# THE STUDY OF ELECTRICAL CONDUCTIVITY OF SALINE WATER: A CASE STUDY OF LAKES; NAKURU, BOGORIA-KENYA AND NATA SALTPAN SANCTUARY-BOTSWANA.

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A Thesis Submitted to the Graduate School in Partial Fulfillment for the Requirement of the Award of Master of Science Degree in Chemistry of Egerton University.

#### **EGERTON UNIVERSITY**

#### **DECLARATION AND RECOMMENDATION**

#### **DECLARATION**

I hereby declare that this thesis is my original work and has not been previously presented for a degree in any other University. All sources of information quoted have been acknowledged by means of a comprehensive list of references.

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# **DEDICATION**

To my wife Nancy Nyaboke, daughter Moraa, parents Duke Omboga and Mary Kwamboka, brothers and sisters. Thanks a lot for believing in me and always being there for me.

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#### **ABSTRACT**

Conductivity measurements have been used to estimate salinity, a feature of salt lakes and pans. Physical and chemical parameters with emphasis on the relationship between electrical conductivity (EC) and salinity were studied for brackish lakes Nakuru, Bogoria-Kenya and Nata saltpan sanctuary-Botswana during dry seasons of the hydrological cycle. Most of the measured variables, conductivity and pH, analyzed variables particularly Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> in lakes Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in Nata saltpan showed extremely high values due to the systems' low water volumes. Nutrients were found in significant concentrations in Lake Nakuru because of agricultural practices in the catchments' basin resulting to nutrient loading unlike Lake Bogoria and Nata saltpan. These studies were based on major ionic composition, which for Lakes Nakuru and Bogoria showed mean absolute salinity of 31.25 and 43.23 g/l respectively and 4.52, 14.80 and 5.54 g/l for the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> saltpans respectively. Regression analysis was used to test the hypothesis that water of relatively high salinity has a different conductivity to salinity relationship than water of low salinity. Regression analysis using log<sub>10</sub>-log<sub>10</sub> linear model provided an adequate approach to the study of the relationship between both variables Models, S  $= 0.6966K_{25}^{0.9981}$  R<sup>2</sup> = 0.972, S = 0.6471K<sub>25</sub><sup>1.018</sup> R<sup>2</sup> = 0.967 and S = 0.7228K<sub>25</sub><sup>1.030</sup> R<sup>2</sup> = 0.745 for lakes Nakuru, Bogoria and Nata saltpan respectively were developed, where S is the salinity in g/l and K<sub>25</sub> is conductivity at 25°C in mScm<sup>-1</sup> to predict salinity from conductivity measurements for Kenya and Botswana saline waters with similar ionic composition. There was no statistical difference in the logarithmic relationship for waters of high and low salinities in the lakes and saltpans. From the concentrations of major ionic species in the lakes and saltpan waters, ionic strength (IS) for each was calculated. Ionic strength for the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> saltpans were 0.038, 0.092 and 0.047M respectively whereas that of Lake Nakuru and Bogoria were 0.166 and 0.195M respectively.

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#### LIST OF ABBREVIATIONS AND ACRONYMS

**AAS** – Atomic Absorption Spectroscopy

**AR** – Analytical Reagent

C<sub>i</sub> – Concentration of Ionic Species i

**Cl–S** – Chloride Salinity Relationship

**C-T** — Conductivity Temperature Meter

**EC** – Electrical Conductivity

**E**<sub>e</sub>, **E**<sub>o</sub> – Energies at Exited and Ground State Respectively

**FES** – Flame Emission Spectroscopy

**g**<sub>e</sub>, **g**<sub>o</sub> – Statistical Weight of Excited and Ground State Electrons Respectively

**GF/C** – Whatman Micro Filters

**HCL** – Hollow Cathode Lamp

**IC** – Ion Chromatography

**IS** – Ionic Strength

**K** – Boltzman Constant

**Meg/l** – Mill equivalent per litre

**mM**<sub>i</sub> – Millimolar Concentration

**mScm**<sup>-1</sup> – Milisiemens per Centimeter

**mSm**<sup>-1</sup> – Millisiemens per Meter

 $\mathbf{pH}$   $-\log[H^+]$ 

**ppm** – parts per million

**PSS** – Practical Salinity Scale

**R**<sub>t</sub> – Salinity Dependence of Conductivity

**TDS** – Total Dissolved Solids

**TSS** – Total Suspended Solids

**Λ** – Equivalent Conductance

λ- Equivalent Conductance of anion

 $\lambda_{+}$  – Equivalent Conductance of Cation

**Λ**<sup>o</sup> – Equivalent Conductance at Infinite Dilution

**μm** – Micro Millimeters

- **h** − Planck's constant (6.6×10<sup>-34</sup>Js)
- $\lambda$  Wavelength
- $|Z_i|$  Absolute Value of the Charge of the Ion

#### **CHAPTER ONE**

#### INTRODUCTION

#### 1.1 Background to the Study

Saline lakes had not received adequate attention from international limnological community until recently (Comin, *et al*; 1992). Besides this, most of the published research has been done on permanent and deeper saline lakes (Hammer, 1986), and only a few studies on shallow, temporary systems (Garcia and Niell, 1993; Garcia, *et al*; 1995). Many shallow and temporary salt lakes are regarded as aberrant, sterile and lifeless ecosystems of little economic value apart from their minable deposits (Williams, 1998). For the last decade, there has been considerable interest in inland saline (anthalassic) lakes as they are different from saline lakes in coastal areas, which are influenced by marine systems (Page, *et al*; 1987).

Dissolved constituents of water bodies are often determined as major component of baseline limnological studies (Gebre, et al; 2002). Large quantities of dissolved compounds render fresh water unsuitable for domestic or industrial use. Total dissolved solids (TDS) refer to total concentration of inorganic solids, which is usually measured in mg/l. A straightforward technique of measuring TDS is to filter out particulate and then evaporate the water in a preweighed dish, getting a weight for the solids left behind from a measured amount of sample (Anderson, et al; 1999). This experimental technique of drying and weighing presents difficulties. It has been observed that the temperatures necessary to drive off last traces of water decompose bicarbonate and carbonates to oxides (M<sub>2</sub>O, where M = Na or K), and halides are lost during heating to dryness (Antonio, et al; 2002). Such results lead to errors in both quantitative and qualitative determination of compounds or elements. Note, that if we weighed the solids caught on the filter, we would have a value for total suspended solids (TSS) in the sample. The ions commonly quantified in water to comprise TDS include Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> (Gebre, et al; 2002). The presence of these major chemical constituents gives water the ability to conduct electricity and essentially constitute the total ionic salinity of waters. Other ions make only very minor contributions (Wetzel and Likens; 1991; Wetzel, 1983). In natural waters, these ions are present in balanced proportions

that are determined by equilibrium between the solution and the geologic formation (Anderson, et al; 1999).

#### 1.2 Surrogate Measures of TDS

A more accurate way to determine TDS is complete chemical analysis of all individual dissolved ions and add the values (Williams, 1998). A limitation of this analytical process is the tedious and time consuming effort involved and cannot be carried out in the field during routine work (Anderson, et al; 1999). The most important surrogate measures involve measurement of density, electrical conductivity and freezing point depression (Williams, 1998). The use of conductivity as an accurate estimator of TDS and a reliable surrogate of salinity has become important because of the ease of measuring this parameter and due to high sensitivity and precision of the method, table 2.5 (APHA, et al; 1995). Limnologists studying fresh water have used conductivity for many years and oceanographers have defined the salinity of seawater in terms of its conductivity (Anon, 1981). Conductivity measurements have also been used by limnologists interested in saline lakes, although with more caution because of the heterogeneity in ionic composition of such waters. When saline lakes are of relatively constant ionic composition, conductivity assumes much greater utility. However, the conventional numerical relationship values do not seem to be applicable across a broad range of lakes thus limnologists often make conversion factors for a given set of lakes (Gebre, et al; 2002). For example, Wood and Talling (1988) derived a model for a set of Ethiopian inland waters. The model between conductivity and dissolved materials derived by Williams (1966) has proved to be particularly useful for Australian limnologists (De Deckker and Geddes, 1980; Geddes, 1976).

Electrical conductivity is expressed in terms of the specific electrical conductivity, which is defined as the reciprocal of electrical resistance in Ohm ( $\omega$ ), in relation to water cube of edge length 1 cm at 25°C (Williams, 1998). The specific EC unit is given in siemens per cm (Scm<sup>-1</sup>), where S= $\omega$ <sup>-1</sup> (AWRI, 2005). Conductivity depends upon the concentration, mobility, oxidation state of dissolved ions and temperature of the water (AWRI, 2005; Williams, 1998). Electrical conductivity does not give specific information about chemical species present in

water, but it gives a determination of TDS, which is an acceptable indicator for water characteristics.

#### 1.3 Estimating TDS from Electrical Conductivity Measurements

Total dissolved solids (mg/l) in a sample can be estimated by multiplying conductivity (in microohms per centimeter) with an empirical factor (Anderson, *et al*; 1999). This factor may vary from 0.55-0.90, depending on the soluble components of the water and on the temperature of measurements (APHA, 1998). Relatively high factors may be required for saline or boiler waters, whereas low factors may apply where considerable hydroxide or free acid is present (APHA, 1995). Even though sample evaporation results in the change of bicarbonate to carbonate, the empirical factor is derived for a comparatively constant water supply system (APHA, 1998).

#### 1.4 Sources of Ions in Water

(i) Geology (rock type): The rock composition determines the chemistry of the watershed soil and ultimately the lake. For example Na-feldspar and calcite weathering results to the following ions in water

$$2NaAlSi_{3}O_{8(s)} + 2CO_{2(g)} + 3H_{2}O_{(l)} - 4SiO_{2(s)} + Al_{2}Si_{2}O_{5}(OH)_{4(aq)} + 2Na^{+}_{(aq)} + 2HCO_{3}^{-}_{(aq)} \\ CaCO_{3(s)} + H_{2}CO_{3(aq)} - Ca^{2+}_{(aq)} + 2HCO_{3}^{-}_{(aq)}$$

- (ii) The size of the watershed (Lake Basin): A bigger watershed to lake surface area means relatively more water draining into the lake because of a bigger catchment source area and more contact with soil before reaching the lake.
- (iii) Other sources of ions to lakes include wastewater from sewage treatment plants, nutrients and atmospheric inputs, which may be reflected by increased electrical conductivity (EC).

Electrical conductivity determination is useful in aquatic studies because it provides an estimate of dissolved ionic matter in water (AWRI, 2005). Low values of specific conductance are characteristics of high quality, oligotrophic (low nutrient) lake waters (AWRI, 2005). High values are observed in eutrophic lakes where pollutants such as fertilizers are in greater abundance. A sudden change in conductivity can indicate a direct discharge or other source of pollution into the water (Fang *et al*, 2005). Conductivity readings

do not provide information about specific ionic composition and concentrations. Chloride, phosphate, sulphate, nitrate, carbonates and bicarbonate anions as well as calcium, magnesium, sodium and potassium cations are major contributors to overall conductivity of the system (Williams, 1998).

#### 1.5 Statement of the Problem

Regular measurement of electrical conductivity by limnologists provides information about total dissolved solids (TDS) but has limitations in determining the ionic strength and specific ions contribution to conductivity. Also there is no information whether empirical relationship between conductivity and TDS is obeyed at all salinity levels. Therefore, there is need to study the relationship between electrical conductivity and total dissolved solids in saline water systems and their ionic strengths.

#### 1.6 General Objectives

The overall objectives of the study was to investigate the concentration of ions in saline waters, establish the relationship between conductivity and salinity in those saline waters and finally through the relationship established develop a model which will be used to determine salinity on only measuring salinity for waters with similar ionic composition

#### 1.7 Specific Objectives of the Study

The objectives of this study were to:

- (i) Determine the concentration of individual dissolved ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>) in saline waters and ionic strength.
- (ii) Empirically test the relationship between conductivity and TDS for saline lakes Nakuru, Bogoria-East Africa and Nata saltpan waters in the Northern part of Botswana, Southern Africa.
- (iii) Develop models from results obtained above, which will be used to determine salinity on measuring only conductivity *in situ*. For saline waters with similar dissolved ions.

# 1.8 Justification of the Study

The relationship between conductivity and TDS is different in highly saline and low saline water systems. Therefore, there is need to compare relationships of these variables in saline waters of different dilution factors. Trace elements are likely to contribute greatly towards total electrical conductivity than major dissolved ions. These waters are particularly suitable for examining this relationships because they exhibit high salinity, moreover they are typified as bicarbonate / carbonate dominated where specific conductance is believed to be very closely proportional to concentrations of major dissolved ions.

#### **CHAPTER TWO**

#### TECHNIQUES FOR MAJOR DISSOLVED ION ANALYSES IN WATER

#### 2.1 Atomic Spectrometric Techniques for Base Cations Analyses

Atomic spectrophotometries are popular detection techniques with the requisite selectivity and sensitivity to measure base cations and trace elements in water and other processed samples. These techniques deal with spectroscopy of atoms (Fifield, *et al*; 2000). Electronic transitions take place within the atom when energy is absorbed, giving line spectra, since the transitions are quantized (Gary, 2004). There are various ways to obtain free atoms (atomic vapor) and to measure the absorption or emission of radiation by the atoms. In Flame Emission Spectrometry (FES), atoms in the form of atomic vapor are created in a flame; a portion of them is thermally and collisionally excited to higher electronic energy and then returned to their ground energy state by emitting photons, to create sharpline emission spectra. While in Atomic Absorption Spectrometry, an amount of radiation absorbed by ground state atoms created in a flame or a minifurnace is measured; the absorption spectrum is created (Gary, 2004). Atomic spectrometry is widely applied and the particular techniques used depend on the sensitivity required, number of samples to be analyzed, and whether single-element or multielement measurements are needed.

#### **2.1.1 Flame Emission Spectroscopy (FES)**

In emission spectrometry the source of excitation energy is a low energy flame giving simple emission spectrum. Consequently, few elements have been determined routinely by FES, especially those that emit line spectra. Only the easily excited alkali metals Na, K and Li are routinely determined by FES (Fifield, *et al*; 1995).

### **Principle**

In FES the sample solution is introduced into the flame as a fine spray, subjected to high temperature to evaporate the solvent, leaving dehydrated salt that is dissociated into free gaseous atoms in the ground state (Gary, 2004). A certain fraction of these atoms absorb energy from the flame enabling them to be raised to an excited electronic state. The excited atoms relax from the excited state to ground state by collision with other particles (Collision

relaxation) or by emission of radiation (Radiative relaxation) emitting photons of characteristic wavelength, with energy equal to  $h\lambda$ , where h is Planck's constant  $(6.6 \times 10^{-34} \text{Js})$  and  $\lambda$  is the wavelength (Robinson, 1996), which is detected with a conventional monochromator detector. The intensity of emission is directly proportional to the concentration of the analyte in the solution aspirated. A calibration curve of emission intensity as a function of concentration is prepared.

The relative populations of ground state  $(N_o)$  and excited state  $(N_e)$  populations at a given flame temperature can be estimated from **Maxwell-Boltzman expression** (Gary, 2004).

$$\frac{N_e}{N_o} = g_e e^{-(Ee-Eo)} KT$$

$$N_o g_o$$

Where  $g_e$  &  $g_o$  are statistical weights of the excited and ground state respectively;  $E_e$  &  $E_o$  are energies of the two states (= hv;  $E_o$  = 0); k is the Boltzman constant (1.3805×10<sup>-16</sup> erg K<sup>-</sup>) and T is the absolute temperature.

#### 2.1.2 Atomic Absorption Spectroscopy (AAS)

AAS is a powerful instrumental technique for the determination of metals in liquid samples. Since the work of Ala Walsh in 1950's (APHA-AWWWA, 1975), the growth of analytical AAS has been phenomenal. With the advent of automation, it has become a rapid method for the detection of metals (Broekaert, 2001).

#### **Principle**

The basic principle of AAS involves atomization of the analyte followed by absorption of radiation (Broekaert, 2001). Sample solution is aspirated into a flame or furnace, and converted to atomic vapor, the flame thermally excites some but the majority remains in the ground state and absorb radiation of a specific wavelength produced by a light source known as hollow cathode lamp (HCL). The absorption follows Beer's law, where absorbance is directly proportional to the path length in the flame and to the concentration of atomic vapor in the flame. Path length is held constant and the concentration of atomic vapor is directly proportional to the concentration of the analyte in the solution aspirated (Gary, 2004).

#### 2.2 Ion Exchange Chromatography

Ion chromatography (IC), introduced in 1975 by H. Small and co-workers is a relatively new approach to the analysis of ionic species in solution (Small, *et al*; 1975). Since its advent, ion chromatography has been used to analyze anions in samples such as radioactive wastes, geothermal well waters, soil samples and a large number of environmental pollutants (Johnson, 1979; Sawicki, 1979). This technique is a variation of high performance liquid chromatography, which employs column packed with pellicular ion exchange resins having high resolution and low ion exchange capacity (Dasgupta, 1992). In suppressed ion exchange chromatography, a mixture of anions is separated by ion exchange and detected by electrical conductivity through removal of unwanted electrolyte prior to conductivity measurement (Daniel, 1999). Determination of the common anions such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and F<sup>-</sup> is desirable to characterize water (APHA, 1998). Although conventional colorimetric, electrometric or titrimetric methods are available for determining individual anions, only IC provides a single instrumental technique used for their rapid, sequential automated measurement (Dasgupta, 1992).

#### **Principle**

In IC, samples containing anion analytes, are injected into a continuously flowing eluent stream at the top of the column, and are dynamically separated into individual bands according to each ion's affinity to the resin (Dionex, 2006). This is based on the premise that different sample ions migrate through the IC column at different rates, depending upon their interactions with the ion exchange sites (Dionex, 2006). The separated anions are directed through a hollow fiber cation exchange membrane bathed in continuously flowing strong acid solution (APHA, 1998). In the suppressor, the separated anions are converted to their highly conductive acid forms and the eluent is converted to weakly conductive acid. The separated sample ions are subsequently detected by electrical conductivity. They are identified on the basis of retention time compared to standards and quantification is by measurement of peak area (Daniel, 1999). Peak heights are used to quantitate the ions but variation in sample matrix and anion concentration peak fluctuations may lead to errors.

#### 2.3 Titrimetry

Titrimetric analyses are derived from the application of the principles of solution chemistry and represent one of the conventional aspects of chemical analysis (Fifield *et al*; 1995). This method remains widely used because of its simple means of operation, which enable comparatively unskilled operator to achieve precise results (Fifield, *et al*; 2000). It is widely spread in-routine and non-routine analysis in industrial and research laboratories in determination of acidic and basic impurities, mineral and metallurgical analysis.

#### **Principle**

Titrimetry involves a controlled reaction between analyte and a standard reagent to stoichiometric point by volumetric method. Reactions suitable for use in titrimetric procedures must be stoichiometric and fast (Fifield, *et al*; 1995). Ionic reactions proceed rapidly and present few problems, but reactions involving covalent bond formation or rapture are frequently slower and a variety of practical procedures are used to overcome this difficulty (Fifield, *et al*; 2000). Ways of driving reaction to completion quickly include heating the solution, use of catalyst, addition of excess titrimetric reagent and perform back titration of the excess reagent (Mendham, *et al*; 1989). If the details of the reaction are known and stoichiometric point is located precisely, the amount of analyte present may be calculated from known quantity of standard reagent consumed in the reaction. Reactions employed in titrimetry may be classified as acid-base; oxidation-reduction; complexation; substitution or precipitation.

#### **End Point Detection**

A prerequisite for precise and accurate titration is the reproducible identification of an end point, which either coincides with the stoichiometric point of the reaction or bears a fixed and measurable relation to it. The common processes observed in end point detection are change in colour; electrical cell potential; electrical conductivity; precipitation or flocculation (Fifield, *et al*; 1995). Visual detection of endpoint is a major factor in maintaining the simplicity of titrimetry; hence the capability of human eye to detect colour change plays an integral role in these techniques. A visual indicator is a compound, which changes from one

colour to another as its chemical form changes with its chemical environment (Fifield, *et al*; 2000). Change in colour is given by the formula below.

$$ln_A = ln_B + nX (i)$$

Colour 1 Colour 2

Where X is H<sup>+</sup>, M<sup>n+</sup> or e<sup>-</sup>. An indicator constant is defined as

$$Kln = \underline{[ln_B] [X]^n}$$

$$[Ln_A]$$
(ii)

Where  $[X]^n = K \ln [\ln_A]$ 

$$[Ln_B]$$
 (iii)

and  $lnpX = lnpK + log10 [ln_B]$ 

$$[\ln_A]$$
 (iv)

A titration reaction regenerating or consuming X species, the indicator will change with concentration of X in the solution and the colour of the solution will be determined by the ratio  $[\ln_B] / [\ln_A]$ . The eye will register a complete colour change when this ratio changes from 10:1 to 1:10 (Fifield *et al*; 1995). Structurally, indicators form three groups; Phthaleins (e.g Phenolphthalein); Sulphonephthalein (e.g Phenol red); and Azo compounds (e.g Methyl Orange).

#### 2.4 Water Analyses

Water analyses for ionic composition should be done immediately after collection in the laboratory, although some other parameters are measured *in-situ*. However, this may not always be possible, especially in developing countries where transportation, electric power and trained personnel are often limiting (Gebre, *et al*; 2002). When resources are not available for measuring certain parameters or when historical data are required for reference, sound estimation of one variable based on another becomes necessary (Mackereth, *et al*; 1978). Conductivity is one such parameter that is used as an estimator of total ionic salinity (TDS) of water samples. It has often been necessary to make such indirect determinations to find values for total ions and TDS for comparative purposes.

#### 2.5 Water Sample Collection and Preservation

Several types of water matrices are sampled and analyzed, including surface, ground and spring water, saline and estuarine among others (Gary, 2004). Metal analyses present challenges right from sampling. The collection of correct samples, both in terms of location and with respect to the analytes to be performed, is fraught with difficulties. The type of sampling containers and method of cleaning them can introduce errors due to release or loss of analytes through adsorption to container surfaces (Florence, 1982). Therefore, glass containers are not recommended for sample collection and preservation because free metal ions adsorb strongly on glass surface (Mackereth, *et al;* 1978). Azlon plastic containers are accepted universally for collecting water samples. Sampling bottles should be cleaned with hot ion free soapy water, soaked in acid bath for 24 hrs, rinsed with ultra pure water and finally with the sample before sample is collected (Florence, 1982; 1977 & Meadows, *et al;* 1978).

Storage of collected samples poses challenges too. Once samples are removed from their natural environment, continuous microbial activity during sample storage may alter sample's physical parameters (Mackereth, *et al;* 1978). Preservation of samples will keep the parameters of interest in the same form as it was prior to the removal from its surroundings. No single technique will preserve all the parameters, so each parameter of interest must be considered and preserved specifically (APHA, 1998). Dissolved metal concentrations change due to their continued uptake or release by living organisms (Ebbinghaus, *et al;* 1994). Addition of concentrated nitric acid (AR) to samples to a pH of about 2 greatly inhibits metabolic processes of microorganisms, which cause changes in the sample and stops precipitation (APHA, 1998). Sulphuric acid should never be used because it leads to rapid gypsum precipitation. Freezing of samples result to ions concentrated in the unfrozen liquid remaining in the center of the container. Storage at 4° C is accepted, many analysts have not observed any significant changes in metal concentrations over a period of weeks (Leonard, 1991).

#### 2.6 Filtration

Filtration has been used to separate high molecular weight and colloidal forms of metals from dissolved species, which are often labile. Most studies have relied on filtration through membranes with 0.45µm pore size (Florence, 1982). This approach is adequate for solutes that tend to partition to the aqueous phase in systems without ion colloids (Kimball, 1995). It has been established that some colloidal materials can pass through 0.45µm pore size, and even 0.1µm filters may allow some ion colloids to pass and be analyzed as dissolved salts (Jones, *et al*; 1974). Ultra filtration membrane filters of apparent pore diameter of 1–15 nm are available, and can be used to separate a metal in true solution from that in colloidal form or to classify colloidal particulate according to their sizes (Batley, *et al*; 1978).

#### 2.7 Electrical Conductivity

Electrical conductivity is a measure of the ability of a solution to carry current and depends on the total concentration of ionized substances dissolved and temperature of water (Williams, 1998). Although all ions contribute to conductivity, their valences and mobilities differ, so their actual and relative concentrations affect conductivity (CWT, 2004). The major positively charged ions in water are sodium (Na<sup>+</sup>), calcium (Ca<sup>2+</sup>), potassium (K<sup>+</sup>) and magnesium (Mg<sup>2+</sup>) while negatively charged ions are chloride (Cl<sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>). Nitrate (NO<sub>3</sub><sup>-</sup>) and phosphate (PO<sub>4</sub><sup>3-</sup>) have minimal contribution towards conductivity even though they have important biological properties (Robert and Gene, 1991).

#### 2.7.1 Typical Conductivity Ranges of Water

**Table 2.1:** Some ranges of conductivity values encountered in the field: Clean Water Team, (2004).

Water Type	Conductivity ( <sup>µ</sup> mhos/cm) at 25° C
Distilled Water	0.5-3.0
Melted snow	2-42
Potable water in U.S.	30-1500
Fresh Water streams	100-2000

Conductivity can be much higher than the maximum values shown above under special conditions in some waters (CWT, 2004), for examples:

- (a) Naturally saline or brackish lakes or ponds.
- (b) Tidally influenced coastal waters
- (c) Rivers or drainage ditches dominated by sub surfaces, agricultural return flows and sewage effluents.

#### 2.7.2 Electrical Conductivity Measurement

Conductivity is a property of water governed by the total ionic content (Stewart, 1989). Although it is non-specific and varies with proportion of species present, it is often measured in characterizing water (Stewart, 1989). This ability depends on the presence of ions; on their total concentration, mobility, and valence and on the temperature of measurement (APHA, 1998). The conductance of a solution, G, is directly proportional to the electrode surface area, A, cm<sup>2</sup>, and inversely proportional to the distance between electrodes, l, cm. K is the constant of proportionality, known as conductivity constant or specific conductance (Crow, 1994) given below.

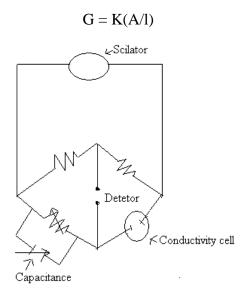


Fig 1: Bridge circuit for conductivity determination

To avoid polarization at the electrode surfaces, conductance measurement is made with an alternating current signal (Willard, *et al*; 1986). The (SI) units of conductivity is reported as millisiemens per meter (mS/m); 1 mS/m = 10  $\mu$ mhos/cm and 1  $\mu$ S/cm = 1  $\mu$ mhos/cm

(Antonio, *et al*; 2002). The digital readout of modern conductivity meter is in C/R units recorded as μS/cm for most fresh waters but often mS/cm for brackish sample (Stewart, 1989). The specific conductance of distilled water is about 1 μS/cm and that of seawater is about 50 mS/cm (CWT, 2004). Temperature of the solution affects ionic velocity and consequently specific conductance (Philip, 1992). Conductivity increases 2-3% per degree Celsius (AWRI, 2005). Therefore, temperature measurements and records must be accurate. Temperature compensation is possible on most conductivity meters by dialing in the temperature of the sample (manual compensation) or by installing a thermistor with the conductivity cell to provide automatic compensation (Philip, 1992).

The following formula can be used to convert conductivity readings made at any temperature to an equivalent conductivity at 25°C (Jeffrey and Bassett, 2001).

$$\mathbf{K}_{25} = {}^{\mathbf{K}}/_{1+0.025 \text{ (t-25)}}$$

In which,  $K_{25}$  is the compensated conductivity measured, K is the measured conductivity in  $\mu$ S/cm and t is the water temperature at which conductivity is measured.

#### 2.7.3 Equivalent Conductivity

Mixed electrolytes are more frequently encountered in practice than single electrolytes. The equivalent conductivity,  $\Lambda$ , of a solution is the conductivity per unit of concentration (APHA, 1998). As the concentration is decreased towards zero,  $\Lambda$  approaches a constant designated as  $\Lambda^{o}$  (Crow, 1994). It is necessary to convert concentration to units of equivalents per cubic centimeters since K is in units of micromhos per centimeter

#### $\Lambda = 0.001$ K/Concentration

Where the units of  $\Lambda$ , K and concentration are mhoscm<sup>2</sup>/equivalent,  $\mu$ mho/cm and equivalent/l respectively. Equivalent conductivity  $\Lambda$ , values for several concentrations of KCl are listed in appendix 10 (Jaspher, 1988). Kohlrausch's law of independent ionic mobility points out that conductivity of a solution is the sum of individual contributions from the positive and negative ions (Crow, 1994). For a single dissolved salt the equivalent conductance can be expressed as

$$\Lambda = \lambda_{+} + \lambda_{-}$$

Where,  $\lambda_{+}$  is the equivalent conductive of the cation and  $\lambda_{-}$  is the equivalent conductive of the anion (Gary and James, 1978). For mixture,  $\lambda_{-}$  would be equal to the sum of the entire individual ionic conductance,  $\lambda_{+}$  s' and  $\lambda_{-}$ s' (Gordon, 1988).

#### 2.7.4 Calculation of Conductivity

For naturally occurring water containing mostly Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg <sup>2+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>and  $SO_4^{2-}$  empirical procedure can be used to calculate conductivity from measured ionic concentrations (Hamilton, 1978). The abbreviated water analysis in Table 2.2 illustrates the calculation procedure. At infinite dilution the contribution to conductivity by different kinds of ions is additive (Gordon, 1988). In general, the relative contribution of each cation and anion is calculated by multiplying equivalent conductance  $\lambda^o_+$  and  $\lambda^o_-$  mho-cm<sup>2</sup> /equivalent by concentration in equivalent per liter (APHA, 1998).

**Table 2.2:** Sample Analysis Illustrating Calculation of Conductivity,  $K_{calc}$  for Natural Waters: Hamilton, C, E, 1978

Ions	mg/l	mM	$ Zi   \lambda^o_{\pm} m M$	$\mathbb{Z}^2$ mM
$Mg^{2+}$	12	0.49	52.0	1.96
$Ca^{2+}$	55	1.38	164.2	5.52
$Na^+$	28	1.22	61.1	1.22
$\mathbf{K}^{+}$	3.2	0.08	5.9	0.08
HCO <sub>3</sub>	170	2.79	124.2	2.79
$SO_4^{2-}$	77	0.80	128.0	3.20
Cl	20	0.56	42.8	0.56
Total			578.2	15.33

Table 2.3 contains a list of equivalent conductance for ions commonly found in natural waters (Dean, 1985). Trace concentrations of ions generally make negligible contribution to the overall conductivity (APHA, 1998).

**Table 2.3:** Equivalent Conductance  $\lambda^{o}_{+}$  and  $\lambda^{o}_{-}$  for Ions in Water at 25°C Hamilton, C, E, 1978

Cation	$\lambda^{o}_{+}$	Anions	λ°.
$SH^{+}$	350.0	OH	198.6
$1/2Ca^{2+}$	59.5	HCO <sub>3</sub>	44.5
$1/2Mg^{2+}$	53.1	$1/2\text{CO}_3^{2-}$	72.0
$Na^+$	50.1	$1/2SO_4^{2-}$	70.0
$K^{+}$	73.5	Cl	76.1
$N{H_4}^+$	73.5	$Ac^{-}$	40.9
$1/2 Fe^{2+}$	54.0	$\mathbf{F}$	54.4
$1/3 \text{Fe}^{3+}$	68.0	$NO_3$	71.4
		$H_2PO_4^-$	33.0
		1/2HPO <sub>4</sub> <sup>2-</sup>	57.0

At finite concentrations as opposed to infinite dilution, conductivity per equivalent decreases with increasing concentration. For solutions composed of single dissolved salt the decrease in conductivity per equivalent with concentration can be calculated using an ionic-strength-based theory of Onsager (Robinson and Stokes, 1959). When mixed salts are present, as is nearly always the case with natural saline waters, the above theory is quite complicated (Harned and Owen, 1958). Therefore, the following semi empirical procedure can be used to calculate conductivity for naturally occurring saline waters.

$$k^{o} = \Sigma \; |Z_{i}| \; (\lambda^{o}_{\; \text{-I}}) \; (mM_{i}) + \Sigma \; |Z_{i}| \; (\lambda^{o}_{\; \text{-I}}) \; (mM_{i})$$

Where,  $|Z_i|$  is the absolute value of the charge of the  $i^{\text{-th}}$  ion,  $mM_i$  is millimolar concentration of the  $i^{\text{-th}}$  ion and  $\lambda^o_{+I}$ ,  $\lambda^o_{-I}$  are equivalent conductance of the  $i^{\text{-th}}$  ion. If mM is used to express concentration, the product  $(\lambda^o_{+I})$   $(mM_i)$  or  $(\lambda^o_{-I})$   $(mM_i)$ , corrects the units from liters to  $cm^3$ . The procedure is as follows

(i) Calculate ionic strength, IS in molar unit

$$IS = 1/2000 \Sigma Zi^2 (mM_i)$$

(ii) Calculate the monovalent ion activity coefficient,  $\gamma$  using Davies equation for IS  $\leq$  0.5 M and for temperature from 20 to 30° C (Robison and Stokes; 1959; Davies, 1962).

$$y = 10^{-0.5[\sqrt{IS}(1+\sqrt{IS})-0.3IS]}$$

(iii) Finally, obtain the calculated value of conductivity  $k_{calc} = k^{o}y^{2}$ 

#### 2.8 Salinity

Salinity is a measure of all dissolved salts, the sum total of all ion concentrations of water (Sherwood *et al*, 1995). High Salinity in inland water systems compromise ecological values of surface water and limits domestic, agricultural, industrial and recreational uses for water (CWT, 2004). One cause of increased salinity is land management practices that increase recharge of water to ground water systems (AWRI, 2005). This brings water tables nearer the surface, and increases discharge of salt laden ground water to stream or the amount of salt washed into streams in runoff (Hammer, 1986). Irrigation causes water table to rise leading to salination of surface waters or in addition, extraction of water from rivers reduces effect on the concentration of dissolved salts (Langbein, 1961).

The salinity of inland water is usually dominated completely by four major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) and the major anions (CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>) (Robert and Gene, 1991). The concentration of these ions generally constitutes over 99% of the total salinity (Mary and Pat, 1987). The salinity of water is variable and is governed by contributions from rock resources of the drainage basin, atmospheric wet and dry deposition and balance between evaporation and precipitation (Robert and Gene, 1991). Concentrations of Mg<sup>2+</sup>, Na<sup>+</sup> and Cl<sup>-</sup> ions are relatively conservative and exhibit minor spatial and temporal fluctuations within lakes and streams from biotic utilization or biotically mediated changes in the environment. On the other hand, concentrations and forms of Ca<sup>2+</sup>, K<sup>+</sup>, inorganic carbon and SO<sub>4</sub><sup>2-</sup> are highly dynamic and are influenced markedly by metabolic activities (Robert and Gene, 1991).

#### 2.8.1 Typical Salinity Ranges of Some Naturally Saline Waters

Saline water in lakes and pans has different salinity measured in g/l as shown in the table 2.4 below.

**Table 2.4:** Some ranges of salinity values of some natural water. (CWT, 2004)

Type of water	Salinity (g/l)	
Sea water	33-37	
Salton sea	46	
Mono lake	90	

#### 2.8.2 Salinity Measurement

Salinity can be determined through determinations of all individual ions and add the values (Williams, 1998). This standard analytical process involves much tedious and time-consuming effort and cannot yield the precision necessary for accurate work (APHA, 1998). Thus to determine salinity, it is important to employ simpler surrogate methods, including determination of density, electrical conductivity, freezing point depression and total dissolved solids (TDS) (Williams, 1998). From an empirical relationship between salinity and the physical property determined for a standard solution it is possible to calculate salinity. The precision of the measurement of a physical property will determine the precision in salinity (APHA, 1998).

**Table 2.5:** Precisions of various physical measurements and the resultant salinity presently attainable with commercial instruments. Antonio *et al*; (2002)

Property	Precision of measurements	Precision of salinity
Conductivity	±0.0002	±0.0002
Density	$\pm 3.0 \times 10^{-6}$	$\pm 0.0040$
Speed Sound	$\pm 0.02 \text{ m/s}$	±0.0100

Although conductivity has the greatest precision; it responds only to ionic solutes. On the other hand density responds to all dissolved solutes but it is less precise (Antonio, *et al*; 2002). This new scale breaks the chloride salinity (Cl-S) relationship in favour of salinity conductivity ratio relationship.

When TDS is measured gravimetrically (by weight), it can be greater or less than salinity, depending on whether loss of bicarbonates (HCO<sub>3</sub><sup>-</sup>) in the gravimetric analysis is more than offset by the presence and, consequently, measurement of dissolved organic carbon (CWT, 2004). A gravimetric measurement of TDS in water in an alkaline lake would probably indicate lower TDS than if TDS were measured by summation or salinity because not enough organic matter would be present in the water to make up HCO<sub>3</sub><sup>-</sup> weight loss (CWT, 2004).

Density can be determined directly by gravimetric methods or indirectly by hydrometers. Since optical density and refractive index of liquid are correlated, refractometer may be used to provide a measure of salinity based on density (Taif and Dipper, 1998).

#### 2.9 Conductivity and Salinity

A more robust approximation of salinity can be achieved by applying the following formula (Jeffrey and Bassett, 2001), instead of multiplying conductivity values by an empirical factor.

Salinity = 
$$a_1 (K_{25}) + a_2 (K_{25})^2 + a_3 (K_{25})^3 + a_4 (K_{25})^4 + a_5 (K_{25})^5 + a_6 (K_{25})^6$$

In which, 
$$K_{25}$$
 is the conductivity at  $25^{\circ}$ C,  $a_1 = 4.98 \times 10^{-1}$ ,  $a_2 = 9.54 \times 10^{-3}$ ,  $a_3 = -3.941 \times 10^{-4}$ ,  $a_4 = 1.092 \times 10^{-5}$ ,  $a_5 = -1.559 \times 10^{-7}$ , and  $a_6 = 8.789 \times 10^{-10}$ .

The salinity dependence of conductivity,  $R_t$ , as a function of temperature of a given sample to standard S = 35 seawater is used to determine salinity by applying the formula below (Antonio, *et al*; 2002).

$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + \Delta S$$
 Where  $R_t = \underline{C(S, t, 0)}$  at pressure = 0 and  $\Delta S$  is given by 
$$C(35, t, 0)$$
 
$$\Delta S = \underline{t-15} \quad (b_0 + b_1 R_t^{1/2} + b_2 R_t + b_3 R_t^{3/2} + b_4 R_t^2 + b_5 R_t^{5/2})$$
 
$$1 + 0.0162(t-15)$$

$a_0 = 0.0080$	$a_1 = -0.1692$	$a_2 = 25.3851$
$a_3 = 14.0941$	$a_4 = -7.0261$	$a_5 = 2.7081$
$b_0 = 0.0005$	$b_1 = -0.0056$	$b_2 = -0.0066$
$b_3 = -0.0375$	$b_4 = 0.0636$	$b_5 = -0.0144$

In order to determine salinity from *in-situ* conductivity measurement for saline lake or pan waters with ionic composition different from that of the seawater, the dependence of conductivity on temperature, pressure and salinity needs to be established for that water (Vollmer, *et al*; 2002). While for fresh water lakes with sufficiently diluted water, these relationships can be calculated (Millero, 2000; Wuest, *et al*; 1996), they would generally have to be determined experimentally for the brackish water to define the lake's salinity scale

(Vollmer, *et al*; 2002). The saline lake water specific conductivity dependence on pressure can be adopted in modified form from Finger (2002). Using the results and ionic absolute salinity of the lake as calculated from major ionic measurement we derive a procedure for computing salinity from C-T measurement (Vollmer, *et al*; 2002). In this procedure we convert the conductivity of brackish water to conductivity that seawater would have at the same pressure and temperature; if diluted to the same salinity as that of the lake. This seawater-equivalent conductivity is then used in the UNESCO (1981a) PSS-78 algorithm to calculate practical salinity (practical salinity S is salinity calculated from conductivity using Unesco 1981a algorithm and reported as a unitless quantity on the practical salinity scale 1978 PSS-78).

#### 2.10 Ionic Strength of Water

Ionic strength is defined as a measure of the interionic effects resulting from electrical attraction and repulsion between ions in solution (Stumm and Morgan, 1981), which includes both positively and negatively charged ions. Operationally, ionic strength is defined as  $\alpha$  in the following equation (Snoeyink and Jenkins, 1980).

$$\alpha = 1/2(\sum Z_i^2 C_i)$$

Where  $Z_i$  is the charge of ionic species i, and  $C_i$  is the concentrations of ionic species i.

Unfortunately, a precise measurement of the ionic strength of water requires a complete chemical analysis (i.e.; a complete cation-anion balance determination). However, standard methods (APHA, *et al*; 1998) notes that a measure of conductivity or total dissolved solids (TDS) can be used to estimate the ionic strength of water in the absence of complete analysis of the ions. In addition to these two surrogate measurements, salinity is also frequently used in the literature as a measure of the ionic strength. Literature regarding ionic strength effects typically does not include a true measure of ionic strength, as strictly defined above, but rather uses one of these three surrogate measurements (Crow, 1994). An excess of major ions in water can create a toxic situation for aquatic organisms. Excessive concentrations overwhelm the osmotic capacities of the organisms, resulting in toxicity (Crow, 1994).

#### 2.11 Occurrence of Salt Lakes and Pans

There must be a suitable geomorphological depression representing the terminus of a closed drainage basin and a balance between the volume of water flowing into the depression and evaporating from it or seeping away through sediments for salt lake and pans to form (Langbein, 1961). In addition to natural processes, many bodies of salt waters have been created by man through mining subsidence, sinks for excess salts (evaporation ponds) and salination of agricultural land by destruction of natural vegetation or excessive irrigation (Williams, 1998). In East Africa salt lakes are wide spread, stretching from Red sea through Ethiopia and Kenya to Tanzania (Vareschi, 1979). Most of these lakes occur within the Great Rift Valley. Salt lakes in Southern Africa mostly take the form of shallow temporary water bodies (salt pans) (Williams, 1998) such as the Makgadikgadi saltpans in Botswana.

#### **CHAPTER THREE**

#### **EXPERIMENTAL WORK**

## 3.1 Description of Study Areas

## 3.1.1 Lake Nakuru in Kenya

Lake Nakuru is a shallow alkaline-saline lake located in the Eastern arm of the Rift valley (0° 22'S, 36° 05'E). The lake has an area of 36-49 km² and a catchment basin of 1800 km² (Vareschi, 1978). It is an endorheic lake which is fed by three major rivers, namely; Njoro, Makalia and Nderit. The lake is protected within a national park and is one of the world's renowned bird sanctuaries with over 400 bird species (Curry Lindahl, 1971). However, the lake is threatened by pollution due to urban and agricultural practices in the catchment basin (Mavura, 2003; Yasindi, 1995). The lake mixes freely and winds with an average speed of 4.0 cms² circulate lake water in the afternoons after stratification during the day (Vareschi, 1982). The lake is a highly buffered system with a pH of 10.0, high salinity and conductivity. Sodium, Carbonate and Bicarbonate are the major ions while Chloride occurs in low concentrations (Milbrink, 1977).

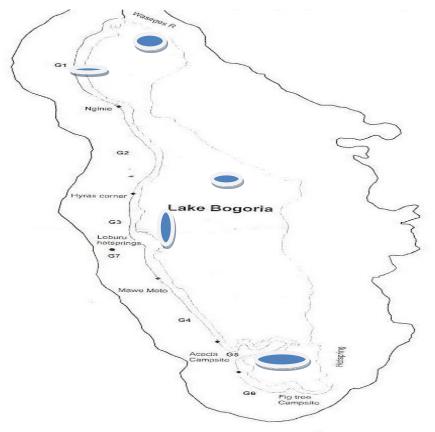


- Map Key Sampling points of Lake Nakuru National Park GPS Latitude: 0° 24′ 0″ S 0
- **GPS Longitude:** 36° 4′ 59" E

Fig 2: Lake Nakuru showing sampling areas

## 3.1.2 Lake Bogoria in Kenya

Lake Bogoria is a saline, alkaline lake with TDS of about 100 g/l and pH of 10.5. Lake Bogoria, like Lake Nakuru is home of the world's largest populations of lesser flamingoes. The lake has been protected by National Reserve since November 29, 1973. Lake Bogoria is shallow (about 10 m depth), and is about 34 km long by 3.5 km wide, with a drainage basin of 700 km². The lake waters contain large concentrations of Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions. They originate from inflow from the Sandai and Emsos rivers, and from about 200 alkaline hot springs that are present at three onshore sites. Other springs discharge directly from the lake floor. The lake has no surface outlet so the water becomes saline mainly through evaporation, which is high in this semi-arid region.



Map Key

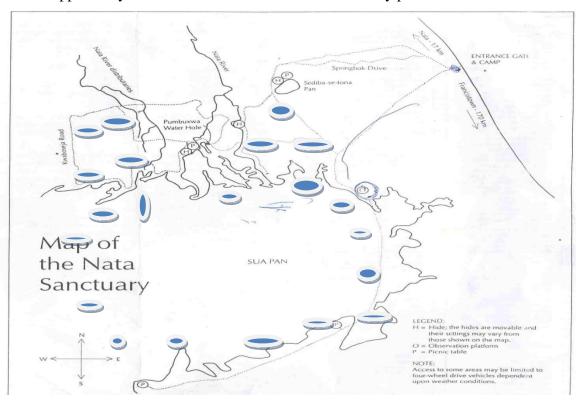
Sampling points for lake Bogoria Latitude 0° 16'33"N

Longitude 36° 06'27"E

Fig 3: Lake Bogoria showing sampling areas

## 3.1.3 Nata Salt Pan Sanctuary in Botswana

The sanctuary is located in an endorheic basin, 170 km Northwest of Francistown on the eastern tip of Makgadikgadi pans. It is shallow, with frequent seasonal drought and high degree of unpredictability. The pans are filled only when the Nata River flows with the summer rains of Zimbabwe. The sanctuary covers approximately 230 km<sup>2</sup> of which 55% is land surface and 45% is pan surface, which was once the site of the largest inland lake in Southern Africa. The pan is protected by Nata conservation committee and provides visitors with an opportunity to view birds and other wildlife in a truly pristine environment.



### Map key

Sampling points at Nata saltpan sanctuary Latitude 20° 12' 34.3044"S Longitude 26° 11' 6.8136"E

**Fig 4:** Nata saltpan showing sampling areas

### 3.2 Instrumentation

## **3.2.1** Ion Meters for Determination of Physico-Chemical Parameters

Field measurements of pH were carried out using OAKLON pH meter (OAKLON instruments; Singapore). In the laboratory, pH was measured using HANNA digital pH meter (HANNA instruments inc; Portugal). Conductivity and temperature measurement in the field and laboratory were carried out using HI 933300 portable microprocessor printing and logging multi-range conductivity model (HANNA instruments inc; Portugal).

## 3.2.2 Atomic Absorption Spectrometer

A Varian SpectrAA 220 FS atomic spectrometer (Varian, Australia) automated and controlled with *intel inside* Pentium *acer* computer using air-acetylene fuel system and equipped with a deuterium background correction was used in the determination of calcium and magnesium in saline water samples.

## 3.2.3 Flame Emission Spectrometer

Sodium and potassium were analyzed using a Sherwood Flame Photometer, model 410 (Sherwood Scientific ltd, Cambridge, UK) with air-butane fuel.

## 3.2.4 Ion Chromatography System

An anion exchange column Chrom-2000 (DIONEX Model, U.S.A) interphased with a suppressor column (ASRS\* ULTRA II 2-mm) automated with *intel celeron'D inside* LG using ultra pure water as eluent and equipped with online continuously eluent generator from de-ionized water was used in the determination of major dissolved anions in water except  $CO_3^{2-}$  and  $HCO_3^{-}$ .

## 3.2.5 A micro pipette

A micro pipette-BOECO Germany (100-1000 µl) was used for samples and standards dilutions during preparations (serial dilutions).

## 3.3 Reagents and Standard Solutions

Both in Kenya and Botswana ultra pure water, obtained by passing distilled water through a reverse osmosis system (Milli-Q water system, millipore) was used always. Redistilled nitric acid used in sample preservation and added to working standards was of spectral purity (Fluka Switzerland). Potassium chloride, sodium carbonate, sodium chloride, sodium fluoride, potassium hydrogen phosphate, sodium nitrate, sodium sulphate, hydrochloric acid, nitric acid, sulphuric acid, ascorbic acid, antimony potassium tartrate, barium chloride, all analytical reagent and metal standard stock solutions (1000 mg/l) were obtained from (SAARCHEM, South Africa). Ammonium molybdate, magnesium chloride and sodium acetate were purchased from (BDH Chemicals Ltd Poole, England). Certified riverine water reference material for base cation and trace metals, SLRS-3 purchased from the National Research Council (Canada) was used to validate the results.

## 3.4 Analytical Procedures

#### 3.4.1 Cleaning of Glassware and Sampling Bottles

The sampling containers and glassware apparatus were cleaned according to the recommended methods (Boltz and Taras; 1978; Mackereth, *et al;* 1978; WHO, 1998; APHA, 1998). They were thoroughly cleaned with metal-free non-ionic detergent solution, rinsed with distilled water, soaked in 10% nitric acid solution for 24 hrs and then rinsed with metal-free water (ultra pure water). Accurate measuring glassware were finally air dried except conical flasks that were oven dried before use.

#### 3.4.2 Preparation of Working Metal Standards

Working standard solutions for each metal were prepared by appropriate dilution of the respective 1000-mg/l stock solutions. A high purity CsCl solution was added to all samples and standards in order to buffer the ionization potential (Mendham. *et al*; 1989). In the case of calcium, a high purity LaCl<sub>3</sub> solution was added to samples and standards to improve

sensitivity in the presence of oxide forming elements such as P and Al (APHA, 1998). The final working standards for calcium and magnesium were acidified to a pH 2 by addition of two drops of concentrated analytical reagent nitric acid to minimize instability and adsorption process (Mackereth, 1978).

## 3.4.3 Preparation of Working Anions Mixture Standards

A series of standard anion stock solutions of 1000 mg/l were prepared by weighing the indicated a mount of salt, dried to a constant weight at 105°C (APHA, 1998).

**Table 3.1:** Amount of analytical reagent salts dissolved in 100 ml volumetric flasks to prepare 1000mg/l standards. Modified from APHA, 1998

Anion	Salt (AR)	Amount
Cl	NaCl	0.1646
$NO_3$	$NaNO_3$	0.1371
$PO_4^{3-}$	$KH_2PO_4$	0.1433
$SO_4^{2-}$	$Na_2SO_4$	0.1478
F	NaF	0.2210

Combined working standard solutions of (5–40) ppm concentration range were then prepared from the above stock solutions by appropriate combinations and dilution.

#### 3.4.4 Calibration of Conductivity, Temperature and pH Probes

The conductivity and temperature probes of HI 933300 portable microprocessor meter model were calibrated according to the instruction manual of the manufacturer and recommended methods (APHA, 1998). A pre calibrated cell was connected on the unit, the SET K position was selected on the RANGE switch and the SET K pot adjusted until the value of the cell was displayed as indicated on the cell. Prior to use the cell was rinsed thoroughly in ultra pure water, shaken to remove internal droplets and outside wiped dry. The display was set to zero using a rear panel zero pot while the probe was in free air. Conductivity cell was rinsed with at least three portions of 0.01M KCl solutions. Temperature of fourth portion was adjusted to

25.0±0.1°C with a probe in it. The meter was adjusted to read 1413μhomS/cm. The pH probe of Oaklon type was also calibrated according to the manufacturer's instruction manual.

## 3.5 Sampling and Sample Preservation

Representative sampling sites of water within the lakes Nakuru, Bogoria and Nata saltpans were established by selecting randomly sampling points 10, 5 and 17 respectively. Surface water samples were collected from sampling points identified during dry season in triplicate using Van Dorn sampler and then transferred to acid-washed polythene bottles. Samples for cation analysis were preserved by adding acid immediately after collection to pH of about 2 using concentrated analar nitric acid (Mackereth, 1978). Collected samples were placed in icebox container before transportation to laboratories for analysis.

## 3.6 Measurement of Physico-Chemical Parameters in-situ

Conductivity, temperature and pH were measured using HI 933300 model C-T conductivity meter and a pH OAKLON probe meters. Measurements were carried out by dipping the calibrated probes into the water and allowing the meter reading to stabilize before a reading was taken. All values were corrected to 25°C using temperature coefficient of 2.3% per °C (Talling and Talling, 1965). On arrival to the laboratory all samples were filtered using Whatman micro filters (GF/C) filter paper (Cellulose Nitrate Membrane filters of 0.45µm) before storage in the cold room at 4°C waiting analysis (Florence, 1982).

#### 3.7 Laboratory Analysis

## 3.7.1 Potassium and Sodium Analyses

A potassium or sodium appropriate filter was selected on Sherwood Flame Photometer 410 Model depending on the cation to be analyzed. De-ionized water in a cuvette was aspirated while regulating the gas supply until blue cones of the flame formed separate cones, one to each burner hole. The sensitivity controls for the galvanometer was calibrated using the strongest standard solution and deionized water. Without changing the instrument controls,

emission reading for the other standard solutions were determined and used to generate a calibration curve versus concentration of the cation (Gary, 2004). At the same instrument controls, samples for sodium and potassium analytes were aspirated separately and their concentrations determined using the calibration curves.

### 3.7.2 Calcium and Magnesium Analyses

A Varian SpectAA 220FS atomic absorption spectrometer using air acetylene fuel equipped with a deuterium background correction was used in the determination of dissolved magnesium and calcium in water samples.

**Table 3.2:** Conditions under which magnesium and calcium were analyzed using Varian SpectAA 2200FS.

Parameters	Magnesium	Calcium
Current in mA	3.00	7.00
Wavelength in Nm	202.60	422.70
Slid width	1.00	0.50
Acetylene flow rate	2.00	2.00
Air flow rate	11.00	13.50

Standards were aspirated starting with blank in the ascending order and finally, in each sample the concentration of the two elements were established by aspirating in turn and absorbance recorded in triplicate. The concentrations were determined by comparing the mean absorbance readings with their respective standard calibration curves, using established methods (Mendham, 1989 and Partin Elmer standard conditions for FAAS).

## 3.7.3 Determination of Carbonate $(CO_3^{2-})$ and Bicarbonates $(HCO_3^{-})$

Carbonate and bicarbonate were determined by titrimetry technique using 0.01N HCl. Phenolphthalein indicator was used for carbonate determination while methyl orange was used for bicarbonates. One drop of phenolphthalein indicator was added to each sample and

titrated with 0.01N standardized HCl drop-wise at an interval of 5 seconds until the colour changed from pink to colorless. The burette reading was designated as Y cm<sup>3</sup>, to the same solution two drops of methyl orange indicator was added and titrated further with the acid to the first orange colour. Burette reading was designated as Z cm<sup>3</sup>. The amount of carbonate and bicarbonate ions present in samples were calculated using the formulas below, expressed in milliequivalent per liter

Meq-CO<sub>3</sub><sup>2</sup>/l ==  $\underline{2Y} \times \text{Normality of Acid} \times 1000 \times \text{Dilution}$ Amount of Sample in ml. Meq-HCO<sub>3</sub>-/l ==  $\underline{(Z - 2Y)} \times \text{Normality of Acid} \times 1000 \times \text{Dilution}$ Amount of Sample in ml.

## 3.7.4 Determination of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup> in samples using IC technique

The pumping rate was set at 1369 psi to allow eluent flow rate of 1.22 ml/min. Each spiked sample was loaded into a sample loop manually and ICS-2000 triggered to inject the sample into the eluent stream. The pump pushed the eluent and sample through the guard and separator columns where ions were separated. The separated sample ions and eluent moved to a suppressor column where selective detection of sample ions was done while suppressing the conductivity of the eluent. The chromatogram generated was compared with that of 10 ml of sample diluted to 50 ml using de-ionized water. This procedure was repeated for all standards used in this study suspect analytes separately and samples. Concentration of analytes in samples was quantified through integration of peak area.

## 3.8 Statistical Data Analysis

Data obtained were analyzed using Excel spreadsheet packages. Linear regression was used to develop predictive models for salinity and TDS based on conductivity (independent variable). Conductivity and salinity (TDS) data were  $\log_{10}$  transformed to normalize them and stabilize the variance (log transformation was necessary to meet the assumption in linear regression of homogeneity of variance. This method provided a better fit than linear regression of untransformed data). Examining relationship at high and low salinity versus conductivity, saline water was categorized as  $(K_{25} \le 6.99 \text{mScm}^{-1} \text{ less saline}$  and  $K_{25} \ge 6.99 \text{mScm}^{-1}$  highly saline) using conductivity as a basis for salinity. The difference in slopes and intercepts of the relationships (Conductivity and salinity) between low and high salinity waters was established using variance analysis. Polynomial regression was used to examine whether a non-linear function is better to fit the joint data sets (low and high salinity waters combined) than a linear function.

# CHAPTER FOUR RESULTS

The three study areas namely lakes Nakuru, Bogoria and Nata saltpan exhibited a pattern of increasing shoreline retreat as the dry season progressed. Although the rate of shoreline retreat varied over the study period, all the three study areas followed a similar pattern. The temperature of the water samples in the study areas in situ mirrored the day to day weather temperature. Mean conductivity measurement was relatively stable in various study areas ranging from 6.99±0.82 to 62.5±0.37 mScm<sup>-1</sup> whereas total dissolved ions ranged from 4.52 to 43.23g/l. The lowest values were from the 1<sup>st</sup> Nata saltpan while the highest values were from Lake Bogoria. The limnological variables analyzed are shown in their respective tables.

## 4.1 Physico-Chemical Parameters

**Table 4.1** Physico-chemical parameters for Nata saltpan.

Sampling Site	Temperature ( <sup>0</sup> C)	PH	Conductivity	Salinity (TDS)
			mScm <sup>-1</sup>	g/l
1 <sup>st</sup> Sanctuary	25.80±1.25	9.66±0.82	6.99±0.44	4.52±0.37
2 <sup>nd</sup> Sanctuary	$27.19 \pm 0.80$	10.18±0.13	$22.80\pm0.21$	$14.80 \pm 0.14$
3 <sup>rd</sup> Sanctuary	$28.04 \pm 0.15$	10.07±0.06	$8.58 \pm 0.34$	$5.54 \pm 0.04$

 Table 4.2 Physico-chemical parameters of lake Nakuru.

Sampling	Temperature in	PH	Conductivity	Salinity(TDS)
Site	°C		in mS/cm	in g/l
MP	26.47	10.62	48.10	32.89
JW	26.71	10.42	48.32	33.43
MM	26.67	10.65	46.61	30.21
MMN	26.93	10.59	47.80	31.54
MMD	26.55	10.41	48.43	29.34
JE	25.84	10.56	46.20	27.85
MJ	26.81	10.60	48.51	33.97
MNJ	26.78	10.62	47.65	28.98
HP	26.66	10.42	47.82	30.56
MN	26.98	10.58	48.33	33.72
Mean	26.64	10.55	47.77	31.25
SD	±0.32	±0.09	±0.78	±2.18

 Table 4.3 Phyico-chemical parameters of lake Bogoria.

Sampling Site	Temperature in	PH	Conductivity	Salinity
	°C		in mS/cm	(TDS) in g/l
Bog NB	26.25	10.15	62.5	43.45
Bog CB	27.82	10.50	62.5	43.23
Bog SB	28.40	10.35	63. 8	43.84
Bog HB	27.75	10.20	63.1	43.52
Bog TB	26.82	10.55	62.9	43.85
Mean	26.25	10.15	62.5	43.23
SD	±0.86	±0.18	±0.37	±0.27

## 4.2 Chemical Composition of Lakes Nakuru, Bogoria and Nata Saltpans Water Bodies.

The tables 4.4 to 4.9, A, values are in mg/l unless stated. B, values meql<sup>-</sup> and C, values as percentage equivalents of either cations or anions.

**Table 4.4** Major base cation compositions of Nata saltpan sanctuaries.

Sanctuary	Value	Conductivity	$\mathbf{K}^{+}$	Na <sup>+</sup> (g/l)	Ca <sup>2+</sup>	$\mathrm{Mg}^{2+}$
		mScm <sup>-1</sup>				
1 <sup>st</sup>	A	6.99±0.44	86.3±4.50	0.18±0.13	1.51±0.18	1.14±0.24
	В		2.21	7.78	0.08	0.09
	C		21.72	76.61	0.79	0.88
$2^{nd}$	A	22.80±0.21	273.8±6.17	$0.63\pm0.12$	$0.28 \pm 0.02$	$0.63 \pm 0.03$
	В		7.00	27.25	0.01	0.05
	C		20.40	79.42	0.03	0.15
$3^{\rm rd}$	A	$8.58 \pm 0.34$	110.61±9.84	$0.22 \pm 0.02$	$0.98\pm0.34$	$0.80 \pm 0.20$
	В		2.77	9.61	0.05	0.07
	C		22.16	76.88	0.40	0.56
Ref SLRS-3			$0.67 \pm 0.01$	$2.09\pm0.32$	5.35±0.35	1.55±0.14
Cert. Value			$0.70\pm0.10$	2.30±0.20	$6.00\pm0.40$	1.60±0.20

 Table 4.5: Major base cation composition of lake Nakuru.

Value	Conductivity	Salinity in	$\mathrm{Mg}^{2+}$	Ca <sup>2+</sup>	$\mathbf{K}^{+}\left(\mathbf{g}/\mathbf{l}\right)$	Na <sup>+</sup> (g/l)
	in mScm <sup>-1</sup>	g/l				
A	47.77±0.78	31.25±2.18	0.02±0.01	0.21±0.04	1.38±0.23	2.37±0.05
В			0.01	0.01	34.86	103.08
C			0.01	0.01	25.27	74.72

Table 4.6: Major base cation composition of lake Bogoria.

Value	Conductivity	Salinity in	$\mathrm{Mg}^{2+}$	Ca <sup>2+</sup>	$\mathbf{K}^{+}\left( \mathbf{g/l}\right)$	Na <sup>+</sup> (g/l)
	in mScm <sup>-1</sup>	g/l				
A	62.5±0.37	43.23±0.27	0.83±0.10	3.63±0.71	0.03±0.01	3.68±0.01
В			0.07	0.18	8.10	160.00
C			0.04	0.11	4.81	95.04

Table 4.7 Major anion compositions of Nata saltpan sanctuaries.

Sanct	Value	Conduc.	Cl <sup>-</sup> (g/l)	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub>	<b>F</b>
Uary		mScm <sup>-</sup>							
1 <sup>st</sup>	A	6.99	2.09±0.13	5.66±0.64	0.35±0.04	137.01±8.29	5.14±2.14	0.03±0.09	2.64±0.53
	В		58.87	0.19	0.01	2.85	0.16	0.05	0.14
	C		94.54	0.31	0.01	4.58	0.26	0.08	0.22
$2^{nd}$	A	22.83	4.59±0.19	14.41±0.99	$0.88 \pm 0.06$	469.20±7.90	$2.07\pm0.41$	$0.04\pm0.65$	$5.65 \pm 0.17$
	В		129.55	0.48	0.01	9.76	0.07	0.05	0.30
	C		92.39	0.34	0.01	6.96	0.05	0.04	0.21
$3^{rd}$	A	8.54	$2.62\pm0.06$	6.15±1.08	$0.38\pm0.07$	171.87±3.35	6.5±0.08	$0.05 \pm 0.08$	$3.70\pm0.66$
	В		73.80	0.21	0.01	3.58	0.02	0.01	0.19
	C		94.85	0.27	0.01	4.60	0.03	0.01	0.24

Table 4.8 Major anion composition of lake Nakuru.

Value	Conduc.	Salinity	Cl (g/l)	CO <sub>3</sub> <sup>2</sup> · (g/l)	HCO <sub>3</sub> (g/l)	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub>
	mScm <sup>-1</sup>	g/l						
A	47.77±0.78	31.25±2.18	0.67±0.05	2.60±0.15	0.15±0.03	0.07±0.04	2.19±0.26	0.53±0.10
В			18.76	86.77	2.51	0.01	0.07	0.01
C			19.45	76.00	4.47	0.01	0.06	0.02

Table 4.9 Major anion composition of lake Bogoria.

Value	Conduc	Salinity	Cl (g/l)	CO <sub>3</sub> <sup>2</sup> · (g/l)	HCO <sub>3</sub> (g/l)	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub>
	mScm <sup>-1</sup>	g/l						
A	62.50±0.37	43.23±0.27	0.12±0.01	3.25±0.28	0.47±0.19	15.52±0.86	7.79±0.54	0.21±0.02
В			3.49	108.17	7.62	0.32	0.24	0.01
$\mathbf{C}$			2.94	90.25	6.36	0.20	0.20	0.01

## 4.3 Logarithimic linear regression relationship between salinity and conductivity

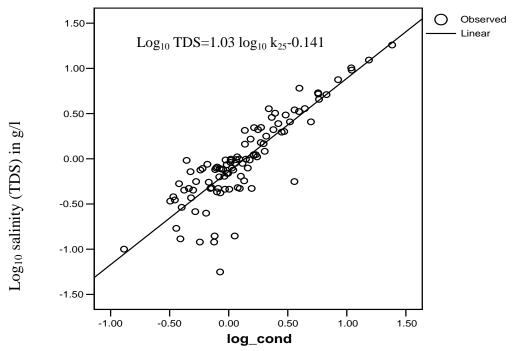
**Table 4.10:** Summary of linear regression analyses between salinity and conductivity for Nata saltpan and Lakes Nakuru, Bogoria water bodies. All variables were log<sub>10</sub> transformed.

Group	Slope	Intercept	$\mathbb{R}^2$	P
1 <sup>st</sup> Sanctuary	0.998	-0.089	0.677	< 0.080
2 <sup>nd</sup> Sanctuary	1.073	-0.161	0.775	< 0.001
3 <sup>rd</sup> Sanctuary	1.169	-0.211	0.660	< 0.005
Com Sanctuary	1.030	-0.141	0.745	< 0.001
Lake Nakuru	0.998	-0.157	0.972	< 0.001
Lake Bogoria	1.018	-0.190	0.967	< 0.001

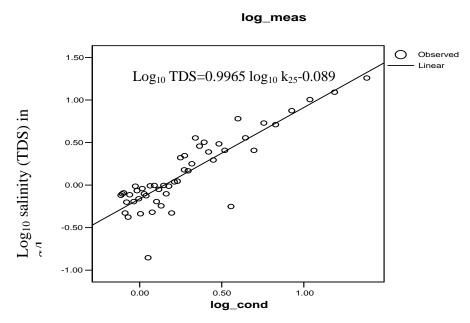
**Table 4.11:** Regression models depicting relationship between conductivity (mScm<sup>-1</sup>, K<sub>25</sub>) and salinity (g/l) for Lakes Nakuru and Bogoria and Nata saltpan. All variables were log<sub>10</sub> transformed.

Sanctuary	Dependent Variable	Equation	N	$\mathbb{R}^2$
1 <sup>st</sup>	Log <sub>10</sub> TDS	$Log_{10} TDS = 0.997log_{10} K_{25} - 0.089$	28	0.677
$2^{\mathrm{nd}}$	$Log_{10}$ TDS	$Log_{10}\ TDS = 1.073log_{10}\ K_{25} - 0.161$	49	0.775
3 <sup>rd</sup>	$Log_{10}$ TDS	$Log_{10}\ TDS = 1.169log_{10}\ K_{25} - 0.211$	21	0.660
Combined	$Log_{10}$ TDS	$Log_{10}\ TDS = 1.003log_{10}\ K_{25} - 0.141$	98	0.745
Lake Nakuru	$Log_{10}$ TDS	$Log_{10}\ TDS = 0.998log_{10}\ K_{25} - 0.157$	30	0.972
Lake Bogoria	$Log_{10}$ TDS	$Log_{10} \ TDS = 1.018log_{10} \ K_{25} - 0.189$	35	0.967

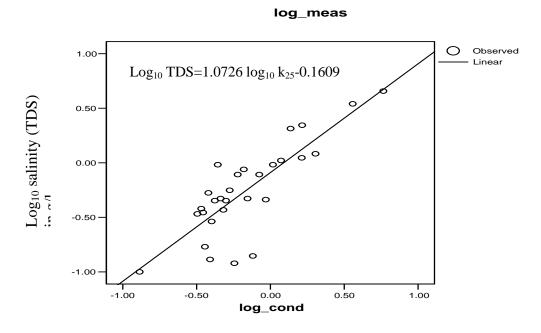
# log\_meas



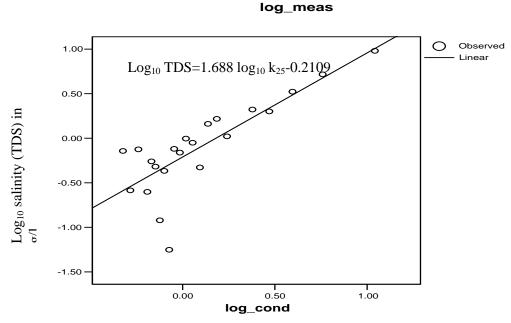
**Figure 5:** Logarithmic relationship between salinity and conductivity for the combined Nata salt pan waters



**Figure 6:** Logarithmic relationship between salinity and conductivity for the first nata salt pan waters



**Figure 7:** Logarithmic relationship between salinity and conductivity for the second nata salt pan waters



**Figure 8:** Logarithmic relationship between salinity and conductivity for the third nata salt pan waters

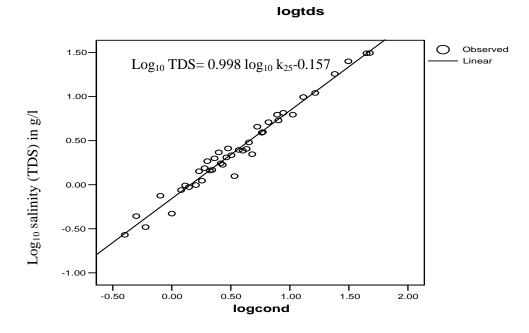


Figure 9: Logarithmic relationship between salinity and conductivity for the Nakuru salt lake

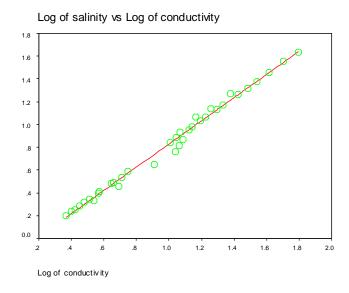


Figure 10: Logarithmic relationship between salinity and conductivity for the Bogoria salt lake

. Table 4.12: Observed measurements of EC  $(k_{25})$  and salinity for Nata saltpans and Lake Nakuru, and predicted values from regression equations

Where equation 1-6 (EQ1=1<sup>st</sup> saltpan; EQ 2=2<sup>nd</sup> saltpan; EQ 3=3<sup>rd</sup> saltpan, EQ 4= Combined saltpan, EQ 5=Lake Nakuru and EQ6=Lake Bogoria) and other models from various researchers.

				Obser	Pred	EQ1	EQ2	EQ 3	EQ 4	LNK	LKB	Williams	Jeffrey
				Ved	Icted					<b>EQ</b> 5	EQ6	1998	al;
													2001
1 <sup>st</sup>	28	6.99	72.44	4.52	4.12	5.66	5.55	5.97	5.36	4.85	4.68	3.87	3.84
$2^{nd}$	49	22.80	174.53	14.80	14.63	18.4	19.78	23.82	18.12	15.80	15.61	14.02	13.78
$3^{rd}$	21	8.58	90.31	5.54	5.13	6.91	6.89	7.55	6.58	5.92	5.77	4.81	4.75
Naku	30	47.77	246.07	31.25	32.92	38.4	43.70	56.35	38.77	33.02	33.14	31.26	30.13
Bogo	35	62.50	288.20	43.23	42.35	50.19	58.26	77.29	51.14	43.18	43.47	44.16	45.20

Tables 4.13: Calculation of Ionic Strength for Natural Nata Saltpan and lakes Nakuru and Bogoria water bodies.

		K <sup>+</sup>	Na⁺	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub>	F <sup>-</sup>	TOTAL
1 <sup>st</sup> Sanc	Mg/l	86.30	179.30	1.51	1.14	2090.0	5.66	0.35	137.10	5.14	0.01	2.64	2509.15
	$mM_i$	2.16	7.80	0.04	0.05	58.87	0.09	0.01	1.43	0.05	0.01	0.14	
	Z <sup>2</sup> mM <sub>i</sub>	2.16	7.80	0.15	0.19	58.87	0.38	0.01	5.71	0.49	0.01	0.14	75.90
2 <sup>nd</sup> Sanc	Mg/l	273.80	627.00	0.28	0.63	4599.0	14.44	0.88	469.20	2.07	0.84	5.65	5993.79
	$mM_i$	6.85	27.26	0.01	0.03	129.55	0.24	0.01	4.88	0.02	0.01	0.30	
	Z <sup>2</sup> mM <sub>i</sub>	6.85	27.26	0.03	0.11	129.55	0.96	0.01	19.53	0.06	0.01	0.30	184.81
3 <sup>rd</sup> Sanc	Mg/l	110.60	221.00	0.98	0.80	2620.0	6.15	0.38	171.80	0.65	0.06	3.70	3136.12
	$mM_i$	2.77	9.61	0.01	0.03	73.80	0.10	0.01	1.79	0.01	0.01	0.20	
	Z <sup>2</sup> mM <sub>i</sub>	2.77	9.61	0.02	0.13	73.80	0.20	0.01	3.58	0.03	0.01	0.20	94.24
L. Naku	Mg/l	1377.03	2370.76	0.21	0.02	666.13	2603.27	153.48	0.07	2.19	0.53		7173.70
	$mM_i$	34.86	103.08	0.01	0.01	18.76	43.39	2.52	0.01	0.02	0.01		
	Z <sup>2</sup> mM <sub>i</sub>	34.86	103.08	0.02	0.01	18.76	173.55	2.52	0.02	0.06	0.01		332.90
L. Bogor	Mg/l	32.00	3680.00	3.63	0.83	124.00	3245.0	465.0	15.52	7.79	0.21		7573.98
	$mM_i$	0.81	160.00	0.09	0.03	3.49	54.08	7.62	0.16	0.08	0.01		
	Z <sup>2</sup> mM <sub>i</sub>	0.81	160.00	0.18	0.06	3.49	108.16	7.62	0.32	0.23	0.01		390.14

#### **CHAPTER FIVE**

#### **DISCUSSION OF RESULTS**

## **5.1 Physico-Chemical Parameters**

## **5.1.1** Temperature

Water temperatures were generally high and consistent with the ambient air temperature as shown in tables 4.1, 4.2 and 4.3. Sampling was done during severe drought seasons, when the regions experienced the highest temperatures. In addition, the waters were shallow with slow movement and in some cases stagnant hence tend to heat up fast. The shallowest points in the saltpan and the lake where highest temperatures were recorded exhibited the greatest conductivity and salinity. Very shallow saltpans and lakes may never stratify and hence have no vertical difference in temperature, while deep salt lakes stratify on seasonal basis resulting to monomictic patterns (Williams, 1998) stratify during warmer season and mix during rainy seasons.

## 5.1.2 The pH Profile

The pH readings were in the range of 6.84-10.31 for the saltpans (table 4.1), while minimal variations were observed in the lakes with mean values of 10.55±0.09, 10.15±0.18 for Nakuru and Bogoria respectively as shown in tables 4.2 and 4.3. These values are outside the range for drinking water (Hutton, *et al*; 1976) and typical of polluted waters. High pH values encountered was due to high concentrations of Na<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> hence typifying the saltpans and lakes water bodies chemically as sodium chloride/sulfate and sodium carbonate-bicarbonate/chloride systems respectively.

The presence of high concentrations of carbonates and bicarbonates may be attributed to the minimal changes observed in the lakes pH levels, tables 4.2 and 4.3. The pH steady state, while water level was receding could be attributed to the

 $HCO_3^-_{(aq)} \longrightarrow H^+_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow CO_{2(g)} + OH^-_{(aq)}$  equilibrium system. Free  $CO_2$  being always in equilibrium with dissolved  $CO_2$  in the surface water, together with equilibria for dissolved ions may be represented according to Wetzel and Likens (1991).

$$CO_{2(air)} + H_2O_{(l)} - CO_{2(diss)} + H_2O_{(l)} - H_2CO_{3(aq)} - H_{(aq)} + HCO_{3(aq)} - 2H_{(aq)}^+ + CO_{3(aq)}^{-2} - 2H_{(aq)}^+ + CO_{3(aq)}^+ - 2H_{(aq)}^+ - 2H_{(aq)}^$$

Through the release and uptake of H<sup>+</sup> depending on its demand in the aquatic system, this enables the pH of the system to be kept in equilibrium (Omondi, 2000). Although pH values are often variable determined by diel changes in photosynthetic rates, lakes Nakuru and Bogoria are not and they are highly buffered systems (Talling and Talling, 1965). Buffering of water with respect to pH occurs when protonated and unprotonated species are both present in significant concentrations; at pH 6.4 this is H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup> and at 10.33 it is HCO<sub>3</sub>-/CO<sub>3</sub><sup>2-</sup> majority of ions present (*htt:/www.*utoronto).

## **5.1.3** Conductivity and Salinity

Mean conductivity of 6.99±0.44, 22.80±0.21 and 8.58±0.34 mScm<sup>-1</sup> were recorded for the1<sup>st</sup>, 2<sup>md</sup> and 3<sup>rd</sup> saltpans respectively (table 4.1). There was no significant spatial variation in conductivity recorded between sampling sites. However, a trend of increase was observed in different saltpans. Salinity (TDS), mean values of 4.52±0.37, 14.80±0.14 and 5.54±0.04 mg/l for the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> saltpans respectively were recorded during the study period, table 4.1. Lakes Nakuru and Bogoria mean conductivity of 47.77±0.78 and 62.5±0.37mScm<sup>-1</sup> respectively recorded during this study as shown in tables 4.2 and 4.3 compared well with (Shivoga, 1998) value of 48.00 mScm<sup>-1</sup> lake Nakuru's but lower than lake Bogoria's 72.00 mScm<sup>-1</sup> (Melack, 1981) and higher than the values recorded for lake Naivasha of between 0.3-0.4 mScm<sup>-1</sup> (Omondi, 2000). The gradual shoreline retreat explained as part of an evaporative "draw down effect" had varying degree of impact on conductivity and salinity. The shallowest, point of the saltpans and the lake exhibited by far the greatest increase in conductivity and salinity over the study period was attributed to increased concentrations of dissolved ions.

Correlation analysis showed that there was significant correlation between conductivity and salinity (TDS), as shown in table 4.10. Conductivity was strongly correlated with TDS ( $R^2 = 0.745$ ) for the salt pans and ( $R^2 = 0.972$ , and 0.967) for lakes Nakuru and Bogoria respectively. TDS is an important contributor to conductivity; the strong correlation was expected since TDS measurement included all major dissolved ions.

Best correlation in Lakes Nakuru and Bogoria was attributed to high concentrations of carbonate and bicarbonates where specific conductance is believed to be very closely proportional to TDS (Rodhe, 1949; Wetzel, 1983).

### 5.2 Chemical Composition of Lakes Nakuru, Bogoria and Nata Saltpan

### **5.2.1** Major base cation composition

Dissolved metals were determined after filtration of acidified samples through 0.45µm membrane filters. The cation concentrations were dominated by Na<sup>+</sup> followed by K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> as shown in tables 4.4, 4.5 and 4.6. In spite of wide fluctuations in the absolute concentration of major cations, expression of their concentrations according to their percentage of equivalent sum of cation (using the method of Kufferath, 1951) showed that cationic proportion remained remarkably constant. Whilst the same major cations are found in freshwater, the proportions are usually different in saline water system. In most freshwaters, it is the divalent cations and carbonates that are important, whereas such combinations are not characteristics of saline waters. For major dissolved cations standards were purchased and certified riverine reference materials SLRS-3 (National Research Council; Canada) was analyzed as checks on accuracy. Analytical errors were estimated to be 9.13%, 4.29%, 10.83% and 3.13% for Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> respectively. Results for the standard reference material were within the estimated errors of the certified values and so no adjustment for systematic offsets were made to the cation data.

#### 5.2.2 Major anion composition

From the results obtained (tables 4.7, 4.8 & 4.9), the saltpan waters can be characterized as low in nutrient content but high in chloride and sulfate whereas lake water had significant amount of trace anions i.e. carbonate, bicarbonate and chlorides. Nitrate content was particularly low in all the saltpan water samples. Since there were no agricultural or other industrial activities around the sanctuaries, nutrient loading was not expected. Concentrations of the other anions were generally high in the 2<sup>nd</sup> and 3<sup>rd</sup> saltpans. This may be due to evaporation leading to increased concentration of dissolved solutes. Temperatures of water in the two saltpans were high

and the water was receding as a result of evaporation. The mean nitrate concentration for Lakes Nakuru and Bogoria recorded during this study were 0.53±0.10 and 0.21±0.02mg/l respectively, as shown in tables 4.8 and 4.9. These values were high and are expected of hypereutrophic lakes (Wetzel, 1983). Talling and Talling (1965) stated that the principal factor that determines phosphate loading in a lake is the geology of the drainage basin through which the rivers supplying it passes. In shallow water bodies, direct sediment resupply may contribute a significant quantity into the water (Scheffer, 1998). This, together with runoffs and river inflows are sources of phosphates in Lakes Nakuru and Bogoria. The higher phosphate contributions may also be attributed to the effects of the waves disturbing the sediments thereby bringing more phosphate from the sediments into the water medium (Omondi, 2000). Lack of variations in the spatial distribution of anions in both saltpans and the lakes suggests high solubility of this analytes coupled with good daily mixing of the waters.

In the absence of anion loading from anthropogenic sources, cations and anions content of water is a function of underlying soil bedrock composition (Kipkore, 2006). The major difficulty encountered was very high chloride levels which swamp out other anions resulting to poorly resolved chromatograms. Therefore in order to analyze other analytes of low concentration using IC, it is necessary to suppress the high chloride levels by some method other than dilution. This suppression must necessarily also be accomplished without the addition of extraneous anions to the sample (Merrill, 1985). Passing samples through a silver form cation exchange column eliminate Cl interference; interferences from large SO<sub>4</sub> concentration can also be eliminated by the addition of barium chloride to the sample prior to treatment with the silver resin.

# 5.3 Linear Regression Analysis Between Salinity and Conductivity for Natasaltpans and Lakes Nakuru, Bogoria.

Mean conductivity measurements in the Natasaltpan water bodies studied varied from 6.99

mScm<sup>-1</sup> to 22.80 mScm<sup>-1</sup>, and TDS ranged from 72.44 meql<sup>-1</sup> to 174.53 meql<sup>-1</sup> as shown in tables 4.1 and 4.12 respectively, whereas mean conductivity recorded for lakes Nakuru and

Bogoria were 47.77±0.78 mScm<sup>-1</sup> and 62.54±0.37 with TDS of 246.07and 288.20 meql<sup>-1</sup> tables 4.2, 4.3 and 4.12 respectively. The lowest values were from 1<sup>st</sup> saltpan while the highest values were from the 2<sup>nd</sup> saltpan. For both high and low saline waters, conductivity was significant predictor of salinity (1<sup>st</sup> saltpan K<sub>25</sub><6.99 mScm<sup>-1</sup>, ANOVA test, F 0.05 (1,28) = 56.557 R<sup>2</sup> = 0.677 P<0.001; 2<sup>nd</sup> saltpan K<sub>25</sub><22.97 mScm<sup>-1</sup>, ANOVA test, F 0.05 (1,49) = 156.254 R<sup>2</sup> = 0.775 P<0.001, 3<sup>rd</sup> saltpan K<sub>25</sub><8.86 mScm<sup>-1</sup>, ANOVA test, F 0.05 (1,21) = 38.833 R<sup>2</sup> = 0.660 P<0.001, lake Nakuru K<sub>25</sub><47.78 mScm<sup>-1</sup>, ANOVA test, F 0.05 (1,29) = 1389.14 R<sup>2</sup>= 0.971 and lake Bogoria K<sub>25</sub><62.54 mScm<sup>-1</sup>, ANOVA test, F 0.05 (1,35) = 4259.34 R<sup>2</sup>= 0.967 tables 4.10& 4.11).

Analysis of covariance detected showed no significant difference in the slopes and intercepts of the three sanctuaries (table 4.10); therefore low and high conductivity data sets from Nata saltpans were combined to derive "joint" predictive model. In the "joint" model conductivity was highly significant predictor of salinity (ANOVA test, F  $_{0.05}$  (1, 98) = 289.25 R<sup>2</sup> = 0.745 P<0.001 table 4.10).

In regions where saltwater are reasonably homogenous with regards to ionic composition, the correlation between conductivity and salinity can be quite close as shown in figs 5, 9 and 10. In the first three figures Na<sup>+</sup> and Cl<sup>-</sup> are the dominant ions, while Na<sup>+</sup>,  $CO_3^{2^-}$  and Cl<sup>-</sup> dominated the last two figures. These figs are based upon a large number of full ion analyses to give salinities and upon contemporaneous dilution and conductivity measurements. Between salinities of  $\approx$ 0.221 and 15.351 gl<sup>-1</sup> the relationship illustrated in fig5 can be described by the joint equation

$$S = 0.7228K_{25}^{1.03}R^2 = 0.745$$

Between salinities of  $\approx$ 0.279 and 32.917 g/l in lake Nakuru, the relationship can be described by the equation

$$S = 0.6966K_{25}^{0.9981} R^2 = 0.972$$

Whereas between salinities of  $\approx$ 0.1.59 and 43.23 g/l in lake Bogoria, the relationship can be described by the equation

$$S = 0.6471 K_{25}^{1.018} R^2 = 0.967$$

Where S is the salinity in g/l and K<sub>25</sub> is conductivity at 25°C in mScm<sup>-1</sup>

The relationship breaks down at very low salinities because of increased ionic heterogeneity and very high because of ion antagonism (Williams, 1998). The latter can be adequately dealt with by appropriate dilution of samples.

# 5.4 Observed Measurements of EC $(k_{25})$ and Salinity for Nata Saltpans and Lake Nakuru, Bogoria and Predicted Values From Regression Equations

To compare these predictive models to previous literature equations (Williams, 1998 and Jeffrey et~al; 2001), first the predicted values were analyzed from conductivity measures and observed values over the study period. The best predictive model was the William's equation ( $\approx$ -13.33%) which was slightly better than the 'joint' equation (18.06%) for saltpan water bodies. For salinity William's model produced very good estimates. Differences between observed and expected results were higher for all equations with the exception of the William's and Jeffrey, et~al models. It is evident that models derived using saltpan water bodies cannot be used to predict TDS in lake waters, since the values obtained using those models were not within the predicted values.

It is clear from this work and earlier studies, that conductivity is generally a very good predictor of salinity. Comparison among models suggests that developing separate equations for low and high saline water bodies has some merit because of ionic heterogeneity and antagonism respectively (Williams, 1998), although no greater statistical differences in slopes and intercepts of the relationships between the three saltpans was found in this study. It is important to develop different models for saline water of different ionic composition.

# 5.5 Conductivity and Ionic Strength for Natural lakes Nakuru, Bogoria and Nata Saltpan Waters

The following semi empirical procedure was used to calculate ionic strength for naturally occurring waters of lakes Nakuru, Bogoria and Nata saltpan water bodies that contain mostly Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>

$$IS = 1/2000 \Sigma Z_{i2} (mM_i)$$

IS = 0.038, 0.092 and 0.047 M for the  $1^{st}$ ,  $2^{nd}$  and  $3^{rd}$  saltpans respectively, while lake Nakuru and Bogoria had IS of 0.166 and 0.195 M respectively.

#### **CHAPTER SIX**

#### CONCLUSIONS AND RECOMMENDATION

#### **6.1 Conclusions**

The cation concentrations were dominated by Na<sup>+</sup> followed by K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> as shown in tables 4.4, 4.5 and 4.6. From the results obtained the saltpan waters can be characterized as low in nutrient content but high in chloride and sulfate whereas lake water had significant amount of trace anions i.e. carbonate, bicarbonate and chlorides. Nitrate content was particularly low in all the saltpan water samples

Ionic strength for naturally occurring waters of lakes Nakuru, Bogoria and Nata saltpan water bodies that contain mostly Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> was IS = 0.038, 0.092 and 0.047 M for the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> saltpans respectively, while lake Nakuru and Bogoria had IS of 0.166 and 0.195 M respectively.

This study suggests that the models developed can be used for Kenya and Botswana saline waters and other waters within their range of conductivity and similar ionic composition to predict salinity on measuring conductivity.

Conductivity calculated using semi empirical approach did not agree with the measured values perhaps because of ionic electrophoretic effect in the samples under study. When mixed salts are present, as is always the case with natural saline water there is need to employ semi empirical procedures to calculate individual ionic contribution to total conductivity when TDS is less than 2500mg/l (APHA, 1998).

#### **6.2 Recommendation**

Since this study was carried out during the dry season, it is crucial for future similar studies carried out during the rainy season.

It is important to have studies carried out to determine the rate of salinisation for these saline water bodies and the effects of trace elements towards electrical conductivity

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## **APPENDICES**

Appendix I: Phyico-Chemical Parameters of Lake Nakuru

Measured immediately after sampling using 3405 Electrochemical Analyzer model and then corrected to temperatures of 25°C.

	Temperature in		<b>Conductivity in</b>	
Sampling Site	°C	PH	mS/cm	Salinity in g/l
MP	26.47	10.62	48.11	32.89
JW	26.71	10.42	48.30	33.43
MM	26.67	10.65	46.62	30.21
MMN	26.93	10.59	47.81	31.54
MND	26.55	10.41	48.42	29.34
JE	25.84	10.56	46.20	27.85
MJ	26.81	10.6	48.53	33.97
MNJ	26.78	10.62	47.74	28.98
НР	26.66	10.42	47.84	30.56
MN	26.98	10.58	48.30	33.72
Mean	26.64	10.55	47.77	31.25
SD	±0.32	±0.09	±0.78	±2.18

## Appendix 2: Phyico-Chemical Parameters of Lake Bogoria

Measured immediately after sampling using 3405 Electrochemical Analyzer model and then corrected to temperatures of 25°C.

Sampling Site	Temperature in	PH	Conductivity	Salinity
	°C		in mS/cm	(TDS) in g/l
Bog NB	26.25	10.15	62.80	43.45
Bog CB	27.82	10.50	62.51	43.23
Bog SB	28.40	10.35	63.52	43.84
Bog HB	27.75	10.20	63.15	43.52
Bog TB	26.82	10.55	62.91	43.85
Mean	26.25	10.15	62.54	43.23
SD	±0.86	±0.18	±0.37	±0.27

## **Appendix 3: Physical Parameters of Nata Saltpans**

Measured in less than 24 hrs after sampling using temperature corrected Crison type conductivity meter and Oaklon pH meter model with temperature probe

## 1<sup>st</sup> Saltpan

Sampling	Conductivity		Temp	Salinityin
Sites	in mS/cm	pН	in °C	g/l
NSP1	6.71	9.83	23.00	4.54
NSP2	6.65	9.80	25.00	4.25
NSP3	6.63	9.81	24.80	4.15
NSP4	6.93	9.90	24.70	4.55
NSP5	7.18	10.10	25.40	5.10
NSP6	7.18	10.00	25.70	4.99
NSP7	8.40	10.20	25.30	5.24
NSP12	7.02	6.84	25.70	4.65
NSP13	6.87	9.86	26.20	4.12
NSP14	6.88	9.79	27.00	4.47
NSP15	6.83	9.77	26.40	4.32
NSP16	6.83	9.70	27.20	4.15
NSP17	6.81	9.74	27.20	4.53
NSP18	6.91	9.94	27.60	4.19
Mean	6.99	9.66	25.80	4.52
SD	±0.44	±0.82	±1.25	±0.37

### 2<sup>nd</sup> Saltpan

Sampling	Conductivity		Temperature	Salinity
Sites	in mS/cm	pН	in °C	in g/l
S 8	22.50	10.31	27.50	14.80
S 9	23.00	10.00	27.67	14.60
S 10	22.90	10.20	27.60	14.90
S 11	22.90	10.21	26.00	14.90
Mean	22.80	10.18	27.19	14.80
SD	±0.21	±0.13	±0.80	±0.14

## 3<sup>rd</sup> Saltpan

Sampling	Conductivity		Temperature	Salinity
Sites	in mS/cm	pН	in °C	in g/l
S 19	8.43	10.10	27.90	5.51
S 20	8.34	10.00	28.03	5.53
S 21	8.96	10.10	28.20	5.59
Mean	8.58	10.07	28.04	5.54
SD	±0.34	±0.058	±0.15	±0.04

Appendix 4: Concentration of Base Cations in Lake Nakuru

Analyzed using Thermo Jerrel Ash AAS and Corning EEL Model 100 Flame Photometer

<b>Sampling Sites</b>	$\mathrm{Mg}^{2+}\left(\mathrm{mg/l}\right)$	Ca <sup>2+</sup> (mg/l)	Na <sup>+</sup> (g/l)	$\mathbf{K}^{+}\left(\mathbf{g}/\mathbf{l}\right)$
MP	0.02	0.17	2.40	1.24
JW	0.02	0.20	2.30	1.49
MM	0.02	0.21	2.35	1.15
MMN	0.02	0.26	2.34	1.59
MND	0.03	0.11	2.44	1.70
JE	0.02	0.23	2.34	1.01
MJ	0.01	0.19	2.43	1.62
MNJ	0.02	0.30	2.37	1.08
HP	0.02	0.27	2.35	1.28
MN	0.02	0.21	2.40	1.60
Mean	0.02	0.21	2.37	1.38
SD	±0.01	±0.04	±0.0.05	±0.23

Appendix 5: Concentration of Base Cations in Lake Bogoria

Analyzed using Thermo Jerrel Ash AAS and Corning EEL Model 100 Flame Photometer

<b>Sampling Sites</b>	$\mathrm{Mg}^{2+}\left(\mathrm{mg/l}\right)$	Ca <sup>2+</sup> (mg/l)	Na <sup>+</sup> (g/l)	K <sup>+</sup> (g/l)
Bog NB	0.74	2.56	3.78	0.03
Bog CB	0.99	4.53	3.53	0.03
Bog SB	0.76	3.75	3.65	0.04
Bog HB	0.86	3.48	3.67	0.03
Bog TB	0.80	3.85 3.75		0.03
Mean	0.83	3.63	3.68	0.03
SD	±0.10	±0.71	±0.10	±0.01

**Appendix 6: Concentration of Major Anions in lake Nakuru** 

Analyzed using titrimetry, turbidimetry, ammonium molybdate and kjedahl techniques

Sampling	Cl <sup>-</sup> (g/l)	$CO_3^{2-}(g/l)$	HCO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub>
Sites			(g/l)	(mg/l)	(mg/l)	(mg/l)
MP	0.66	2.60	0.17	0.04	2.12	0.49
JW	0.72	2.57	0.16	0.05	1.75	0.54
MM	0.70	2.54	0.11	0.03	2.31	0.41
MMN	0.63	2.55	0.16	0.02	1.92	0.56
MND	0.61	2.64	0.17	0.06	2.59	0.69
JE	0.72	2.68	0.14	0.07	2.03	0.53
MJ	0.74	2.65	0.16	0.04	2.33	0.39
MNJ	0.57	2.60	0.18	0.05	2.27	0.66
HP	0.62	2.54	0.18	0.04	2.16	0.47
MN	0.70	2.66	0.13	0.06	2.44	0.62
Mean	0.67	2.60	0.15	0.07	2.19	0.53
SD	±0.05	±0.15	±0.03	±0.04	±0.26	±0.10

**Appendix 7: Concentration of Major Anions in lake Bogoria** 

Analyzed using titrimetry, turbidimetry, ammonium molybdate and kjedahl techniques

Sampling Sites	Cl' (g/l)	CO <sub>3</sub> <sup>2-</sup> (g/l)	HCO <sub>3</sub> - (g/l)	SO <sub>4</sub> <sup>2</sup> - (mg/l)	PO <sub>4</sub> <sup>3</sup> · (mg/l)	NO <sub>3</sub> (mg/l)
Bog NB	0.13	<b>3.</b> 25	0.79	17.75	8.75	0.24
Bog CB	0.14	3.46	0.88	15.52	9.25	0.26
Bog SB	0.15	3.52	0.75	16.45	7.79	0.25
Bog HB	0.12	3.94	0.47	15.86	8.28	0.21
Bog TB	0.14	3.26	0.98	16.20	8.56	0.25
Mean	0.12	3.25	0.47	15.52	7.79	0.21
SD	±0.01	±0.28	±0.19	±0.86	±0.54	±0.02

#### **Appendix 8: Concentrations of Base Cations in Nata saltpans**

Analyzed using Varian SpectAA AAS and Sherwood Flame Photometer, model 4100

#### 1<sup>st</sup> Saltpan

Sampling	$Mg^{2+}$	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>
sites	(mg/l)	(mg/l)	(g/l)	(mg/l)
NSP1	0.98	1.71	0.17	87.07
NSP2	1.55	1.66	0.18	88.18
NSP3	1.37	1.61	0.17	85.13
NSP4	1.38	1.67	0.18	86.25
NSP5	1.29	1.57	0.19	89.04
NSP6	1.28	1.70	0.19	88.49
NSP7	0.58	1.13	0.22	99.36
NSP12	0.96	1.57	0.17	83.74
NSP13	1.06	1.47	0.18	84.87
NSP14	0.95	1.46	0.18	83.18
NSP15	1.13	1.52	0.17	81.23
NSP16	1.04	1.46	0.17	81.79
NSP17	1.16	1.16	0.18	83.19
NSP18	1.15	1.39	0.18	86.81
Mean	1.14	1.51	0.18	86.31
SD	±0.24	±0.18	±0.01	±4.50

### 2<sup>nd</sup> Saltpan

Sampling	$Mg^{2+}$	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>
sites	(mg/l)	(mg/l)	(g/l)	(mg/l)
NSP 8	0.60	0.26	0.63	276.32
NSP 9	0.61	0.26	0.62	269.06
NSP 10	0.66	0.29	0.61	268.49
NSP 11	0.67	0.30	0.64	281.35
Mean	0.63	0.28	0.63	273.80
SD	±0.03	±0.02	±0.01	±6.17

## 3<sup>rd</sup> Saltpan

Sampling	$Mg^{2+}$	Ca <sup>2+</sup>	Na <sup>+</sup>	$\mathbf{K}^{+}$
sites	(mg/l)	(mg/l)	(g/l)	(mg/l)
NSP19	0.92	1.33	0.23	107.46
NSP20	0.57	0.54	0.22	102.73
NSP21	0.90	1.07	0.22	121.64
Mean	0.80	0.98	0.22	110.61
SD	±0.20	±0.40	±0.01	±9.84

**Appendix 9: Concentrations of Major Anions in Nata saltpans** 

Analyzed using an Ion Chrom-2000 (Dionex model, USA) and titrimetry technique

1<sup>st</sup> Saltpan

Sampling	Cl	SO <sub>4</sub> <sup>2</sup> -	PO <sub>4</sub> <sup>3</sup> -	NO <sub>3</sub>	F <sup>-</sup>	CO <sub>3</sub> <sup>2</sup> -	HCO <sub>3</sub>
Sites	(g/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
NSP1	2.04	133.75	3.30	0.01	1.50	5.27	0.32
NSP2	2.00	131.71	6.37	0.01	2.86	6.12	0.41
NSP3	1.99	132.70	9.99	0.01	3.07	5.10	0.31
NSP4	2.04	135.31	6.27	0.01	2.96	6.46	0.39
NSP5	2.20	142.32	4.98	0.01	3.10	4.76	0.29
NSP6	2.19	144.33	5.79	0.01	3.30	6.72	0.41
NSP7	2.50	162.70	7.56	0.01	3.00	5.61	0.34
NSP12	2.04	134.12	5.15	0.01	2.41	5.70	0.35
NSP13	2.03	134.01	2.21	0.01	2.77	5.44	0.33
NSP14	2.01	131.09	4.90	0.01	2.44	4.76	0.29
NSP15	2.04	134.70	3.59	0.01	3.10	5.44	0.33
NSP16	2.02	132.00	5.79	0.01	2.04	6.72	0.41
NSP17	2.04	134.74	4.34	0.01	2.56	5.53	0.34
NSP18	2.08	136.11	1.75	0.01	1.88	5.53	0.34
Mean	2.09	137.10	5.14	0.03	2.64	5.66	0.35
SD	±0.13	±8.29	±2.14	±0.02	±0.53	±0.64	±0.04

## 2<sup>nd</sup> saltpan

Sampling	Cl -	SO <sub>4</sub> <sup>2</sup> -	PO <sub>4</sub> <sup>3-</sup>	NO <sub>3</sub>	F <sup>-</sup>	CO <sub>3</sub> <sup>2</sup> -	HCO <sub>3</sub>
Sites	(g/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
NSP8	4.39	463.70	1.97	0.01	5.71	15.47	0.94
NSP9	4.61	468.01	1.84	1.32	5.48	14.88	0.91
NSP10	4.57	464.31	2.68	0.01	5.54	14.11	0.86
NSP11	4.84	480.72	1.80	0.03	5.86	13.18	0.80
Mean	4.60	469.20	2.07	0.34	5.65	14.41	0.88
SD	±0.19	±7.90	±0.41	±0.65	±0.17	±0.99	±0.06

# 3<sup>rd</sup> Saltpan

Sampling	Cl	SO <sub>4</sub> <sup>2</sup> -	PO <sub>4</sub> <sup>3</sup> -	NO <sub>3</sub>	F	$CO_3^{2-}$	HCO <sub>3</sub>
Sites	(g/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
NSP19	2.64	171.30	0.70	0.01	3.40	7.40	0.45
NSP20	2.55	168.71	0.69	0.01	3.24	5.44	0.33
NSP21	2.66	175.32	0.56	0.04	4.46	5.61	0.34
Mean	2.62	171.80	0.65	0.02	3.70	6.15	0.38
SD	±0.06	±3.35	±0.08	±0.01	±0.66	±1.08	±0.07

Appendix 10: Equivalent Conductivity,  $\Lambda$ , and Conductivity of Potassium Chloride at  $25^{0}\mathrm{C}$ 

KCl	Equivalent	Conductivity,
<b>Concentration M</b>	conductivity, A	μmho/cm
or equivalent/l	mho-cm²/ equivalent	
0	149.9	
0.0001	148.9	14.9
0.0005	147.7	73.9
0.001	146.9	146.9
0.005	143.6	717.5
0.01	141.2	1412
0.02	138.2	2765
0.05	133.3	6667
0.1	128.9	12890
0.2	124.0	24800
0.5	117.3	58670
1.0	111.9	1119000

**Jaspher, W.S** (1988)

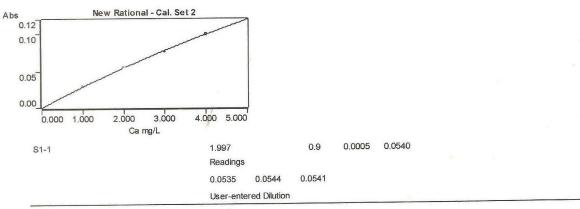
**Appendix 11: Standard Calibration Graph for Magnesium analysis** 

SpectrAA Repo	VI G			25/10/200			Page 1
Analyst Date Started Worksheet Comment	19:23 25/10/2006 SAMUEL						
Methods	Mg						
	Method: Mg (Flame)						
Sample ID		Conc mg/L	_	%RSD	Mean Abs		
CAL ZERO		0.000 Readings		63.8	-0.0038	50	
		-0.0033	-0.0017	-0.0064	(6)		
		User-enter	ed Dilution				
STANDARD 1		1.000 Readings		2.7	0.0368		
1		0.0372	0.0376	0.0357	-		
		User-enter	red Dilution				2
STANDARD 2		2.000 Readings		3.9	0.0658		
		0.0688	0.0646 red Dilution	0.0641			
		User-enter	rea Dilution				
STANDARD 3		3.000 Readings		2.8	0.0984		
		0.1000	0.0952	0.0999			
		User-enter	red Dilution				
STANDARD 4		4.000 Readings		1.9	0.1215		
		0.1240	0.1199	0.1205		4	
		User-enter	red Dilution				
STANDARD 5		5.000 Readings		2.6	0.1481		
		0.1495	0.1510	0.1438			
Manager and Property and the Control of the Control	17	User-ente	red Dilution				
N	ew Rational - Cal. Set 6						
.17]		A LANGE TO THE REAL PROPERTY OF THE PARTY OF					
.10							
.05							
0.000 1.000	2.000 3.000 4. Mg mg/L	000 5.000					
SC1-1		1.312 Readings		9.8	0.0460		
		0.0409	0.0480	0.0491			

User-entered Dilution

**Appendix 12: Standard Calibration Graph for Calcium analysis** 

Analyst Date Started Worksheet Comment Wethods	sunday 16:03 29/10/2006 Ca Sam 05 Ca,Ca								
	Method: Ca (Flame)								
Sample ID		Conc mg/L		%RSD	SD	Mean Abs			
CAL ZERO		0.000 Readings		1.1	0.0003	-0.0287			
		-0.0284 User-enter	-0.0290 ed Dilution	-0.0287		100			
STANDARD 1		1.000 Readings		0.9	0.0003	0.0292			
		0.0294	0.0289	0.0294					
		User-enter	ed Dilution					1	
STANDARD 2		2.000 Readings		2.2	0.0012	0.0542			
		0.0529	0.0548	0.0550					
	L.	User-enter	ed Dilution				-		
STANDARD 3		3.000 Readings		0.9	0.0006	0.0755			
		0.0748	0.0755	0.0761					
		User-enter	ed Dilution						
STANDARD 4		4.000 Readings		1.8	0.0018	0.0989			
	, , , , , , , , , , , , , , , , , , , ,	0.0968 User-ente	0.1003 red Dilution	0.0996			10		
STANDARD 5	n	5.000 Readings	3	1.4	0.0016	0.1201			con a liberary
	100000000000000000000000000000000000000	0.1190	0.1220	0.1194					
	,	User-ente	red Dilution						



#### **Appendix 13: Standard Chromatogram for Anions Analysis**

Operator:Administrator Timebase:UniversityBotswana Sequence:161206

Page 1 2006/12/16 5:48 PM

Sample Name:	mixstds	Inj. Vol.:	30.0
Sample Type:	standard	Dilution Factor:	1.0000
Program:	AS18 Anions 37 mM	Operator:	n.a.
Inj. Date/Time:	16.12.06 12:14	Run Time:	10.50

No.	Time min	Peak Name	Туре	Area µS*min	Height µS	Amount
25	3.60	Fluoride	M	15.032	107.114	6.4895
26	4.63	Chloride	M	50.643	401.503	29.9771
27	5.79	Sulfate	M	20.439	116.233	15.7669
29	7.91	Phosphate	M	6.678	30.898	6.0397
30	8.98	Nitrate	M	4.828	12.837	5.5076
		тоти	AL:	97.62	668.59	63.78

