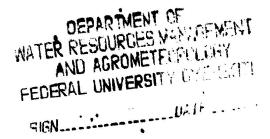
METHODS OF ESTIMATION OF IONIC STRENGTH IN HAND DUG WELL WATER OF IKOLE-EKITI EKITI STATE NIGERIA

BY

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A THESIS SUBMITTED TO

THE FACULTY OF AGRICULTURE, DEPARTMENT OF WATER
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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR IN WATER RESOURCES AND AGRO-METEORLOGY DEGREE OF THE FEDERAL UNIVERSITY OYE-EKITI EKITI STATE, NIGERIA.

NOVEMBER, 2017

DECLARATION

I declare that the work in this project entitled "METHODS OF ESTIMATION OF IONIC STRENGTH IN HAND DUG WELL WATER OF IKOLE-EKITI, EKITI STATE, NIGERIA", was written by me and that it is the record of my research wok.

The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this project was previously presented for another degree or diploma at this or any other institution.

EMEREMGINI KENECHUKWU EMEKA

11/11/2017

CERTIFICATION

This project entitled "METHODS OF ESTIMATION OF IONIC STRENGTH IN HAND DUG WELL WATER OF IKOLE-EKITI, EKITI STATE, NIGERIA", by EMEREMGINI KENECHUKWU EMEKA meets the regulations and requirement governing the award of a Bachelor of Water Resources Management and Agro-Meteorology degree of Federal University Oye Ekiti, and is approved for its contribution to knowledge and literary presentation.

Prof. J.O. Agbenin
Supervisor
Date:
Prof. A. A. Ogunwole
Head of Department
Date:

DEDICATION

This project work is dedicated to the Almighty God the owner and lover of my soul and to the memory of my late father Mr Patrick Emeremgini, whose words of encouragement have kept me going. To my wonderful mother Mrs Evelyn Emeremgini your prayer and love has being of great inspiration to me.

ACKNOWLEDGEMENTS

My appreciation goes to God for giving me the privilege of undergoing the course of this work. To Him be all glory, honour and praise.

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LIST OF SYMBOLS

AAS - Atomic Absorption Spectrophotometer

BOD - Biochemical Oxygen Demand

DO - Dissolved Oxygen

COD - Chemical Oxygen Demand

I- Ionic Strength

EC - Electrical Conductivity

Mol/L- Mole per Litre

Mg/L - Milligram per Litre

μg. l⁻¹- Microgram per Litre

dS/m- DeciSeimen per meter

meq/L- Milliequivalents per litre

μS cm⁻¹- MicroSiemen per centimeter

mi- Molar concentration of a free ion

γι - Free ion activity coefficient for that species

m_T - Total ion concentration

ai - Activity of the free ion.

f_i - Percent free ion.

SPSS - Statistical Package for the Social Science

WHO - World Health Organization

ABSTRACT

The estimation of ionic strength and its activities in well water source within the vicinity of Ikole local government Ekiti state was conducted. A total of fifteen (15) water samples were collected from five locations (A1, A2, A3, B1, B2, B3, C1, C2, C3, D1, D2, D3, E1, E2 and E3) from the study area. These samples were examined for major cations and major anions using Atomic Absorption Spectro-photometer (210/211VGP (AAS)) and Technicon Autoanalyzer AAII system respectively. From the result, it was deduced that the Electrical conductivity, temperature, pH. major cations and anions of the water samples were all within the WHO (2008) acceptable permissible limit. The ionic strength was calculated using the major anions and cations. The calculated ionic strength was graphically plotted against determine electrical conductivity to obtain linear regression equation which is used as new model of determining ionic strength (Predicted ionic strength). The result obtained from the comparism of the linear regression and coefficient of determination between ionic strength and Griffin and Jurinak, Marion and Babcock and Gillman and Bell only occurred at 8% except for Predicted ionic strength whose coefficient of determination is 4%. This proves that it is difficult to determine ionic strength from electrical conductivity variables obtained. This is in contrast to reports of excellent relationship between ionic strength and electrical conductivity. The lack of significant relationship between ionic strength and electrical conductivity is probably caused by errors in measurement of electrical conductivity of these water samples. However, Ca concentration appears to be the major factor responsible for variation in the ionic strength between samples level, ionic strength can be predicted by Ca concentration up to 92% in the water samples. Institutions around the study area should be equipped with the necessary experimental equipment and laboratory for research purposes and also to maintain the integrity of the samples.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

Water is an essential resource ever known man and his environment. Habitation of man is obviously and largely dependent on the availability of natural water. This is because in every activities known to man is definitely dependent of water. It is a vital resource for human activities like industry, agriculture, transportation, recreation and domestic activities (Awomeso et al, 2010).

Water being excessive resource to man also came with its own attentive quality concern. The quality of water determines the usable factor to man and his environment. For example, salt water from the sea is not advisable for irrigation of livestocks and other agricultural usage.

Water is classified under two main categories based on its location, which are namely; surface water and ground water (Appelo et al, 2005). The access of the ground water to the surface for usage includes the development bore holes and hand dug wells. Hand dug wells being the aim of this project is described as the excavation or structure with an estimated depth, water volume and cemented wall developed by local contractors with local tools for the assessment of ground water to the surface. The well water is drawn to the surface with the use of containers like iron, rubber or plastic buckets.

Natural waters such as mineral water and seawater have often a non-negligible ionic strength due to the presence of dissolved salts which significantly affects their properties. The ionic strength of a solution is a measure of the individual concentration of ionic either cation or anion in that solution (Wikipedia). Increased ionic strength and changes in ion composition may lead to shifts in community composition and function based on factors such as taxa-specific preferences and adaptations. Measurements of electrical conductivity, salinity, and total dissolved solids (TDS) are often used to represent the ionic strength of water and generally increase with increasing ion content. This module provides advice for deciding whether or not to include increased ionic strength as a candidate cause of biological impairment.

lonic strength is required for the theory of double layer and related electrokinetic phenomena and electroacoustic phenomena in colloids and other heterogeneous systems. That is, the Debye length,

which is the inverse of the Debye parameter (κ) , is inversely proportional to the square root of the ionic strength. Both molar and molal ionic strength have been used, often without explicit definition. Debye length is characteristic of the double layer thickness. Increasing the concentration or valence of the counterions compresses the double layer and increases the electrical potential gradient (Wikipedia).

lonic compounds are natural constituents of both inland and marine systems, and are not harmful unless levels exceed or fall below the tolerance range of aquatic organisms. Being exceeded can be as a result of pollution or other factors. Pollution in affects not only water quality but could also be dangerous to aquatic life (Sunnudo-Wilhelmy et al, 1999). Ground water can also be contaminated by naturally occurring element sources. These natural occurring element sources are mostly from soil and geological formations of the earth crust containing high level of these ions which leaches through infiltration or percolation of water into the ground water.

Indeed, some constituents of ionic compounds are essential elements, necessary for the survival of aquatic organisms and humans too. Salts are ionic compounds composed of cations (positive charge) and anions (negative charge). Common salt ions include:

- Cations: Na^+ Ca^{2+} Mg^{2+} K^+
- Anions: Cl HCO₃ CO₃² SO₄²

lonic strength may significantly impact freshwaters through interactions with other stressors, and it may be difficult to distinguish among proximate stressors and interacting stressors. Potential interactions include:

- Increased salinity may foster or hinder uptake of toxic substances by organisms (Bidwell and Gorrie 2006, Zalizniak et al. 2006, Environment Canada and Health Canada 2001).
- Salts impact soil structure, potentially decreasing soil permeability (Rengassamy 2002), increasing runoff volume, and increasing soil erosion (Environment Canada and Health Canada 2001).
- Salt solubility increases as temperature increases.

1.2 Justification

The presence of these high ionic components in water can cause some complicated health problems. With the high increase in population and human activities in Ekiti state, there is need for high quality of water since the source of water is mainly from hand dug wells. This provokes the necessity for estimating or measuring of the ionic strength and its activities in these well waters. These methods include; measurement based on molar concentration of dissolved ions and their valences and measurement based on electrical conductivity.

1.3 Aim and Objectives of the Study

The aim of the study is to prove that evaluation of ionic strength from electrical conductivity is easier and convenient than ionic strength from major ions in the selected environs of Ikole Ekiti.

Therefore, the objectives of this project or study are to:

- I. Compare of methods of estimating the ionic strength and activities in hand dug well water.
- II. Determine the major ions affecting ionic strength of the well water.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Water Quality Assessment

Ground water constitutes 20% of water present as freshwater. The value of groundwater lies not only in its wide spread occurrence and availability but also in it's consistent good quality, which makes it an ideal supply for drinking water (UNESCO, 2000). Contaminated water resources have important implications on health and environment (Peterson et al., 1971). The importance of water quality in human health has recently attracted a great deal of interest. In developing world, 80% of all diseases are directly related to poor drinking water and unsanitary conditions (Olajire and Imeokparia, 2001; Chung et al., 2007).

Water quality is determined by the concentration of physical, chemical and biological contaminants. It is the measure of the condition of water relative to the requirements of one or more biotic species and to any human need or purpose.

2.1.1 Physical quality assessment

Most common physical contaminants of water are suspended sediments. These are properties which are often apparent to casual observer such as colour, odour, taste and turbidity. Most of these sediments have some humic matter which tends to change the physical content of the water (resulting to colour change). Also the suspended sediment on the surface of the water tends to blur out the clarity or transparency of the water avoiding the easy passage of transcending sun light resulting to water turbidity. Odour and taste in water may have natural origins, such as earthly, fishy, rotten hydrogen sulphide, aromatic swampy, clayey or Industrial effluent into the water system can also change the natural state of the water, for instance, of chlorine, camphor, pharmaceuticals, e.t.c. (Nikoladze and Mints, 1989).

2.1.2 Chemical Quality Assessment

Chemicals are the major sources of water contamination. Some chemicals are introduced during movement through geological materials or by manufactured chemicals. These chemical parameters includes: pH, Electrical conductivity (E.C), Total solids (TS), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Total Hardness, Calcium Hardness, Magnesium Hardness, Nitrates,

Phosphates, Sulphates, Chlorides, Dissolved Oxygen (D.O), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Fluorides, Free Carbon-di-oxide, Potassium and Sodium.

The ground water quality is relatively uniform throughout an aquifer. Changes in quality occur slowly due to the fact that it is not exposed to the air and is not as subject to direct pollution and contamination from runoff as surface water. Due to natural filtering action of the aquifer, the ground water is relatively free from microbes than surface water. In most cases contamination results either from improper well construction or poor waste disposal facilities (American Water Works Association, 1971). The urbanization process threatens the ground water quality. The urban population in Ikole town of Ekiti state does not match with provision of basic infrastructure like water supply, sanitation and waste management.

Chemical parameters of drinking water quality give an indication of water acceptability for human consumption, which can be domestic use, agricultural use and industrial use (Chatwell et al., 1989). The chemical parameters must be taken into consideration in the assessment of water quality, such as source protection, treatment efficiency and reliability and protection of the distribution network (WHO, 1996).

2.1.3 Biological quality assessment

Biological contaminants are primarily from animal and human wastes. The presence of organic matter and bacteria are measured by Biological Oxygen Demand (BOD) and coliform count. BOD is a measure of oxygen required to oxidize the organic matter present in a sample, through the action of microorganisms contained in a sample of wastewater. It is the most widely used parameter of organic pollution applied, to wastewater, as well as, surface and groundwater (Bhatia, 2009). Microorganisms use the oxygen to decompose complex organic molecules present in the water in their aerobic metabolic processes. The coliform count is used to determine the presence of harmful bacteria in the water. This is done by looking for the presence of a common bacterium, Escherichia coli, which is present in excrement. The idea is that, if the water is contaminated with this common bacterium, there is a possibility of contamination by pathogenic or harmful bacteria as well.

2.2 Indices of Chemical Quality of Water

Water quality index can be evaluated on the basis of various physical, chemical and bacteriological parameters (TirkeyPoonam and BhattacharyaTanushree, November 2015). Therefore chemical parameters in this study are to evaluate the sample parameters and compare them to the provided guidelines. The essence of this experiment is to avoid or present the excessive intrusion of those chemical parameters into the water as well as human bodies and the habitats in the surrounding environments.

2.2.1 Electrical conductivity

Electrical conductivity is widely used to indicate the total ionized constituents of water. It is widely related to the sum of cations or anions as determined chemically and is closely correlated, in general, with the total salt concentration (http://www.duluthstreams.org)

Human activities also influence conductivity. Acid mine drainage can add iron, sulphate, copper, cadmium and other ions if minerals containing them are exposed to air and water. Sewage and farm runoff can raise conductivity due to the presence of nitrate and phosphate. Runoff roads can also carry salt and other materials that contribute ions to water. WHO (1984) recommended 1000μS/cm as maximum contaminant limit for drinking water. The conductivity of most freshwaters ranges from 10 to 1,000 μS cm⁻¹ but may exceed 1,000 μS cm⁻¹, especially in polluted waters, or those receiving large quantities of land run-off. In addition to being a rough indicator of mineral content when other methods cannot easily be used, conductivity can be measured to establish a pollution zone, e.g. around an effluent discharge, or the extent of influence of run-off waters.

2.2.2 Total Dissolved Solid

The TDS in water consist of organic salts and dissolved materials. In natural waters, salts are chemical compounds comprise of anions such as carbonates, chlorides, sulphates and nitrates (primarily in ground water), and cations such as potassium, magnesium, calcium and sodium. In ambient conditions, these compounds are present in portions that create a balanced solution (http://www.duluthstreams.org). According to WHO (1984), there has not been any deleterious physiological reactions occurring in persons consuming drinking water that have TDS values in excess of 1000mg/l. WHO, however, recommends the low level of the latter as a guideline value

for TDS. Kempster *et al.*, (1997) reported a critical TDS value of 2450mg/l above which some long term health problems might be anticipated due to excessive concentrations of dissolved particles in drinking water. TDS is determined using Gravimetric method (APHA, 1998).

2.2.3 Alkalinity and Acidity

Alkalinity

The capacity of water to accept H+ ions is called alkalinity. Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids.

Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of water to support algae growth and other aquatic life, so it can be used as a measure of water fertility. Alkalinity is usually given in the unit mEq/L (milliequivalent per liter), ppm (part per million), or mg/L (milligram; per liter). (http://www.advacedaquarist.com/issues/feb2002/chemistry.htm). Water with high alkalinity is said to be "hard." The most prevalent mineral compound causing alkalinity is calcium carbonate, which can come from rocks such as limestone or can be leached from dolomite and calcite in the soil.

(http://www.ehow.com/about_5098791_causes-high-alkalinity-water.html#ixzz1Hfw7KCsE). Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonation, and hydroxide ion.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

 $CO_3^{2-} + H^+ \rightarrow HCO_3^-$
 $OH^- + H^+ \rightarrow H_2O$

Acidity

Acidity is produced by substances that yield hydrogen ions on hydrolysis. The definition for acidity is the reciprocal of that used for alkalinity with the substitution of the word hydrogen for hydroxyl. In other words, a substance is acidic if it neutralizes hydroxyl ions. The determination of acidity is made at the indicator used in a titration. The titrated acidity of water is expressed in terms of milliequivalents per liter (meq/L) of hydrogen ions or as equivalent concentration of calcium carbonate or of sulfuric acid.

The importance of hydroxide ions in the attack of neutral waters on rock minerals has been indicated by the presence of hydrogen ions in most of the reaction equations. The three sources of the [H⁺] that participate in such reactions are;

- 1. Hydrolysis, as in $[H_2O] = [H^+] + [OH_-]$,
- 2. The disassociation of acidic solutes $H_2CO_3 = [H^+] + [HCO^{3-}]$, and
- 3. Oxidation reactions such as $[H_2S] + 4[H_2O] = [SO_4^{2-}] + 10[H^+] + 8$ electrons.

2.3 Cation and Anion Concentration

• Main Ions

Mineral substances contained in natural waters in the dissolved state (in the form of ions, complex ions, undissociated compounds and colloids) are conventionally subdivide into macro components and micro components. The macro components comprise the so-called main ions that determine water chemical type and account for the bulk of natural water mineral content (up to 95% for fresh water and up to 99% for highly mineralized waters). The micro components comprise substances occurring only under certain conditions and in very small concentration (µg.1-1 and < mg.1-1). An immediate position is occupied by ions of hydrogen, compounds of nitrogen, phosphorus and silicon dissolved in water.

The concentration of all minerals is related to two main factors – the abundance of chemical elements in the Earth's crust and the solubility of their compounds.

The main anions contained in natural waters are Cl⁻, SO_4^{2-} , HCO_3^- , and CO_3^{2-} and the main actions are Ca^{2+} , Na^+ , Mg^{2+} and K^+ .

2.3.1 Major Anion Concentration

Chloride ions (Cl⁻) have a large migratory ability in connection with the very high solubility of chloride of sodium, magnesium and calcium. That is chlorides are widely distributed in nature as salts of sodium (NaCl), potassium (KCl), and calcium (CaCl₂) [Department of National Health and Welfare (Canada), 1992]. Their presence water is naturally associated with the process of leaching from minerals (e.g. gallite, sylvite, carnallite, bischofite), from rocks (e.g. nephelines), and from saline deposits. It is also present in atmospheric precipitation, and today it is particularly associated with industrial and municipal wastes. Chloride ions occur in all types of water in concentrations from parts of mg.1⁻¹ to hundreds of g.kg⁻¹ (in brines). Chloride increases the electrical conductivity

of water and thus increases its corrosivity. In metal pipes, chloride reacts with metal ions to form soluble salts (WHO Regional Office for Europe, 1979), thus increasing levels of metals in drinking-water. In lead pipes, a protective oxide layer is built up, but chloride enhances galvanic corrosion (Gregory, 1990). It can also increase the rate of pitting corrosion of metal pipes.

Sulfate ions (SO₄²⁻) are contained in all surface waters, and their content is limited by the presence of calcium ions together with which they form a slightly soluble CaSO₄. Sulphates are discharged into the aquatic environment in wastes from industries that use sulphates and sulphuric acid, such as mining and smelting operations, kraft pulp and paper mills, textile mills and tanneries (Delisle et al., 1977). The main source of sulfate in water is various sedimentary rocks which include gypsum and anhydride. Water enrichment by sulfates takes place both by the process of oxidation of sulfide, which is abundant in the Earth's crust, and oxidation of hydrogen sulfide which is created during volcanic eruption and is present in atmospheric precipitation. The process of decompositions and oxidation of substances of vegetable and organic origin containing sulfur, and also human economic activity, have an effect on sulfur content in water bodies. The sulfate content of waters of rivers and freshwater lakes reaches several tens of mg.1⁻¹. USEPA as well as WHO set the Maximum contaminant level of sulphate in drinking water at 250 mg/L

Hydrocarbonate and carbonate ions (HCO³⁻ and CO₃²⁻) occur in natural waters in dynamic equilibrium with carbonic acid in certain quantitative proportions and form a carbonate system of chemical equilibrium connected with the pH of water. When the pH of water system is 7 to 8.5 the predominant ion is hydrocarbonate. When pH is less than 5, the content of the hydrocarbonate ions is close to zero. Carbonate ions dominate when pH > 8. The sources of HCO₃⁻ and CO₃²⁻ are various carbonate rocks (limestones, dolomites, magnesites), from which dissolution takes place with the participation of carbon dioxide. The degree of hardness of drinking water may be classified in terms of its calcium carbonate concentration as follows: soft, 0 to <60 mg/L; medium hard, 60 to <120 mg/L; hard, 120 to < 180 mg/L; and very hard, 180 mg/L and above (Thomas 1953).

Hydrocarbonate ions always dominate in water with low mineralization, and often in waters with moderate mineralization. Accumulation of hydrocarbonate ion is limited by the presence of calcium ions, forming with HCO₃-, a poorly dissolved salt. Usually in surface fresh water HCO₃-

content does not exceed 250 mg.1⁻¹ (with the exception of soda alkaline water sin which HCO₃⁻¹ and CO₃²⁻¹ content can reach grams and even dozens of grams per kilogram)

2.3.2 Major Cation Concentration

lons of sodium (Na⁺). The migratory ability of sodium as an element is rather high, as all its salts have high solubility. In waters with low mineralization Na⁺ is third in concentration. With higher mineralization, the content of sodium rises, all in waters have mineralization of some g.kg⁻¹ it becomes a dominant ion.

The source of Na⁺ in waters are deposits of various salts (rock-salt), weathering products of limestone rocks, and its displacement from the absorbed complex of rocks and soils by calcium magnesium. An excessive level of sodium is easily detected by taste. In solutions at room temperature, taste thresholds for sodium present in salts such as sodium chloride and sodium sulphate are approximately 130 to 140 mg/L. Domestic water softeners can give levels of over 300 mg/litre, but much lower ones are usually found [WHO Regional Office for Europe, 1979 (EURO Reports and Studies No. 2)]. Generally, the taste is offensive at a concentration of >200 mg/L sodium (whether chloride or sulphate) [WHO Regional Office for Europe, 1979 (EURO Reports and Studies No. 2)].

the solubility of its compounds is very similar to sodium. However, it occurs in lower concentration in surface waters as it has weak migratory ability. This is due to its active participation in biological processes, e.g. absorption by living plant and micro-organisms. Case-studies of toxicity resulting from high doses of salt substitutes have described chest tightness, nausea and vomiting, diarrhoea, hyperkalaemia, shortness of breath and heart failure (WHO, 2009). WHO set maximum contaminant level at 30mg/l. adverse health effects due to potassium consumption from drinking-water are unlikely to occur in healthy individuals. Potassium intoxication by ingestion is rare, because potassium is rapidly excreted in the absence of pre-existing kidney damage and because large single doses usually induce vomiting (Gosselin, Smith & Hodge,

Ions of calcium (Ca²⁺). The basic sources of calcium are carbonate rocks (limestones, dolomites) that are dissolved by carbonic acid contained in water. When the availability of carbon dioxid (with

which it is in a balance), is low, however, the reaction begins to proceed in a reverse direction, accompanied by precipitation of CaCO₃. Another source of Ca²⁺ in natural water is gypsum, is common in sedimentary rocks. Calcium ions dominate in the cation composition of low-mineralized waters. Calcium is essential to human health (http://www.lenntech.com/Periodic-chart-clements/Ca-en.htm). Calcium is unique among nutrients, in that the body"s reserve is also functional: increasing bone mass is linearly related to reduction in fracture risk (WHO, 2004).

The WHO Guideline maximum contaminant level of calcium in drinking water is 200mg/l.

leas of magnesium (Mg2+). Magnesium is less abundant than calcium in the Earth's crust. It enters surface water as a result of the process of chemical weathering and dissolution of dolomites, marls, and other rocks. Magnesium ions occur in all natural waters, but very seldom dominate. Its concentration in river waters ranges from one to tens of mg.1-1. The weaker biological activity of magnesium, as compared with calcium and also the higher solubility of magnesium sulfate and bydrocarbonate as compared with calcium, equivalent compounds of calcium, favour increase of concentration in water. With higher water mineralization, the ratio between calcium and begins to change towards predominance of the latter. However, due to the role guesium plays in water hardness, WHO drinking water guideline has maximum contaminant red to be 150mg/l (WHO, 2006). The WHO concluded that the magnesium content of water is acardiovascular risk factor and that supplementing drinking water with magnesium should priority, much became fluoride one w.nsf.org/international/press release.asp?p id=12041).

Conversion of concentration of dissolved cations and anions to ionic activities

The activity coefficient is the ratio of an ion's activity to its concentration in solution. The activity

coefficient of ions in solution may be estimated from ionic strength using a variety of equations,

and as the Debye-Huckel and Davies equations.

we need to do an equilibrium calculation of the percent free which we express as f_i . Thus:

 $m_i = m_T \times f_i$

For the case where we have Ca_T but we want Ca²⁺ we need to calculate the ratio:

$$fCa^{2+} = [Ca^{2+}]/Ca_T = [Ca^{2+}]/([Ca^{2+}] + [CaSO_4^{\circ}] + [CaCO_3^{\circ}])$$

Once we have the concentration of the free ion (m_i) we need to convert it to the activity of the free ion (a_i) . To do that we use the free ion activity coefficient (γ_i) that corrects for electrostatic shielding by other ions. This correction is written as:

$$a_i = \gamma_i \times m_i$$

 m_i = molar concentration of a free ion

 γ_i = free ion activity coefficient for that species

The total expression with both correction factors is then written as:

$$a_i = \gamma_i \times f_i \times m_T$$

m_T is the total ion concentration

 $f_i = \%$ of the total concentration, m_T , that is free

Sometimes γ_i and f_i are combined together and called the total activity coefficient, γ_T .

Then,

$$a_i = \gamma_T m_T$$

Where, the total activity coefficient = $\gamma_T = \gamma_i f_i$

How do we obtain values for γ_i and f_i .

• γ_i --- Free Ion Activity Coefficient

The free ion activity coefficient describes the relation between the activity and concentration of a free ion species. We use either some form of the Debye-Huckel type equations or the mean salt method

• fi --- % free = We obtain this from a chemical speciation calculation done by hand or using a computer program like MINTEQA2 or HYDRAQL.

2.5 Methods to Measure Ionic Strength of Water

Ionic strength is defined as:

$$I = \frac{1}{2} \left(\sum_{i} M_{i} z_{i}^{2} \right)$$

Where M = the molar concentration of ion i, and z = the valence of ion i. However, the identities of all ions present in surface and ground waters are generally not known. Therefore, the ionic strength of such waters cannot be accurately calculated from the concentration of ions present.

2.5.1 Measurement Based On Molar Concentration of Dissolved Ions and Their Valences

Most surfaces in contact with a highly polar liquid (such as water) acquire a surface charge, either by dissociation of ions from the surface into the solution or by preferential adsorption of certain ions from the solution. The surface charge is balanced by a layer of oppositely charged ions (counterions) in the solution at some small distance from the surface. In dilute solution, this distance is the Debye length k^{-1} which is purely a property of the electrolyte solution. The Debye length falls with increasing ionic strength (i.e., with the molar concentration M_i and valency z_i) of the ions in solution.

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_{\rm B} T}{e^2 N_{\rm A} \sum_i z_i^2 M_i}\right)^{1/2}$$

Where I is the ionic strength of the electrolyte, ε_0 is the permittivity of free space, ε_r is the dielectric constant, k_B is the Boltzmann's constant, T is the Temperature, N_A is Avogadro's Number. e is the elementary charge,

2.5.2 Measurement Based On Electrical Conductivity

Electrical conductivity or conductance: Ability of a solution to conduct current (measured in μS/cm, mS/cm, μmho/cm, or mmho/cm), which is related to ionic strength, temperature, and the mobility of ions. One siemen (S) is equal to one mho, and these terms are used interchangeably. "Specific conductivity" indicates the measurement has been normalized to a reference temperature (usually 25°C). Conductivity increases approximately 2% for every 1°C increase in water temperature (Wetzel 2001).

An approximation of ionic strength from surface water conductivity

- Griffin & Jurinak. Ie $(dS/m) = 0.0127*E.C-0.0003\times10^{-3}$
- Marion & Babcock. $Ie(dS/m) = 0.01442*E.C^{1.009} \times 10^{-3}$
- Gillman & Bell. $Ie(dS/m) = 0.012*E.C 0.004 \times 10^{-3}$

2.6 Actual Calculations of Ionic Activities in Water

Debye-Huckel Equations:

Extended Debye-Huckel

Log
$$\gamma_i$$
 = -A $z_i^2 I^{1/2} / (1 + a_i. B. I^{1/2})$ for $I < 10^{-1}$

For water at 25°C the constants are:

$$A = 0.51$$

$$B = 0.33 \times 10^8$$

Because the Debye-Huckel limiting law has a limited range of application chemists added a term to take into account that the central ion has a finite radius. Thus the extended D-H equation has a term called the ion size parameter (a). This term is supposed to take into account the fact that ions have a finite radius and are not point charges.

The ion size parameter has no clear physical meaning. It is too large to correspond to the ionic radii of the ions. It therefore must include some aspect of the hydrated radii. In reality it is merely an adjustable parameter that has been used by modellers to empirically extend the fit of the equation to higher ionic strength.

Table 2.1 Parameters of Ion size and activity coefficients for ionic strength by J. Kielland (1937).

Ion Size		Activity Coefficients Calculated with (2) of Table 3.3 for Ionic Strength					
Parameter, a (Å) ⁴	Ion	10-4	10-3	10-2	0.05	10-1	
9	H ⁺ Al ³⁺ , Fe ³⁺ , La ³⁺ , Ce ³⁺	0.99	0.97 0.74	0.91 0.44	0.86 0.24	0.83 0.18	
8	Mg^{2+} , Be^{2+}	0.96	0.87	0.69	0.52	0.45	
6	Ca ²⁺ , Zn ²⁺ , Cu ²⁺ , Sn ²⁺ , Mn ²⁺ Fe ²⁺	0.96	0.87	0.68	0.48	0.40	
5	Ba ²⁺ , Sr ²⁺ , Pb ²⁺ , CO ₃ ²⁻	0.96	0.87	0.67	0.46	0.39	
4	Na ⁺ , HCO ₃ , H ₂ PO ₄ , CH ₃ COO ⁻ SO ₄ ⁻ , HPO ₄ ⁻ PO ₄ ⁻	0.99 0.96 0.90	0.96 0.87 0.72	0.90 0.66 0.40	0.81 0.44 0.16	0.77 0.36 0.10	
3	K ⁺ , Ag ⁺ , NH ₄ ⁺ , OH ⁻ , Cl ⁻ ClO ₄ ⁻ , NO ₃ ⁻ , I ⁻ , HS ⁻	0.99	0.96	0.90	0.80	0.76	

^e After J. Kielland, J. Am. Chem. Soc., 59, 1675 (1937). Reproduced with permission from American Chemical Society.

Davies Equation

Log
$$\gamma_i$$
 = -A $z_i^2 \{I^{1/2} / (1 + I^{1/2}) - 0.3 I\}$; for $I < 0.5$ (almost seawater)

In this version of the Debye-Huckel equation a simple term, linear in I, was added at the end of the equation. This term improves the empirical fit to higher I but it has no theoretical justification. So this equation is purely empirical. Because of its simplicity it is used in many of the chemical equilibrium computer programs.

In this equation all ions of the same charge have the same value of γ_i because there is no ion size parameter.

• Guntelberg Equation

Log γ_i = -A $z_i^2 I^{1/2} / (1 + I^{1/2})$; for I < 0.10 (useful in solutions of several electrolytes)

This is an alternative form of extended Debye-Hückel equation. At ionic strengths greater than 0.1, extended Debye-Hückel and Guntelberg Equation can be modified to the Davis equation by adding a further term:

Log
$$\gamma_i = -A z_i^2 \{I^{1/2} / (1 + Ba_0 I^{1/2}) + 0.3 I\};$$

or

Log
$$\gamma_i = -A z_i^2 \{I^{1/2} / (1 + I^{1/2}) + 0.3 I\}.$$

Table 2.2: Summary of Debye-Huckel type, Guntelberg and Davies equations. The f in these equations is the same as what we are calling γ .

Approximation	Equation ^a		Approximate Applicability [ionic strength (M)]
Debye-Hückel	$\log f = -Az^2 \sqrt{I}$	(1)	<10-2.3
Extended Debye-Hückel	$= -Az^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}}$	(2)	< 10 ⁻¹
Güntelberg	$= -Az^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$	(3)	< 10 ⁻¹ useful in solutions of several electrolytes
Davies	$= -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$	$(4)^{b}$	•

[&]quot;I (ionic strength) = $\frac{1}{2}\sum C_i z_i^2$; $A = 1.82 \times 10^6 (\varepsilon T)^{-3/2}$ (where ε = dielectric constant); $A \approx 0.5$ for water at 25°C; z = charge of ion; $B = 50.3(\varepsilon T)^{-1/2}$; $B \approx 0.33$ in water at 25°C; a = adjustable parameter (angstroms) corresponding to the size of the ion. (See Table 3.4.)

Davies has proposed 0.3 (instead of 0.2) as a coefficient for the last term in parentheses.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of Study Area.

In general, Ekiti State is underlain by metamorphic rocks of the pre cambrian basement complex, the great majority of which are very ancient in age. These basement complex rocks show great variations in grain size and in mineral composition. The rocks are quartz gneisses and achist's consisting essentially of quartz with small amounts of white micaceous minerals. The rocks vary from very coarse grained pegmatite to grained gneisses with strong foliation.

Ikole local government area is geographically located between longitudes point of 5° 30′ 31.1′′ (5.5087°) east of green wich and latitude point of 7°47′29.3′′ (7.7915°) north Equator in Ekiti state. The state is mainly an upland zone, rising over 250 meters above sea level. Nigeria bordered by Kwara state to the north, kogi state to the north east. The local government headquarter of Ikole Ekiti is about 22.5km from Ado-Ekiti in Ekiti state. Ikole Ekiti has an area of 321 km² and a population of 168,436 at the 2006 census (Wikipedia.org).

Ikole Ekiti is situated in the deciduous forest area of state. The raining season life spam ranges from April to October, dry season from November to March. Temperature ranges from 21°c to W28°c with high humidity. Rainfall is about 70 inches per annum. The good drainage of land makes it suitable for agricultural purpose. The two season - dry season and raining season are quite distinct and are important to the agriculture pursue of the people (The Official Website of the Government of Ekiti State, Nigeria » Ikole LGA .2016).

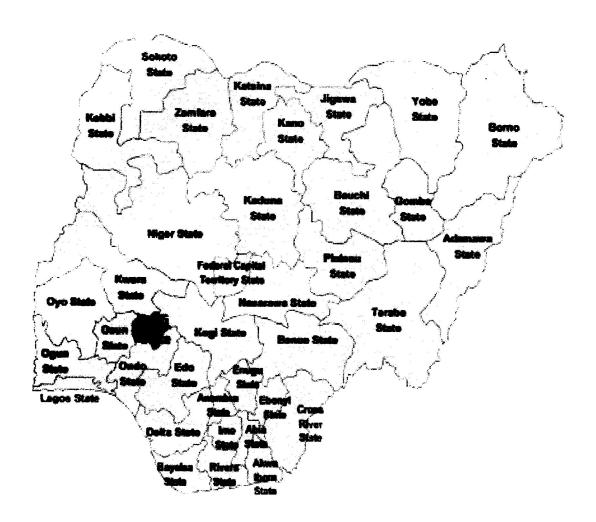


Figure 1: Map of Nigeria showing Ekiti State.

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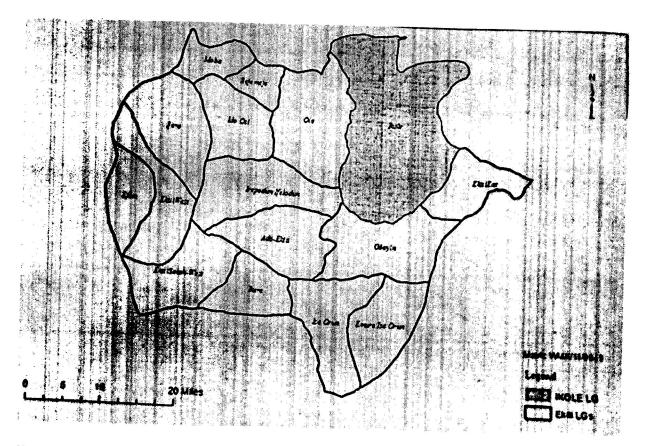


Figure 2: Map of Ekiti state showing the study area at Ikole Local Government Area.

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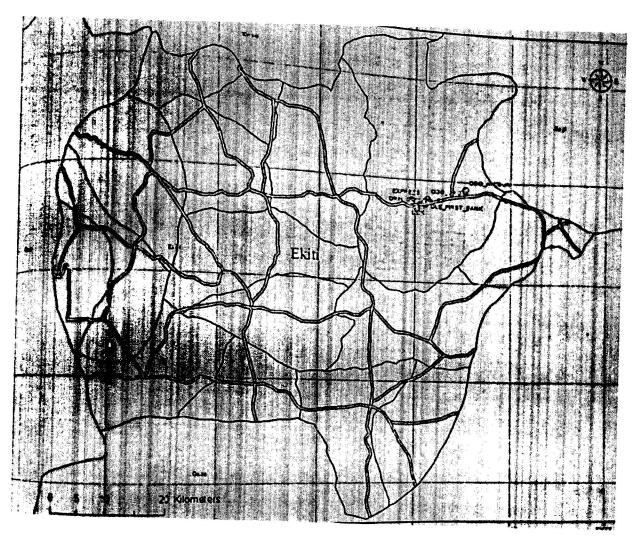


Figure 3: Map of Ekiti state showing the sampling points.

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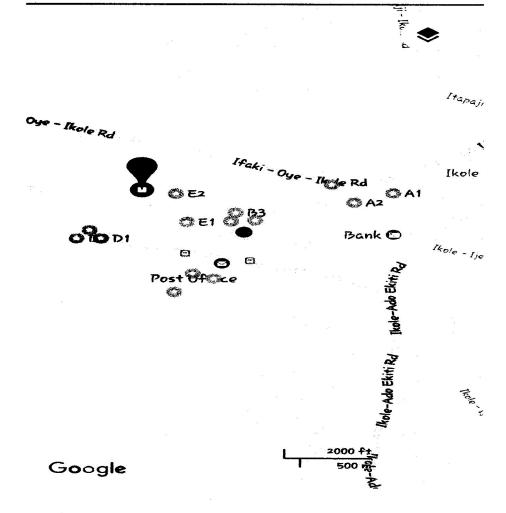


Figure 4: Road map of Ikole showing the sampling points.

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3.2 Materials and methods

The main experimental materials used were the different hand-dug wells. Three samples of water randomly collected from four locations in five communities (Usin, Asin, Isaba, Ootunja and Ilotin) in Ikole L.G.A.Ekiti State, making it a total of fifteen samples.

3.3 Location

The locations where the water samples will be collected from include: Usin, Asin, Isaba, Ootunja and Ilotin all within Ikole Local Government Area of Ekiti State.

Table 3.1: The location and the geographical coordinate points of the wells sampled (water samples).

		Geographical coordinates				
Locations	Water samples	Latitude points	Longitude points			
	Al	7.796185	5.510114			
ILOTIN	A2	7.779552	5.507673			
	A3	7.797041	5.506208			
	Ві	7.793262	5.499806			
USIN	B2	7.793381	5.501357			
	B3	7.794156	5.500109			
	C1	7.787432	5.498729			
ISABA	C2	7.786064	5.496217			
	C3	7.787959	5.497388			
	D1	7.791489	5.491552			
ASIN	D2	7.791489	5.490002			
	D3	7.792330	5.490832			
	EI	7.793179	5.497013			
OOTUNJA	E2	7.796058	5.496325			
	E3	7.796424	5.494163			

3.4 Field Studies

Three samples of water will be collected from three different wells in each communities in Ikole Ekiti. This implies that a total of fifteen samples of water will be collected. The water samples will be collected with plastic bottles. Pre-washed in 0.1m HCl and mixed with deionized or distilled water five times. The samples were taken to the laboratory for analysis.

3.5 Sample Collection and Treatment

Water from the study area which comprised fifteen sampling wells were collected between the dates of May (25th and 26th of May) the peak of raining season. The wells earmarked for sampling were picked from each zone to give a good representation of the entire study area. Seven of these wells are sited in private residence, four are public wells, two of the wells are located along the flow path of pit latrines and two are sited by a market. The choice of wells sited with different activities around them is to ascertain how this contributes to variation in their quality. The sample bottles were thoroughly rinsed with the water collected and then corked. The collection process of the water samples from the hand dug wells involves the use of bucket to manually collect the water from the bucket was transferred into the bottle, determine the pH and electrical conductivity of water samples before adding two to three drops of 0.1m HNO₃ to limit microbial activity and immediately transferred to a cooler containing ice block with a view to minimizing solute precipitation, microbial activities and loss of dissolved gases.

3.6 Laboratory Analysis

1

The ion contents of the water samples will be analyzed to determine the ionic strength of the water samples in Ikole Ekiti. The main anions contained in natural waters to be analyzed are Cl⁻, SO₄²⁻, HCO₃⁻, and CO₃²⁻ and the main cations are Ca²⁺, Na⁺, Mg²⁺ and K⁺. Two methods will be employed in the estimation of the ionic strength:

- i. Method based on Electrical conductivity
- ii. Method based on dissolved Cation and Anions.

3.7 Major ions analysis of the water samples

Standard methods as recommended by authorities such as world health organization (WHO). United State Environmental Protection Agency (US-EPA) was employed for the preparation of reagents and determination of all water quality parameters. The temperature and electrical

conductivity (EC) was measured using mercury thermometer and conductivity meters immediately after sampling. Water sample collected in the field were analyzed in the laboratory for the major cations (Ca, Mg, Na & k) using Atomic Absorption Spectrophotometer (210 / 211VGP (AAS)) and major anions (Cl, SO₄, NO₃, PO₄, HCO₃ & CO₃) using Technicon Autoanalyzer AAII system.

3.7.1 Determination of major cations

Major cations includes ca, k, mg and na in the well water samples were determined by Atomic Absorption Spectro-photometer, (210 / 211VGP (AAS)) using appropriate wave length for each cation. The Atomic Absorption Spectro-photometer, (210 / 211VGP (AAS)) was operated in the air-acetylene flame mode and single element holo cathode lamp.

The procedure involves;

- Sample in solution which may contain proportion of organic solvent to enhance signal.
- Nebulization; production gas liquid aerosol, by atomizer. Large drops drained off.
- Flame and burner; this is to remove solvent, break molecular bonds and excite the atoms
- Monochromator; the function of monochromator is to isolate the energy of the desired wavelength from that of neighboring wavelength emitted from the source.
- The photomultiplier tube (PMT) is employed to measure the amount of unabsorbed radiant energy (photon) passing through the flame and exiting slit of monochromator, converts to voltage pulse.

The detection limit for the major cations at different wavelength includes; Ca(422.7nm), Mg(285.2nm), K(766.5nm) and Na(589.0nm).

3.7.2 Determination of major Anions

Major anions (Cl, SO₄, NO₃, PO₄, HCO₃ & CO₃) using Technicon Autoanalyzer AAII system. This method of determination involves colour development, the deeper the colour the more the concentration.

3.7.2.1 Determination of chlorine

Reagents

- Potassium chromate, K₂CrO₂, 0.1 M and
- Silver nitrate, AgNO₃, 0.1 N.

Procedure

Take 10 ml aliquot of the water sample into a 250 ml conical flask and dilute to 50 ml.

Add 2 ml of 0.1 M K_2CrO_2 solution and mix thoroughly.

Titrate with 0.1 N AgNO₃ solution from a burette. The endpoint is reached when the solution gives a rather muddy yellow colour. Record the titre value.

Calculate Cl⁻ in the water sample from the amount of 0.1 N AgNO₃ solution required to titrate the aliquot to the end point.

Calculation: Cl⁻ (meq) = titre value × normality =
$$X(ml) \times N$$

 $\underline{Meq \times 35.5 \times 10^3}$

 $Cl^{-}(mg/L) = Sample aliquot (ml)$

3.7.2.2 Determination of sulphate

Reagents

- Barium chloride, Dissolve 1.526 g of barium chloride dihydrate (BaCl2-2H20) in 500 ml of distilled water and dilute to 1 liter.
- Methylthymol blue Dissolve 0.1182 g of methylthymol blue (3'3"-bis-N,N-biS carboxymethyl)-ammo methylthymolsulfone-phthalem pentasodium salt) in 25 ml of barium chloride solution. Add 4 ml of 10 N hydrochloric acid which changes the color to bright orange Add 71 ml of water and dilute to 500 ml with ethanol, The pH of this solution is 2.6. This reagent should be prepared the day before and stored in a brown plastic bottle m the refrigerator.
- Buffer, pH 10.5 ± 0.5, Dissolve 6.75 g of ammonium chloride in 500 ml of distilled water,
 Add 57 ml of concentrated ammonium hydroxide and dilute to one liter with distilled water.
- Buffered EDTA, Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer, and dilute to one liter with buffer.
- Sodium hydroxide solution, (50%) Dissolve 500 g NaOH in 600 ml of distilled water, cool, and dilute to 1liter.
- Sodium hydroxide 0.18N Dilute 14.4 ml of sodium hydroxide solution to 1liter.
- Dilution Water Add 0.75 ml of sulfate stock solution and 3 drops of Brij-35 to 2 liters of distilled water.

- Sulfate stock solution, 1 ml = 1 mg SO₄ Dissolve 1479 g of dried (105°C) Na₂SO₄ in distilled water and dilute to 1 liter.
- Dilute sulfate solution, 1 ml = 0.1 mg SO₄ Dilute 100 ml of sulfate stock Solution to 1liter.

Procedure

- The lon exchange column is prepared by pulling slurry of the resin into a piece of glass tubing 7.5 inches long, 2 0 mm ID and 3 6 mm OD. This is conveniently done by using a pipet and a loose fitting glass wool plug m the tubing. Care should be taken to avoid allowing air bubbles to enter the column. If air bubbles become trapped, the column should be prepared over again. The column can exchange the equivalent of 35 mg of calcium for the high level manifold this corresponds to about 900 samples with 200 mg/l Ca The column should be prepared as often as necessary to assure that no more than 50% of its capacity is used up.
- Allow the colorimeter, recorder and printer to warm up for 30 minutes Pump all reagents until a stable baseline is achieved.
- Analyze all working standards in duplicate at the beginning of a run to develop a standard curve The A and B control standards are analyzed every hour to assure that the system remains properly calibrated Since the chemistry is non-linear the 180 mg/l standard is set at 50% on the recorder using the standard calibration control on the colorimeter.
- At the end of each day, the system should be washed with the buffered EDTA solution.

 This is done by placing the methylthymol blue line and the sodium hydroxide line in water for a few minutes and then in the buffered EDTA solution for 10 minutes.

3.7.2.3 Determination of Nitrate

Reagents

Color developing reagent, to approximately 500 ml of distilled water add 200 ml concentrated phosphoric acid (sp gr I 834), 10 g sulfanilamide (H₂NC₆H₄S0₂NH₂) followed by 0.8 g N (1-Naphthyl) ethylenediamine dihydrochloride. Dilute the solution to 1 liter with distilled water and store in a dark bottle in the refrigerator. This solution is stable for approximately 1month.

Copper sulfate stock solution, Dissolve 2.5 g of copper sulfate (CuS0₄.5H₂0) in distilled water and dilute to 1 liter.

Copper sulfate dilute solution, Dilute 20 ml of stock solution to 2 liters with distilled water.

Sodium hydroxide stock solution, (10N) Dissolve 400 g NaOH in 750 ml distilled water, cool and dilute to 1 liter.

Section hydroxide (1.0N). Dilute 100 ml of stock NaOH solution to 1 liter.

Hydrazine sulfate stock solution Dissolve 27.5 g of hydrazine sulfate (N₂H₄.H₂SO₄) in 900 ml of water and dilute to 1 liter. This solution is stable for approximately 6 months.

CAUTION Toxic if ingested, Mark container with appropriate warning.

Hydraciae sulfate dilute solution. Dilute 22 ml of stock solution to 1 liter.

Stack mixed solution (100 mg/1 N03-N) Dissolve 0.7218 g of KN03, oven dried at 100-105°C for 2 hours, in distilled water and dilute to 1 liter, Add 1 ml chloroform as a preservative Stable for 6 months 1 ml = 0 1 mg N.

Suck nitrite solution (100 mg/1 NO₂-N), Dissolve 0.6072 g KNO₂ in 500 ml of distilled water and other to 1 liter Preserve with 2 ml of chloroform and keep under refrigeration 1 ml = 0.1 mgN.

Suched nitrate solution, Dilute 100 ml of stock nitrate solution to 1 liter 1 ml = 0.01 mgN

Thing the stock nitrate solution, prepare the following standards in 100 ml volumetric flasks At the concentration to verify the efficiency of the reduction.

Presidents

The continuous filter must be used to remove the precipitate

to colorimeter and recorder to warm up for 30 minutes obtain a stable baseline with all feeding distilled water through the sample line.

NO3-N and a 20 mg/1 NO2-N standard through the system to check for 100% of mirror to nitrite. The two peaks should be of equal height. If they are not, the standard of the hydrazine sulfate solution must be adjusted as follows. If the NO3 peak is that of the NO2 peak the concentration of hydrazine sulfate should be increased until the concentration of the hydrazine sulfate when the correct concentration of hydrazine sulfate has been determined, no a standard through the system to check for 100% the syste

contact nitrate standards in the sampler in order of decreasing concentration of nitrogen.

Contact leading tray with unknown samples. Use a 2 minute sampling rate.

3.7.2.4 Determination of phosphate

Respent

Salfuric acid solution, 5N slowly add 70 ml of conc. H₂SO₄ to approximately 400 ml of distilled water. Cool to room temperature and dilute to 500 ml with distilled water.

Antimony potassium tartrate Solution, Weigh 0.3 g K(SbO)C₄H₄O ₆.1/2H₂O, dissolve in 50 ml distilled water in 100 ml volumetric flask, dilute to volume Store at 4°C m a dark, glass-stoppered house.

Ammonium molybdate Solution, Dissolve 4 g (NH₄)6Mo₇O₂₄.4H₂O in 100 ml distilled water Store in a plastic bottle at 4°C.

Ascorbic acid, 0.1M Dissolve 1.8 g of ascorbic acid in 100 ml of distilled water. The solution IS stable for about a week if prepared with water containing no more than trace amounts of heavy metals and stored at 4°C.

Mix the above reagents in the following proportions for 100 ml of the mixed reagent 50 ml of 5N H₂SO₄, 5 ml of antimony potassium tartrate solution, 15 ml of ammonium molybdate solution, and 30 ml of ascorbic acid solution. Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed m the order given. If turbidity forms m the combined reagent, shake and let stand for a few minutes until the turbidity disappears before processing. This volume is sufficient for 4 hours operation. Since the stability of this solution is limited, it must be freshly prepared for each run. NOTE 1: A stable solution can be prepared by not including the ascorbic acid in the combined reagent. If this is done, the mixed reagent (molybdate, tartrate, and acid) is pumped through the distilled water line and the ascorbic acid solution (30 ml of ascorbic diluted to 100 ml with distilled water) through the original mixed reagent line.

Sulfuric acid solution, 11 N slowly adds 310 ml conc. H₂SO₄ to 600 ml distilled water. When cool, dilute to 1 liter.

Ammonium persulfate

Acid wash water. Add 40 ml of sulfuric acid solution to I liter of distilled water and dilute to 2 liters (Not to be used when only orthophosphate is being determined).

Phenolphthalein indicator solution (5 g/l) D1ssolve 05 g of phenolphthalein in a solution of 50 ml of clayl or isopropyl alcohol and 50 ml of distilled water.

Stock phosphorus solution, D1ssolve 0.4393 g of pre-dried (105° C for 1 hour) KH2PO4 in distilled water and dilute to 1000 ml 1.0 ml = 0.1mg P

Standard phosphorus solution, Dilute 100.0 ml of stock solution to 1000 ml with distilled water 1.0 ml = 0.01 mg P.

Standard phosphorus solution, Dilute 100.0 ml of standard solution to 1000 ml with distilled water 1.0 ml = 0.001 mg P.

Prepare a series of standards by diluting suitable volumes of standard solutions to 1000 ml w1th distilled water.

Procedure

Add 1 drop of phenolphthalein indicator solution to approximately 50 ml of sample. If a red color **develops**, add sulfuric acid solution drop-wise to just discharge the color. Acid samples must be **neutralized with 1N** sodium hydroxide (40 g NaOH/I).

Set up manifold,

Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable base line with all **reagents**, feeding distilled water through the sample line.

For the AAII system, use a 30/hr, 2.1cam, and a common wash

Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples. Switch sample line from distilled water to Sampler and begin analysis.

3.7.2.5 Determination HCO₃ and CO₃

Bicarbonate can be determined by titrating 20 ml of the water sample with 0.002 N HCl to pH 4.5 and 8.3. The water sample is titrated with 0.002 N HCl to pH 8.5 which is the inflection point for CO₃²⁻. The volume of acid used is recorded. The titration is continued to pH 4.5 which is the inflection point for HCO₃⁻. Titration curve of pH versus volume of 0.002 N HCl used can then be constructed to observe these inflection points. Bicarbonate and CO₃²⁻ ions in the sample can be calculated as follows;

Normality of acid used = 0.002Vol. of acid titrated at pH 8.3 = X (ml) Vol. of acid titrated at pH 4.5 = Y (ml)

$$CO_3^{2-}$$
 (mg L⁻¹) = $\frac{2x \times 120}{\text{Sample aliquot (ml)}}$

OR

$$CO_3^{2-}$$
 (mg L⁻¹) = $\frac{2x \times N \times 10^3}{\text{Sample aliquot (ml)}}$

$$HCO_3^{2-}$$
 (mg L⁻¹) = $\frac{(Y-2X) \ 122}{Sample \ aliquot \ (ml)}$
 OR
 HCO_3^{2-} (mg L⁻¹) = $\frac{(Y-2X)N \times 10^3}{Sample \ aliquot \ (ml)}$

Where N = normality of HCl used.

3.8 Statistical Analysis

Pearson Correlation among the chemical constituent (anions and cations) and ionic strength using PROC correlation, were all done using SAS (2012).

The graphs were collected using statistical tool for agricultural research STAR (2013).

CHAPTER FOUR

4.0 RESULT AND DISCUSSION

Table 4.1: Mean Separation for Major cations in the Water samples

	•					4.6	Z
Location	E.C	Temperature	Ph	చ్	Mg	4	
					()	101.7	
	(mS/cm)	(၃)				(a n	
						000 1 200	12+09
A	0.026 ± 0.013	26	7.7 ± 0.02	700 ± 510	69. 1 ± 2.0	0.87 ± 0.20	7.0 -1 -7.1
							00-01
B	0.021 ± 0.011	25	7.2 ± 0.01	600 ± 480	62.3 ± 1.7	7.39 ± 0.21	12 ± 0.9
						101.01	11 + 0.7
C	0.038 ± 0.025	26	8.1 ± 0.03	600 ± 480	65.2 ± 2.1	5.21 ± 0.13	\\ 11 \\
						210.002	0.8+0.3
D	0.023 ± 0.012	26	7.2 ± 0.01	600 ± 480	69.4 ± 2.0	5.79 ± 0.15	7.0 ± 0.7
						7 10 1 0 10	10 + 0 6
E	0.027 ± 0.015	26	8.3 ± 0.03	600 ± 480	79.3 ± 2.1	6.18 ± 0.18	0.0 ± 0.1
	8						S

Values are mean \pm standard error of the selected physic-chemical and units of anions and cations are in μ mol/L,

Table 4.2: Mean Separation for Major anions and ionic strength in the Water samples

				_		
IONIC_St 1/2∑Ci.Zi²) × 10 ^{−3}	(m/Sp)	0.41 ± 0.31	0.34 ± 0.21	0.37 ± 0.25	0.35 ± 0.22	0.37 ± 0.25
CO3		21 ± 0.9	22 ± 1.0	19 ± 0.7	18 ± 0.6	19 ± 0.7
нсо3		1.49 ± 0.05	1.54 ± 0.06	1.34 ± 0.03	1.29 ± 0.02	1.36 ± 0.04
P04		1.08 ± 0.07	1.16 ± 0.09	0.81 ± 0.021	0.91 ± 0.023	0.97 ± 0.027
NO ₃	(µmol/L)	0.80 ± 0.021	0.85 ± 0.023	0.73 ± 0.020	0.67 ± 0.018	0.69 ± 0.019
70 8		3.67 ± 0.17	3.90 ± 0.19	3.36 ± 0.16	3.15 ± 0.15	3.1 6 ± 0.15
ō		22 ± 1.1	24 ± 1.2	20 ± 1.0	19 ± 0.7	19 ± 0.7

Values are mean ± standard error of the selected physic-chemical and ionic strength, units of anions and cations are in µmol/L and ionic strength in dS/m.

Table 4.3: Mean Separation for different methods of estimating ionic strength

	Griffin-Jurinak	Marion-Babcock	Gillman-Bell	Predicted ionic strength
Location	0.0127*E.C-0.0003×10 ⁻³	0.01442*E.C*1.009×10 ⁻³	0.012*E.C - 0.004×10 ⁻³	1.522 *E.C+0.3324 × 10^{-3}
		(m/Sb)	n)	
A	0.32 ± 0.21	1.01 ± 0.90	0.26 ± 0.18	0.37 ± 0.22
B	0.19 ± 0.09	0.61 ± 0.46	0.14 ± 0.09	0.36 ± 0.22
O	0.47 ± 0.32	1.48 ± 1.27	0.40 ± 0.26	0.39 ± 0.25
Q	0.20 ± 0.16	0.64 ± 0.48	0.15 ± 0.09	0.36 ± 0.22
ш	0.34 ± 0.22	1.06 ± 0.92	0.27 ± 0.18	0.37 ± 0.22

Values are mean ± standard error of the selected methods of estimation of Ionic strength. Unit for methods of estimation of Ionic strength are in

The result for the mean separation of cations and anions in the water samples is shown in Table 1. Among the locations investigated, the highest E.C value was obtained in Location C (0.038) while the least value was obtained in Location B (0.021). The other locations were intermediate between the two extreme. For temperature, all the locations had similar locations as Location A, C and D had temperatures of 26°C while Location B had a temperature of 25°C. The values of the physical parameters are within approved WHO (2004) drinking water standard values. The low values of EC<1000mS/cm indicates fresh water (Freeze and Cherry, 1979).

In the case of Ca, the highest value was obtained in Location A (700 μ mol/L) while the least value was obtained in location B (550 μ mol/L), the other locations recorded values intermediate of the two extremes. In the case of Mg, the highest value was obtained in Location E (79 μ mol/L), followed by Location A, D, C, and B in the range of 62 – 69 μ mol/L.

The value of K was in the range of 5.2 to 7.4μmol/L in Location C and Location B respectively. The highest value for Na was recorded in Location A and B at 12μmol/L, followed by Location C, E and D at 11, 10 and 9.8μmol/L respectively. In respect to Cl⁻, the values were in the range of 19 to 24μmol/L. The highest value was obtained in Location B while the lowest value was recorded in Location D and E. Location C and A recorded values of 22 and 20 respectively. The values of SO₄ were in the range of 3.15 to 3.90μmol/L in Location D and B respectively. The values for the other locations were intermediate of the two extremes. A similar trend was observed for NO₃ as the highest values of 0.85μmol/L was obtained in Location B while the least value of 0.67μmol/L was obtained in Location D. The other locations had values intermediate these two extremes.

In respect to PO₄, the highest value of 1.2μmol/L was recorded in Location B, followed by Location A, E, C and D in the range of 0.81 to 1.1μmol/L. A similar trend of result was obtained in HCO₃ as the highest value of 1.54μmol/L was obtained in Location B while the least value of 1.29μmol/L was obtained in Location D, while the other locations recorded values in between the extremes. For CO₃, the values were in the range of 18 and 22μmol/L in Location D and B respectively. Location A recorded value of 21μmol/L while locations C and E recorded value of 19μmol/L apiece. The value for ionic strength was recorded within the range of 0.34 – 0.41dS/m. The highest value was obtained in location A while the least was recorded in location B. The other locations had values intermediate these two extremes.

Well water samples analyzed in the study area exhibited an overall ionic dominance of $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ for the major cations on the one hand and $Cl^{-} > CO_3^2 > SO_4^{2+} > HCO_3^{-} > PO_4^3$

> NO₃ on the other hand. This order was in contrast with the ionic dominance of freshwater which was in the order of Na⁺ > Mg²⁺ > Ca²⁺ > K⁺ and HCO₃⁻ > SO₄²⁻ > Cl⁻ reported by Burton and Liss, (1976). This observation is a clear indication of variability from one location to other in the major factors (climate, lithology and anthropogenic) controlling chemical concentrations of groundwater.

The amount of bicarbonate ions released from carbonates or made available as buffers to the acid radicals are found to control the level of acidity and relating the effectiveness of the aquifer to the concentration of Ca²⁺ present. The result shows a general dominance of chloride, calcium, magnesium and sodium ions in the water. Although all the parameters recorded showed concentration, below the WHO standard recommended for drinking water.

The process of leaching in soils and contributions from runoff increase some of the activities of ions which in turn increase electrical conductivity and ionic strength of the water sample in different locations. However, all the well water samples studied met the WHO standard for drinking water quality and other domestic usage.

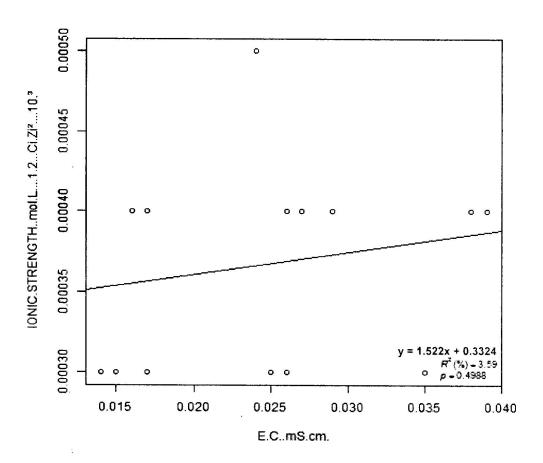
Water hardness is primarily the amount of calcium and magnesium and to a lesser extent, iron in the water and is commonly expressed as milligrams of calcium carbonate equivalent per litre. Water containing calcium carbonate at concentrations below 60 mg/L is generally considered as soft; moderately hard (60–120 mg/L), hard (120–180 mg/L) and very hard (>180 mg/L) (McGowan, 2000). Water in the study areas is suitable for domestic uses as shown by this classification.

4.1 Methods of estimating ionic strength

The result for different methods of estimating ionic strength is shown in Table 4.2. Using Griffin & Jurinak method of estimating ionic strength, the highest value was recorded in Location C (0.47), followed by Location E (0.34), A (0.32), D (0.20) and B (0.19). The same order of magnitude was found with Marion & Babcock, Gillman & Bell method, as well as Predicted Ionic Strength. Using the Marion & Babcock, the highest value was obtained in Location C (1.48), while the least value was recorded in Location B (0.61), the other locations had values in between the two extremes. Gillman & Bell recorded the highest value of ionic strength in Location C (0.40) and the least value in Location B (0.14), with other locations recording values in between the two extremes. On the other hand, using Predicted Ionic Strength method of ionic strength estimation, the highest value was also recorded in Location C (0.39), followed by Locations A and E (0.37) and Locations B and D (0.36).

4.2 Prediction of ionic strength

The calculated ionic strength from Table 1 was graphically plotted against the determined electrical conductivity. The equation obtained from the trend among the ionic strength and electrical conductivity is y = 1.522x + 0.3324. This equation obtained is used as the **predicted** ionic strength.



Graph 1: Predicted form of ionic strength

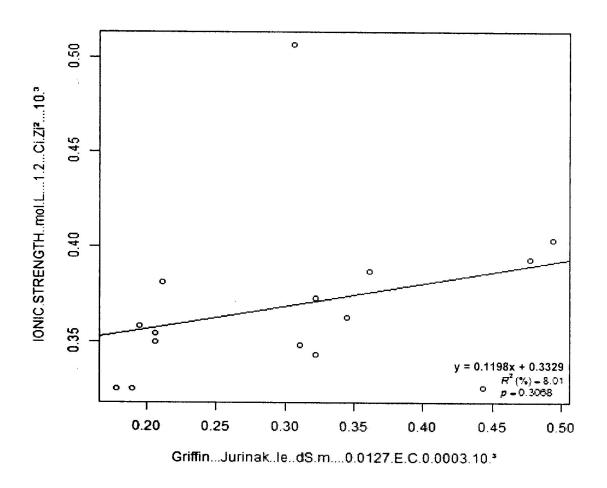
The linear regression between ionic strength and electrical conductivity is y = 1.522x + 0.3324. Y is the independent representing ionic strength and X is representing electrical conductivity.

R² is the coefficient of determination, when is higher it describes that there is a good fit between the two factors that is being compared but when is very low the fit of the two factors being compared is not very good. This is describes how fit is the relationship the two factors being compared.

In this case, R^2 is 3.59 which very low. This show that the ability of electrical conductivity predicts ionic strength is 4%. That is the linear regression or linearity between ionic strength and electrical conductivity will only occur 4 out of 100 of times. Between ionic strength and electrical conductivity there is a linear relationship y = 1.522x + 0.3324.

4.3 Comparison between ionic strength and other methods of estimation of ionic strength

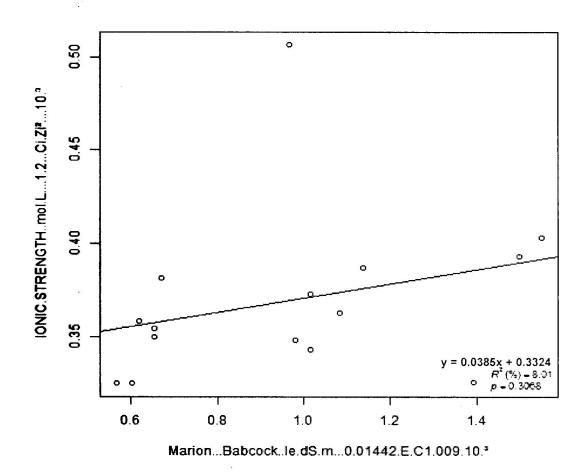
Graphical representation showing the linear relationship or regression and coefficient of determination R^2 between Ionic strength and Griffin and Jurinak.



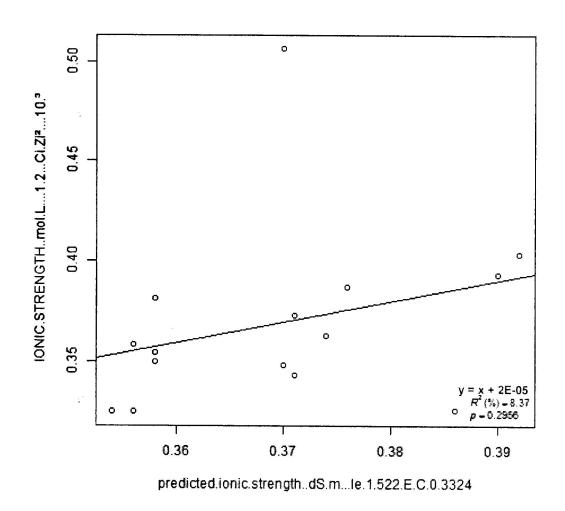
Graph2: Comparison between ionic strength against Griffin and Jurinak

R² is 0.08 which very low. This shows that the ability of Griffin and Jurinak to occur in the compared ionic strength is 8%. That is the linear regression or linearity between ionic strength

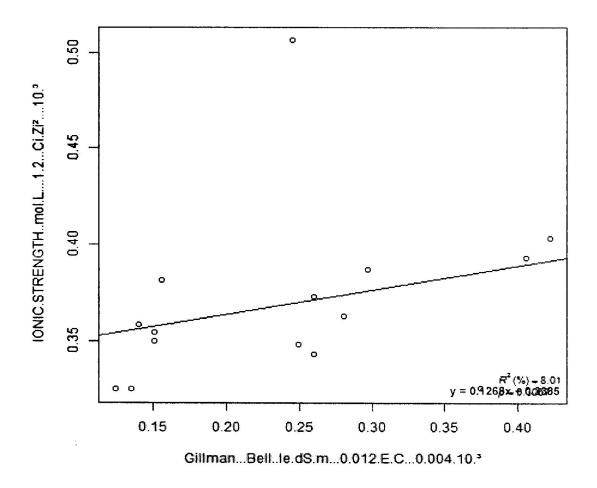
and Griffin and Jurinak will only occur 8 out of 100 of times. The linear regression y = 0.1198x + 0.3329 shows the relationship between Ionic strength and Griffin and Jurinak.



Graph3: Comparison between ionic strength against Marion-Babcock



Graph4: Comparison between Ionic strength against Predicted ionic strength



Graph5: Comparison between Ionic strength against Gillman & Bell

Graph 2, 3, 4 and 5 all represent the comparison between ionic strength against Griffin and Jurinak, Marion and Babcock, Predicted ionic strength and Gillman and Bell respectively. Each of these graphs have different linear regression equations which are y = 0.1198x + 0.3329, y = 0.0385x + 0.3324, y = x + 2E-05 and y = 0.1268x + 0.3385 but the coefficient of determination R^2 of each graphs are similar (0.08).

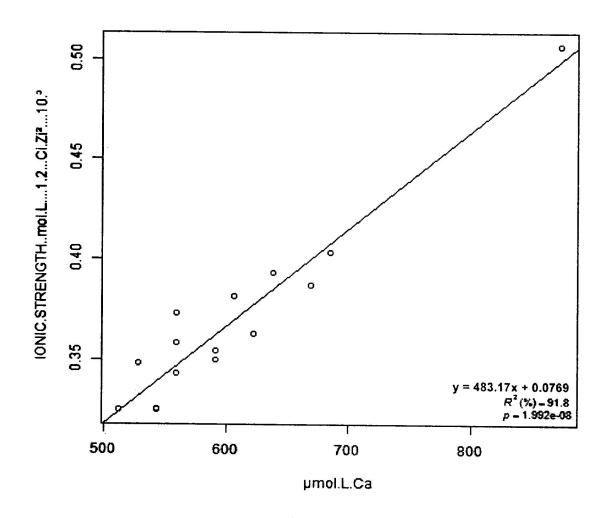
This shows that the ability of each of these methods of estimation of ionic strength is 8 out of 100. That is the linear regression or linearity between ionic strength and Griffin and Jurinak, Marion and Babcock, Predicted ionic strength and Gillman and Bell will only occur 8 out of 100 of times. This proves that it is difficult to determine ionic strength from electrical conductivity variable of the water samples.

4.4 Correlation among individual ions and ionic strength

Table 4.4: Comparison of (upper diagonal) and the similarity (lower diagonal) of the paired major cation and anion in water samples from the five different locations

IONIC_St	0.92***	0.20724	-0.03951	0.0739	0.07389	0.07387	0.07413	-0.03958	0.1068	0.10689
CHEMICAL COMPOSITION OF IONS	Са	Mg	¥	Na	D	S04	No3	Po4	нсо3	Co3

^{*, **, *** -} Significance at P = 0.05, 0.01 and 0.001.



Graph6: Comparison between Ionic strength against Calcium

The strong correlation between ionic strength and Ca (r = 0.92) indicates that Ca is almost the sole determination of ionic strength in these water samples.

The major ion affecting ionic strength of the well water is of the cation which is calcium evidenced by the correlation coefficient of 0.92***.

CHAPTER FIVE

5.0 CONCLUSIONS

This research on the physiochemical characteristics of hand dug wells water around Ekiti State **Ikole-Ekiti, Southwest Nigeria** revealed that all major ionic concentrations as well as the physical **parameters** (Temperature (°C), pH and EC (mS/cm) of the well water were within WHO(2004) **approved standard values** for drinking water. Well water samples analyzed in the study area **exhibited an overall ionic** dominance of $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ for the major cations on the one **hand and Cl > CO₃² > SO₄²⁺ > HCO₃⁻ > PO₄³ > NO₃ on the other hand.**

The ionic strength against Griffin and Jurinak, ionic strength against Marion and Babcock, ionic strength against Gillman and Bell all showed that there were differences among the method of estimation of ionic strength in all the locations.

The linear regression or linearity between ionic strength and Griffin and Jurinak, Marion and Babcock, Predicted ionic strength and Gillman and Bell produced $r^2 = 0.08$. This proves that it is difficult to determine ionic strength from electrical conductivity variables obtained. This is in contrast to reports of excellent relationship between ionic strength and electrical conductivity. The lack of significant relationship between ionic strength and electrical conductivity is probably caused by errors in measurement of electrical conductivity of these water samples.

However, Ca concentration appears to be the major factor responsible for variation in the ionic strength between samples level, ionic strength can be predicted by Ca concentration up to 92% in the unter samples.

5.1 RECOMMENDATION

The following is hereby recommended as possible solution to the well water quality in the study

• Institutions around the study area should be equipped with the necessary experimental equipment and laboratory for research purposes and also to maintain the integrity of the samples.

APPENDICES Appendix 1: Selected sample locations with their physic- chemical and major cations and

_	عارسا	EC	Temp	р рН	Ca	Mg	K	Na	Cl	SO ₄	NO ₃	PO ₄	HCO ₃	CO ₃
	Al	0.0244	26.0	7.5	0.8729	0.0923	0.0095	0.0059	0.0114	0.0019	0.0004	0.0015	0.0011	0.0157
	AZ	0.0248	27.0	7.7	0 .5279	0.0729	0.0073	0.0173	0.0332	0.0055	0.0012	0.0011	0.0020	0.0291
	A3	0.0274	26.0	7.9	0.6220	0.0414	0.0039	0.0116	0.0224	0.0037	0.0008	0.0006	0.0013	0.0188
	81	0.0165	25.0	6.8	0.5906	0.0632	0.0102	0.0058	0.0111	0.0018	0.0004	0.0016	0.0010	0.0143
	112	0.0143	25.0	7.5	0.5122	0.0414	0.0085	0.0174	0.0335	0.0055	0.0012	0.0013	0.0020	0.0281
	B 3	0.0157	26.0	7.3	0.5592	0.0826	0.0034	0.0138	0.0266	0.0044	0.0009	0.0005	0.0017	0.0237
	CI	0.0352	27.0	8.2	0.5435	0.0632	0.0068	0.0065	0.0126	0.0021	0.0004	0.0011	0.0010	0.0142
	CZ	0.0392	26.0	7.9	0.6847	0.0462	0.0056	0.0137	0.0264	0.0043	0.0009	0.0009	0.0016	0.0225
	G	0.0379	26.0	8.1	0.6376	0.0850	0.0033	0.0116	0.0224	0.0037	0.0008	0.0005	0.0015	0.0208
	DI	0.0152	27.0	6.8	0.5435	0.0559	0.0079	0.0076	0.0147	0.0024	0.0005	0.0012	0.0011	0.0157
	D2	0.0170	25.0	7.4	0.6063	0.0874	0.0067	0.0115	0.0221	0.0036	0.0008	0.0011	0.0015	0.0220
f	D3	0.0165	27.0	7.3	0.5906	0.0632	0.0027	0.0102	0.0197	0.0032	0.0007	0.0004	0.0012	0.0177
	EI	0.0287	26.0	8.4	0.6690	0.0632	0.0085	0.0056	0.0108	0.0018	0.0004	0.0013	0.0009	0.0135
	E2	0.0257	26.0	8.1	0.5592	0.0535	0.0065	0.0130	0.0250	0.0041	0.0009	0.0010	0.0016	0.0222
	B	0.0257	27.0	8.4	0.5592	0.1214	0.0035	0.0114	0.0219	0.0036	0.0008	0.0006	0.0016	0.0224
N	lean	0.024	26.13	7.69	0.61	0.07	6.3E-3	0.011	0.021	3.4E-3	7.5E-4	9.9E-4		
C	.V(%):	6.96	2.84	3.17	16.03	37.40	10.71	15.73	15.75	15.76	15.78	10.67		12.54

Appendix 2: Selected methods of estimating ionic strength

Sample	Ionicstrength	Griffin_Jurinak	Marion_Babcock	Gillman_Bell	P.I.S
1	0.5063	0.3066	0.9667	0.2453	0.370
2	0.3487	0.3109	0.9801	0.2494	0.370
3	0.3632	0.3444	1.0843	0.2810	0.374
4	0.3500	0.2062	0.6541	0.1504	0.358
5	0.3255	0.1783	0.5672	0.1241	0.354
6	0.3584	0.1950	0.6193	0.1399	0.356
7	0.3257	0.4435	1.3930	0.3746	0.386
8	0.4034	0.4937	1.5493	0.4221	0.392
9	0.3936	0.4769	1.4972	0.4062	0.390
10	0.3253	0.1895	0.6019	0.1346	0.356
11	0.3815	0.2118	0.6714	0.1557	0.358
12	0.3549	0.2062	0.6541	0.1504	0.358
13	0.3875	0.3611	1.1364	0.2968	0.376
14	0.3435	0.3220	1.0148	0.2599	0.371
15	0.3732	0.3220	1.0148	0.2599	0.371
ean:	0.30	0.96	0.24	0.24	0.37
V(%):	13.87	7.05	6.96	8.34	0.7

Dimension; the units are in dS/m(10⁻³)

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