore is pyrolusite (MnO_2) which contains 63% manganese (Olsen, *et al*, 2007). In Kenya, expansive deposits are yet to be tapped in Ganze and Mrima Hill at the coastal region.

2.2.10 Gypsum

This consists of hydrated calcium sulphate ($CaSO_4.2H_2O$) and is plenty in El Wak, Tana River, Garissa, Kajiado and Turkana; this mineral is used in the production of plaster of Paris, fertilizers, cement, shampoos and hair products. It is also used in food to provide calcium especially by vegetarians (Cornelis, *et al*, 1985).

2.2.11 Diatomite

Diatomite, also called Diatomaceous Earth (DE), is a substance composed primarily of fossilized diatoms. The purest natural diatomite is completely white in colour and consists mainly of opaline silica ($SiO_2.2H_2O$), with only very small amounts of impurities such as clay, iron oxide, carbonates

of calcium and magnesium, organic carbonaceous matter and water (Strens, 1976). Significant deposits of this mineral, used as absorbent, are found on the base of the Rift Valley, mostly around Gilgil and Gicheru area. Other uses of diatomite are in the manufacture of soap, detergents, bricks and paints. Because of its high porosity, it is also used in purification of liquid substances like grease, beer and wines among others (Fields, *et al*, 2003).

2.2.12 Gemstones

Sapphires, ruby, garnets, emerald, aquamarine, amethyst and other precious gemstones are found in varying but still significant quantities in Tana River, Taita Taveta, Kitui, Kajiado, Mwingi, Embu, Meru, Isiolo and Turkana. These are mostly cut into jewels and ornamental objects and are currently being mined haphazardly by individuals, both locals and foreigners (Wise, 2006).

2.2.13 Limestone and Marbles

Limestone is a sedimentary rock that is dominantly composed of the calcium-bearing carbonate minerals calcite ($CaCO_3$) and dolomite $CaMg(CO_3)_2$. This is perhaps the one mineral Kenya is synonymous with. Virtually every corner of the country has limestone whose uses touch everyday life. From the manufacture of cement, chalk, paper and glass to medicines, floorings and farm conditioners (Putris, 1992). This is one mineral that can earn this country a lot of foreign exchange if the capacity of its exploitation is greatly enhanced. Cement has the potential to become a leading foreign exchange earner for Kenya. Demand for cement for instance, has over the last few years increased exponentially as a result of rapid growth in the construction industry (Taylor, *et al*, 2003).

2.2.14 Petroleum and Gas

Since March 2012, significant oil deposits estimated at 250 million barrels have been struck at Ngamia-1, Twiga South-1, Etuko-1 and Ekales-1 in Turkana County by Tullow Oil Plc. The company has already disclosed that the oil deposits are commercially viable. Energy specialists says all ingredients for a major oil find are present in Kenya, adding that the presence of oil in western

India shows high possibility that oil is available in plenty in Lamu, going by similarity of the two regions based on their plate tectonic relationship. The southern coastal area most likely has natural gas and Kenya is most likely sitting on immense oil and gas wealth reserves. This has already been confirmed by the Apache company of Australia who have declared the presence of natural gas in the off shore region near Lamu.

2.3 Saratoga Springs, New York

The Saratoga springs are located approximately 40 KM north of Albany, New York and just south of the Adirondack Park. Approximately 18 springs and hot well discharged carbonated mineral water along the Saratoga fault. These springs originate in layers of limestone 100 to 1000 feet (30 to 300 Meters) below the surface and rise to the surface through the Saratoga fault (Loam, 1992). Most of the mineral water has been obtained by drilling wells, the sites selected where the bubbles of carbon dioxide issue from the ground. The spring waters have been used for drinking and bathing in Spas where it has been considered a cure for everything from skin disorders to digestive problems and inflammation of the eyes. The carbonated water is bottled and sold as commercial product. However, water rich in iron and carbon dioxide gas produced headaches for some people who drank the water (Zink, 1993).

By the close of the nineteenth century, carbonic acid gas (H_2CO_3) was found in a free state in many of the Saratoga Springs. This "dry gas" was discovered accidentally when a well blew out upon hitting a pocket of this gas. It was dry, clear and free from any impurities, and thus was preferred over chemical extraction processes of the time. The gas was ideally suited for use as an additive of food or drink. It was in great demand because of its use to artificially carbonate water used in ice cream, sodas and also found an important use in refrigeration. Companies were formed to collect the natural gas and to extract it from the mineral water, and in the process almost "killed" the famous mineral Springs of Saratoga (Swanner, 1988). The analyses of the mineral waters of Saratoga Spa Park are listed in Table 2.1.

Table 2.1: Saratoga mineral springs analyses in mg/l.

Element or Radical	Geyser spring	Polaris spring	Haves spring	Orenda spring	Hatthorn spring	Lincoln spring	State seal spring*
Sodium	850	560	3025	2420	3820	1150	2
Potassium	83	80	333	266	340	219	0.15
Lithium	2.1	5	11.9	8	10	6.3	0.01
Calcium	375	370	724	672	872	348	32.2
Magnesium	75	95	277	224	353	171	4.4
Barium	12.5	2.1	12	15.6	25	8.1	0.038
Strontium	1	-	10.5	10	12	9.9	0.11
Ammonium	12	1.2	13	13	14	6	Trace
Iron	4	1.1	1.8	1.7	2.2	8.2	0.4
Aluminium	4.1	6	9	8	4	3	0.034
Manganese	Trace	-	0.3	0.3	0.4	None	0.002
Bicarbonate	2562	2130	4550	3600	4850	2608	104
Chloride	820	1000	4500	3800	6030	1538	4.8
Bromide	16	5	51	46	53	34	None
Iodide	0.9	-	2.1	2	2.9	1.3	None
Metaborate	6	0.9	7	7.5	7	4.1	0.25
Silica	12	17	11	11	12	51	5
Sulphate	None	None	None	None	None	None	22
Total solids at 110 ^{o}C	4836	3260	13,539	11,105	16,407	6,166	175
Radium,226(Pico curies per liter)	-	102	284	232	430	48	-

Source: Zink (1993).

*All of the above waters, except State Seal, are highly effervescent as they flow from the springs, containing from two to four litres of carbon dioxide per litre of mineral water (Swanner, 1988).

The results in table 2.1 illustrate high levels of sodium, potassium, calcium, magnesium, radium, hydrogen carbonate, chloride and total dissolved solids. The large amount of the bicarbonate ion may be due to free CO_2 from the earth's crust, metamorphic process, carbonate rocks or organic matter (Mao, *et al*., 2009).

2.4 Carbon Dioxide Mining in Kenya

The gas was discovered in 1918 in fissures and holes in volcanic rocks on the mount Margaret Estate, Kedong Valley and was tapped and sold on a small scale for aerating bottled drinks such as soda water. In 1922, seepages of the gas were reported from the soil and rocks south of Lake Magadi. The first discovery of major economic importance did not occur until 1946 when a borehole drilled for water at Esageri near Eldama Ravine struck gas at a depth of 450 feet and at a pressure of 80 p.s.i averaging 98 per cent CO_2. Commercial exploitation began in 1951. In 1957, a borehole was sunk at Kireita, near Uplands, some 20 miles northwest of Nairobi where a spring was known to give out CO_2. The borehole encountered gas at a pressure of about 35 p.s.i. with 97.8% CO_2 (Bubois and Walsh, 2007). The gas is mined by Carbacid Company and sold in compressed steel cylinders, and also in the solid state, known as 'dry ice'. It is employed extensively as a refrigerant in the transportation of meat, fish and vegetables. Unlike ordinary ice it leaves no moisture on evaporation and cannot therefore spoil food or food packages. The CO_2 gas which it gives off also inhibits the growth of bacteria and moulds. It is possible then, since the gas issues under pressure to use it as prime-mover and a small reciprocating engine has been worked by this means in order to operate a generator to supply electric power for one of the factories.

2.5 Previous Geological work in Meru-Isiolo Area

Few reports of previous geological work in this area have been found. In 1914, Parkinson passed through the area en route to Northern Frontier District (the former North Eastern Province) and in his report described a gneisses inlier eleven miles north east of Meru, the hill mentioned is known as Gwathini. Parkinson also noted the basalts in the vicinity of Isiolo. A reconnaissance survey of the area was undertaken between December 1950 and April 1951, in order to ascertain whether or not more detailed work and prospecting would be advisable (Manson, 2007). The primary reason for geological mapping of the area was a supposed occurrence of granitic intrusion on the southern slopes of the Nyambene range, as has been indicated on the geological map of Kenya published in

1942. The presence of a granitic intrusion suggests the possibility of the occurrence of valuable minerals. Examination of the supposed intrusion proved that it is an inlier of quartzo-felspathic biotite gneisses and granitoid gneisses of Precambrian age, surrounded by much more recent lavas and thick brown soils. The full extent of the inlier could not be determined in the time available owing to the thick forest which covered that part of the area (Manson, 2007). It is worth noting that there is no intensive geochemistry study that has been done around the Rurii spring so far. This fact underscores the purpose of this investigation.

2.6 Water Quality Parameters for Domestic Use

Safe water for drinking is one that may be consumed in any desirable amount without concern for adverse effects on the health of the consumer (WHO, 2004). It must meet high quality standards of physical, chemical and biological purity. Such water must be free from pathogenic micro-organisms, minerals and substances capable of producing adverse physical effects. In addition it must be aesthetically acceptable free from turbidity, colour, odours and all objectionable taste as provided by World Health Organisation, WHO (Thompson, 2007). Some important water quality parameters which were analysed in the Rurii spring water are described in the following sections.

2.6.1 Electrical Conductivity (EC)

Electrical conductivity also called specific conductance refer to the measure of water ability to conduct an electric current. EC depends on the temperature of the water and the concentration of dissolved mineral salts (Murigi, 2004). Total dissolved solids should not exceed 2,000 mg/l (WHO, 2004). Pure water should have very low conductivity and can be said to be a non-conductor. EC is usually measured in micro-Siemens per centimetre (μScm^{-1}), which is equivalent to specific conductance, that is, the capacity of a 1 cm cube of a substance at 25 ^{o}C to conduct an electric current. As a general rule, the higher the conductivity, the greater the concentration of total dissolved solids.

2.6.2 pH

The pH (Hydrogen ion potential) is a measure of acidity or alkalinity of water. It determines the ability of water to dissolve mineral salts from rocks. Overall pH of most groundwater results from the balance between dissolved CO_2 gas derived from the atmosphere and biological activity in the environment, and dissolved carbonate and bicarbonate derived from the carbonate rock. pH of natural water lies between 6.5 to 8.5. Groundwater is generally alkaline due to presence of mineral salts (Orata, 2003).

2.6.3 Temperature

The temperature governs the solubility of mineral salts in water in addition to controlling most geochemical and biological activities. Water having temperature between $10 - 15$ ^oC is most palatable (Thomson, 2007).

2.6.4 Total Dissolved Solids

Total dissolved solid (TDS) refers to the total dissolved solids in water. It determines the water quality in terms of its suitability for any particular use (Ngugi, 2009). The recommended TDS range is not more than 200 mg/l. However, water up to 2000 mg/l TDS is often used if no other source is available (WHO, 2004). Table 2.2 shows classification of water based on total dissolved solids (APHA, 2005).

Table 2.2: Classification of water based on TDS.

Classification	TDS
Fresh water	0-1,000
Brackish water	1,000 – 10,000
Saline water	10,000 – 100,000
Brine water	More than 100,000

Source: Gray (2008).

2.6.5 Total Suspended Solids

Total suspended solids (TSS) refer to all the tiny insoluble particles suspended in water. These are discrete particles which can be trapped by filtering a sample through a fine paper (Rono, 2008).

2.2.6 Total Hardness

Amount of Ca^{2+} and Mg^{2+} contribute to the total hardness (TH) of water. These cations react with soap rendering it ineffective by forming insoluble scum (Equation 2.2).

$$2C_{17}H_{35}COO^-Na^+ + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2Na^+ \qquad\qquad 2.2$$
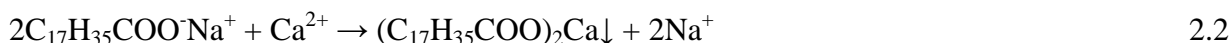
Hard water when heated forms kettle fur and boiler scale in electric kettles and boilers, respectively, which reduce their efficiency and increase the running costs (Shadrack, 2006). Temporary hardness which is due to bicarbonate ions is removed by boiling water while permanent hardness arising from sulphates and chlorides can be removed by exchanging Ca^{2+} and Mg^{2+} with Na^+ (Eqn 2.2 and 2.3).

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2 \qquad\qquad 2.3$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 \qquad\qquad 2.4$$

Total hardness is determined by titration of the sample of water with a standard solution of EDTA using Erio-chrome Black T indicator (Equation 2.5).

$$Mg\,In\,(wine\,red) + EDTA^{4-} \longrightarrow MgEDTA^{2-} + In^{2-}\,(blue) \qquad\qquad 2.5$$

Example:

If one is using EDTA with molarity of 0.0080 for the titration and 50.0 ml of water sample is titrated using 10.68 ml of EDTA, concentration of Ca^{2+} ions per litre is given as follows;

$$= \frac{(\text{molarity EDTA})\,(\text{ml EDTA added})}{50\,\text{ml of water sample titrated}}$$

$$= \frac{0.0080\,M \times 10.68\,ml}{50.0\,ml\,water} = 0.0017\,M$$

Total water hardness;

$$= 0.0017\,mol/l \times 100\,g/mol\,CaCO_3 \times 10^3 = 170\,mg\,/l\,CaCO_3$$

Water can be classified according to total hardness content in $CaCO_3$ mg/l as shown in Table 2.3 (Hersi, 2003).

Table 2.3: Classification of Water based on TH.

mg $CaCO_3$/l	Description
0 – 60	Soft
61 – 120	Moderately hard
121 – 180	Hard water
Over 180	Very hard water

Source: Hersi (2003).

2.6.7 Free Carbon Dioxide

Free carbon dioxide is a measure of the concentration of free CO_2 in water which equates to the amount of dissolved CO_2 gas in water. CO_2 is an indicator of the health of the ecosystem in that there is a balance of O_2 consumed and CO_2 produced between flora and fauna. If the CO_2 levels are too high, then the O_2 levels will be too low (Irwin, *et al*., 2012). In most cases, surface water contains less than 10 mg/l CO_2. while in some groundwater the concentration may be higher. Dissolved CO_2 usually is the major acidic component of unpolluted surface waters (Mathew, *et al*., 2008). In a sample containing only carbon dioxide-bicarbonates-carbonates, titration to pH 8.3 at 25 $^{\circ}$C corresponds to stoichiometric neutralization of carbonic acid to bicarbonate (Equation 2.6). Because the colour change of phenolphthalein indicator is close to pH 8.3, this value is generally accepted as a standard end-point for titration of total acidity.

$$OH^- + CO_2 \longrightarrow HCO_3^- \hspace{4cm} 2.6$$

2.6.8   Total Alkalinity

Alkalinity of water is a measure of its capacity to neutralise acids (Equations 2.7 and 2.8). Substances that exhibit a pH greater than 7 are said to be alkaline. The carbonates, bicarbonates and hydroxyl ions represent the major form of alkalinity in groundwater. Groundwater is commonly in

the range of pH 6.5 to 8.5, hence the contribution of total alkalinity by OH^- and CO_3^{2-} is negligible and alkalinity due to HCO_3^- is the only capacity actually measured (Hyeon, *et al.*, 2005). Total alkalinity is expressed in mg/l $CaCO_3$. In large quantities, alkalinity imparts a bitter taste to the water. Determination of alkalinity is of importance in water softening as it helps in calculating the amount of lime or soda ash required and in corrosion control.

$$HCO_3^- + H^+ \longrightarrow H_2CO_3 \qquad\qquad\qquad 2.7$$

$$CO_3^{2-} + 2H^+ \longrightarrow H_2CO_3 \qquad\qquad\qquad 2.8$$

2.6.9   Chemical Oxygen Demand

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Dichromate ion $Cr_2O_7^{2-}$ is the specified oxidant which is reduced to chromate ion Cr^{3-}. Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic component predominates and is of the greatest interest. COD is often used as a measurement of pollutants in wastewater and natural waters. The COD test is used to measure the content of organic matter of both wastewater and natural water. The oxygen equivalent of organic matter that can be oxidised is measured by using a strong oxidising agent in acidic media (WHO, 2004). The sum of all oxidizable substances in water is determined. These are mainly organic constituents which are oxidised during a heating of 2 hours at 150 ^{o}C by chromosulphuric acid with silver sulphate as a catalyst. The dichromate present in the reaction mixture is the oxidising agent. During the reaction, the green chromate ion is formed from yellow dichromate. The increase in absorption at 600 nm in UV-VIS spectrometer is in relation to the amount of oxidizable substances in the sample (Andrew, 2005). It is also possible to follow this reaction at 446 nm where the decrease of dichromate can be monitored. The later calibration curve has a negative slope. Potassium hydrogen phthalate standard solution is used for the calibration curve.

20

2.6.10 Colour

Pure water has a pale green-blue tint in large volumes. The guideline value is true colour units (TCU). Most people can detect levels of colour above 15 TCU in a glass of water (WHO, 2004). The appearance of colour in drinking water is caused by the absorption of certain wavelengths of normal white light by dissolved or colloidal dispersed substances, by inflorescence in the visible wavelength region from substances that absorb white or ultraviolet light, by the presence of coloured suspended solids, and by the preferential scattering of short wavelengths of light by the smallest suspended particles. Colour measured in water that contains suspended matter is defined as "apparent colour"; "True colour" is measured in water samples from which particulate matter has been removed by centrifugation. In general, the true colour of a given water sample is substantially less than its apparent colour.

One True Colour unit (TCU) or platinum- cobalt unit corresponds to the amount of colour exhibited under the specified test conditions by a standard solution containing 1.0 mg of platinum per litre. Thus, a sample exhibiting a colour of 15 TCU has a closer colour match with a standard containing 15 mg of platinum per litre than with standards containing 14 or 16 mg/l. A colour of 15 TCU can be detected in a glass of water by most consumers and 5 TCU will be apparent in large volumes of water, such as in bathtub; few people can detect a colour level of 3 TCU (Obuya, *et al*, 2012). One major factor that affects the colour of natural surface water is pH. The increase in colour with increasing pH of the test sample is commonly referred to as the <u>indicator</u> <u>effect</u>, and it is widely recommended that the pH of the sample be recorded together with the colour measurement to allow for this effect. The alternative is that all colour measurement be done at a standard pH of 8.3.

2.6.11 Turbidity

Turbidity is the measure of the cloudiness of water. Turbid water contains suspended matter that interferers with passage of light through the water or in which visual depth is restricted. It is usually expressed in terms of reduced light transmission by water Nephelometric Turbidity Unit (NTU).

Absolute turbidity is the fractional decrease of incident monochromatic light through a 1cm layer of a sample, integrating both scattered and transmitted light. Nephelometric turbidity is an empirical measurement of the light scattering characteristic (Tyndall effect) of the suspended matter in a sample (Murigi, 2004). It is determined by reference to a chemical mixture that produces a reproducible refraction of light. The method requires use of a nephelometer or turbidimeter. The water sample is put in a nephelometer bottle and the outside of the bottle is wiped with a soft, clean cloth to remove all fingerprints. Then the bottle is placed gently into a nephelometer and the "Read" button pushed. The reading is record in NTUs (Hersi, 2003). Table 2.4 shows categorisation of water in NTUs.

Table 2.4: Nephelometer turbidity measurement.

Turbidity	Approximate readings in NTUs
Clear	0-3 NTUs
Cloudy	4-12 NTUs
Muddy	>12 NTUs

Source: WHO (2004).

A simpler method of determining turbidity involves filling a transparency tube with sampled water. Then look straight down into the tube and visually observe ability to see black and white disk at the bottom of the tube (Table 2.5).

Table 2.5: Transparency tube turbidity measurement.

Category	Observation
Clear	Black and white disk can be seen clearly
Cloudy	Black and white disk can be seen but not clearly
Muddy	Black and white disk cannot be seen

Source: WHO (2004).

2.6.12 Coliforms

Coliform bacteria are broad group that has members which live in soil, water, vegetation and in the gut of mammals. Coliform group bacteria present in the gut of warm-blooded animals generally include organisms capable of producing gas from lactose in a suitable culture medium at $44.5\pm0.2\ ^{\circ}\text{C}$ (Rono, 2008). Water for domestic use must be free from diseases causing pathogens. For water to be portable, the total coliform counts per 100 ml of sample should be zero (WHO, 2004). Coliform group of bacteria is one of the principle indicators of suitability of water for domestic, industrial or other uses. In particular faecal coliforms or *Escherichia coli (E. coli)* are very significant as criterion of the degree of pollution and thus sanitary quality of water. They include faecal *streptococci* and *enterococci.*

Bacteria reproduce rapidly if conditions are right for growth. Most bacteria grow best in dark, warm, moist environments with food. Some bacteria form colonies as they multiply which may grow large enough to be seen. By growing and counting colonies of coliform bacteria from a sample of water, the amount of bacteria originally present can be determined (Mbaka, 2003).

Membrane filtration is the method of choice for the analysis of faecal coliforms (*E. coli*) in water. A 100 ml volume of water sample is drawn through a membrane filter (0.045 µm pore size) through the use of a vacuum pump. The filter is placed on a Petri dish containing M-FC agar and incubated for 24 hours at $44.5\ ^{\circ}\text{C}$. This elevated temperature shocks non-faecal bacteria and suppresses their growth. As the faecal coliform colonies grow they produce an acid (through fermenting lactose) that reacts with the aniline dye in the agar thus giving the colonies their blue colour. Coliform density using membrane filter with 20 to 80 coliform colonies and not more than 200 colonies per membrane is calculated by the following equation (Andrew, 2005).

Total coliforms/100 ml= coliform colonies counted $\times$ 100
                        ml sample filtered

Newer methods for coliform detection are based on specific enzyme substrates as indicators of coliform. These assays make use of a sugar linked to a dye which, when acted on by the enzyme beta-galactosidase produces a characteristic colour. The enzyme beta-galactosidase is a marker for coliforms generally and may be assayed by hydrolysis of the sugar glucoside-nitrophenyl beta-D-galactose. Assays typically include a second sugar linked to a different dye which, when acted on by the enzyme beta-glucuronidase, produces a fluorescent product. Because *E. coli* produces both beta-galactosidase and beta-glucuronidase, a combination of these two dyes makes possible the unique ability to use one test to differentiate and quantify coliforms and *E.coli* (Table 2.6).

Table 2.6: Colour change for various cultures.

Substrate	Total coliform positive	*E. coli* positive	Negative result
ONPG-MUG	Yellow	Blue fluorescence	Colourless or No fluorescence
CPRG-MUG	Red or Magenta	Blue fluorescence	Yellow or No fluorescence

Source: Rono (2008).

2.6.13 Sulphate

Sulphates can occur in surface, ground and waste waters in different concentrations. The highest levels occur in groundwater originating from natural source. It may occur in dissolved and undissolved forms. High concentrations between 1,000 – 1,200 mg/l lead to laxative effect .It also causes noticeable taste and corrosion in the distribution systems. The maximum limit of sulphate in water according to WHO is 400 mg/l (Mepham, 2003). Sulphate ions in water are determined by turbidimetric method which involves adding $BaCl_2$ crystals to the sample under controlled conditions to form insoluble $BaSO_4$ (Equation 2.9). The resulting turbidity is determined by UV/VIS spectroscopy at 420 nm or using turbidimeter.

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4(s)$$ 2.9

2.6.14 Nitrate and Nitrite

Nitrates are naturally produced from atmospheric nitrogen through nitrogen fixation but may accumulate in excess amount from anthropogenic sources of fertilizer. Nitrates in groundwater may result from point sources such as sewage disposal systems and livestock facilities, non-point sources such as fertilized cropland, parks or naturally occurring sources of nitrogen (Ngugi, 2009).

Nitrite and nitrate are readily interchangeable through reduction of nitrate to nitrite and oxidation of nitrite to nitrate. Reducing conditions in the gut, for example, can cause nitrate to convert to nitrite, while exposure to oxygen does reverse. Nitrite is a common pollutant of rivers, streams, lakes and water supplies. It has an element of toxicity and in high doses is linked with cancer as it can make carcinogenic nitrosamine and N-nitroso compounds. Nitrite is usually an indicator of direct contamination by sewage or manure because nitrites are unstable and quickly become nitrates. Levels of both are regulated in drinking water. The WHO allowed limits for nitrates and nitrites are 10 mg/l and 1 mg/l, respectively (Mfashwanayo, 2009).

2.6.15 Ammonia-Nitrogen

Ammonia can occur in all kinds of surface waters, some groundwater and wastewaters from industries and households. Whether ammonia-nitrogen is found as NH_4^+ ion or NH_4OH or NH_3 depends on the pH value of the water. According to WHO standards a maximum of 0.5 mg/1 NH_3-N is recommended (Thomson, 2007).

2.6.16 Phosphorus

Phosphorus can occur in different concentrations in all kinds of waters. It can occur in dissolved and undissolved forms. Depending on sample pre-treatment, the following forms of phosphorus can be determined by molybdate/ascorbic acid method. These are orthophosphate, hydrolysable and orthophosphate, total phosphorus and the dissolved forms of the above types (Murigi, 2004).

2.6.17 Chloride

Chloride ion is one of the major inorganic anions in groundwater and wastewater. Chloride is widely distributed in nature, generally as NaCl and KCl salts. By far, the greatest amount of Chloride found in the environment is in the oceans. Chloride in drinking water sources can come from dissolving salt deposits, salting of highways to control ice and snow, effluent from chemical industries, sewage and irrigation drainage. Small amounts of chlorides are required for normal cell functions in plant and animal life. The salty taste of water is produced by the chloride in combination with sodium ions. A high Chloride content makes water taste bad and may corrode metallic pipe structures as well as harm growing plants and marine life. Therefore, water that is used in industry or processed for any use has a recommended maximum chloride level. This is 250 mg/l as per WHO and KEBS standards (Hersi, 2003). Chloride in water is determined by argentometric method which involves titration of the sample with standard 0.0141 N $AgNO_3$ in the presence of K_2CrO_4 indictor. Silver chloride is precipitated quantitatively before the red silver chromate is formed (Equation 2.10).

$$Cl^- + Ag^+ \longrightarrow AgCl(s) \qquad\qquad 2.10$$

2.6.18 Fluoride

Fluoride occurs naturally in most groundwater wells and in surface waters. Fluoride containing compounds are added to drinking water to help prevent dental cavities. Groundwater can also contain high concentrations of fluoride due to leaching from rocks. Fluoride level between 1.0 and 1.5 mg/1 is desirable in drinking water. Fluoride of approximately 1.0mg/1 in drinking water effectively reduces dental caries without harmful effects on health. However, Fluorosis may occur when the fluoride level exceeds the recommended limits (Kithia, 2006). Fluoride in a water sample is determined by measurement with a fluoride ion selective combination electrode. A 1:1 dilution of all samples with TISAB provides a high total ionic strength background, swamping out variations in ionic strength between samples and buffers the samples at pH 5-6. In acid media, HF forms; while in alkaline media, OH^- ion interferes in the electrode response (Christian, 2004).

Tables 2.7 and 2.8 summarises the water quality parameters and drinking water standards according to the World Health Organisation (WHO) and Kenya Bureau of Standards (KEBS), respectively. Most of the quality parameters between WHO and KEBS are in agreement.

Table 2.7: WHO Water quality parameters and drinking water standards.

Parameter	Units	Amount in Drinking Water	
		Desirable	Maximum
Coliforms	MPN	Absent in 100ml	-
Colour	TCU	5	25
Odour	TON	Unobjectionable	-
Taste	-	Agreeable	-
Turbidity	NTU	5	10
pH value	pH scale	6.5 – 8.5	No relaxation
Total hardness as $CaCO_3$	mg/l	300	600
Iron	mg/l	0.3	1.0
Chloride	mg/l	250	1000
Residual chlorine	mg/l	0.2	-
Dissolved solids	mg/l	500	2000
Calcium	mg/l	75	200
Copper	mg/l	0.05	0.1
Manganese	mg/l	0.1	0.3
Sulphate	mg/l	200	400
Nitrate	mg/l	50	No relaxation
Fluoride	mg/l	1.0	1.5
Phenolic compounds	mg/l	0.001	0.002
Mercury	mg/l	0.001	No relaxation
Cadmium	mg/l	0.01	No relaxation
Selenium	mg/l	0.01	No relaxation
Arsenic	mg/l	0.05	No relaxation
Cyanide	mg/l	0.05	No relaxation
Lead	mg/l	0.05	No relaxation
Zinc	mg/l	5	15
Anionic detergents	mg/l	0.02	1.0
Chromium	mg/l	0.05	No relaxation
Poly-nuclear aromatic hydrocarbons	mg/l	-	-
Mineral oil	mg/l	0.01	0.03
Pesticides	mg/l	Absent	0.001
Radio-active materials			
a. alpha emitters	a. Bq / l	-	a. 0.1
b. beta emitters	b. Pci/l	-	b. 0.037
Alkalinity	mg/l	200	600
Aluminium	mg/l	0.03	0.2
Boron	mg/l	1	5

Source: WHO (2004).

Table 2.8: KEBS Aesthetic quality requirements for drinking water and bottled drinking water.

Substance or characteristic	Unit	Maximum Level	
		Drinking water	**Bottled drinking water**
Coliforms	MPN	Absent in 100 mls	Absent in 100 mls
Colour	TCU	15	15
Taste and odour	TON	Not offensive	Not offensive
Suspended matter	mg/l	Nil	Nil
Turbidity	NTU	5	1
Total dissolved solids	mg/l	1,500	1,500
Hardness as $CaCO_3$	mg/l	500	500
Aluminum	mg/l	0.1	0.1
Chloride	mg/l	250	250
Copper	mg/l	0.1	0.1
Iron	mg/l	0.3	0.3
Manganese	mg/l	0.1	0.1
Sodium	mg/l	200	200
Sulphate	mg/l	400	400
Zinc	mg/l	5	5
pH	pH Scale	6.5 to 8.5	6.5 to 8.5
Magnesium	mg/l	100	100
Chlorine	mg/l	0.2 ± 0.5	Nil
Calcium	mg/l	250	250
Ammonia	mg/l	0.5	0.5
Fluoride*	mg/l	1.5	1.5
Arsenic	mg/l	0.05	0.05
Cadmium	mg/l	0.005	0.005
Lead	mg/l	0.05	0.05
Mercury(total Hg)	mg/l	0.001	0.001
Selenium	mg/l	0.01	0.01
Chromium	mg/l	0.05	0.05
Cyanide	mg/l	0.01	0.01
Phenolic substances	mg/l	0.002	0.002
Barium	mg/l	1.0	1.0
Nitrate	mg/l	10	10

Source: Water Resources Management Authority (2012).

*The local and climatic conditions necessitate adaptation of fluoride concentration in excess of 1.5 mg/l.

2.7 Classification of Rocks and Minerals

2.7.1 Rocks

Rocks are composed of assemblages of minerals. According to the manner of formation, rocks are divided into three main classes namely; igneous, sedimentary and metamorphic rocks (Rutley, 1988).

Igneous rocks are formed from molten rock of magma, which has originated well below the earth's surface, has ascended towards the surface, consolidated or crystallized as solid rock, either on the surface as lava, or deep within the earth's crust as its temperature fell. In spite of there being over hundred elements, only eight of these are abundant in igneous rocks on the earth's surface, in form of oxides as shown in Table 2.9.

Table 2.9: Major Oxides in Igneous rocks.

Constituent oxide	Range of concentrations wt. - %
SiO_2	30 – 78
Al_2O_3	3-34
Fe_2O_3	0-5
FeO	0-15
MgO	0-40
CaO	0-20
Na_2O	0-10
K_2O	0-15

Source: Rutley (1988).

Sedimentary rocks are formed from the accumulation and compaction of either fragments from pre-existing rocks which have been disintegrated by erosion, organic debris such as shell fragments or

dead plants or material dissolved in surface waters or groundwater which is precipitated in conditions of oversaturation; or some combinations of these.

Metamorphic rocks are formed from pre-existing rocks of any type which have been subjected to increase of temperature or pressure or both, such that the rocks changed from their original parental material in appearance, texture and mineralogy (Putnis, 1992).

2.7.2 Minerals

The chemical classification usually used begins with the elements and then follow with subdivisions based on the anion groups present. In the scheme employed by the American mineralogist, J.D Dana, the following sub-divisions were made (Rutley, 1988).

These are;

Native elements - gold, silver mercury, copper.

Sulphide – Selenides, tellurides, arsenides, antimonides.

Sulphosalts – sulpharsenites, sulphantimonites, sulphobismuthites.

Halides – Chlorides, bromides, Iodides, fluorides.

Oxides and Hydroxides – bauxite, rutile, cuprites.

Oxygen salts – carbonates, titanates, niobates, tantalates, phosphates, arsenates,

              vanadates, Antimonates, nitrates, borates, urinates, sulphates,

              chromates, tellurates, tungstates, and molybdates.

Salts of organic acids- Oxalates, mellates.

Hydrocarbon compounds.

Silicates.

2.8 Classification of analyte level

The constituents determined in an analytical procedure can cover a wide range in concentration as shown in Table 2.10. Analyte present in the range of 1% (10,000 ppm) and above are usually termed

major constituents, those present in amounts between 0.01% (100 ppm) to 1% are said to be minor, whereas those present in amounts between 1 ppb and 100 ppm are termed trace substances. Components present in amounts less than 1 ppb are usually considered to be ultra-trace constituents.

Table 2.10: Classification of constituent analytes

Analyte Level	Classification
> 1% (10,000 ppm)	Major
0.01% (100 ppm) – 1%	Minor
1 ppb – 100 ppm	Trace
<1 ppb	Ultra-trace

(Skoog, 2004).

2.9 Instrumentation

In this study, Flame Emission Spectrophotometry, Atomic Absorption Spectrophotometry (AAS), X-Ray Fluorescence (XRF) and Ultra-Violet/Visible (UV/VIS) spectroscopy methods were used.

2.9.1 Flame Emission Spectrophotometry

At temperatures reached in a flame, appreciable numbers of atoms gain sufficient excess energy to excite their outer electrons into high energy states, from which they can subsequently go back to the ground state with emission of radiation of a characteristic wavelength. At its simplest level, this forms the basis of the well-known flame test used to detect elements such as Potassium, Sodium, Calcium, Strontium, Barium and Copper by the colour they impart to a Bunsen burner flame. The same principle is used in flame emission spectrophotometry but the characteristic light is produced under carefully controlled conditions and analysed spectroscopically and intensities at the various wavelengths present are monitored electronically.

Flame photometer is an easy and convenient instrument for the determination of strongly emitting elements, especially alkali metals and alkaline earth metals, and provides a useful and rapid method of routine analysis for such elements capable of measuring accurately concentrations as low as 0.1 mg/l or less (Jeffery, 1975).

The flame is usually produced in a special burner which is supplied with a mixture of butane gas and air which are carefully regulated at flow rates capable of maintaining flame conditions as constant as possible. Before reaching the burner, the air passes through the nebuliser where venturi effect aspirates the sample solution through a capillary tube and disperses it as a fine mist so that it is introduced into the flame in a uniform manner. Quite accurate results can be obtained with flame photometer provided that care is taken to standardize the conditions in the instrument and particularly in the flame. It is important that the operating conditions in the nebuliser and burner units be carefully controlled, especially that the flow rate of the gas and the air streams be kept constant to ensure that the concentration of the required element in the flame, and hence the intensity of its emission will remain constant.

The instrument is calibrated using standard solutions containing the required element in an appropriate range of known concentrations. The concentration of the unknown is determined from the calibration curve by interpolation (Figure 2.2).
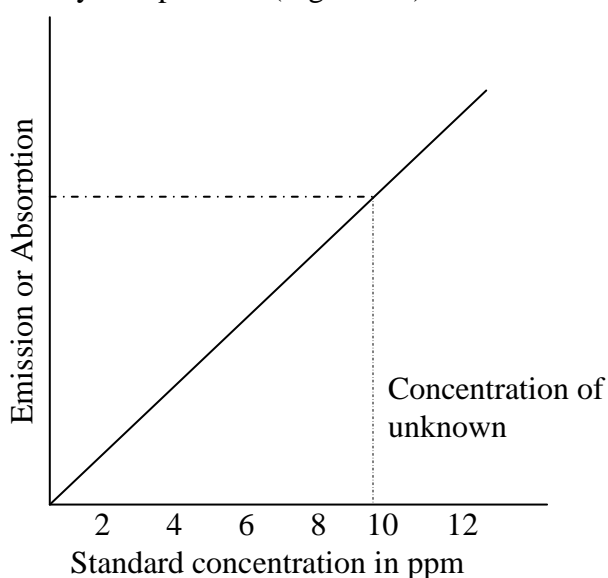
Figure 2.2: Normal calibration curve.

It is important that the chemical and physical characteristics of the standard solution should be as close as possible to those of the test solution with regard to viscosity and concentrations of dissolved substances to minimize potential source of error (Skoog, 2004).

An alternative calibration technique is the method of standard addition in which known, increasing amounts of the required element in an appropriate solution form are added to aliquots of the test (unknown) solution. When the observed intensity readings of the resulting solutions are plotted against the known concentrations due to the additions alone, it is found that these lie on a straight line. When this is extrapolated to zero intensity, the "the negative intercept" on the concentration axis corresponds to the original concentration of the element in the test solution (Figure 2.3). This method of internal calibration is recommended particularly in its ability to standardize the physical properties of the standard solutions and the test solutions and this checks the problem of interference.
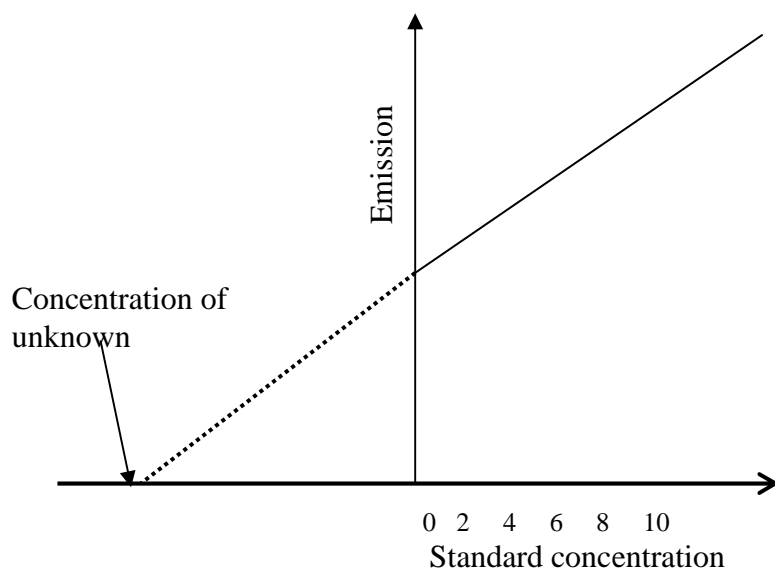
Figure 2.3: Standard addition calibration curve.

Working standard solutions are prepared by diluting respective stock solutions of the metals using the equation 2.11.

$$C_0V_0 = C_1V_1 \qquad\qquad 2.11$$

Where; V_0 is the initial volume (ml) of stock solution required to make C_1, C_0 is the concentration of the metal (ppm) in the stock solution, C_1 is the concentration of the metal (ppm) required in V_1 and V_1 is the volume (ml) needed (Odero, 1998). Calibration standards are prepared from the working standards using the same equation.

2.9.2 Atomic Absorption Spectrophotometry (AAS)

AAS was introduced by Walsh in 1955. The method is based on the ability of atoms formed in a flame to absorb energy from a light beam of a suitable wavelength, thus resulting in transition of these atoms from the ground state to excited state.

$$A \xrightarrow{\text{h}\upsilon} A^*$$

Ground state atom   Excited state atom
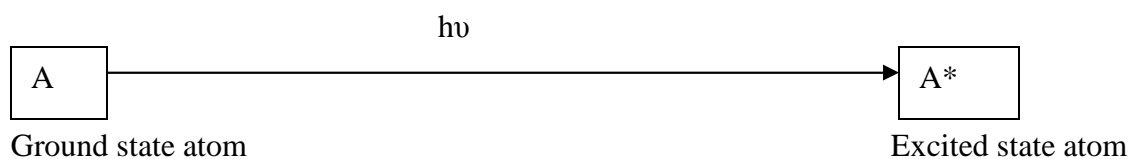
Where h is the Plank's constant and υ is the frequency of radiation (Maxwell, 1968). The AAS comprises three main sections; light source, absorption flame, and the wavelength selector (monochromatic) and detector. The light source is the heart of the AAS and is normally a hollow cathode lamp or an electrodeless discharge lamp (EDL) which produces a line spectrum specific to the element being determined. This gives the great advantage of high specificity to the source and leads to high levels of accuracy and sensitivity with a minimum of interference, but this very specificity is a disadvantage in another way. Since each element requires its own lamp, the lamp must be changed for each element being determined in a multi-element analysis and hollow cathode lamps are quite expensive. Multi-element hollow cathode lamps can be available but are generally of lower quality than single element lamp. EDLs take a longer time to warm up compared to the hollow cathode lamp (Andrew, 2005).

The test liquid is aspirated into the flame via nebuliser, and carried forward by a mixture of fuel and oxidant as a fine cloud, where it is atomized. The light from the hollow cathode source passes first

through the flame into which the absorption occurs. The flame is usually produced by a slot burner, usually oriented with its long axis parallel to the direction of the light beam to produce longest possible absorption path (Nicol, 1975). Conditions in the flame must be maintained as homogenous as possible. The flame is normally an acetylene – air mixture, but acetylene – nitrous oxide mixture is used for high temperatures (Appendix II). After passing through the flame, the light next passes through either a prism or an optical grating and a slit system which selects a narrow band of wavelength for final transmission to the detector. The detector unit, which usually incorporates a photomultiplier, transmits a signal to the recorder (Figure 2.4).

Slits

Detector

Dual grating

Slits

Chopper

Hollow Cathode
Lamp

Flame area
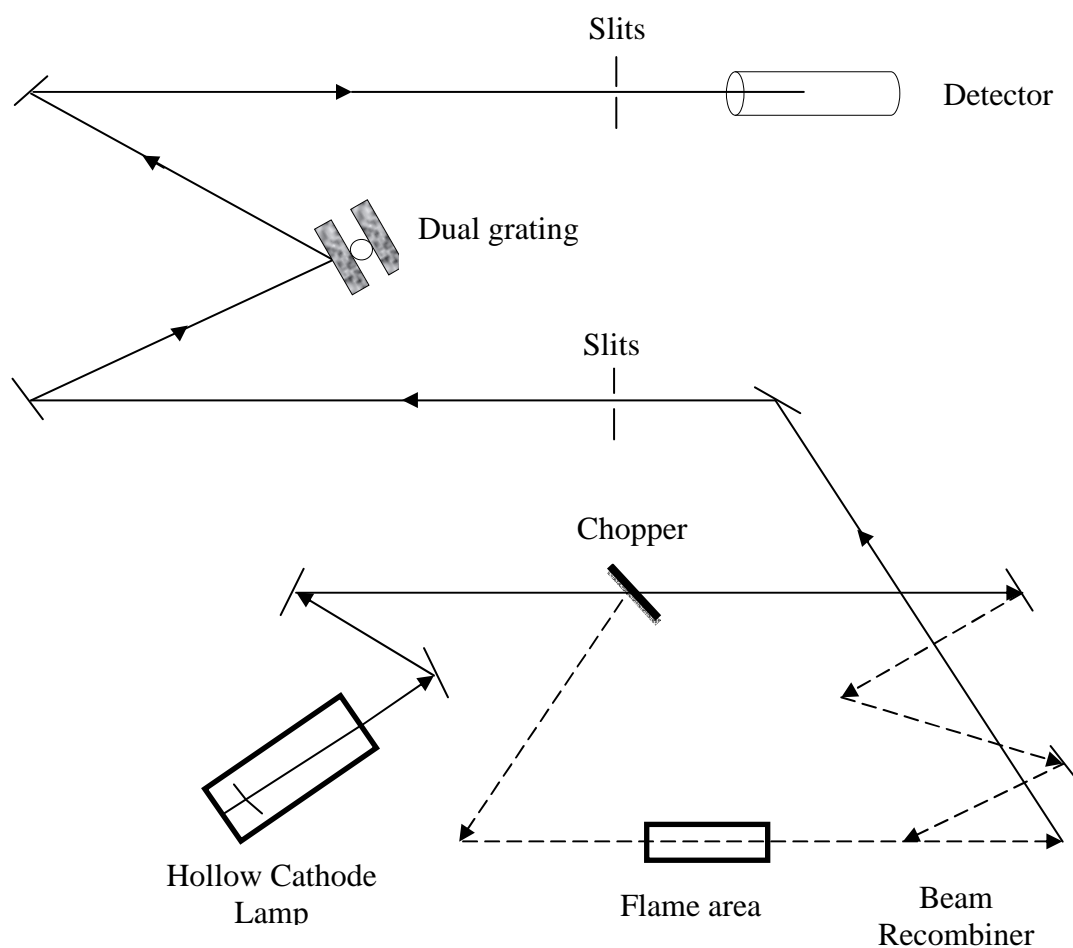
Beam
Recombiner

Figure 2.4: Principle of operation of Double – Beam AAS (Perkin – Elmer 303).

AAS has proved to be reliable and flexible technique for the analysis of many elements particularly metals and is limited only by the availability of a suitable hollow cathode discharge lamp for the element in question. The concentration of the unknown sample is determined from the calibration

curve of standard solutions, of the element under analysis (Parker, 1972). Most atomic absorption instruments are also equipped for operation in an emission mode, which may provide better linearity for some elements such as sodium.

2.9.3 X-Ray Fluorescence

The features of primary interest in X-ray fluorescence technique are the existence of discrete energy levels (K, L, M, and N) shells, for the electrons surrounding the central nucleus. When sufficient energy is applied to the atom, electrons may be ejected from an inner shell and replaced within 10 – 15 seconds by electrons from the outer shells. At each step in this process a photon of electromagnetic radiation is emitted with a wavelength in the X-ray region corresponding to the energy differences between the shells. The photon energies and their associated wavelengths are given by the following equation (2.12).

$$\Delta E = (E_{outer} - E_{Inner}) = \frac{hc}{\lambda} \qquad\qquad 2.12$$

Where E is the photon energy, h is Plank's constant, c is the velocity of light and λ is the wavelength of the X- ray radiation generated (Jeffery, 1975).

In an X-ray tube, the electrons from heated filament strike a positively charged metal target, such as tungsten, molybdenum or chromium and produce primary X-ray radiation as mentioned above and have a continuous spectrum (continuum). The irradiation of a sample by this primary photons having sufficient energy to eject electrons from the inner K and L shells of the constituent atoms, with the resultant appearance of the characteristics spectra of these atoms as other electrons move to fill the vacated positions and emit secondary fluorescence X-rays in the process (Figure 2.5). The wavelengths of the secondary fluorescence X-rays are independent of the primary radiation, depending only upon the nature of the excited atoms (Van, *et al*., 2002).
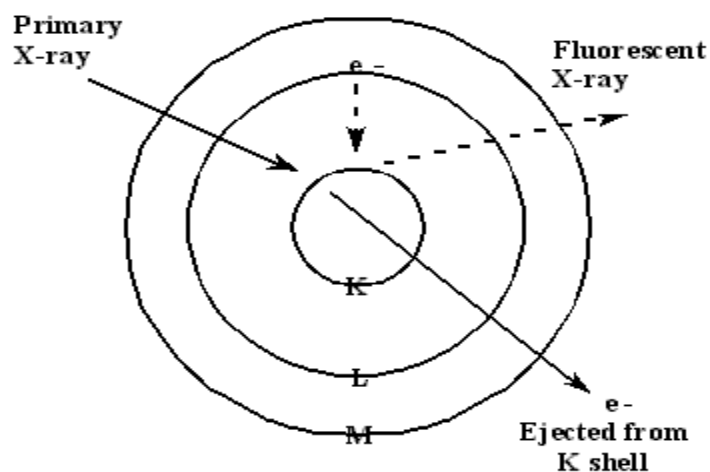
Figure 2.5: Formation of Secondary (Fluorescent) X-Ray.

Because there are only two electrons in the K shell, and not more than eight in the L shell, the resulting secondary X-ray spectra consists of only a few strong lines. The main transitions are given names: an L→K transition is called K_α, an M→K transition is called K_β, an M→L transition is called L_α, and so on. It is necessary to separate the various wavelengths (wavelength-dispersive analysis) or energies (energy-dispersive analysis) of the emitted secondary X-ray radiation in order to identify the elements responsible for it and to measure the corresponding line intensities. This is done by utilizing diffraction by analyser crystals in WDXRF while EDXRF uses silicon semi-conductors to sort out the energy of the photons.

The unique or characteristic line spectra produced by each element could be used to identify the element. Relative intensities of the elemental lines in different samples would also give an estimate of concentrations. Because the X-ray fluorescence method is fast, non- destructive and readily applied, it is particularly well suited to qualitative analysis. The simplicity of the X-ray spectrum makes the identification of all elements in a given range a simple process (Orata, 2003). Figure 2.6 illustrates a simplified diagram of XRF spectrometer.
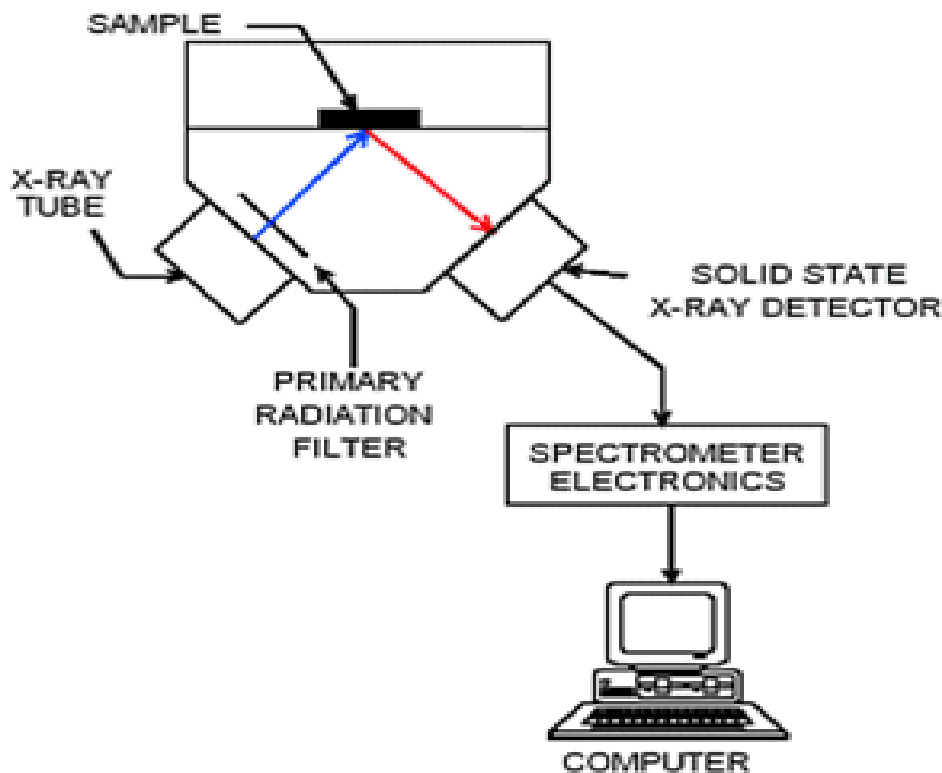
Figure 2.6: Simplified XRF Diagram.

2.9.4 Ultra-Violet / Visible Spectroscopy (UV / VIS)

Light of wavelength between about 400 nm – 750 nm is visible. Just beyond the red end of the visible spectrum above 750 nm lays infrared region. Just beyond the violet end of the visible spectrum below 400 nm lays the ultraviolet region. The UV/VIS spectrometers commonly used measure absorption of light in the visible and near ultraviolet region, which is 200 – 750 nm range. This light is of higher frequency and greater energy. The absorption of UV / VIS light by a molecule cause the promotion of an electron from a ground electronic state to an excited electronic state. The electronic transitions of most concern are $n \longrightarrow \pi^*$ in which the electrons of unshared pair goes to unstable anti-bonding π orbital and $\pi \longrightarrow \pi^*$ in which an electron goes from a stable bonding π orbital to unstable anti-bonding π orbital (Skoog, 2004).

The Beer – Lambert's law states that the absorbance of a solution is directly proportional to the concentration of the solution. Thus UV/VIS spectroscopy can be used to determine the concentration of a solution as given in equation 2.13.

$$A = -\log (I/I_o) = \log (I_o/I) = \varepsilon.C.L \qquad\qquad 2.13$$

Where A is the measured absorbance, I_o is the intensity of the incident light at a given wavelength, I is the transmitted light intensity through the solution, L is the path length through the sample, C is the concentration of the absorbing species and ε is a proportionality constant known as molar absorptivity.

UV/VIS spectroscopy is routinely used in quantitative determination of solution of transition metal ions and highly conjugated compounds. It is an important analytical technique in modern mineral analysis. Many cations and anions in a sample can be determined with high selectivity and sensitivity (Brewer, 1964). The common principle of water analysis is that the sample is mixed with specific complexing reagents which react with the constituent to be analysed. In most cases a coloured compound or complex is formed. The intensity of the colour is a measure of the concentration and can be quantified using UV / VIS spectroscopy. Here the attenuation of radiation of a specific wavelength can be measured and a relation between absorbance and concentration is made by establishing a calibration curve. However, Beer Lambert's law is only valid in a limited absorbance or concentration range. In practice, it is recommended that measurements be made in the linear range of the calibration curve (Nicol, 1975).

In the majority of spectrophotometric procedures, the amount of the required substance present is determined directly from the absorbance of the test solution, but in some, a measurement is made of the amount of a reagent remaining after an excess of it has reacted with the required material in a manner analogous to " back titration" in volumetric analysis (Tebbutt, 1983). Figure 2.7 illustrates the principle of operation of a double beam UV/VIS spectrophotometer.
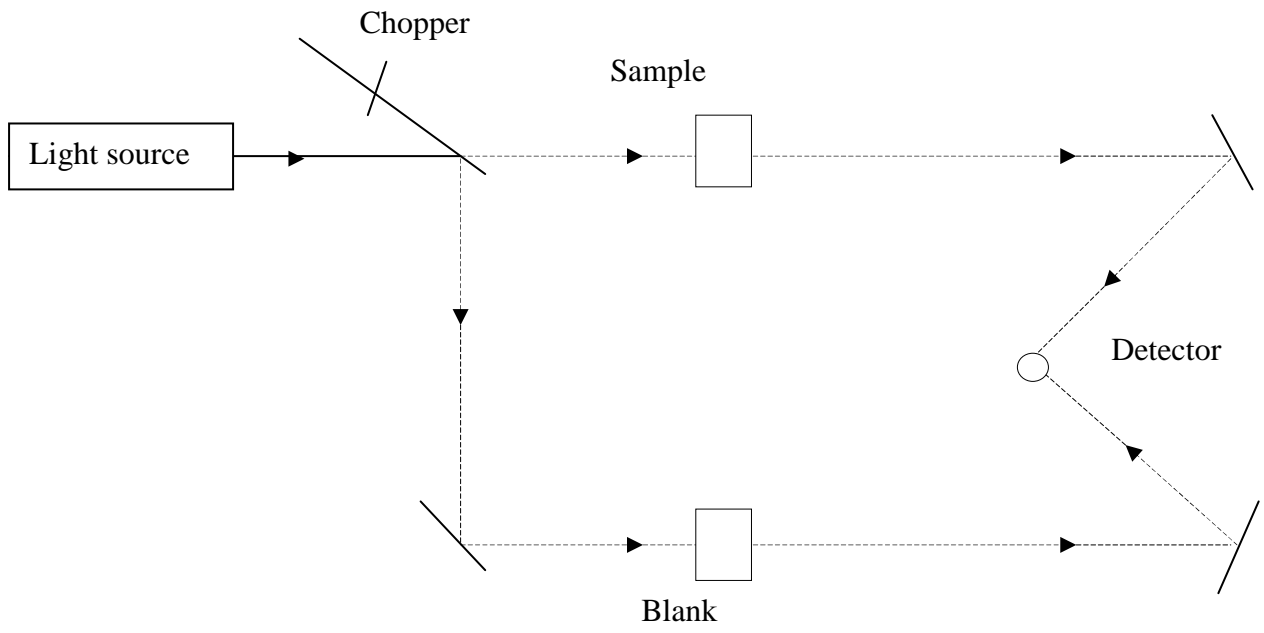
Figure 2.7: Principle of operation of double beam UV/VIS spectrophotometer.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter highlights the sampling procedures, materials used, preliminary treatment of samples, preparation of standards and calibration curves, quality control, methods of sample analyses and data analyses.

3.2 Sampling

Two sets of samples were collected from the study area in the months of September and November 2012, representing the dry and rainy seasons, respectively. The materials sampled included mineral water, sediments and rocks from the Rurii spring (An area approximately 50 M^2). Ten samples (replicates) of each material were collected at random per visit. This was to ensure a good representative of the area under study (Orata, 2003). Water samples for AAS analysis were collected straight from the spring in thoroughly cleaned and sterilized polypropylene bottles and carried in an ice box. The surface rock and sediment samples were collected in clean polythene bags at intervals of 5 metres distance away from the spring. Water samples for bacteriological analysis were collected in non-reactive borosilicate bottles that had been cleaned, rinsed carefully with deionised water and sterilised. Sterilising had been done in an autoclave at 121 ^{o}C and 115 p.s.i for 15 minutes. The samples were transported to the laboratory in ice boxes and investigation started immediately.

3.3 Laboratory Apparatus, Chemicals and Instruments

The apparatus used included but not limited to the following: volumetric flasks, beakers, burette, pipette, conical (Erlenmeyer) flasks, magnetic stirrer, weighing balance, heating block, ice box, oven and mercury thermometer. Analytical grade chemicals used included hydrochloric, nitric and hydrofluoric acids. sodium sulphate, potassium nitrate, sodium nitrite, ammonium chloride,

diammonium hydrogen phosphate, barium chloride, sodium hydroxide, silver nitrate, Nessler reagent, EDTA, sulphanilic acid, NED, potassium hydrogen phthalate, chromosulphuric acid, molybdivanadate, boric acid, Erio-chrome Black T, potassium chromate, phenolphthalein, Colilert ONPG and MUG nutrient indicators and distilled water. The pure reagents were imported from the National Institute of Standards and Technology (NIST) through the Mines and Geology Department and other collaborating laboratories. The instruments comprised of fluoride ion meter (ORION 330), pH meter (ORION 290A), nephelometer (HANNA Instruments Lp 200), AAS (VARIAN SPECTRA A-10), XRF (MINIPAL 2) and UV/VIS Spectrophotometer (T 80+), Quanti tray sealer (2X IDEXX), Fluorescent analysis cabinet (CM-10), Long wave (UV 365 nm) source and Incubator.

3.4 Preliminary treatment of samples

Water samples intended for AAS analysis were filtered after sampling and then preserved immediately to pH <2 by adding 1.5 ml concentrated nitric acid per litre to minimize precipitation and adsorption of cations on the container walls. The acidified samples were stored in a refrigerator at approximately 4 ^{o}C to prevent change in volume due to evaporation. The containers and caps used had been thoroughly cleaned with non-ionic detergent solution, rinsed with tap water, soaked in 50% HNO_3 (v/v) for 24 hours at 70 ^{o}C, and then rinsed with metal-free de-ionized water. The preserved water samples were digested in order to reduce interference by organic matter and convert metals associated with particulates into free form that could be analysed by AAS (Christian, 2004). The rock and sediment samples were also digested before execution of the AAS analysis.

3.5 Digestion of water

To 100 ml of each water sample, 5ml of concentrated HNO_3 were added. The samples were evaporated to almost dryness on hot plate, cooled and transferred to 100 ml volumetric flask then diluted to the mark.

3.6 Digestion of rocks and sediments

The samples were first dried in an oven at 110 °C for 24 hours and then grinded into fine powder. 0.1000 g of each sample was weighed into a beaker. 1 ml of concentrated HCl and HNO_3 in the ratio of 3:1 (aqua-regia) respectively was added followed by 3 ml of concentrated HF. Then the samples were left overnight. 50 ml of saturated Boric acid were added the following morning and the samples left to stand for 1 hour after which 46 ml of distilled water were added to the samples. 5 ml were taken from each digested sample and diluted to 50 ml with 50% (v/v) boric acid.

3.7 Preparation of standards and reagents

The stock solutions (1000 mg/l) were prepared using the respective pure salts or metals. The amount of salt weighed was calculated using the formula (3.1) given below.

$$M = Mw/Aw \text{ x } 100/P \text{ x } V/1000 \qquad\qquad 3.1$$

Where,

M: Amount of salt to be weighed in grams

Mw: Molecular weight of the metal salt

P: Percentage purity of the salt

V: Volume (ml) of the stock solution to be prepared

Aw: Atomic weight of the metal element or the formula mass of the anion

The volume of stock solution required to prepare 100 mg/l working standards and the calibration standards for each parameter was obtained using the formula expression (3.2):

$$C_0V_0 = C_1V_1 \qquad\qquad 3.2$$

Where:

V_0 is the initial volume (ml) of stock solution required to make C_1.

C_0 is the concentration of the metal (mg/l) in the stock solution.

C_1 is the concentration of the metal (mg/l) required in V_1, and

V_1 is the volume (ml) required.

Calibration standards were freshly prepared and treated in the same way as the samples before analysing them to obtain the specific calibration curves. The standards prepared were within the methods working range. Several stock solutions and reagents were prepared as follows.

80 NTU and 40 NTU standards:

1.0 g of hydrazine sulphate, $(NH_2)_2H_2SO_4$, was dissolved in distilled water and diluted to 100 ml in a volumetric flask. 10.0 g hexamethylenetetramine, $(CH_2)_6N_4$, was dissolved in distilled and diluted to 100 ml in a volumetric flask. 5 ml of the first solution and 5 ml of the second solution were mixed in 100 ml volumetric flask and let to stand for 24 hours at room temperature. The mixture was diluted to the mark to make a stock solution with turbidity of 400 NTU. 20 ml and 10 ml of the 400 NTU stock solutions were separately diluted in 100 ml volumetric flasks to get 80 NTU and 40 NTU standards, respectively.

Potassium hydrogen phthalate stock solution (500 mg/l): 0.850 g of potassium hydrogen phthalate (KHP), $C_8H_5KO_4$, was dissolved in 800 ml of distilled water in a 1000 ml volumetric flask and diluted up to the mark with distilled water.

Sulphate stock solution (1000 mg/l): 1.479 g of pure sodium sulphate, Na_2SO_4, was dissolved in 800 ml of distilled water in a 1000 ml volumetric flask, and then diluted to the mark with distilled water.

Nitrate stock solution (100 mg/l): 1 g of potassium nitrate, KNO_3, was dried in an oven at 105 ^0C for 24 hours. 0.7218 g of the dry KNO_3 was dissolved in 400 ml of distilled water in a 1000 ml volumetric flask and diluted to the mark with distilled water. The solution was preserved with 2 ml of chloroform, $CHCl_3$.

Nitrite stock solution (250 mg/l): 1.232 g of sodium nitrite, $NaNO_2$, was dissolved in 400 ml of distilled water and then filled to the mark with distilled water.

Ammonia-Nitrogen stock solution (1000 mg/l): 3.819 g of ammonium chloride, NH_4Cl, dried at 100 ^0C for 24 hours was dissolved in 400 ml of ammonia free water in a 1000 ml volumetric flask and made up to the mark with the same water.

Phosphorus stock solution (50 mg/l): 0.2192 g of di-ammonium hydrogen phosphate, $(NH_4)_2HPO_4$, was dissolved in 400 ml of distilled water and diluted to the mark.

Fluoride stock solution (100 mg/l): 0.221 g of anhydrous sodium fluoride, NaF, was dissolved in about 400 ml of distilled water and then diluted to 1000 ml mark.

Total hardness buffer: 16.9 g of NH_4Cl was dissolved in 163 ml conc. NH_4OH. 1.25 g of magnesium salt of EDTA was added to the solution and diluted to 250 ml.

Eriochrome Black T Indicator: 0.5 g of Eriochrome Black T and 100 g of NaCl were mixed together and stored in a tightly stoppered bottle.

0.02 N EDTA: 3.723 g of analytical grade reagent of disodium ethylenediaminetetraacetate dihydrate, $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$, was dissolved in about 400 ml of distilled water in a one litre volumetric flask and diluted to the mark with distilled water.

Chromosulphuric acid (digestion solution): 10.2 g of potassium dichromate, $K_2Cr_2O_7$, (previously dried at 103 ^{0}C for 2 hours), 167 ml of conc. sulphuric acid, H_2SO_4, and 33.3 g of mercury sulphate, $HgSO_4$, were added to 500 ml of distilled water. The mixture was cooled and diluted to the mark with distilled water in 1000 ml volumetric flask.

Silver sulphate catalyst solution: 5.5 g of silver sulphate, Ag_2SO_4, crystals were weighed accurately and added to 500 ml of concentrated sulphuric acid carefully. The mixture was allowed to stand for 24 hours to enable the, Ag_2SO_4, crystals to dissolve completely.

Sulphate buffer: 75 g of sodium chloride, NaCl, was added into 300 ml distilled water and stirred. 30 ml of conc. HCl, 100 ml of Isopropyl alcohol, C_3H_8O, and 50 ml of glycerol, $C_3H_8O_3$ were added to the solution. Then stirred to form a homogenous solution and stored it in a brown bottle.

Nitrate buffer: 528g of ammonium sulphate, $(NH_4)_2SO_4$, was dissolved in 800 ml of distilled water in a one litre volumetric flask and made to the mark.

Ammonia free water: 500 ml of distilled water was redistilled in a Pyrex apparatus from a solution containing 1 g of potassium permanganate, $KMnO_4$, and 1 g of anhydrous sodium carbonate, Na_2CO_3. The first 100 ml of the distillate was discarded and about 300 ml was then collected.

Nessler Reagent: 100 g of mercuric iodide, HgI, and 70g of potassium iodide, KI, were dissolved in 100 ml of ammonia free water. The mixture was added to a cooled solution of 160 g NaOH in 500 ml of ammonia free water and diluted up to the 1000 ml mark with the same water. The solution was stored in a coloured bottle and the precipitates formed allowed to settle for two days before using the yellow supernatant.

Molybdivanadate solution: 0.2197 g ammonium metavanadate, NH_4VO_3, was dissolved in 400 ml of 50% HNO_3. 50 g of ammonium molybdate, $(NH_4)_2MoO_4$, was dissolved in 400 ml distilled water. The two solutions were mixed and diluted to one litre with distilled water.

Potassium chromate indicator: 50 g of potassium chromate, K_2CrO_4, was dissolved in 400 ml of distilled water. Silver nitrate, $AgNO_3$, solution was added until a definite red precipitate was formed. The solution was allowed to stand for 12 hours, filtered and then diluted to one litre mark with distilled water.

Standard 0.0141 N silver nitrate: 2.395 g of silver nitrate, $AgNO_3$, was dissolved in 400 ml of distilled water and diluted to 1000 ml mark. The solution was stored in dark brown bottle.

Standard 0.0141 N sodium chloride: 0.824 g of NaCl dried at 140 ^0C for 24 hours was dissolved in 400 ml of distilled water and then diluted to 1000 ml mark.

Fluoride buffer (TISAB): About 500 ml of distilled water was placed in a one litre beaker. 57 ml of glacial acetic acid, CH_3COOH, 58 g of sodium chloride and 4.0 g of 1, 2-cyclohexanediaminetetraacetic acid[1] (CDTA), $C_{14}H_{22}N_2O_8$, were added and stirred to dissolve. (CDTA complexes with polyvalent cations like Si^{4+}, $Al^{3+}$and Fe^{3+}, which otherwise would complex F^- and change its concentration). The beaker was transferred to a cool water bath and about 125 ml of 6 N sodium hydroxide added until the pH was between 5.3 and 5.5. The contents of the beaker were then transferred to a one litre volumetric flask and filled to the mark.

3.8 Reliability and Quality Control

In order to raise the validity of the research findings, the three materials namely water, sediments and the rocks were sampled and analysed from the study area. Sampling was done during the dry and rainy seasons in September and November 2012, respectively. Ten samples of each material were collected and analysed per visit. This helped to check the reproducibility of the work. To achieve high level of reliability, element analysis was done using AAS and XRF techniques in order to compare the results. Pure standard reference materials were subjected to the same procedure as the samples and analysed alongside them for the verification of the analytical method. The certified reference materials (CRMs) were traceable from the National Institute of Standards and Technology (NIST), Canada Centre for Mineral and Energy Technology and others from the Academy of Sciences Institute for Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) in Russia. The CRMs were procured by the Mines and Geology Department.

Calibration verification was done periodically during each run for quality control. This was done by analysing a midpoint calibration standard and calibration blank at the beginning and the middle of sample run or adding a known amount of the metal of interest and re-analysed it to confirm the percentage recovery. Recovery of added metal between 85% and 115% was accepted.

3.9 Water Analysis

The following water quality parameters were analysed.

3.9.1 Temperature

Temperature was recorded during the sampling of water using a mercury thermometer.

3.9.2 pH

The pH meter was calibrated using buffers pH 4.0 and pH 7.0. About 50 ml of each sample were measured and put in a beaker. The pH electrode was inserted into the sample and the stable pH value recorded. The pH was determined in situ.

3.9.3 Electrical Conductivity (EC)

The conductivity meter was calibrated using standard 0.01 N KCI solution which has conductivity of 1413 μS/cm at 25 $^{\circ}$C. The equipment electrode was rinsed with distilled water and then placed in 50 ml of the sample in a beaker; conductivity value was recorded in micro-Siemens per centimetre (μS/cm). The test was carried out in situ.

3.9.4 Colour

A 50 ml sample was measured and transferred into a special lovibond comparator test tube and put in the lovibond comparator. The colour of the sample was matched against a platinum-cobalt scale colour disc and recorded in true colour units (TCU).

3.9.5 Turbidity

The turbidity meter was set at zero using distilled water and then standardised using 80 NTU and 40 NTU standards. The sample was poured in a cuvette and the meter reading recorded.

3.9.6 Total Alkalinity

The pH meter was calibrated using the buffers pH 4.0 and pH 7.0. Exactly 50 ml of each sample were measured and put in a beaker. The pH electrode was inserted and the stable pH value recorded. The sample was titrated with 0.02 N H_2SO_4 using a burette until the pH reached 4.5.

Total alkalinity in mg $CaCO_3$/l = $\dfrac{\text{Titre x } 0.02 \text{ N} \times 50000}{\text{Volume of sample taken}}$

Bicarbonate alkalinity, HCO_3^- as mg $CaCO_3$/l = $\dfrac{T - 5.0 \times 10^{(pH-10)}}{1 + 0.94 \times 10^{(pH-10)}}$

Where, T = total alkalinity in mg $CaCO_3$/l

Carbonate alkalinity, CO_3^{2-} as mg $CaCO_3$/l = $0.94 \times B \times 10^{(pH-10)}$

Where B = bicarbonate alkalinity in mg $CaCO_3$/l

3.9.7 Free Carbon Dioxide

A 50 ml sample was measured into a beaker and 2-3 drops of phenolphthalein indicator added and stirred. The sample was titrated drop-wise using 0.0227 N NaOH until the solution changed to permanent pink colour.

$$\text{mg } CO_2/l = \frac{\text{Volume of titrant used} \times 0.0227 \text{ N} \times 44000}{\text{Volume of the sample}}$$

3.9.8   Total Hardness (TH)

A 50 ml sample was taken and 1.0 ml of total hardness buffer solution added followed by a spatula of Erio-chrome Black T indicator powder. The sample was titrated slowly with continuous stirring using standard 0.02 N EDTA at pH 10 ($\pm$ 0.1) until the colour changed from red to blue.

$$\text{Total hardness as mg } CaCO_3/l = \frac{\text{Titre} \times 0.02 \text{ N} \times 50000}{\text{Volume of sample}}$$

3.9.9   Total Suspended Solids (TSS)

Filter paper (Whatman no.542) was dried in the oven for 30 minutes at 110 ^{o}C. Then allowed to cool in a desiccator and weighed. 200 ml of the sample were filtered through the filter paper using a vacuum pump. The filter paper and the residue were dried in the oven at 110 ^{o}C for 2 hours then cooled in the desiccator and re-weighed to a constant weight.

$$\text{mg/l TSS} = \frac{(A-B) \times 1000}{\text{Sample volume (ml)}}$$

Where: A = weight (mg) of filter paper + residue

B = weight (mg) of filter paper

3.9.10 Total Dissolved Solids (TDS)

A 250 ml beaker was cleaned and dried in the oven for 30 minutes at 110 ^{o}C then removed from the oven and allowed to cool and weighed. 200 ml of the sample were filtered into the weighed beaker through filter paper (Whatman no. 542) using a Buchner funnel. The sample was evaporated on a hot

plate to near dryness. The residue in the beaker was further dried in the oven at 110 ^{o}C to a constant weight.

mg/l TDS = $\frac{(A-B) \times 1000}{\text{Sample volume (ml)}}$

Where: A= weight (mg) of beaker + residue

B= weight (mg) of beaker

3.9.11 Chemical Oxygen Demand (COD)

A 10 ml portion of each of the standard potassium hydrogen phthalate solutions (20, 50, 100, 200 and 400 mg/l) were transferred in culture tubes, treated with 6 ml of chromosulphuric acid and mixed thoroughly. 14 ml of silver sulphate catalyst solution were added to each of the standards down the side of the culture tubes. The tubes were placed in a block digester at 150 ^{0}C for 2 hours, and then cooled allowing any precipitates to settle. The absorbance of the standards was measured at 600 nm using UV/VIS spectrophotometer (Model T 80+). 10 ml of the samples were similarly treated like the standards and COD values determined from the calibration curve. A blank solution was treated and analysed as the samples and used for background correction.

3.9.12 Total Coliforms and *E. coli*

The samples were analysed by multi-well procedure using quanti- trays with 51 wells. The samples were poured into quanti-trays containing colilert ONPG and MUG nutrient indicators. The sample filled quanti-tray was placed into the quanti-tray rubber and insert of the quanti-tray sealer with the well of the quanti-tray facing down, then sealed and incubated at 37 ^{o}C for 24 hours. After 24 hours the number of yellow wells (positive wells) was counted and the total coliform results read from the table for MPN of coliforms (Appendix III). With the help of UV 365 nm machine, the number of *E. coli* per 100 ml of water was determined by counting the blue wells and reading the results from the MPN table.

3.9.13 Sulphate

The turbidity meter was calibrated using 80 NTU and 40 NTU standards. Sulphate, SO_4^{2-}, standards were prepared at an increment of 5.0 mg/l up to 40 mg/l in 100 ml volumetric flask. The solutions were transferred into 250 ml Erlenmeyer flask and 2.5 ml of sulphate buffer solution added to each and stirred. A spatula of $BaCl_2.2H_2O$ crystals of size 20 to 30 mesh was added to each solution while stirring at constant speed for 1 minute. Turbidity of the standards was recorded and the calibration curve was obtained. The water samples and a blank were treated like the standards, turbidity values measured and the concentrations of sulphate present were read from the calibration graph.

3.9.14 Nitrate

A series of nitrate, NO_3^-, standards ranging from 1-5 mg/l were prepared in 50 ml volumetric flasks and 1ml of nitrate buffer added to each. The nitrate electrode connected to the ion meter was inserted in each standard and mV readings recorded. A plot of mV readings verses concentration produced calibration curve. 50 ml of the samples and a blank were measured and put in beakers. 1ml of buffer was added to each sample and the mV readings recorded from the ion meter. The concentration of samples was obtained from the graph in mg/l NO_3^-.

3.9.15 Nitrite

Nitrite standards of 0.01, 0.03, 0.05 and 0.1 mg/l were prepared in 50 ml volumetric flasks. 1ml of sulphanilic acid was added to each standard and let to stand for 2 minutes. 1 ml of N-(1-Naphthyl)-ethylenediamine dihydrochloride (NED), $C_{12}H_{14}N_2.2HCl$, was added and let to stand for 10 minutes. Absorbance of the standards was measured at 540 nm using UV/VIS spectrophotometer and the calibration curve was obtained. 50 ml of the samples and a blank were treated like the standards and their concentration determined from the calibration curve.

3.9.16 Ammonia – Nitrogen

A series of ammonia-nitrogen, NH_3-N, standards ranging between 0.1-5 mg/l were prepared in 50ml volumetric flasks and 1ml of Nessler reagent added to each. The solutions were mixed thoroughly

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and then allowed to stand for 10 minutes. Absorbance of the standard solutions was measured at 420 nm using UV/VIS spectrophotometer. 50 ml of the samples and a blank were treated like the standards and the concentration obtained from the calibration curve.

3.9.17 Total phosphorus

To 50 ml of each sample, 1 ml of concentrated H_2SO_4 and 5 ml of concentrated HNO_3 were added and digested on a hot plate to a volume of about 10 ml. Digestion was continued until the solutions became colourless. The solutions were cooled and about 20 ml of distilled water and one drop phenolphthalein indicator solution were added. 1 N NaOH solution was added gradually until a faint pink colour was formed. The solutions were transferred to 100 ml volumetric flasks and filled to the mark with distilled water. 10 ml of digested samples were pipetted into 100 ml beakers. 10 ml of molybdivanadate solution and 25 ml of distilled water were added to each solution, and then allowed to stand for 5 minutes. A series of di-ammonium hydrogen phosphate, $(NH_4)_2HPO_4$, standards of 1-10 mg/l and a blank were treated likewise. Absorbance of the standards was measured at 430 nm using UV/VIS spectrophotometer and the calibration curve obtained. Concentration of the samples was determined from the calibration curve.

3.9.18 Chloride

To 50ml of each sample, 2 ml of concentrated HNO_3 were added and boiled for about 10 minutes. The solution was neutralised with solid $CaCO_3$ until effervescence stopped. The solution was filtered and topped to 100 ml with distilled water. A blank sample of distilled water was treated likewise. 1 ml of K_2CrO_4 indicator was added to 25 ml of each sample and the blank followed by titration with standard 0.0141 N $AgNO_3$ (The $AgNO_3$ was first standardised against 0.0141 N sodium chloride before titration).

$$\text{mg/l Cl} = \frac{(A\text{-}B) \times N \times 35450}{\text{Volume of sample}}$$

Where:

        A- Volume of titre used for the sample

        B- Volume of the titre used for the blank

        N- Normality of silver nitrate

3.9.19 Fluoride

Fluoride ion meter was calibrated using 25 ml of NaF standards of 1mg/l and 10 mg/l each added with 25 ml of fluoride buffer. The difference between meter readings of the two standards was kept within the acceptable range of 54-60 before the samples were tested. 25 ml of each sample were mixed with 25 ml of fluoride buffer and the ion meter reading recorded.

3.9.20 Metals

Digested water samples were analysed for various metals using AAS after calibrating the instrument with the respective standards. Another set of water samples were analysed for heavy elements using XRF instrument.

3.10 Rock and Sediments Analysis

Digested rock and sediment samples were analysed to determine the percentage of the major oxides (SiO_2, Na_2O, K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, MnO and TiO_2), using AAS method after calibrating the instrument with the respective standards. In another round of analysis, 5 g of each sample for both rocks and sediments were transferred into the sample holder and scanned with EDXRF using a current of 2 µA and a potential of 25 keV to obtain the percentage of the major oxides.

3.11 Data Analysis and Interpretation

The results were analysed using statistical package for social sciences (SPSS) and MS Excel programs. Standard deviation was determined among the ten samples. The *F* test (95% confidence level) was done to establish if the variance of the dry and rainy seasons were statistically different. The conclusion made was based on deductive and inductive interpretation of the analysed data.

## RESULTS AND DISCUSSION

4.1 Introduction

The sampling of water, rocks and sediments was done during the hot and wet seasons in September and November 2012, respectively. Ten samples or replicates of each material were collected per visit and analysed individually. Statistical analysis of the data generated was carried out using MS Excel and SPSS. The analysed results are contained in the tables below and accompanied by discussions.

4.2 Calibration Curves

The Tables and Figures numbered 4.1 and 4.2 contain results for the analyses of sodium and nitrate standards used and the corresponding calibration curves.

Table 4.1: Sodium Standards.

Standards (mg/l)	Intensity
2	0.092
4	0.187
6	0.281
8	0.371
10	0.463
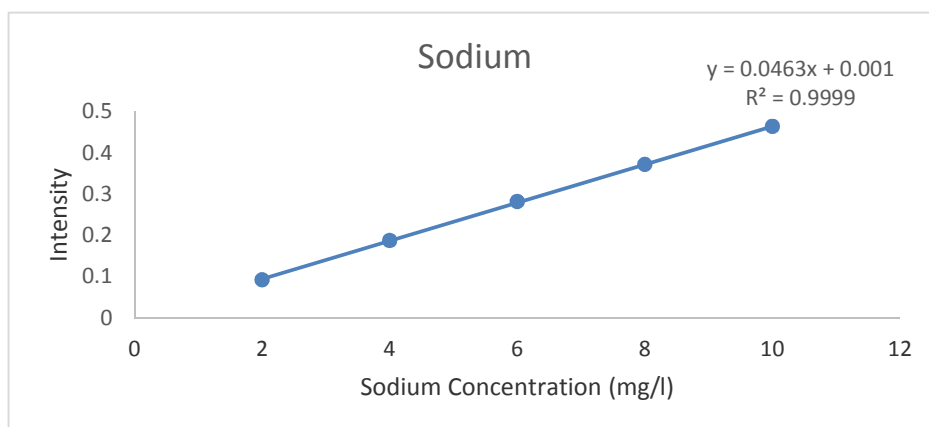
Figure 4.1: Sodium Calibration Curve.

Table 4.2: Nitrate Standards.

Standards (mg/l)	Absorbance
1	0.298
2	0.671
3	0.93
4	1.273
5	1.581
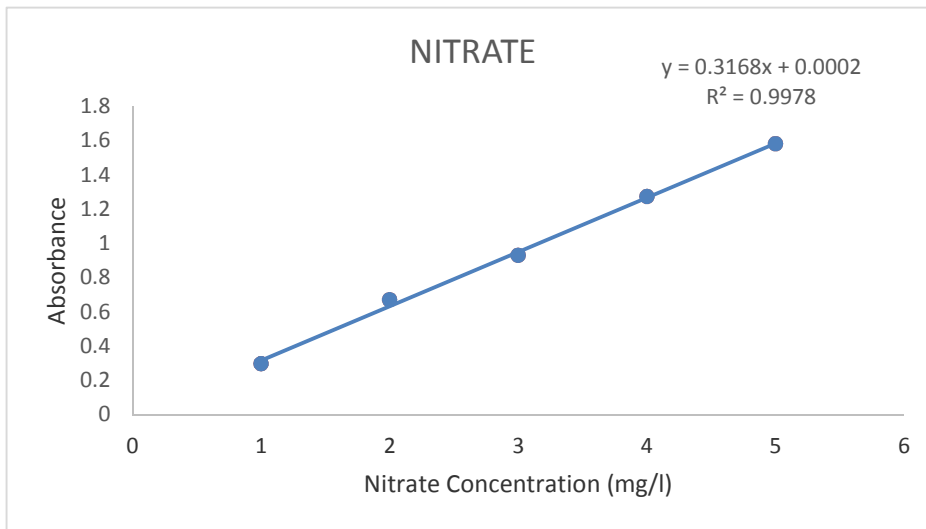
Figure 4.2: Nitrate Calibration Curve.

Good linear curves were obtained in Figures 4.1 and 4.2 in accordance with the Beer-Lambert's law. This is depicted by the high R^2 (> 0.99) values and was therefore adopted in the analyses of the samples. Similar calibration curves are given in appendix V.

4.3 Mineral Water Analysis

The results of water quality analysis for the dry and rainy seasons are contained in Tables 4.17 to 4.22. The *F* test at 95% confidence level was used to determine if the variances for the two seasons were statistically different. Where, the variance is the square of the standard deviation, s^2.

$F = \dfrac{s^2_1}{s^2_2}$ (The variances are arranged so that the F value is > 1, where $s^2_1 > s^2_2$).

Table 4.17: Physical Analysis of Water.

Parameters	Units	Dry Season*	Rainy Season**	*F* Values***
pH	pH scale	7.5±0.1	7.5±0.1	1.0
Temperature	^{o}C	20.8 ± 0.2	19.8±0.3	2.2
Colour	TCU (mg Pt/l)	<5	<5	-
Turbidity	NTU	10.0 ± 0.5	11.1±0.5	1.0
Conductivity (25 ^{o}C)	µS/cm	6,014 ± 41.0	5,986±40.0	1.0
Total Alkalinity	mg/l CaCO$_3$	5,528 ±67.0	5,649±64.0	1.1
Total Hardness	mg/l CaCO$_3$	407.4 ± 1.6	391.3±1.4	1.3
TSS	mg/l	22.5 ± 0.4	40.3±0.5	1.6
TDS	mg/l	5,056.7±51.2	4,923.1±40.7	1.6
COD	mg/l	14.8±0.8	15.2±0.5	2.6

*September 2012, **November 2012. ***The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference between the variance of the dry and rainy seasons.

From the results in Table 4.17, the pH was slightly alkaline at 7.5±0.1 which was mainly contributed by HCO_3^- ion. The temperature was 20.8±0.2 ^{o}C and 19.8±0.3 ^{o}C which was very close to the room temperature (21.5 ^{o}C and 20.5 ^{o}C, respectively) of the surrounding environment. The colour was <5 TCU and hence not objectionable. The results reflected high conductivity at 6,014±41 mg/l and 5,986±40 mg/l, for dry and wet seasons respectively, which can be attributed to the large TDS value. Total alkalinity was very high at 5,528±67 mg/l and 5,649±64 mg/l due to the great amounts of HCO_3^- , dissolved CO_2 and CO_3^{2-}. Total hardness was 407.4±1.6 mg/l and 391.3±1.4 mg/l which indicated the presence of significant levels of calcium and magnesium in the water. The amount of COD was14.8±0.8 mg/l and 15.2±0.5 mg/l hence the organic matter in the water was minimal. The TDS was significantly high at 5,056.7±51.2 mg/l and 4,923.1±40.7 mg/l as a result of the large mineral content. The TSS was 22.5±0.4 mg/l and 40.3±0.5 mg/l, hence the water should be filtered before use. The conductivity and TDS values were lower in the wet season due to increase in the

volume of water. The TSS and COD were higher in the wet season because of the water runoff from

the surrounding area.

Table 4.18: Chemical Analysis of Water in mg/l.

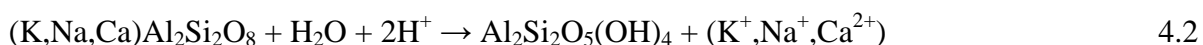| Parameters	Dry Season*	Rainy Season**	*F* Values****
Free carbon dioxide	931.3±2.0	1,015.0±2.9	2.1
Carbonate	16.7±0.2	17.1±0.2	1.0
Hydrogen Carbonate	5,511.4±67.2	5,632.6±64.2	1.0
Sulphate	492.5±17.7	420.1±25.3	1.4
Nitrate	2.8±0.3	2.0±0.2	2.2
Nitrite	0.0055±0.0	0.0037±0.0	-
Ammonia-Nitrogen	Not detected	Not detected	-
Phosphorus	115.68±1.5	96.42±1.7	1.3
Chloride	950.9±13.1	853.6±10.0	1.7
Fluoride	0.73±0.1	0.67±0.1	1.0
Bromide	0.97±0.1	0.59±0.1	1.0
Sodium***	1,043±35.0	954.4±20.3	3.0
Potassium***	121.6±2.1	116.7±2.2	1.1
Calcium***	124.2±1.8	94.2±1.6	1.1
Magnesium***	73.6±0.5	70.4±0.3	2.8
Iron***	0.82±0.1	0.49±0.1	1.5
Manganese***	0.097±0.0	0.075±0.0	-
Lead***	<0.05	<0.05	-
Barium***	0.677±0.1	0.537±0.1	1.0
Strontium***	1.469±0.1	1.304±0.1	1.0
Cadmium***	<0.002	<0.002	-
Copper***	<0.01	<0.01	-
Aluminium***	0.290±0.0	0.205±0.0	-
Chromium***	0.056±0.0	0.055±0.0	-
Zinc***	<0.005	<0.005	-

*September 2012, **November 2012, < Below AAS detection limit, ***AAS Analysis. ****The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference between the variance of the dry and rainy seasons.

According to Table 4.18, the amount of free carbon dioxide was very high at 931.3 ± 2.0 mg/l and $1,015.0\pm2.9$ mg/l. This is equivalent to 531 cm^3 and 554 cm^3 of CO_2/l, respectively, at room temperature (Molar Gas Volume = 24 dm^3 at 25 ^{o}C). It shows the likelihood of existence of pure CO_2 coming from underground through a volcanic fault which gets mixed with water to form weak carbonic, H_2CO_3. The amount of CO_2 was higher during the rainy season because solubility of gases in water is more at low temperature. The level of HCO_3^- was very high at $5,511.4\pm67.2$ mg/l and $5,632.6$ mg/l mainly due to the dissolved CO_2. The amount of CO_3^{2-} was 16.7 ± 0.2 mg/l and 17.1 ± 0.2 mg/l which was not significant. Chloride level was high at 950.9 ± 13.1 mg/l and 853.6 ± 10.0 mg/l followed by sulphate at 492.5 ± 17.7 mg/l and 420.1 ± 25.3 mg/l, total phosphorous at 115.68 ± 1.5 mg/l and 96.42 ± 1.7 mg/l, in dry and rainy seasons, respectively. Nitrate 2.8 ± 0.3 mg/l and 2.0 ± 0.2 mg/l, bromide 0.97 ± 0.05 mg/l and 0.59 ± 0.02 mg/l, fluoride 0.73 ± 0.03 mg/l and 0.67 ± 0.08 mg/l, nitrite 0.0055 ± 0.0 mg/l and 0.0037 ± 0.0, were not significant.

Among the cations, sodium was the highest at $1,043\pm35.0$ mg/l and 954.4 ± 20.3 mg/l followed by potassium 121.6 ± 2.1 mg/l and 116.7 ± 2.2 mg/l, calcium 124.2 ± 1.8 mg/l and 94.2 ± 1.6 mg/l, magnesium 73.6 ± 0.6 mg/l and 70.4 ± 0.3 mg/l. Levels of strontium 1.469 ± 0.1 mg/l and 1.304 ± 0.1 mg/l, iron 0.82 ± 0.1 mg/l and 0.49 ± 0.1 mg/l, barium 0.667 ± 0.1 mg/l and 0.537 ± 0.1 mg/l, aluminium 0.290 ± 0.0 mg/l and 0.205 ± 0.0 mg/l, manganese 0.097 ± 0.0 mg/l and 0.075 ± 0.0 mg/l, chromium 0.056 ± 0.0 mg/l and 0.055 ± 0.0 mg/l, were generally low. Lead, Cadmium, Copper and Zinc were below the detection limits of the AAS instrument used. The mineral content was lower during the rainy season due to the increase in the volume of water.

Most of these minerals originated from the salts in the surrounding rocks. Dissolution of carbonate and feldspar rocks could be the main source of Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^- in the water (Chan Ho, *et al*, 2005).

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad\qquad 4.1$$

$$(K,Na,Ca)Al_2Si_2O_8 + H_2O + 2H^+ \rightarrow Al_2Si_2O_5(OH)_4 + (K^+,Na^+,Ca^{2+}) \qquad 4.2$$

These results indicate why Rurii spring discharges mineral water which can be packed and sold as a healthy drink (soda water). The water has therapeutic value such as neutralization of excess acid in the stomach due to its high level of alkalinity and also acts as an alternative source of calcium in the body which is essential for bone and teeth formation. About two to three litres of CO_2 per litre can be extracted from the water for use in carbonated beverages, refrigeration, solvents and fire extinguishers. More CO_2 can be mined by drilling the area near the spring. The various minerals in the rocks can be utilised in the production of salt licks for livestock, baking powder, cement, fertilizers, laboratory chemicals and pharmaceutical products.

Table 4.19: Bacteriological Analysis of Water/100ml.

Parameters	Units	Dry Season*	Rainy Season**
Total Coliforms	MPN	>200	>200
E.coli	MPN	15 ±1	17±1

*September 2012, **November 2012.

The total coliforms and *E.coli* were considerably high as per the results in Table 4.19 because uncontaminated water should not have any coliforms per 100 ml of water sample (Chemuliti, 2009). Therefore, this water was very contaminated with harmful micro-organisms which could have emanated from the livestock and human wastes. This is as a result of the frequent visits to the spring by the local people and their livestock. Consequently, this water needs to be treated or boiled before human consumption.

Table 4.20: XRF Analysis of Water.

Element	Dry season (mg/l)*	Rainy Season(mg/l)**	*F* Values***
Chloride	292.52±26.57	261.87±19.46	1.9
Bromide	0.970±0.05	0.587±0.03	2.8
Potassium	124.140±0.12	120.709±0.09	1.8
Calcium	96.237±1.50	59.072±1.00	2.2
Iron	0.502±0.08	0.447±0.07	1.3
Manganese	0.178±0.02	0.087±0.02	1.0
Strontium	1.254±0.01	0.920±0.01	1.0
Copper	<0.001	<0.001	-
Zinc	<0.001	<0.001	-
Rubidium	0.069±0.00	0.063±0.00	-

*September 2012, **November 2012. ***The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference between the variance of the dry and rainy seasons.

According to the results in Table 4.20, the water contained the following metals: potassium 124.140±0.12 mg/l and 120.709±0.09 mg/l, calcium 96.237±1.50 mg/l and 59.072±1.00 mg/l, iron 0.502±0.08 mg/l and 0.447±0.07 mg/l, manganese 0.178±0.07 mg/l and 0.087±0.02 mg/l, strontium 1.254±0.01 mg/l and 0.920±0.01 mg/l, copper <0.001 mg/l, zinc <0.001 mg/l, rubidium 0.069±0.00 mg/l and 0.063±0.00 mg/l. The non-metals present were chloride 292.52±26.57 mg/l and 261.87±19.46 mg/l, and bromide 0.970±0.05 mg/l and 0.587±0.02 mg/l, in dry and rainy seasons, respectively. Potassium, calcium and chloride levels were relatively high. The XRF technique was used for a general survey of most elements, except for lighter elements like sodium and magnesium. The purpose of using XRF technique was to identify the presence of any heavy metals in the water which were very minimal.

Table 4.21: Comparison between AAS and XRF Elemental Analyses of Water.

Element	AAS Results (mg/l)		XRF Results (mg/l)	
	Dry season	**Rainy season**	**Dry season**	**Rainy season**
Chloride	-	-	292.52±26.57	261.87±19.46
Bromide	-	-	0.970±0.05	0.587±0.02
Sodium	1,043±35.0	954.4±20.3	-	-
Potassium	121.6 ± 2.1	116.7±2.2	124.140±0.12	120.709±0.09
Calcium	124.2 +1.8	94.2±1.6	96.237±1.50	59.072±1.00
Magnesium	73.6±0.6	70.4±0.3	-	-
Iron	0.82±0.1	0.49±0.1	0.502±0.08	0.447±0.07
Manganese	0.097+0.0	0.075±0.0	0.178±0.07	0.087±0.02
Lead	<0.05	<0.5	<0.001	<0.001
Barium	0.677±0.1	0.537±0.1	<0.001	<0.001
Strontium	1.469±0.1	1.304±0.1	1.254±0.01	0.920±0.01
Cadmium	<0.002	<0.002	<0.001	<0.001
Copper	<0.01	<0.01	<0.001	<0.001
Aluminium	0.290±0.0	0.205±0.0	<0.001	<0.001
Chromium	0.056+0.0	0.055±0.0	<0.001	<0.001
Zinc	<0.005	<0.005	<0.001	<0.001
Rubidium	-	-	0.069±0.00	0.063±0.00

- Not analysed, < Less than detection limit

From Table 4.21, potassium, Calcium, Iron, Manganese and Strontium were detected by both AAS and XRF techniques. There was some degree of agreement of results for potassium, iron and strontium between the two techniques. In both analyses the levels of Pb, Cd, Cu and Zn were equally low.

Table 4.22: Rurii Water Quality Parameters compared to WHO and KEBS maximum limits.

Parameters	Units	Dry season	Rainy season	WHO	KEBS
pH	pH scale	7.5±0.1	7.5±0.1	6.5 – 8.5	6.5 – 8.5
Temperature	^{o}C	20.8 ± 0.2	19.8±0.3	-	-
Colour	TCU	<5	<5	15	15
Turbidity	NTU	10.0 ± 0.5	11.1±0.5	10	10
Conductivity (25 ^{o}C)	μS/cm	6,014 ± 41.0	5,986±40.0	2500	-
Free CO_2	mg/l	931.3 ± 2.0	1,015±1.9	-	-
Total Alkalinity*	$mgCaCO_3$	5,528 ±67.0	5,649±64.0	600	600
Total Hardness	$mgCaCO_3$	407.4 ± 1.6	391.3±1.4	600	500
TSS	mg/l	22.5 ± 0.4	40.3±0.5	-	-
TDS*	mg/l	5,056.7±51.2	4,923.1±40.7	2000	1500
COD	mg/l	14.8 ±0.8	15.2±0.5	-	-
Total coliforms*	MPN	>200	>200	None/100ml	None/100ml
*E. Coli**	MPN	15±1	17±1	None/100ml	None/100ml
Carbonate	mg/l	16.7±0.2	17.1±0.2	-	-
Bicarbonate	mg/l	5,511.4±67.2	5,632.6±64.2	-	-
Sulphate*	mg/l	492.5 2±17.7	420.1±25.3	400	400
Nitrate	mg/l	2.8±0.3	2.0±0.2	10	10
Nitrite	mg/l	0.0055± 0.0	0.0037±0.0	0.1	0.1
Ammonia-Nitrogen	mg/l	Not detected	Not detected	Max 0.5	0.5
Phosphorous	mg/l	115.68 ±1.5	96.42±1.7	-	-
Chloride*	mg/l	950.9 ±13.1	853.6±10.0	250	250
Fluoride	mg/l	0.73 ±0.03	0.67±0.08	1.5	1.5
Bromide	mg/l	0.97± 0.05	0.59±0.02	-	-
Sodium*	mg/l	1,043±35.0	954.4±20.3	200	200
Potassium*	mg/l	121.6 ± 2.1	116.7±2.2	50	50
Calcium	mg/l	124.2 +1.8	94.2±1.6	100	150
Magnesium	mg/l	73.6±0.6	70.4±0.3	100	100
Iron	mg/l	0.82±0.1	0.49±0.1	0.3	1.0
Manganese	mg/l	0.097+0.0	0.075±0.0	0.1	0.1
Lead	mg/l	<0.05	<0.05	0.05	0.05
Barium*	mg/l	0.677±0.1	0.537±0.1	0.05	0.05
Strontium	mg/l	1.469±0.1	1.304±0.1	-	-
Cadmium	mg/l	<0.002	<0.002	0.005	0.005
Copper	mg/l	<0.01	<0.01	0.1	0.1
Aluminium*	mg/l	0.290±0.0	0.205±0.0	0.1	0.1
Chromium	mg/l	0.056+0.0	0.055±0.0	0.05	0.05
Zinc	mg/l	<0.005	<0.005	0.05	0.05

<less than detection limit, - not stated, *substance exceeded WHO and KEBS allowable limits.

The results in Table 4.22 indicates that water pH (7.5±0.1) was within the WHO (2005) and KEBS (2012) pH range (6.5-8.5). The colour (<5 TCU) was acceptable. Turbidity (10.0±0.5 NTU and 11.5±0.5) was slightly above the limits for WHO (10 NTU), therefore, cloudy and required filtration. Conductivity was very high at 6,014±41 µS/cm and 5,986±40 µS/cm as compared to WHO (250 µS/cm). This arose due to the huge mineral content in the water. Thus excessive consumption of the water may affect the osmotic balance of the body and on the other hand provide vital minerals like calcium.

The total alkalinity 5,528±67.0 mg/l and 5,649±64.0 mg/l was rather high than WHO and KEBS standards which is 600 mg/l. This would make the water to neutralize excess acid in the stomach and give therapeutic effect. Total hardness at 407.4±1.6 mg/l and 391.3±1.4 mg/l, was moderately high but had not exceeded the 600 mg/l and 500 mg/l maximum limits for WHO and KEBS, respectively. The water can be a source of calcium to the body but would be unsuitable for washing due to precipitation of soap. Total dissolved solids were 5,056±51.2 mg/l and 4,923.1±40.7 mg/l which was very high compared to 1500 mg/l standard limit. That means the water contained a lot of dissolved salts which was supported by the plenty amounts of sodium, potassium calcium, chlorides, carbonates and hydrogen carbonates.

Total coliforms were excessively high at >200 MPN while *E.coli* number were 15±1 MPN and 17±1 MPN. The Bacteria should be absent per 100 ml of water, according to WHO and KEBS standards. This suggests pollution by human and/or animal waste matter and therefore the water should be treated before drinking it to avert the risk of contracting waterborne diseases like cholera.

The sulphate level at 492.5±17.7 mg/l and 420.1±25.3 mg/l was slightly over the 400 mg/l standard limits. Nitrate and nitrite were below the recommended range. The latter has a maximum standard limit of 0.1 mg/l and the former 10 mg/l. The chloride content was 950.9±13.1 mg/l and 853.6±10.0 mg/l and far beyond the 250 mg/l maximum limit for WHO and KEBS. The combination of the chloride and sodium ions gives the water a characteristic salty taste.

The fluoride level was 0.73±0.03 mg/l and 0.67±0.08 mg/l which was below the recommended limit of 1.5 mg/l. The sodium level was very high at 1,043±35.0 mg/l and 954.4±20.3 mg/l compared to the allowed limit 200 mg/l. It means the surrounding rocks and soil contain a lot of sodium salts which dissolve in the water because sodium compounds are very soluble. Potassium (121.6±2.1 mg/l and 116.7±2.2 mg/l) was still above the 50 mg/l standard limit and again points at potassium containing rocks in the surrounding area. The amount of calcium was 124.2±1.8 mg/l and 94.2±1.6 mg/l which falls between the WHO and KEBS maximum limits of 100 mg/l and 150 mg/l, respectively. Hence the rocks contain substantial amounts of calcium.

Iron (0.82±0.1 mg/l and 0.49±0.1 mg/l) was slightly above 0.3 mg/l WHO standard limits but below 1.0 mg/l KEBS limit. Manganese (0.097±0.0 mg/l and 0.075±0.0 mg/l) was slightly below 0.1 mg/l allowed limits. Barium (0.677±0.1 mg/l, 0.537±0.1 mg/l) and aluminium (0.290±0.0 mg/l, 0.205±0.0 mg/l) were above the WHO (0.05 mg/l) and KEBS (0.1 mg/l) standard limits, respectively. Chromium at 0.056±0.0 mg/l and 0.055±0.0 mg/l was slightly above the maximum limit of 0.05 mg/l. Lead (<0.05 mg/l) and zinc (<0.005 mg/l) were below the detection limit of the instrument and also lower than the standard limits (0.05 mg/l).

4.4 Rocks Analysis

The AAS and XRF techniques were used for the analysis of rocks. The results showing the major oxides found in rocks are represented in Tables 4.23, 4.24 and 4.25.

Table 4.23: AAS Analysis of the Major Oxides[a] in the Rocks.

Oxides	Dry Season (%)*	Rainy Season (%)**	*F* Values***
SiO_2	38.773±2.818	36.344±1.613	3.052
Al_2O_3	13.534±1.009	13.074±1.518	2.263
CaO	9.264±1.019	10.360±1.241	1.483
MgO	3.261±0.265	3.084±0.228	1.350
Na_2O	4.203±0.640	4.593±0.558	1.315
K_2O	1.770±0.495	1.683±0.305	2.633
TiO_2	2.355±0.381	2.461±0.249	2.341
MnO	0.340±0.052	0.360±0.040	1.690
Fe_2O_3	18.420±0.970	19.08±1.100	1.286
LOI	6.380±2.190	7.042±1.866	1.377
Total (%)	98.3±9.837	98.081±8.724	1.271

*September 2012, **November 2012. ***The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference between the variance of the dry and rainy seasons.

[a]The certified (standard) reference materials used for AAS calibration were already computed in oxide form, hence it was possible to obtain directly the percentage oxide in the samples.
Example % Al = $\frac{13.534\% \ Al_2O_3 \times 27 \ g/mol \ Al \times 2 \ mol \ Al}{102 \ g/mol \ Al_2O_3 \times 1 \ mol \ Al_2O_3}$

The results in Table 4.23 showed that all the expected major oxides were present in the rocks. The mean percentages obtained were in the following order: SiO_2 38.773±2.218% and 36.344±1.613%, Fe_2O_3 18.420±0.970% and 19.080±1.100%, Al_2O_3 13.534±1.009% and 13.074±1.518%, CaO 9.264±1.019% and 10.360±1.241, Na_2O 4.203±0.640% and 4.593±0.558%, MgO 3.261±0.265% and 3.084±0.228%, TiO_2 2.355±00.381% and 2.461±0.249%, K_2O 1.770±0.495% and 1.683±0.305%, and MnO 0.340±0.052% and 0.360±0.040% in dry and rainy seasons, respectively. The loss on ignition (LOI) was 6.380±2.190% and 7.042±1.866%. The total percentage was slightly below 100 since there may be other minor metal oxides in the rocks that were not accounted for. There was no

much difference between the results for the hot and wet seasons. The findings did not deviate very much from what was expected especially for silicon, aluminium and iron which are the most abundant in the earth's crust with the following percentages, 28%, 8% and 4.6% in that order. However, it can be noted from the analysis, that the percentage of Fe_2O_3 was more than that of Al_2O_3. Hence, iron minerals are more prevalent in this area compared to aluminium minerals. TiO_2 in the rocks was also quite high; however, titanium species are usually insoluble in water. This accounts for the absence of titanium metal in water. The average abundance of manganese in the earth's crust is only 1060 mg/l and that is why MnO is quite low. The percentage of Na_2O, K_2O, CaO and MgO were reasonably high and this could explain why these metals were present in the spring water in large amounts especially sodium which is very soluble (Table 4.18). The loss on ignition (LOI) was significant showing the presence volatile substances in the rocks.

Table 4.24: XRF Results of the Major Oxides in the Rocks.

Oxide	Dry Season (%)*	Rainy Season (%) **	*F* Values***
SiO_2	39.00±2.60	38.40±2.30	1.28
Al_2O_3	21.80±2.20	21.41±1.93	1.30
CaO	11.043±0.85	10.982±0.90	1.12
K_2O	1.83±0.39	1.747±0.36	1.17
TiO_2	1.95±0.22	1.94±0.19	1.34
MnO	0.452±0.05	0.417±0.06	1.44
Fe_2O_3	23.10±2.70	22.94±2.04	1.75
Total	99.114±9.01	97.897±7.78	1.34

*September 2012, **November 2012. ***The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference between the variance of the dry and rainy seasons.

As in shown the previous Table 4.23, the results in Table 4.24 indicate that SiO_2 had the highest percentage at 39.00±2.60% and 38.40±2.30% followed by Fe_2O_3 23.10±2.70% and 22.94±2.04%, Al_2O_3 21.80±2.20% and 21.41±1.93%, CaO 11.043±0.85% and 10.982±0.90%, TiO_2 1.95±0.22% and 1.94±0.19%, K_2O 1.83±0.39% and 1.747±0.36%, and MnO 0.452±0.05% and 0.417±0.06%, in dry and rainy seasons, respectively. XRF spectrometer does not analyse precisely the light elements such as sodium and magnesium. That is why the percentage of Na_2O and MgO were missing. This could also help to explain the reason why there was an increase in the percentage of Al_2O_3, Fe_2O_3 and CaO due to interference. There is no much difference between the results for the dry and rainy seasons.

Table 4.25: Comparison between AAS and XRF Analyses of Rocks.

Oxides (%)	AAS Results		XRF Results		*F* Values*	
	Dry season	Rainy season	Dry season	Rainy season	Dry season	Rainy season
SiO_2	38.773±2.818	36.340±1.613	39.00±2.60	38.40±2.30	1.17	2.03
Al_2O_3	13.534±1.009	13.074±1.518	21.80±2.20	21.41±1.93	4.75	1.62
CaO	9.264±1.019	10.360±1.241	11.043±0.85	10.982±0.90	1.44	1.78
MgO	3.261±0.265	3.084±0.228	-	-	-	-
Na_2O	4.203±0.640	4.593±0.558	-	-	-	-
K_2O	1.770±0.495	1.683±0.305	1.83±0.39	1.747±0.36	1.61	1.39
TiO_2	2.355±0.381	2.461±0.249	1.95±0.22	1.94±0.19	3.00	1.72
MnO	0.340±0.052	0.360±0.040	0.452±0.05	0.417±0.06	1.08	2.25
Fe_2O_3	18.420±0.970	19.080±1.100	23.10±2.70	22.94±2.04	7.75	3.44
LOI	6.38±2.190	7.042±1.866	-	-	-	-
Total (%)	98.3±9.837	98.181±8.724	99.114±9.07	97.897±7.78	1.18	1.26

-Not analysed. *The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference (except for Al_2O_3 and Fe_2O_3) in the precision of both AAS and XRF analyses.

The comparison between the results for AAS and XRF analysis of rocks are shown in Table 4.25. These AAS and XRF analyses were largely in agreement as depicted by the results, looking at the order of percentages from the highest (SiO_2) to the lowest (MnO). However, Al_2O_3 is greatly higher for XRF possibly due to interference by sodium and magnesium. In other words, XRF was used to validate the results obtained by AAS.

4.5 Sediments Analysis

Tables 4.26, 4.27 and 4.28 give the major oxides in the sediments. The analysis was done using AAS and XRF techniques.

Table 4.26: AAS Results for the Major Oxides[a] in the Sediments.

Oxides	Dry Season (%)*	Rainy Season (%)**	*F* Values***
SiO_2	57.515±2.116	57.165±2.410	1.297
Al_2O_3	12.537±1.806	11.804±1.675	1.162
CaO	1.598±0.344	1.742±0.462	1.804
MgO	0.671±0.107	0.497±0.093	1.324
Na_2O	2.659±0.080	2.349±0.102	1.626
K_2O	2.229±0.454	2.185±0.317	2.051
TiO_2	1.346±0.248	1.008±0.294	1.405
MnO	0.193±0.024	0.121±0.026	1.174
Fe_2O_3	11.331±0.762	11.836±1.214	2.538
LOI	8.947±2.097	8.707±1.746	1.442
Total (%)	99.026±8.038	97.414±8.340	1.077

*September 2012, **November 2012. ***The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference between the variance of the dry and rainy seasons.

[a]The certified (standard) reference materials used for AAS calibration were already computed in oxide form, hence it was possible to obtain directly the percentage oxide in the samples.

The average percentage of oxides in Table 4.26 were in the following order SiO_2 57.515±2.116%
and 57.165±2.410%, Al_2O_3 12.537±1.806%% and 11.804±1.675%, Fe_2O_3 11.331±0.762% and
11.836±1.214%, Na_2O 2.659±0.080% and 2.349±0.102%, K_2O 2.229±0.454% and 2.185±0.317%,
CaO 1.598±0.344% and 1.742±0.462%, TiO_2 1.346±0.248% and 1.008±0.294%, MgO
0.671±0.107% and 0.497±0.093%, and MnO 0.193±0.024% and 0.121±0.026% .The loss on ignition
(LOI) was 8.947±2.097% and 8.707±1.746% in dry and rainy seasons, respectively. The total
percentage was slightly below 100 since there may be other minor metal oxides in the rocks that
were left out in the analysis. As earlier mentioned, the percentage of SiO_2, Al_2O_3 and Fe_2O_3 are
usually expected to be high because of the higher abundance of Si, Al, and Fe in the earth's crust.
There were fairly large amounts of Na_2O, K_2O and CaO which accounts for the presence these
metals in the mineral water. There was no large variation between the results in hot and wet seasons.

Table 4.27: XRF Analysis of the Major Oxides in the Sediments.

Oxides	Dry Season (%)*	Rainy Season (%)**	*F* Values***
SiO_2	56.100±2.80	56.320±2.42	1.34
Al_2O_3	20.030±1.34	19.700±1.20	1.25
CaO	1.785±0.24	1.594±0.12	1.19
K_2O	3.020±0.99	2.893±0.80	1.53
TiO_2	1.745±0.26	1.768±0.24	1.17
MnO	0.285±0.01	0.234 ±0.01	1.00
Fe_2O_3	16.756±1.16	15.661±1.47	1.60
Total (%)	99.721±6.80	98.170±5.96	1.14

*September 2012, **November 2012. ***The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix
IV); hence, there was no significant difference between the variance of the dry and rainy seasons.

According to the results in Table 4.27, the XRF average percentage were in the following order; SiO_2 56.100±2.80% and 56.320±2.42%, Al_2O_3 20.030±1.34% and 19.7±1.20, Fe_2O_3 16.756±1.16% and 15.661±1.47%, K_2O 3.02±0.99% and 2.893±0.80%, CaO 1.785±0.24% and 1.594±0.22%, TiO_2 1.745±0.26% and 1.768±0.24%, and MnO 0.285±0.01% and 0.234±0.01% in dry and rainy seasons, respectively. As explained in table 4.24, the percentage for Al_2O_3 in the sediments increased when using XRF method. However, a similar trend in the amounts from one oxide to the next was maintained. This is clearly seen in table 4.28.

Table 4.28: Comparison between AAS and XRF Analyses of Sediments.

Oxides (%)	AAS Results		XRF Results		*F* Values*	
	Dry season	Rainy season	Dry season	Rainy season	Dry season	Rainy season
SiO_2	57.515±2.116	57.165±2.410	56.100±2.80	56.320±2.42	1.75	1.01
Al_2O_3	12.537±1.806	11.804±1.675	20.030±1.34	19.700±1.20	1.82	1.95
CaO	1.598±0.344	1.742±0.462	1.785±0.24	1.594±0.22	2.05	4.41
MgO	0.671±0.107	0.497±0.093	-	-	-	
Na_2O	2.659±0.050	2.349±0.102	-	-	-	
K_2O	2.229±0.454	2.185±0.317	3.020±0.99	2.893±0.80	4.76	6.37
TiO_2	1.346±0.248	1.008±0.294	1.745±0.26	1.768±0.24	1.10	1.28
MnO	0.193±0.014	0.121±0.026	0.285±0.01	0.234 ±0.01	1.96	6.76
Fe_2O_3	11.331±0.762	11.836±1.214	16.756±1.16	15.661±1.47	2.32	1.47
LOI	8.947±2.097	8.707±1.746	-	-	-	-
Total (%)	99.026±8.458	97.414±8.340	99.721±6.80	98.170±6.36	1.54	1.72

-Not analysed. *The tabulated *F* values for *N*-1=9 (95% confidence level) is 3.18 (Appendix IV); hence, there was no significant difference (except for K_2O, CaO and MnO) in the precision of both AAS and XRF analyses.

The results in Table 4.28 indicate that AAS and XRF analysis of the sediments were consistent to a large extent. Absence of Na_2O and MgO in the case of XRF analysis could have resulted in the

increase of Al_2O_3 and Fe_2O_3 due to interference. Therefore, the AAS results for the sediments were reliable when compared with the XRF results.

Table 4.29: Comparison between AAS Analyses of the Key Metals in Water, Rocks and sediments.

Metal	Water (mg/l)		Rocks (%)		Sediments (%)	
	Dry season	Rainy season	Dry season	Rainy season	Dry season	Rainy season
Na	1,043±35.0	954.4±20.3	3.118±0.475	3.408±0.414	1.973±0.037	1.743±0.076
K	121.6 ± 2.1	116.7±2.2	1.469±0.412	1.396±0.253	1.850±0.378	1.813±0.263
Ca	124.2±1.8	94.2±1.6	6.617±0.728	7.400±0.890	1.141±0.246	1.244±0.330
Mg	73.6±0.6	70.4±0.3	1.957±0.159	1.850±0.137	0.403±1.00	0.298±0.056
Fe	0.82±0.1	0.49±0.1	12.89±0.680	13.36±0.770	7.932±0.533	8.285±0.850
Mn	0.097+0.0	0.075±0.0	0.263±0.040	0.279±0.031	0.150±0.011	0.094±0.020
Al	0.290±0.0	0.205±0.0	7.165±0.534	6.922±0.804	6.637±0.956	6.249±0.887
Ti	-	-	1.413±0.229	1.477±0.149	0.808±0.149	0.605±0.176

-Not analysed.

Table 4.29 gives a summary of the AAS results for the three sampled materials (water, rocks and sediments) when compared together. It is apparent that group one (Na, K) and group two (Ca, Mg) metals were the most abundant in water with sodium in the lead. This is expected because they form the most water soluble compounds compared with the other metals. The huge presence of these metals in water is also reflected in the rocks and sediments. The fact that calcium is not as soluble as sodium and potassium explains why calcium was lower in water but higher in rocks than the group one metals.

4.6 Evaluation of Analytical Procedure

Recovery experiments were done to validate the AAS procedure used by adding a known amount of the metal in question to the water samples and the blank. The results are as shown in Tables 4.30 and 4.31. For further quality control, certified reference materials were also analysed as illustrated in Table 4.32.

Table 4.30: Percentage Recoveries in the Water samples using AAS.

Metal	Present(mg/l)	Added (mg/l)	Total (mg/l)	Found (mg/l)	Recovery (%)
Na	1,043.0±35.0*	50	1,093.0	1,091.0±32.0	99.8
	954.4±20.3**	50	1,004.4	997.0±19.4	99.3
K	121.6±2.1*	10	131.6	129.7±1.9	98.6
	116.7±2.2**	10	126.7	126.3±2.0	99.7
Ca	124.2±1.8*	10	134.2	133.5±1.9	99.5
	94.2±1.6**	10	104.2	102.8±1.3	98.6
Mg	73.6±0.6*	10	83.6	82.9±0.4	99.2
	70.4±0.3**	10	80.4	80.2±0.2	99.8

*Dry season, **Rainy season

Table 4.31: Percentage Recoveries in the Blank using AAS.

Metal	Present(mg/l)	Added (mg/l)	Total (mg/l)	Found (mg/l)	Recovery (%)
Na	1.42±0.02*	50	51.42	51.39±1.61	99.94
	1.13±0.02**	50	51.13	50.8±1.47	99.35
K	0.05±0.01*	10	10.05	9.93±0.66	98.80
	0.03±0.01**	10	10.03	10.00±0.57	99.70
Ca	0.11±0.01*	10	10.11	10.02±0.51	99.11
	0.08±0.01**	10	10.08	9.95±0.74	98.71
Mg	0.004±0.01*	10	10.004	9.90±0.71	98.96
	0.003±0.01**	10	10.003	9.94±0.55	99.37

*Dry season, **Rainy season

It is quite evident from the results in Tables 4.30 and 4.31 that the percentage recoveries of the metals in water samples and the blank were within the generally acceptable range of 85-115%. Therefore, the AAS analytical procedure adopted was valid.

Table 4.32: AAS Analysis of metals in Certified Reference Materials (CRMs).

Element	Found Value (mg/l)	Certified Value (mg/l)	Accuracy (%)
Sodium	4.96±0.12	5.0±0.1	99.2
Potassium	4.92±0.11	5.0±0.1	98.4
Calcium	4.97±0.13	5.0±0.1	99.4
Magnesium	4.95±0.11	5.0±0.1	99.0

The accuracy of the results in Table 4.32 ranged from 98.4% to 99.4% which was considered acceptable.

4.7 Discussion of the Results

The occurrence and economic significance of the minerals established during the study is explained in the following paragraphs:

The amount of free CO_2 in the water was found to be 931.3±2.0 mg/l and 1,015±1.9 mg/l, in dry and rainy seasons, respectively. The gas possibly comes from the earth's crust and rises through volcanic vent (Mao, *et al.*, 2009). Surface waters normally contain less than 10 mg/l of free CO_2, while some groundwater may easily exceed that concentration. Free carbon dioxide is currently being mined in Kenya at Kireita springs in Kiambu County. The amount of CO_2 mined in year 2011 was 16,275 tones which earned the Country Kshs 105 million in foreign exchange (Table 1.1 and 1.2). CO_2 has wide application in making of dry ice used for refrigeration and cloud seeding, fire extinguishers, carbonated drinks which include sodas and beer. The area around Rurii spring can be drilled to extract large amounts of free CO_2 from underground for industrial use.

The level of sodium was 1,043±35 mg/l and 954.4±20.3 mg/l in water; 3.118±0.475% and 3.408±0.414% in rocks; 1.973±0.0.037% and 1.743±0.0.076% in sediments, in dry and wet seasons respectively. The average abundance of sodium in the earth's crust is 2.8%, in soils it is 0.02 to 0.62 %, in streams it is 6.3 mg/l and in groundwater it is generally >5 mg/l (Andrew, 2005). Sodium occurs with silicates and with salt deposits. Sodium compounds are used in many ways including caustic soda and chloride manufacture, table salt, fertilizers and water treatment. Sodium minerals ores include feldspar $NaAlSi_3O_8$, rock salt $NaCl$, soda nitre $NaNO_3$, thenardite Na_2SO_4 ˌ mirabilite $Na_2SO_4.10H_2O$, glauberite $Na_2Ca(SO_4)_2$, thermonitrite $Na_2CO_3.H_2O$, trona $Na_3H(CO_3)_2.H_2O$, borax $Na_2B_4O_7.10H_2O$, ulexite $NaCaB_5O_9.8H_2O$ and cryolite Na_3AlF6 (Rutley, 1988).

Sodium in the studied region was mostly in form of carbonates, hydrogen carbonates, chlorides and sulphates. Because these anions were contained in the water in considerable amounts as follows; carbonates 16.9±0.2mg/l, hydrogen carbonates 5,572.0±67.7mg/l, chlorides 902.2±11.6 mg/l and sulphates 456±26.5 mg/l. Soda ash is the key sodium mineral found in Kenya at lake Magadi, the country exported Kshs 7.352 billion worth of soda ash in year 2011 (Table 1.1).

Potassium was 121.6±2.1 mg/l and 116.7±2.2 mg/l in water; 1.469±0.412% and 1.396±0.253% in rocks; 1.850±0.0.378% and 1.813±0.263% in sediments, in dry and rainy seasons respectively. The average abundance of potassium in the earth's crust is 1.84%, in soils it has a range of 0.1 to 2.6%, in streams it is 2.3 mg/l and in groundwater it has a range of 0.5 to 1.0 mg/l. Potassium minerals are sylvine KCl, carnallite $KMgCl_3.6H_2O$, Kainite $KCl. MgSO_4.3H_2O$, Polyhalite $K_2Ca_2Mg(SO_4)_4.2H_2O$, alunite $KAl_3(SO_4)_2(SO_4)_2(OH)_6$, nitre KNO_3, orthoclase feldspar $KAlsi_3O_8$, leucite $KAlSi_2O_6$ and muscovite or potassium – mica $KA1_2 [Si_3A1O_{10}](OH)_2$ (Watson, 1979).

In this particular area of study potassium would likely occur as bicarbonate, carbonate, phosphate, chloride or sulphates which were some of the major anions in the water. Potassium compounds are used in the manufacturer of glass, fertilizers, baking powder, soft drinks, explosives, electroplating, pigments, soaps and detergents. Potassium is an essential element in both plants and animals and

occurs in groundwater as a result of mineral dissolution from potassium containing silicate minerals (feldspars) such as $KAlSi_3O_8$, from decomposing plant material and from agricultural runoff.

Calcium was established to be 124.2±1.8 mg/l and 94.2±1.6 mg/l in water; 6.617±0.728% and 7.40±0.89% in rocks; 1.141±0.246% and 1.244±0.330% in the sediments, in hot and wet seasons respectively. The average abundance of calcium in the earth's crust is 3.5%, in soils it is 0.07 to 1.7%, in streams it is about 15 mg/l and in groundwater it ranges from 1 to >500 mg/l . The presence of calcium in water supplies results from passage over deposits of limestone, dolomite, gypsum and gypsiferous shale (Putris, 1992).

Calcium is necessary in plant and animal nutrition. It is an essential compound of bones, shells and plants structures. Small concentrations of calcium carbonate prevent corrosion of metal pipes by lying down a protective coating. Other calcium compounds are used in pharmaceuticals, photography, lime, de-icing salts, pigments, fertilizers and plasters. Calcium minerals are anorthite feldspar $CaAl_2Si_2O_8$, wallastonite $CaSiO_3$, calcite $CaCO_3$ (trigonal), aragonite $CaCO_3$ (orthombic), dolomite $CaMg(CO_3)_2$, gaylussite $Na_2Ca(CO_3)_2.5H_2O$, barytocalcite $BaCa(CO_3)_2$, anhydrite $CaSO_4$, gypsum $CaSO_4.H_2O$, glauberite $Na_2Ca(SO_4)_2$, polyhalite $K_2Ca_2Mg(SO_4).2H_2O$, apatite $Ca_5(F,Cl)(PO_4)_3$, fluorite CaF_2, ulexite $NaCaB_5O_9.8H_2O$ and colemanite $CaB_6O_{11}.5H_2O$ (Zussman, 1992). However, the most common forms of calcium are calcium carbonate (calcite) and calcium magnesium carbonate (dolomite).

Magnesium level was 73.6±0.6 mg/l and 70.4±0.3 mg/l in water; 1.957±0.159% and 1.850±0.137% in rocks; 0.403±0.100% and 0.298±0.056% in sediments, in dry and rainy seasons respectively. The average abundance of the magnesium in the earth's crust is 2.7% in soils, it is 0.03% to 0.84%, in streams it is 4 mg/l and in groundwater it is >5 mg/l. Magnesium minerals include: periclase MgO, brucite $Mg(OH)_2$, magnesite $MgCO_3$, dolomite $MgCa(CO_3)_2$, epsomite $MgSO_4.7H_2O$, kieserite $MgSO_4H_2O$, polyhalite $K_2Ca_2Mg(SO_4)_4.2H_2O$, kainite $MgSO_4.KCl.3H_2O$, carnallite $KMgCl_3.6H_2O$,

boracite $Mg_3B_7O_{13}Cl$ and spinel $MgAl_2O_4$. Magnesium occurs mainly in the minerals magnesite and dolomite (Maxwell, 1968). Magnesium is an essential element in chlorophyll and in red blood cells. Magnesium is widely used in alloys, pyrotechnics, flash photography, drying agents, refractories (furnace linings), fertilizers, pharmaceuticals and foods. Magnesium concentrations greater than 125 mg/l can have cathartic and diuretic effects (MC Divitt, 1974).

Strontium was detected in water at 1.469 ± 0.009 mg/l and 1.304 ± 0.005 mg/l, in dry and rainy seasons respectively. The average abundance of strontium in the earth's crust is 38.4 mg/l, in soils strontium ranges from 3.6 to 160 mg/l, in streams its average is 50 mg/l and in groundwater it is 0.01 to 10 mg/l. Strontium is found chiefly in celestite, $SrSO_4$ and strontianite, $SrCO_3$ (Dunning, 1970). Strontium compounds are used in pigments, pyrotechnics, ceramics flares or fireworks.

Iron detected was 0.82 ± 0.16 mg/l and 0.49 ± 0.13 mg/l in water; $12.894\pm0.679\%$ and $13.36\pm0.77\%$ in rocks; $7.932\pm0.533\%$ and $8.285\pm0.850\%$ in sediments, during the hot and wet seasons respectively. The average abundance of iron in the earth's crust is 4.6% and the second most widely distributed metal after aluminum. In soils iron ranges from 0.5 to 4.3%, in streams it averages about 0.7 mg/l and in groundwater it is 0.1 to 10 mg/l. Soluble iron in groundwater is usually in the ferrous state (Fe^{2+}), on exposure to air or addition of oxidants ferrous iron is oxidized to the ferric state (Fe^{3+}). Elevated iron levels in water can cause stains in plumbing, laundry and cooking utensils and can impact objectionable tastes and colours to foods (Bradley, 1989).

The chief minerals of iron are magnetite Fe_3O_4 (74% Fe), hematite Fe_2O_3 (70% Fe), goethite FeO(OH) (68.5 Fe) and siderite or chalybite (48.3% Fe). Other minerals are native iron Fe, Limonite FeO (OH).nH_2O), turgite $Fe_2O_3.nH_2O$, pyrite FeS_2, Marcasite FeS_2, pyrrhotite $Fe_{1-n}S$, copperas $FeSO_4.7H_2O$, vivianite $Fe_3P_2O_8.8H_2O$, ilvaite $CaFe^{2+}Fe^{3+}O[Si_2O_7]$ (OH), ilmenite $FeTiO_3$, chromite $FeCr_2O_4$, franklinite (Fe, Zn, Mn)$_2O_4$, chalcopyrite CuFeS, arsenopyrite FeAsS, and ilvaite $CaFe^{2+}Fe^{3+}O$ (Si_2O)OH, and other forms of iron silicates (Rutley, 1988). Cast iron, wrought iron and

steel are the main forms in which iron appears in commerce. Their different properties are primarily due to the presence of varying amounts of carbon. Iron forms the foundation of modern construction industry where it is used in enormous quantities and widely used in other alloys.

Barium was found to be 0.677 ± 0.135 mg/l and 0.537 ± 0.110 mg/l in water, in dry and rainy seasons respectively. The average abundance of barium in the earth's crust is 390 mg/l, in soils it is 63 to 810 mg/l, in streams it is 0.05 to 1 mg/l. The solubility of barium in water is controlled by the solubility of $BaSO_4$ and by adsorption on hydroxides. High concentration of barium occurs in some brine. Concentrations exceeding 1 mg/l is toxic to marine life. The main barium minerals are barite $BaSO_4$ and witherite $BaCO_3$. Others are bromlite (Ba, Ca) $CaCO_3$, barytocalcite $BaCa (CO_3)_2$. Barium is used in mud slurries in drilling oil and exploration wells, pigments, rat poisons, pyrotechnics and in medicine (Strens, 1976).

Aluminium was 0.290 ± 0.005 mg/l and 0.205 ± 0.005 mg/l in water; $7.165\pm0.534\%$ and $6.922\pm0.804\%$ in rocks; $6.637\pm0.956\%$ and $6.249\pm0.887\%$ in sediments, in hot and wet seasons respectively. The average abundance of Aluminium in the earth's crust is 8.1% and is the most widely distributed metal. In the soils it is 0.9 to 6.5%, in streams it is 400 µg/l and in groundwater it is <0.1 µg/l (Andrew, 2005). Aluminium occurs in the earth's crust in combination with silicon and oxygen to form feldspars, micas and clay minerals.

The most important minerals are bauxite (hydrated Al_2O_3), and corundum Al_2O_3, others are leucite $KAlSi_2O_6$, spinel $MgAl_2O_4$, chrysoberyl $BeAl_2O_4$, diaspore $HAlO_2$, boehmite $AlO(OH)$, gibbsite $Al(OH)_3$, websterite or aluminite $Al_2O_3.SO_3.9H_2O$, alunogene $Al_2(SO_4)_3.16H_2O$, alum $KAl(SO_4)_2.12H_2O$, alunite $KAl_3(SO_4)_2(OH)_6$, cryolite Na_3AlF_6, turquoise, $CuAl_6(PO_4)(OH)_8.4H_2O$ and wavellite $Al_6(PO_4)_4(OH)_6.9H_2O$ (Watson, 1979). Aluminium and its alloys are used for heat exchangers, aircraft parts, building materials and containers; aluminium potassium sulphate (alum) is

used in water treatment process to flocculate suspended particles. It is also employed in manufacture of household articles, wrapping foil, building sheet and electrical equipments.

Manganese was found to be 0.097 ± 0.002 mg/l and 0.075 ± 0.002 mg/l in water; $0.263\pm0.040\%$ and $0.279\pm0.031\%$ in rocks; $0.150\pm0.011\%$ and $0.094\pm0.020\%$ in sediments, during dry and rainy seasons respectively. The average abundance of manganese in the earth's crust is 1060 mg/l, in soils it is 61 to 1010 mg/l, in streams it is $7\mu g/l$ and in ground water it is <0.1 mg/l. Manganese is associated with iron minerals and occurs in nodules in oceans, fresh waters and soils.

The common ores are pyrolusite MnO_2 and Psilomelane (Hydrated oxide with Ba and K). Other Manganese mineral are hausmannite Mn_3O_4, braunite Mn_2O_3, manganite $MnO(OH)$, polianite MnO_2 , franklinite (Fe, Zn, Mn) (Fe, Mn)$_2O_4$, dialogite or rhodochrosite $MnCO_3$, rhodonite $MnSiO_3$ and alabandite MnS. In addition to these specifically manganese minerals, the element enters into many silicates such as manganese garnet and spessartite (Putnis, 1992). Manganese is used in steel alloys, batteries, food additives, manufacture of oxygen, and permanganates of potassium and sodium which are used in disinfectants. It is used as a drier in manufacture of paints, vanish and in in decolourisation of glass. Manganese is considered an essential trace element for plants and animals.

Chromium present in water was 0.056 ± 0.002 mg/l and 0.055 ± 0.002 mg/l, in hot and wet seasons respectively. The average abundance of chromium in the earth's crust is 122 mg/l, in soils it is 11 to 22 mg/l, in streams it is about $1\mu g/l$ and in groundwater it is generally100 $\mu g/l$. In natural waters, trivalent chromium exists as Cr^{3+}, Cr (OH)$^{2+}$, Cr (OH)$_2^+$ and $Cr(OH)_4^-$ (Andrew, 2005). In hexavalent form, chromium forms strong complex with amines and would be absorbed by clay minerals. Chromium is found chiefly in chrome iron ore called chromite $FeO.Cr_2O_3$. But it is also found in several silicate minerals such as chrome diopside, chrome zoisite and uvarovite or garnent (Brewer, 1964). Chromium is used in alloys, electroplating, pigments, corrosion control, tanning, photography and refractory material for furnace lining. Hexavalent compound of chromium have been shown to

be carcinogenic by inhalation and are corrosive to tissue. Chromium is considered nonessential in plants but an essential trace element for animals.

Titanium was found to be $1.413\pm0.229\%$ and $1.477\pm0.149\%$ in the rocks; $0.808\pm0.149\%$ and $0.605\pm0.176\%$ in the sediments, in dry and rainy seasons. The average abundance of titanium in the earth's crust is 0.6%, in soils it is 1700 to 6600 mg/l, in streams it is 3µg/l and in groundwater it is <0.l mg/l. Titanium species are usually insoluble in natural waters, with the Ti^{4+} species being the most common when found. The element is commonly associated with iron minerals like ilmenite $FeTiO_3$. Other titanium minerals include titanite, $CaTiSiO_5$, rutile TiO_2, brookite TiO_2 and anatase TiO_2 (Perrin, 1975). Titanium is used in making corrosion resistant alloys for aircraft, marine and food handling equipment. It is also used in artificial hip joints, cardiac pacemakers, ship building, artificial tooth to give an ivory tint and pottery manufacture. Titanium carbide is an extremely obdurate material and can be employed for cutting tools (Appello and Postma, 1993).

The percentage of silicon in rocks was $18.094\pm1.315\%$ and $16.960\pm0.753\%$; in sediments it was $26.840\pm0.987\%$ and $26.677\pm1.125\%$, in hot and wet seasons respectively. Silicon constitutes about 28% of the earth's crust. Silicon does, not occur in a free state in nature but its compounds are extraordinarily abundant. Silicates are the most important rock forming minerals. Silica (SiO_2), commonly known as sand is the only oxide of silicon (Watson, 1979). It occurs in the form of quartz, chalcedony, agate and flint. Silicon is obtained from silica rich sands, sandstones or quartzites. Silicon is used in the manufacturer of silicon chips and semiconductors, as a de-oxidiser in steel making, as ferrosilicon alloy, aluminium casting and other metallurgical process (Rutley, 1998).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Introduction

From the outcome of the research undertaken at Rurii spring, the study established that the spring water and the neighbouring rocks had a wide range of appreciable minerals. Based on these results, the following conclusion and recommendations were attained.

5.2 Conclusion

Rurii spring water had the following important minerals in large quantities: free carbon dioxide 931.3 ± 2.0 mg/l and $1,015\pm1.9$ mg/l; sodium $1,043\pm35$ mg/l and 954.4 ± 20.3 mg/l; potassium 121.6 ± 2.1 mg/l and 116.7 ± 2.2 mg/l; calcium 124.2 ± 1.8 mg/l and 94.2 ± 1.6 mg/l; and magnesium 73.6 ± 0.6 mg/l and 70.4 ± 0.3 mg/l. The anions were: bicarbonates $5,511.4\pm67.2$ mg/l and $5,632.6\pm64.2$ mg/l; chlorides 950.9 ± 13.1 mg/l and 853.6 ± 10.0 mg/l; sulphates 492.5 ± 7.7 mg/l and 420.1 ± 25.3 mg/l; total phosphorus 115.68 ± 1.56 mg/l and 96.42 ± 1.7 mg/l; carbonates 16.7 ± 0.2 mg/l and 17.1 ± 0.2 mg/l, in dry and rainy seasons respectively. Sodium bicarbonate and sodium chloride were the most abundant salts in the water considering the large quantity of these specific ions.

Other valuable minerals that were found in water but in smaller quantities were: strontium 1.469 ± 0.009 mg/l and 1.304 ± 0.005 mg/l, iron 0.82 ± 0.16 mg/l and 0.49 ± 0.13 mg/l, barium 0.677 ± 0.135 mg/l and 0.537 ± 0.110 mg/l, aluminium 0.290 ± 0.005 mg/l and 0.248 ± 0.004 mg/l, manganese 0.097 ± 0.002 mg/l and 0.075 ± 0.002 mg/l, and chromium 0.056 ± 0.002 mg/l and 0.055 ± 0.002 mg/l, in dry and rainy seasons respectively. These mineral salts found in the water originated from neighbouring rocks which contained substantial oxide percentages of calcium $9.264\pm1.019\%$ and $10.360\pm1.241\%$, sodium $4.203\pm0.640\%$ and $4.593\pm0.558\%$, magnesium $3.261\pm0.265\%$ and $3.084\pm0.228\%$, and potassium $1.77\pm0.495\%$ and $1.683\pm0.305\%$, in dry and rainy

seasons respectively. The rocks comprised of bicarbonates, carbonates, chlorides and sulphates which were the major anions present in the water.

The water had high conductivity of 6,014±41 µS/cm and 5,986±40 µS/cm; TDS was 5056.7±51.2 mg/l and 4923.1±40.7 mg/l during the dry and rainy seasons, respectively. This was as a result of the excessive mineral content. The total alkalinity of water was very high at 5,528±67 mg $CaCO_3$/l and 5,649±64 mg $CaCO_3$/l in hot and wet seasons, respectively, especially due to the presence of large amount of bicarbonate. The total hardness was found to be 407.4±1.6 mg $CaCO_3$/l and 391.3±1.4 mg $CaCO_3$/l, in dry and rainy seasons, respectively. This reflected high presence of calcium and magnesium in the water. The water was significantly contaminated with coliforms. The total coliforms were >200 MPN while faecal coliforms were 15±1 MPN and 17±1 MPN, during the hot and wet seasons, respectively. Therefore, treatment is necessary before use. The water was slightly turbid measuring 10.0±0.5 NTU and 11.1±0.5 NTU in the dry and rainy seasons, respectively, hence ought to be filtered before drinking.

In connection with the quality, the water had too much sodium, potassium, barium, aluminium, chloride, sulphate, total dissolved solids, total alkalinity and coliforms which exceeded the WHO and KEBS limits. Hence, it is necessary to reduce the level of these substances closer to the acceptable standards before it is made available for human consumption.

From the results obtained, the most important minerals at Rurii spring were carbon dioxide, sodium, potassium, calcium and magnesium metals in form of their hydrogen carbonates, chlorides, sulphates, phosphates and carbonates. These minerals can be utilized commercially in the production of mineral water, salt licks for livestock, baking powder, solvents, pharmaceutical products, cement, laboratory chemicals, fertilizers, carbonated drinks, dry ice for refrigeration and fire extinguishers. Moreover, the spring can be developed into a modern Spa Park. Mining of such minerals can create employment; generate additional foreign exchange and speed up the Country's economic growth as envisaged in the Kenya Vision 2030.

5.3 Recommendations

Based on the results and the conclusion of this study, the following pertinent issues need to be addressed.

1. This research should be advanced further to cover the entire geochemistry of the study area and determine the full extent of commercial worth of the minerals found there. In addition to AAS and XRF, other analytical methods such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD) and Inductively Coupled Plasma (ICP), are required for the detailed mineral analysis. It is also necessary to analyse further for the ^{13}C isotope of the CO_2-rich water to determine the external source of the CO_2 and know whether it is derived from the mantle, metamorphic processes, biogenic activity or from the surrounding carbonate rocks.

2. Such mineral resources in this region and other areas in our Country should not lie idle. It is imperative for the Government, Private Sector and Universities to invest widely in mining research and production. This work should be co-ordinated by the experts in Chemistry, Physics, Geology and Mining Engineers.

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Date: 20th September 2012

George Ng'ang'a Mungai
University of Nairobi
P.O.Box 30197-00100
Nairobi.

RE: RESEARCH AUTHORIZATION

Following your application for authority to carry out research on "*An investigation of minerals in the water and rocks of Rurii Mineral Spring in Meru County, Eastern Kenya*," I am pleased to inform you that you have been authorized to undertake research in **Meru County** for a period ending **30th April**, *2013*.

You are advised to report to **the District Commissioners and the District Education Officers, Meru County** before embarking on the research project.

On completion of the research, you are expected to submit **two hard copies and one soft copy in pdf** of the research report/thesis to our office.

DR M.K. RUGUTT, PhD, HSC.
DEPUTY COUNCIL SECRETARY

Copy to:

The District Commissioners
The District Education Officers
Meru County.

"The National Council for Science and Technology is Committed to the Promotion of Science and Technology for National Development".

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APPENDIX II

OPERATING CONDITIONS FOR AAS

Metals	Slit Width (nm)	Flame Matrix*	Detection Level (mg/l)**	Wavelength (nm)
Na	0.5	A-AC	0.002	589
K	1.0	A-AC	0.005	766.5
Ca	0.5	A-AC	0.003	422.7
Mg	0.5	A-AC	0.0005	285.2
Fe	0.2	A-AC	0.02	248.3
Mn	0.2	A-AC	0.01	279.5
Pb	1.0	A-AC	0.05	217.0
Ba	0.5	N-AC	0.03	553
Sr	4.5	A-AC	0.03	460.7
Cd	0.5	A-AC	0.002	228.8
Cu	0.5	A-AC	0.01	324.5
Zn	1.0	A-AC	0.005	213.9
Al	0.5	N-AC	0.1	309.3
Cr	0.2	A-AC	0.02	357.9
Si	0.2	N-AC	0.3	251.6
Ti	0.5	N-AC	0.3	364.3

Source: Standard Methods for Examination of Water and Waste Water, 21st Edition (2005).

*A-AC=Air-Acetylene, N-AC=Nitrous Oxide-Acetylene

**Detection level is the concentration that produces absorption equivalent to twice the

magnitude of the background fluctuation.

APPENDIX III

MPN INDEX AND 95% CONFIDENCE LIMIT

Number of wells giving positive reaction per 100ml sample	Most Probable Number (MPN)	95% Confidence limit	
		Upper	Lower
1	1.0	0.0	3.7
2	2.0	0.6	5.6
3	3.1	1.1	7.3
4	4.2	1.7	10.7
5	5.3	2.3	12.3
6	6.4	3.0	13.9
7	7.5	3.7	15.5
8	8.7	4.5	17.1
9	9.9	5.3	18.8
10	11.1	6.1	20.5
11	12.4	7.0	2.1
12	13.7	7.9	23.9
13	15.0	8.8	25.7
14	16.4	9.8	27.5
15	17.8	10.8	29.4
16	19.2	11.9	31.3
17	20.7	13.0	33.3
18	22.2	14.1	35.2
19	23.8	15.3	37.3
20	25.4	16.5	39.4
21	37.1	17.7	41.6
22	28.8	19.0	43.9
23	30.6	20.4	46.3
24	32.4	21.8	48.7
25	34.4	23.3	51.2
26	36.4	24.7	53.9
27	38.4	26.4	56.6
28	40.6	28.0	59.5
29	42.9	29.7	62.5
30	45.3	31.5	65.6
31	47.8	33.4	69.0
32	50.4	35.4	72.5
33	53.1	37.5	76.2
34	56	39.7	80.1
35	59.1	42.0	84.4
36	62.4	44.6	88.8
37	65.9	47.2	93.7
38	69.7	50.0	99.0
39	73.8	53.1	104.8
40	78.2	56.4	111.2
41	83.1	59.9	118.3
42	88.5	63.9	118.3
43	94.5	68.2	135.4
44	101.3	73.1	146
45	109.1	78.6	158.7
46	118.4	85	174.5
47	129.8	92.7	195
48	144.5	102.3	224.1
49	165.2	115.2	272.2
50	200.5	135.8	387.6
51	>200.5	146.1	Infinite

Source: WRMA (2012).

APPENDIX IV

VALUES OF *F* AT THE 95% CONFIDENCE LEVEL

N-1	2	3	4	5	6	7	8	9	10	15	20	30
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

Source: Christian (2004).

CALIBRATION CURVES

Table 4.3: Potassium Hydrogen Phthalate Standards.

Standard (mg/l)	Absorbance
20	0.008
50	0.019
100	0.035
200	0.073
400	0.145
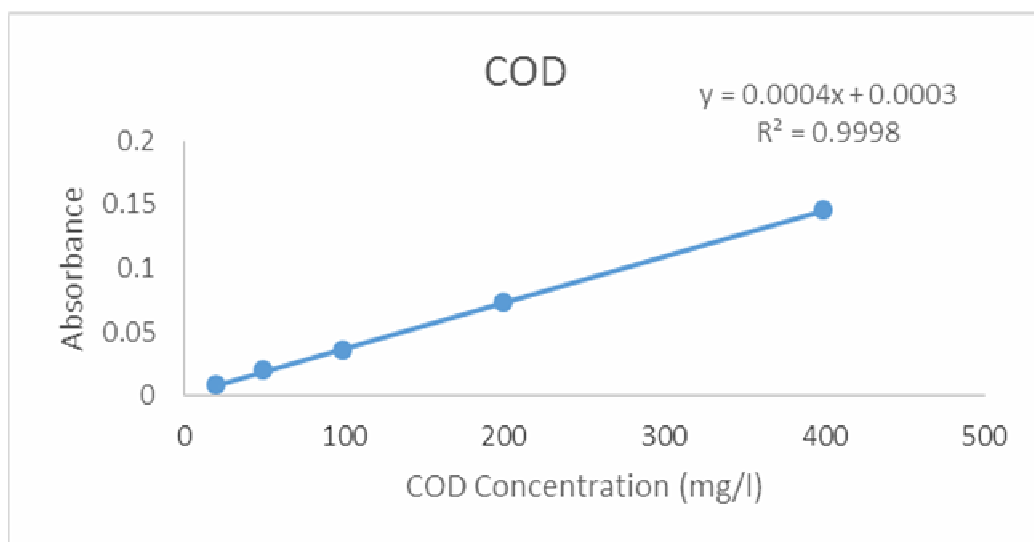
Figure 4.3: COD Calibration Curve.

Table 4.4: Sulphate Standards.

Standards (mg/l)	Turbidity(NTU)
5	10.94
10	19.21
20	39.93
30	56.95
40	80.92
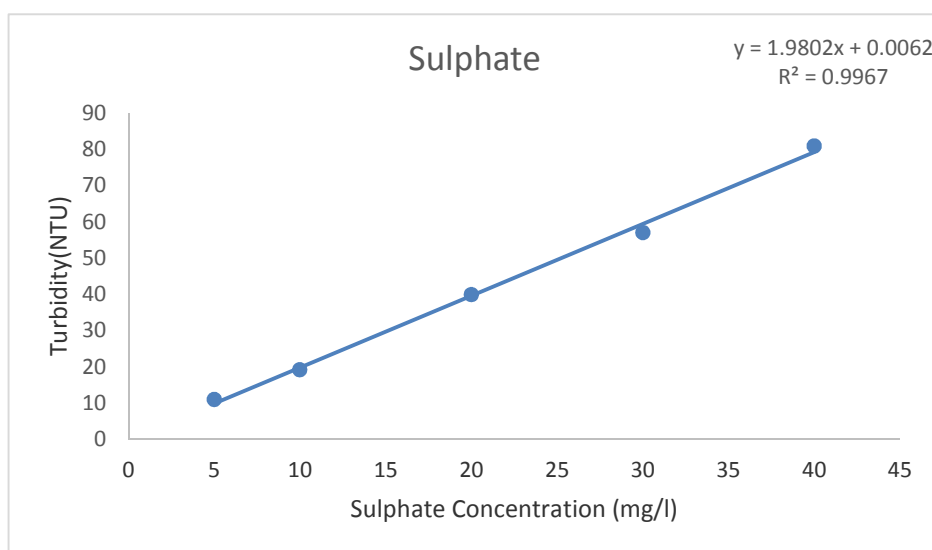
Figure 4.4: Sulphate Calibration Curve.

Table 4.5: Nitrite Standards.

Standards(mg/l)	Absorbance
0.01	0.009
0.03	0.028
0.05	0.05
0.1	0.093
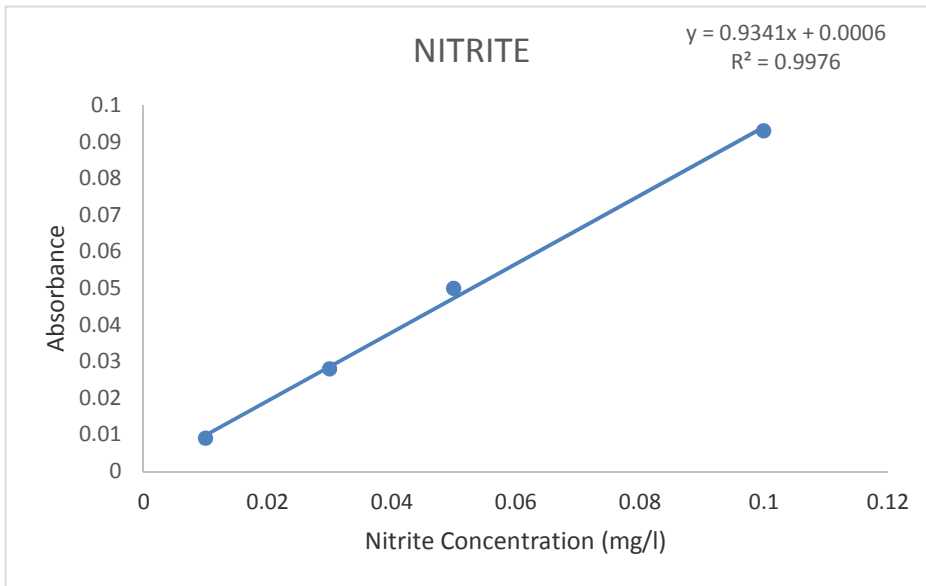
Figure 4.5: Nitrite Calibration Curve.

Table 4.6: Ammonia-Nitrogen Standards.

Standards(mg/l)	Absorbance
0.5	0.025
1	0.07
2.5	0.153
5	0.306
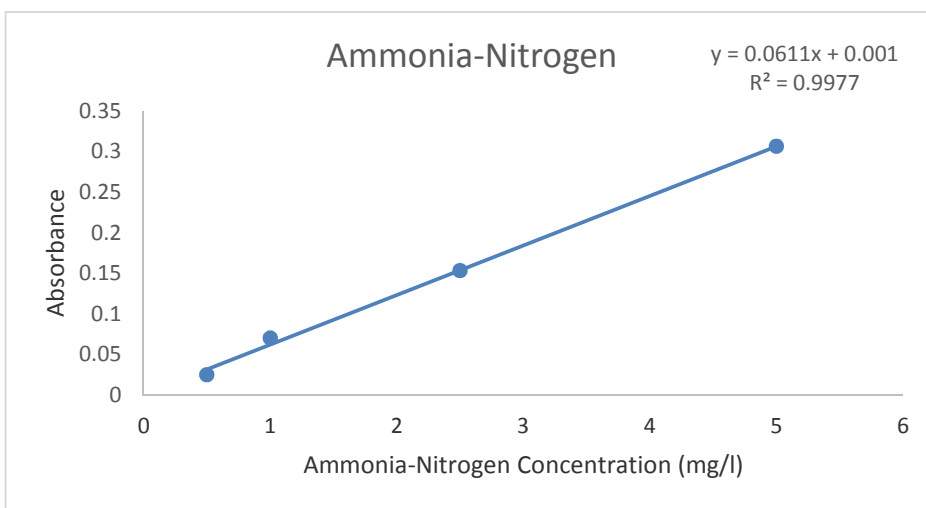
Figure 4.6: Ammonia-Nitrogen Calibration Curve.

Table 4.7: Phosphorus Standards.

Standard (mg/l)	Absorbance
1	0.005
2.5	0.02
5	0.038
7.5	0.054
10	0.071
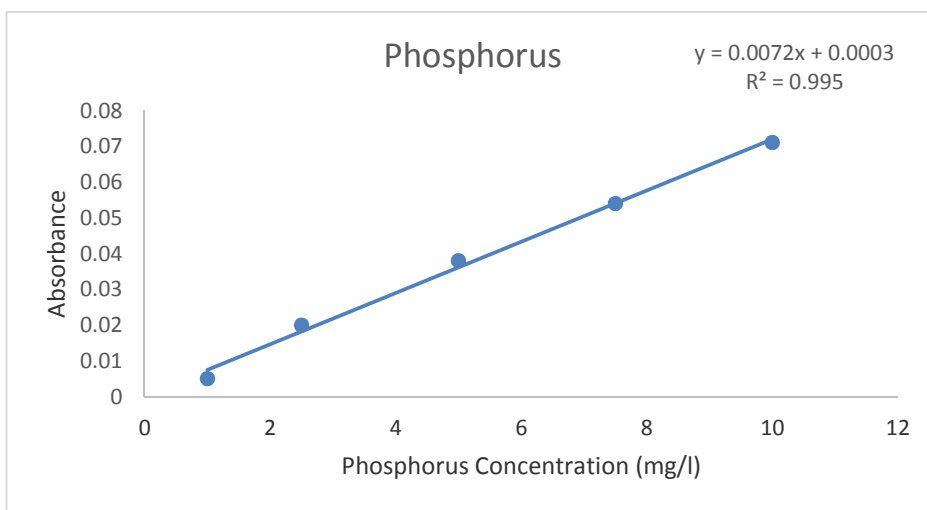
Figure 4.7: Phosphorus Calibration Curve.

Table 4.8: Potassium Standards.

Standards (mg/l)	Intensity
2	0.082
4	0.184
6	0.285
8	0.373
10	0.441
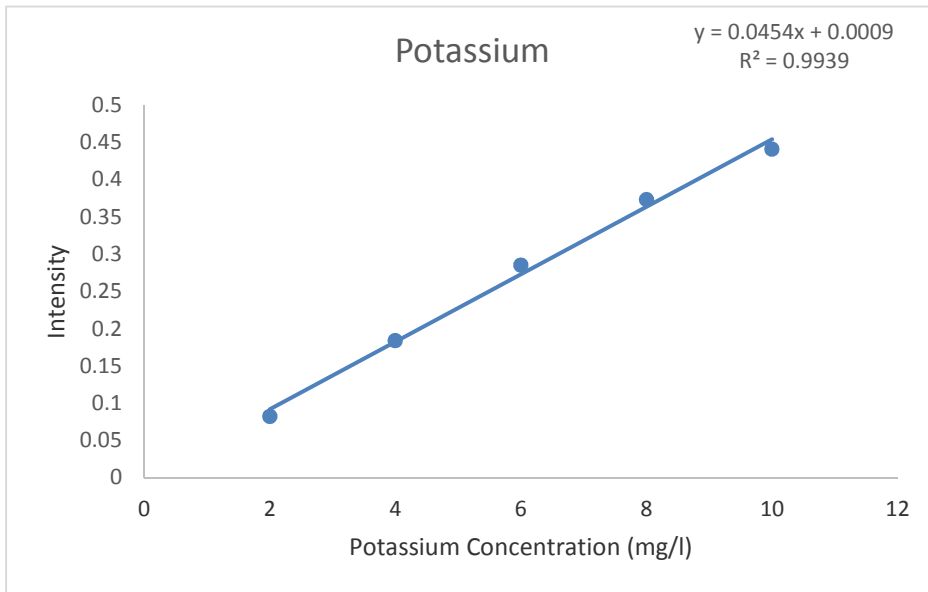
Figure 4.8: Potassium Calibration Curve.

Table 4.9: Calcium Standards.

Standards (mg/l)	Intensity
2	0.117
4	0.213
6	0.331
8	0.422
10	0.558
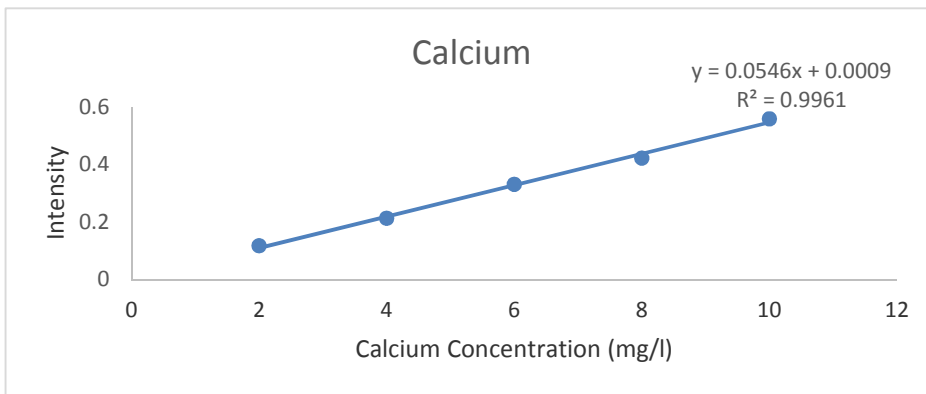
Figure 4.9: Calcium Standard Curve.

Table 4.10: Magnesium Standards.

Standards (mg/l)	Intensity
2	0.047
4	0.101
6	0.143
8	0.198
10	0.241
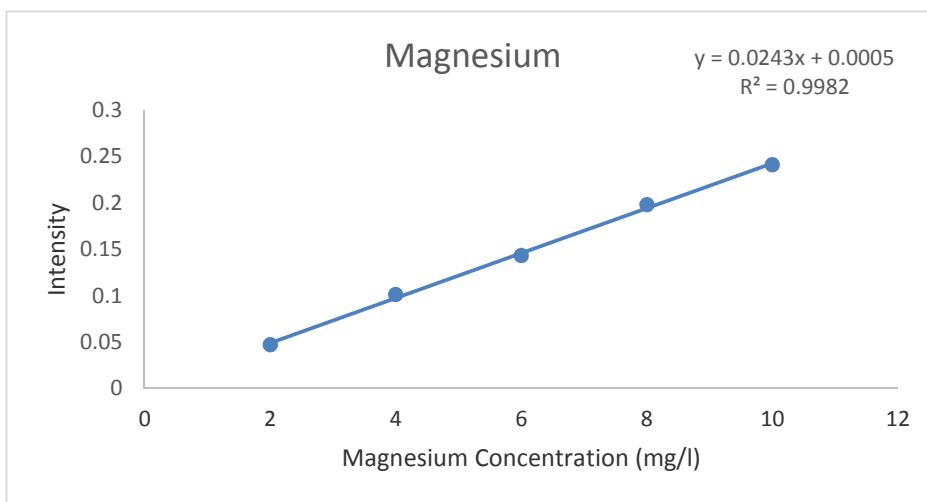
Figure 4.10: Magnesium Standard Curve.

Table 4.11: Iron Standards.

Standards (mg/l)	Intensity
1	0.016
5	0.108
10	0.223
15	0.327
20	0.423
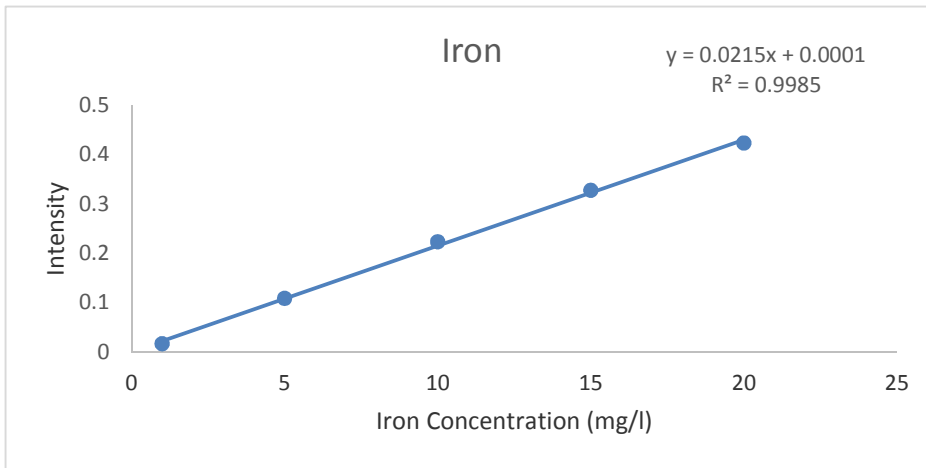
Figure 4.11: Iron Calibration Curve.

Table 4.12: Aluminium Standards.

Standards (mg/l)	Intensity
10	0.042
20	0.074
30	0.11
40	0.147
50	0.194
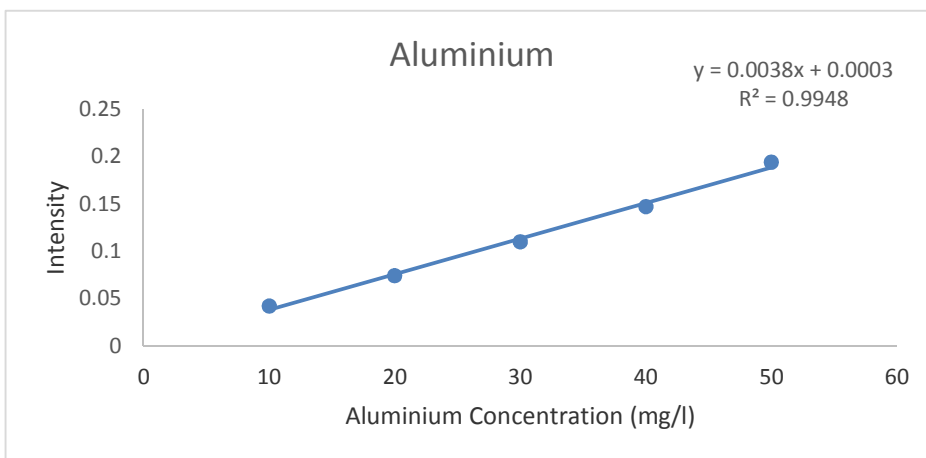
Figure 4.12: Aluminium Standard Curve.
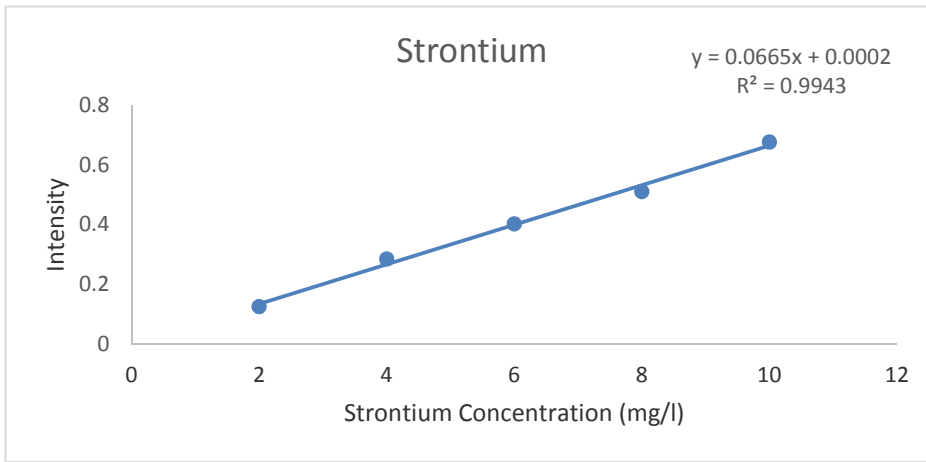
Table 4.13: Barium Standards.

Standards (mg/l)	Intensity
20	0.037
40	0.076
60	0.125
80	0.157
100	0.191
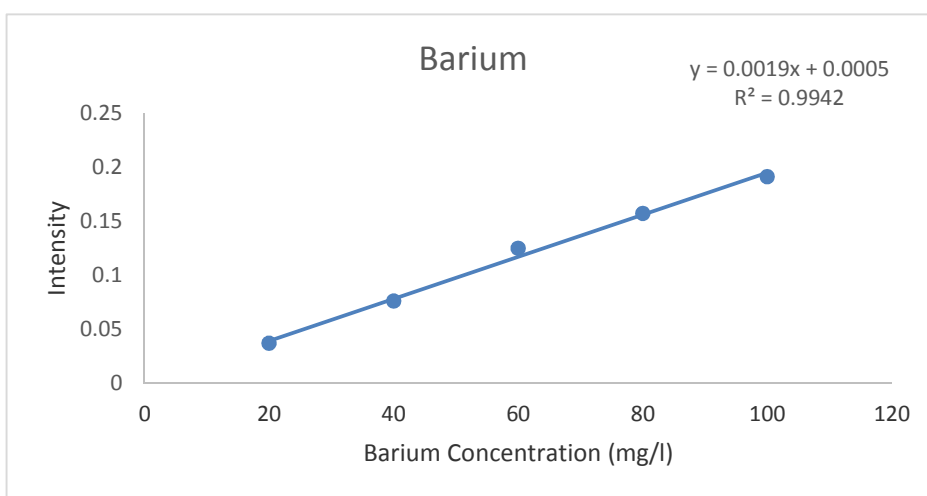
Figure 4.13: Barium Calibration Curve.
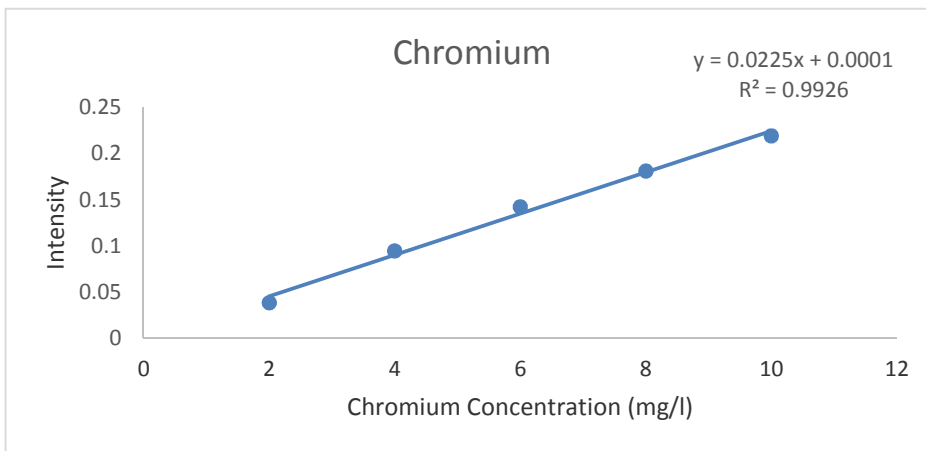
Table 4.14: Strontium Standards.

Standards (mg/l)	Intensity
2	0.124
4	0.284
6	0.402
8	0.51
10	0.676

Figure 4.14: Strontium Standard Curve.
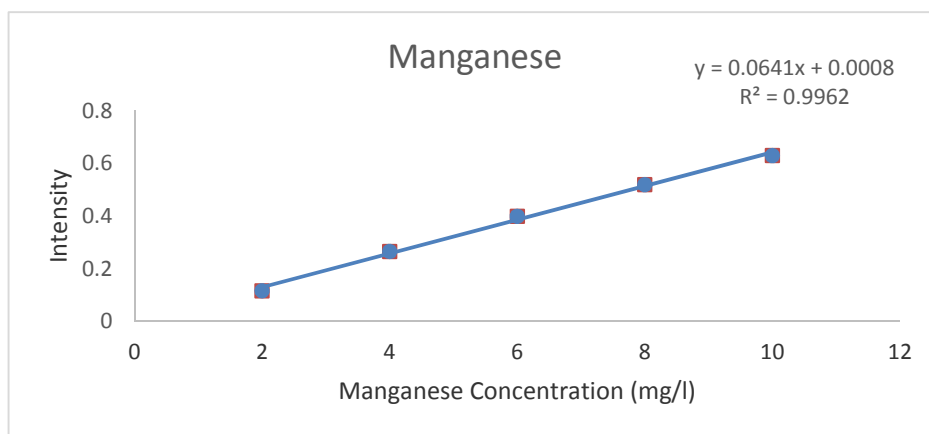
Table 4.15: Chromium Standards.

Standards (mg/l)	Intensity
2	0.038
4	0.094
6	0.142
8	0.181
10	0.219

Figure 4.15: Chromium Standard Curve.

Table 4.16: Manganese Standards.

Standards (mg/l)	Intensity
2	0.115
4	0.265
6	0.399
8	0.519
10	0.629

Figure 4.16: Manganese Standard Curve.

APPENDIX VI

THE RURII SPRING PHOTOGRAPHS