COMPARATIVE STUDY ON DETERMINATION OF PERCENTAGE PURITY AND ESSENTIAL ELEMENTS ON ROCK SALT SAMPLES OF DIFFERENT ORIGINS

A DISSERTATION

SUBMITTED FOR THE

PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

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BY

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This dissertation entitled **"Comparative Study on Determination of Percentage Purity and Essential Elements on Rock Salt Samples of Different Origins"**, by "Saraswati Pandeya", under the supervision of Asst. Prof. Dr. Bhanu Bhakta Neupane, Central Department of Chemistry, Tribhuvan University, Nepal, is hereby submitted for the partial fulfillment of the Master of Science (M. Sc.) Degree in Chemistry. This dissertation has not been submitted in any other university or institution previously for the award of degree.

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This is certify that the dissertation work entitled, **"Comparative Study on Determination of Percentage Purity and Essential Elements on Rock Salt Samples of Different Origins "** has been carried by **'Saraswati Pandeya'** as a partial fulfillment for required of M Sc. Degree in Chemistry under my supervision. To the best of my knowledge, this work has not been submitted to any other degree in this institute.

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I, "**Saraswati Pandeya**", hereby declare that the work presented herein is genuine work done originally by and has not been published or submitted elsewhere for that requirement of a degree program. Any literature, data or works done by others and cited in this dissertation has been given due acknowledgement and listed in the reference section.

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LIST OF ABBREVIATIONS

IDD	Iodine Deficiency Disorder
WHO	World Health Organization
EDTA	Ethylene Diamine Tetra acetic Acid
AAS	Atomic Absorption Spectroscopy
XRD	X-ray Diffraction
SEM/EDS	Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy
ICP-OES	Inductive Coupling Plasma Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
XRF	X-ray fluorescence (XRF)
FTIR	Fourier Transform Infrared Spectroscopy
UNSCEAR	United Nations Committee on the Effects Of Atomic Radiation
nm	nanometer
ppm	Parts Per Million
µg	Micro Gram
ppb	Parts Per Billion

ABSTRACT

Black and white rock salts are one of the highly used ingredients in daily meal and different types of food industries. Black rock salt is called as *bire noon* and white rock salt is called as *sinde noon* in Nepali. These rock salts are being highly used in herbal formulations too. Rock salts of Indian and Tibetan origins are primarily found in Nepalese market. Salt of Nepalese origin, available from Mustang district, is also sold in market. Majority of these salt samples are found to be sold in unprocessed form. Hence, it is likely that these samples may have different level of toxic impurities. Salt containing high amount of essential elements is considered to be of high nutritional value. Therefore, information on level of toxic impurities and essential elements in the salt samples is an important task to know nutritional value of any salt. However, such information on salts of Nepalese market is not available in literature.

The amount of sodium in the black salt sample determined potentiometrically was found to be in the range of 30-37mg/100mg of salt sample. In white salt samples, relatively lower amount of sodium in the range of 23-35mg/100g was obtained. Iron was detected in all the collected white and black rock salt samples. The amount of iron in the black and white salt samples was found to be in the range 12-24 and 7-14 ppm, respectively. This tells that black salt is better source of iron than white salt. The low level of magnesium was found two black salt samples only, whereas it was detected in nine white salt samples in the range of 0.1-5 ppm. On the other hand calcium in not detected in all the white and black salt samples. The preliminary AAS measurement in few selected samples showed that Hg and As beyond the WHO safe limit. This study showed that white and black salt is a good source of sodium and iron.

Key words: Rock salt, Essential elements, Toxic elements, Percentage purity

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CHAPTER I

INTRODUCTION

1.1 Background

Salt is an important ingredient in food products. It is a highly used component in food industry. Historically, salt was added in food for its preservation but today few foods are preserved solely by the addition of salt. However, salt remains a commonly used component for creating an environment resistant to spoilage and inhospitable for the survival of pathogenic organisms in foods. Pathogenic organisms undergo osmotic shock on addition of salt to food as cells tend to loss water thereby causing cell death or retarded growth [1]. The rate of microbial growth can retarded by different mechanisms in different microorganisms such as salt may limit oxygen solubility, interfere with cellular enzymes, or force cells to expend energy to exclude sodium ions from the cell [2]. Salt is also very rich in nutritional value. It enhances the taste of food. Besides this, human body needs salt to produce digestive acids, stimulate liver function, regulate osmotic pressure in cell level, and for proper functioning of brain. Proper amount of salt intake is reported to boost immune system of our body [3].

Table or white salt is added in almost all food products. In Nepal, the authorized distributer of table salt is Nepal Salt Trading Corporation. Since iodine is one of the most important micronutrients, as in other countries, the table salt is fortified with iodine and sold as trade name *Aayo noon*. Iodine is an essential component of the thyroid hormones, thyroxin and triiodothyronine. Therefore, inadequate iodine leads to insufficient production of these hormones which adversely affects many body parts like muscle, heart, liver, kidney, and the development of brain. The iodine deficiency disorder (IDD) is the major cause of mental retardation amongst the world's population. Iodine deficiency also causes physical sluggishness (inertia), goiter (enlarged thyroid), hypothyroidism, delayed neurological development, slow physical growth, and reproductive failure. In this respect the iodized table salt is found to be very useful to prevent iodine deficiency associated health problems.

Besides white salt (iodized or non-iodized), unprocessed black (locally called as bire noon in Nepali and Kala namak in Hindi) and white rock salts (called as sinde noon in Nepali and Sinda Namak in Hindi), mostly of Tibetan and Indian origins, is sold by retailers and also sold openly in streets in Nepal. These salt, also known as volcanic or Himalayan rock salt, deposits also exist in Mustang districts of Nepal.

Figure 1.1. Black rock salt

Figure 1.2. White rock salt

Himalayan rock salt (black and white) are believed to be very beneficial for patients with high blood pressure because of its low sodium content. It is claimed that these salt consists of 84 major and minor trace elements including iron [4].

Since ancient time, black rock salt has been used in various ways. In South Asian Countries, black salt is used in salads, tofu, pickles, and many more food products as taste enhancer. Small amount of black salt is also added in beverages and tea products to enhance the taste. Black salt smells like hydrogen sulfide, which is also one of the component of rotten eggs. So, it is also accepted in vegan's dishes as it mimics the taste of egg [5]. Black salt is believed to have high medicinal values. It is added in many herbal/ayurvedic formulations as laxative and digestive aid. Local people frequently use black salt to treat flatulence, gastrointestinal disorders, heart burn and goiter [6]. Black salt is also used to treat hysteria and for making toothpastes by combining it with other mineral and plant ingredients [7].

Similarly, white rock salt is also being used for different purpose. In Hindu culture, it is believed to be most sacred form of salt. Sinde noon is the only allowed form of salt especially to someone observing rituals, ceremony in the memory of close family member and in any kind of religious fasting.

Rock salt is harvested from natural salt mines that believed to exist in various sites due to transformation of sea during various geological events. Because of its natural occurrence, rock salt can contain various minerals distributed in different proportions. The elemental composition of salt varies depending upon its location and climatic condition [8]. It is possible that percentage purity and nutritional value-which is measured in terms of distribution of useful elements/minerals-in salt sample can be different based on their geographical deposition. A rock salt sample is of high nutritional value if it contains useful elements in high proportions and toxic metals in low portions i.e. to the level as recommended by WHO safe limit.

The consumption of salt on daily basis provides our body with various useful minerals. So, salt is being a most important component of every cuisine. If salt of low quality is consumed then it can pose various health issue. Salt also contain different types of heavy metals in more or less amount and consumption of salt having concentration of metals more than WHO safe limit cause different health problems. Heavy metal poisoning of body is a condition that results from accumulation of certain metals in body due to exposure through food water etc.

Heavy metals like lead, mercury and arsenic adversely affects the nervous system, damage the kidney, and increases the risk of stone formation [9].

According to codex standard for food grade salt, the salt should contain at least 97% of NaCl on dry matter basis, exclusive of additives. Salt having toxic metals in low portions can be used for human consumption. The maximum limit of arsenic and cadmium in a consumable salt should not exceed 0.5 mg/kg, whereas maximum limit for copper and lead is 2mg/kg and that for mercury is 0.1mg/kg [10].

1.2 Methods used in estimation of some of the elements in salt

Different types of essential and toxic elements in salt samples can be determined by using different methods. Some of the methods are briefly described below.

1.2.1 Potentiometric titration for estimation of sodium

Potentiometric titration method is a versatile method used in chemical analysis. It is usually employed to find the concentration of solute in solution. This method uses two electrodes inserted in two different solutions connected by a salt bridge. Salt bridge is a glass tube filled with electrolyte solution which allows the free flow of ions from one cell to another cell therefore makes the electrical connection between two half cells. By using a high impedance voltmeter, potential between these two electrodes can be measured. Since the high impedance voltmeter ensures that current flow is negligible, there are no net electrochemical reaction. Hence, the system is in equilibrium.

For the estimation of sodium chloride in salt sample, a known amount of analytic solution is titrated against a standard silver nitrate solution using a standard saturated calomel electrode as reference electrode and silver-silver chloride electrode as working electrode. Electrode potential of reference electrode is a constant value.

The sharp change in potential indicates the end point of the potentiometric titration. After titration with silver nitrate, end point can be accurately located with the help

of first derivative curve. When an aqueous solution of silver nitrate ($AgNO_3$) is added to the aqueous solution of sodium chloride (NaCl), a white precipitate of silver chloride (AgCl) is formed that is indicated by the following chemical reaction.

$$Ag^+ (aq) + NO_3^- (aq) + Na^+ (aq) + Cl^- (aq) \longrightarrow AgCl (s) + Na^+ (aq) + NO_3^- (aq)$$

At the end point, formation of white precipitate of silver chloride (AgCl) will ceased due to complete consumption of chloride ion from the analytic solution. Therefore the percentage purity and amount of sodium can be calculated [11].

1.2.2 Spectrophotometric method for estimation of iron

Spectrophotometry is a branch of science which studies the interaction of electromagnetic radiation with matter. It is a very simple and economic means for quantitative analysis of minute quantity of substances. It is being widely used for quantitative chemical analysis because of its sensitivity and precision.

Spectrophotometry in the visible region of electromagnetic spectrum is often called colorimetry. Visible region of electromagnetic spectrum generally ranges from 380nm to 780nm. In colorimetry, the color intensity of the unknown is compared with that of standard solution. Colorimetric method gives more accurate results even at very low concentration and it is easy to carry out. Colorimetric method can be applied to a system if it follows Beer's law and if the color produced is sufficiently stable to permit an accurate reading to be taken.

Beer's law is the basis for infrared chemical analysis. It is stated that the concentration of any analyte in the solution is directly proportional to the absorption of the solution [12] i.e.

$$A = \varepsilon bc$$

Where,

A is absorbance,

ε is molar absorptivity expressed in $Lmol^{-1}cm^{-1.}$,

b is path length of sample expressed in cm,

c is the concentration of the compound in solution expressed in $molL^{-1}$.

Total iron in salt sample also, can be determined spectrophotometrically using 1'10-phenanthroline ($C_{12}H_8N_2$) as complexing agent. A spectrophotometric determination of iron dependent on the formation of the iron (II) - 1, 10-phenanthroline complex, which is reddish orange in color, may be oxidized to a blue complex. Upon standing, this blue complex changes to a yellow complex, which also may be produced by complexing iron (II) and 1, 10-phenanthroline directly.

1, 10- phenanthroline is a heterocyclic nitrogen compound. It has been extensively used for the colorimetric determination of small quantities of iron. The iron is first reduced to the ferrous state in a reaction with hydroxylamine hydrochloride; a reducing agent. It was then reacted with 1, 10-phenanthroline to form a colored complex, known as ferroin. This method is routinely used for the determination of iron in wine, beer, foods, chemicals and many other products. It has been adopted as the official method for determining iron in water [13].

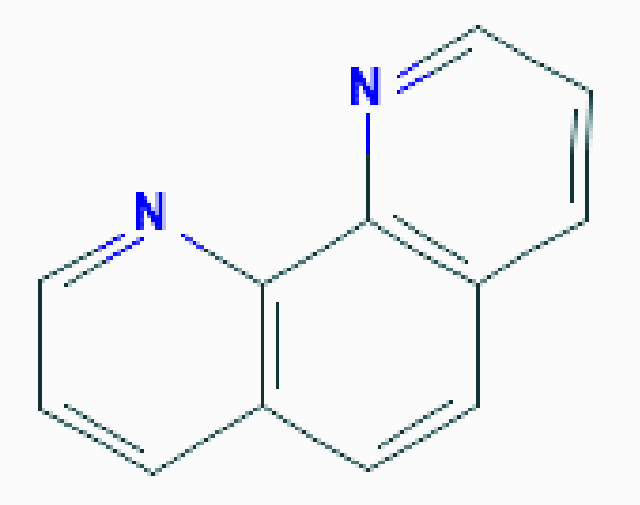

Figure 1.3. Structure of 1, 10- phenanthroline.

In this method, standard solution of iron in the range of 0.5 to 5ppm is made at first using Mohr's salt. Absorbance of each standard solution of iron is measured at maximum wavelength (λ_{max}). Wavelength of maximum absorption is known as λ_{max}. This wavelength is characteristic of each compound. In the given figure 1.4, the peak of the curve whose wavelength correspond to maximum absorption is λ_{max}.

A calibration curve, also known as reference curve, is then obtained by making absorbance *versus* concentration plot as in figure 1.5. With the help of obtained calibration curve, the concentration of total iron can be determined in all the salt samples.

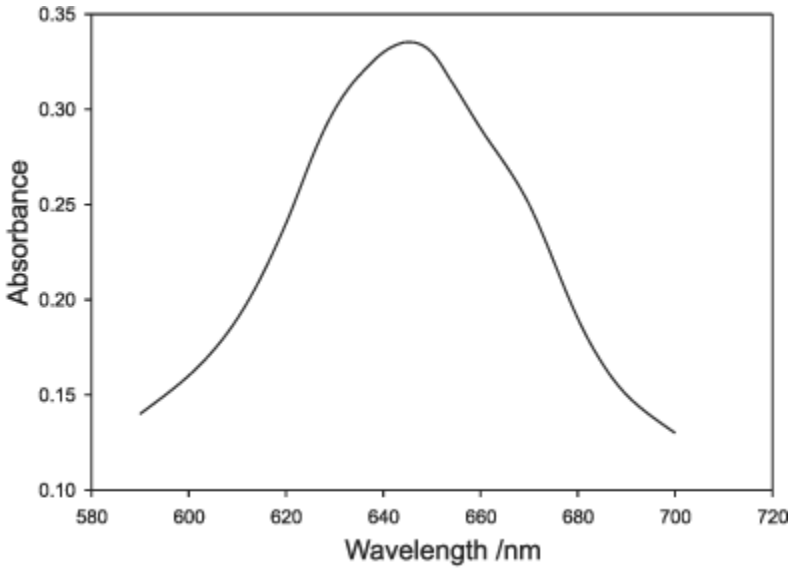

Figure 1.4. Absorbance *versus* wavelength plot showing λ_{max}.

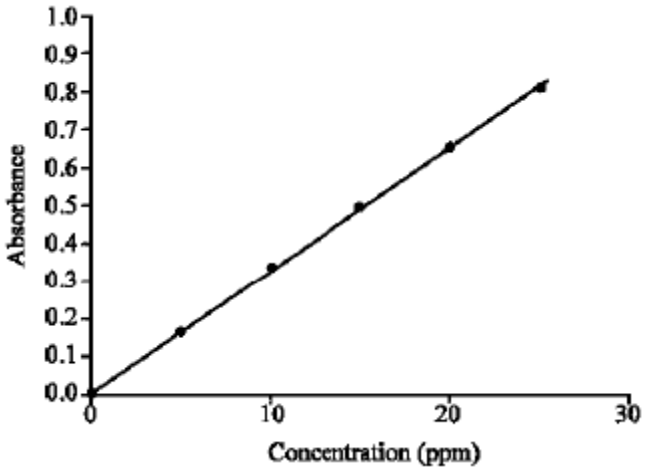

Figure 1.5. Theoretical calibration curve to measure concentration of iron.

Certain amount of salt sample is first boiled with hydroxylamine hydrochloride ($NH_2OH.HCl$), which converts all the iron in ferrous as indicated by the reaction below.

$$4Fe^{+3} + 2NH_2OH.HCl \longrightarrow 4Fe^{+2} + N_2O + 4H^{+} + H_2O$$

The reduced iron then form complex with 1, 10- phenanthroline and its concentration can be determined spectrophometrically.

$Fe^{2+} + 3Phen \longrightarrow Fe(Phen)_3^{2+}$

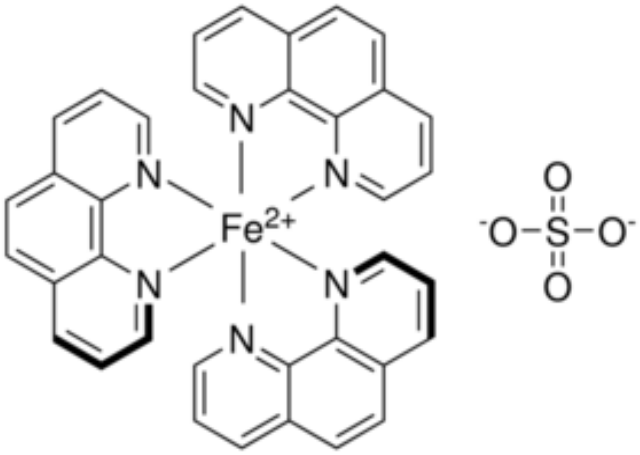

Figure 1.6. Structure of Iron-phenanthroline complex.

Since iron complex has more solubility at acidic pH, it has to be maintained at 3.2-3.3. Appropriate amount of acidic buffer, i.e. ammonium acetate buffer or potassium citrate solution has to be added to the analytic solution [14].

1.2.3 EDTA titration for estimation of magnesium and calcium

EDTA titration is also known as complexometric titration method. EDTA is a hexadentate chelating ligand which binds with metal ions in water to give stable chelate complex.

For estimation of the magnesium and calcium, in first step total amount of calcium and magnesium present in salt sample is performed in presence of Erichrome black T indicator. Then, amount of calcium only is determined in presence of murexide as an indicator.

The difference between the total calcium and magnesium obtained and the total calcium obtained is equivalent to total magnesium in the salt sample [15].

pH of the solution is most important factor to observe during EDTA titration since different metal forms stable complex with EDTA at different pH value. The minimum pH at which calcium and magnesium forms stable complex with EDTA is 8-10 [16].

1.2.4 AAS method for the determination heavy metals

Atomic absorption spectrometer (AAS) is a spectro analytical instrument for the quantitative determination of chemical elements and the procedure is known as atomic absorption spectroscopy. A vapor containing atoms of the metal is formed when a solution containing metallic salt or other metallic compound is aspirated into flame. Some of these gaseous atoms may be excited to higher energy level. Since, excited atoms cannot stay longer in higher energy level they return to lower energy level by emission of radiation characteristic of metal. But there may be a large number of the gaseous metal atoms remain in ground state. Such metal atom can absorb radiant energy of their own specific resonance wavelength, which in general is the wavelength of the radiation that the atom would emit if excited from the ground state.

Hence, some part of light will be absorbed if the light of the resonance wavelength is passed through a flame containing the atoms to be analyzed. The extent of absorption is proportional to the number of ground state atoms present in flame. This is the basic principle of atomic absorption spectroscopy. The absorption A is given by the logarithmic ratio of the intensity of the incident light signal I_0 to the transmitted light, I_t, i.e.

$$A = \log \frac{I0}{It} = KLN_0$$

Where,

N_0= the concentration of atoms in the flame (no. of atoms per milliliter)

L= the path length through the flame (cm)

K= a constant related to the absorption coefficient

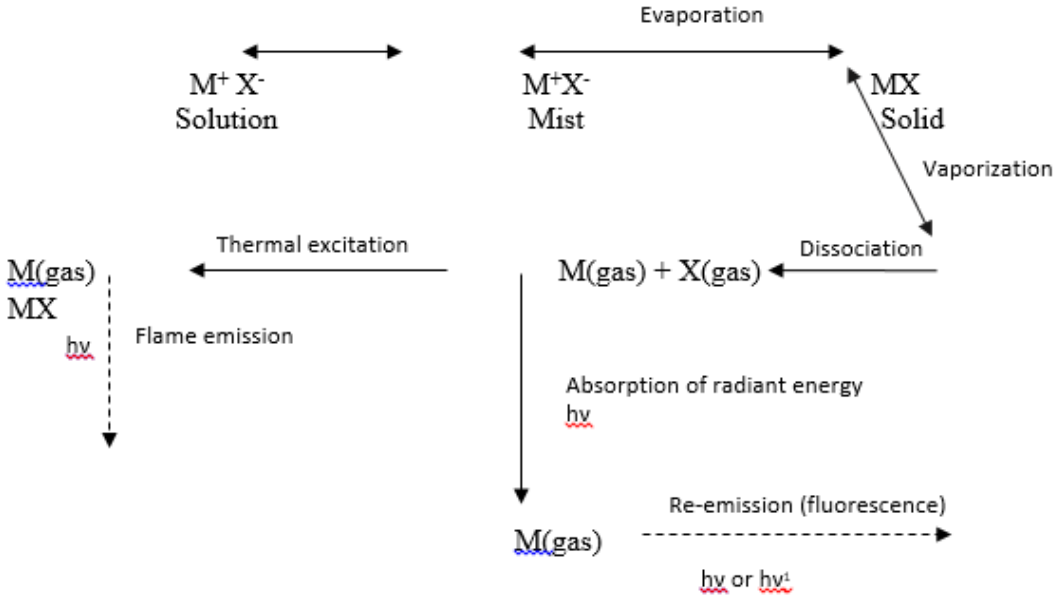

Figure 1.7. Overall process involved in atomic emission.

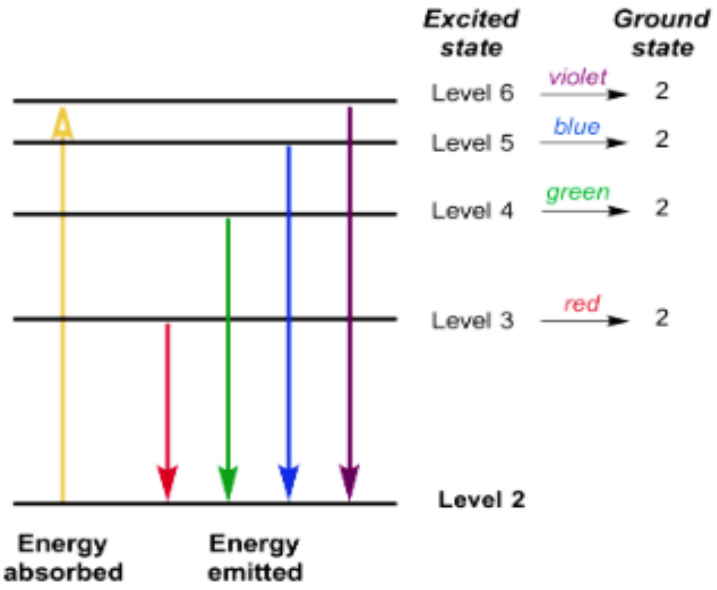

Figure 1.8. Energy levels involved in atomic absorption and emission processes.

Atoms in ground state gets promoted to excited state by the absorption of radient energy ΔE which is determined by Bohrs equation

$\Delta E = E_3 - E_2 = h\nu = hc/\lambda$.

Where,

c = velocity of light

h= Planks constant

ν= frequency

λ= wavelength of radiation absorbed.

The relationship between the number of atoms in ground state and excited state is given by the Boltzmann equation [16]

$$N_1/N_0 = (g_1/g_0)e^{-\Delta E/KT}.$$

Where,

N_1 = number of atoms in excited state

N_0 = number of atoms in ground state

g_1/g_0 = ratio of statistical weight for ground and excited state

ΔE = energy of excitation

K= Boltzmann constant and

T = temperature in Kelvin

1.3 Literature review

Elemental analysis in salt samples of different countries is reported by researchers. Determination of trace metal contaminants such as Pb, Cd, Zn, Fe, Cu and Al in edible salt samples obtained from different places of Iran was reported by Khaniki *et al.* by using atomic absorption spectroscopy. The study was carried on 60 different types of salt and it was found that concentration of some of the toxic metals in some samples exceed the WHO safe limit. Since the concentration of heavy metals in some salt sample exceed the permitted value it was recommended to use a suitable method for clarification and purification during salt processing [17].

Characterization of six different salt samples namely, source salt, Himalayan salt, rock salt, sea salt, lake salt and reduced sodium salt (minsalt) that obtained from markets of Turkey was made by Yalcin *et al.* In the study, identification of different minerals and their structural characterization was carried out. They had used various spectroscopic and microscopic techniques such as X-ray powder diffraction (XRD), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM/EDS) inductive coupling plasma optic emission spectroscopy(ICP-OES), X-ray fluorescence (XRF) spectrometer and the Fourier transform infrared (FTIR) spectroscopy. In this study it was found that sodium and chlorine is primarily found in all types of salt. Besides sodium and chlorine some other elements like Al, Ca, Cu, Fe, K, Mg and P were also identified [18].

Duggal *et al.* made elemental analysis of various edible salt samples obtained from Indian markets by X-ray fluorescence technique (XRF). From this study, it was concluded that apart from the major elements Na and Cl, the Mg (0.06-1.07 %), S (0.05-2.06 %), K (0.02-21.86 %), Ca (0.011.26 %), Mn (up to 0.02 %), Fe (up to 0.29 %), Br (0.00530.04 %) and Si (0.01-0.92 %) trace elements were detected. Low NaCl composition i.e. 80-84% was reported in *Lahori* black salt whereas average composition of NaCl in commercial iodized salt was 99.87% [19].

Yüksel, Z., & Tufan, M. Ç. determined the radioactive levels of salt minerals using gamma spectrometry units with HPGe detector. In this study, it is noted that Iranian salt sample has the maximum radioactivity level whereas Turkish salt samples has lower level of radioactivity concentration however the effective doses for all salt samples are lower than that of UNSCEAR 2000 values [20]

Determination of uranium content in commercial iodized salt was made by Simon *et al.* it was reported that the uranium content of the iodinated commercially available sodium salt sample is ≤ 10 ppb [21]

The level of lead (Pb), cadmium Cd), mercury (Hg), copper (Cu) and Iron (Fe) in unrefined and refined salt was determined by Heshmati *et al.* using atomic absorption spectroscopy method. Analyzed heavy metal contents were generally at high level in unrefined salts as compared to refined salt. All values for toxic metals were lower than the permitted maximum for human consumption as prescribed by Codex Alimentarius commission [22].

Heavy metal contamination of table salt consumed in Iran was observed by Cheraghali *et al.* One hundred samples of rock and refined table salts were analyzed using atomic absorption spectrophotometric methods for the presence of toxic heavy metals such as Cd, Pb, Hg and As. The concentrations of tested heavy metals were well below the maximum levels set by Codex [23].

Heavy metal contaminants in natural salt samples was also determined by Peerawat *et al*. by using inductively coupled plasma atomic emission spectrophotometry [24].

Zsigmond *et al*. conducted the morphological and microchemical surface characterization of Himalayan salt sample using SEM/EDS techniques. Very heterogeneous morphological surface and eleven elements (Cl, Na, O, S, Ca, K, Mg, Si, Al, Fe, F) detected in the samples [25].

The contents of Ca, Fe, K, Mg and Na were studied in 23 common and gourmet salt samples by Almeida *et al*. using atomic spectrometry. They found that the concentration levels found for those mineral elements were low [26].

Attah Danil *et al.* carried out a comparative study of local and commercial table salt marketed in Wukari, Nigeria. This study concluded that Akwana mineral salt and table salts processed from it contained nitrate, phosphate, iron and ammonia with concentration ranges from 0.4 to 1.0, 1.0 to 2.0, 0.5 to 12 and 0.5 mg/kg, respectively [27].

The level of essential and non-essential heavy metals in the table salt refined with recrystallization and washing methods was determined by Eftekhari *et al.* The level of lead, cadmium, copper, zinc, nickel and cobalt was determined using Voltammetric method. It was found that values for toxic metals were lower than the permitted maximum for human consumption as prescribed by Codex and Institute of Standards and Industrial Research of Iran [28].

By using XRD and FTIR techniques Santhanakrishnan *et al.* analyzed the elemental and structural characterization of solar evaporated salts from Tamilnadu, India. Besides Na and Cl, other elements like Fe, Pb, Cu, Ni, Cd, Zn were also reported in salt samples but with the limit accepted by WHO for human consumption[29].

1.4 Statement of the problem

Rock salt, mostly of Indian and Tibetan origins, is highly used in Nepalese community as food additive and in herbal formulations. Sample of Nepalese origin, mostly obtained from Mustang, is also in use. The rock salt samples may or may not be refined ones. Also, nutritional value in the salt sample is not reported in literature.

If the rock salt sample is impure and contains heavy metal contaminants then the salt is unfit for consumption. Salt being one of the highly used food additive, consumption of low quality salt or salt lacking useful minerals can pose different short and long terms health issue.

1.5 Objectives

The broad objective of this research is to make a comparative study on percentage purity and amount of trace metals in rock salt samples of different origins. This will provide useful information on the nutritional value of different salt samples.

The specific objectives of this research are as listed.

1. Determine the percentage purity in salt samples.
2. Determine the amount of useful metals particularly sodium, iron, calcium, and magnesium present in different salt samples.
3. Determine the amount of toxic heavy metals arsenic and mercury.
4. Compare the percentage purity, and contents of useful and heavy elements in the salt samples using different statistical parameters.

CHAPTER-II

EXPERIMENTAL METHODS

2.1. Determination of % Purity and Amount of Sodium

The % purity and amount of sodium in the collected salt samples was determined by following Euro salt standard (EuSalt/AS 016-2005) [9]. Detail of the method used is described below:

2.1.1. Reagent Preparation

All regents were prepared in double distilled water having pH of 7.2±0.05. The conductivity of the water sample was 20±2 micro Siemens.

a. Preparation of 500mL solution of 1.4 M HNO_3

50mL of concentrated HNO_3 (ρ=1.40g/mL, 65% m/m) was taken in a measuring cylinder and was transferred into a 500mL volumetric flask with the help of funnel. It was then diluted up to marked level.

b. Preparation of 100mL solution of 2g/L PVA

0.200g of PVA was weighted in an analytical balance and was transferred into a 100mL volumetric flask with the help of a funnel and was diluted up to the marked level.

c. Preparation of 1000mL solution of 25g/L NaCl

25.000g of NaCl (99%) was weighted in an analytical balance and it was transferred into a 100mL volumetric flask with the help of a funnel and it was diluted up to marked level.

d. Preparation of 100mL solution of 0.05 N $AgNO_3$

0.849g $AgNO_3$ was weighted in an analytical balance and it was transferred into a 100ml volumetric flask with the help of a funnel and was diluted up to marked level.

e. Preparation of salt bridge

About 50ml of water was taken into a 100ml beaker. 7.500g of KNO_3 was weighted using analytical balance and it was poured into the beaker. It was then started to heat. 1.500g agar-agar was added into the same beaker and it was heated to boil with continuous stirring using a glass rod. After it forms a thick gel, it was allowed to cool down. A glass tube was made U shaped. From one end of the tube the gel was sucked into it with the help of a sucker. It was then kept in inverted position.

f. Preparation of stock solution of collected salt sample

Black and white rock salt samples were collected from different places of Nepal. Retailers from different cities was claimed that some salt is of Tibetan origin and some salt is of Indian origin. Besides these, rock salt sample of Nepali origin was collected from Mustang. All the salt samples were stored into different glass vials and were labelled as follow.

Table 1. Sample collection sites and place of origin for black salt samples

Collected from	**Origin**	**Labelled as**
Kathmandu	Tibet	BS1
Bhatbhateni(KTM)	India	BS2
Butwal	India	BS3
Gulmi	India	BS4
Baitadi	Tibet	BS5
Pokhara	India	BS6
Palpa	India	BS7
Factory(Testy)	India	BS8
Kathmandu(I)	Tibet	BS9
Kathmandu(II)	India	BS1O

Table 2. Sample collection sites and place of origin for black salt samples

Collected from	Origin	Labelled as
Kathmandu	India	WS1
Bhatbhateni(KTM)	India	WS2
Butwal	Tibet	WS3
Gulmi	India	WS4
Baitadi	Tibet	WS5
Pokhara	India	WS6
Palpa	India	WS7
Factory(Testy)	India	WS8
Mustang(I)	Nepal	WS9
Mustang(II)	Nepal	WS10

Each sample was dried in hot air oven at 50-60 for 10 minutes then 2.500g of each was weighted in an analytical balance and it was then transferred into a 100mL volumetric flask using a funnel. It was diluted up to marked level.

2.1.2 Method Validation

Study of % recovery is an essential parameter for method validation, which provides confidence to conduct research. Percentage purity of each salt sample was determined by following Euro salt standard (EuSalt/AS 016-2005) by potentiometric titration method [9].

For this, titration solution was made by adding 0.5ml stock solution of NaCl, 0.1mL of HNO_3, 0.2mL of PVA was added into a titration vessel using a pipette. After

adding 20ml of water into this titration vessel titration was carried out using 0.05 N $AgNO_3$ solution, potentiometrically.

2.1.3 Estimation of amount of sodium in collected salt samples

2.0mL of samples stock solution, 2mL of HNO_3, 4mL of PVA was taken into a conical flask with the help of a pipette. About 20mL of water was added into it. Potentiometric titration was carried out for each sample using 0.05N $AgNO_3$, calomel electrode as reference electrode and Ag-AgCl electrode.

The % purity and amount of sodium was in the sample can be calculated by using the following approach.

Since 1mL of solution ≡ 24875µg of NaCl, theoretical weight of NaCl (x) in 1000ml of solution is given by:

$$x = 24875mg \text{ (99.5\% of 25000mg)}$$

Experimental weight of NaCl in the salt sample is calculated as:

$$x' = 0.05 \times V \times 58.5 \times 1000\mu g$$

Where, V is end point of titration i.e. volume of $AgNO_3$ consumed.

The % error in the measurement can be calculated as:

$$\% \text{ error} = (x\text{-}x') \times 100/x'$$

The determination of % error helps to calculate the % recovery in each sample.

2.2 Determination of Total Iron

Total iron in each of the collected salt samples was determined by following a standard procedure described by Harvey *et al.* [10]. The detail of this method is provided in later section.

2.2.1 Reagent Preparation

a. Preparation of 1000mL solution of 1000ppm Mohrs salt (stock solution)

7.021 g of Mohrs salt was weighted in an analytical balance and it was carefully transferred in 1000mL volumetric funnel. 50mL of distilled water was added into it and was shaken till it dissolves completely. Then it was diluted up to marked level.

b. Preparation of 1, 10- phenanthroline

0.100 g of 1, 10 – phenanthroline was weighted using an analytical balance and it was carefully transferred in a beaker.100mL of distilled water was added into it and it was heated just to boil with continuous stirring using a glass rod. After cooling it was transferred into a glass bottle.

c. Preparation of ammonium acetate buffer

62.5 g of ammonium acetate was weighted using an analytical balance and it was transferred into 250mL volumetric flask. 40mL of water and 175mL of glacial acetic acid was added using measuring cylinder and funnel.

d. Preparation of hydroxyl amine

10 g of $NH_2OH.HCl$ was weighted using an analytical balance and it was carefully transferred in a 100mL volumetric flask. 10mL of distilled water was added and shaken till the content dissolved completely then diluted upto marked level.

e. Preparation of calibration standard solutions of Fe^{++}

Calibration standard solution of Fe^{++} of different concentration i.e. 0.5ppm, 1ppm, 2ppm, 3ppm, and 4ppm were prepared using stock solution, by following dilution technique.

At first 100mL of 100ppm of Fe^{++} solution was made by taking 10mL of stock solution. It was further diluted to make it 10ppm in 50mL volumetric flask, by taking required volume then it was used to make calibration standard solutions. To make calibration standard solutions i.e.50mL of 0.5ppm, 1ppm, 2ppm, 3ppm and

4ppm of Fe^{++}; calculated (using dilution method) 2.5mL, 5mL, 10mL, 15mL and 20mL solution of 10ppm Fe^{++} was taken respectively into 5 separate conical flask. 1mL of HCl and 0.5mL of hydroxyl amine was added into each conical flask and was heated till the volume reduced to half. After cooling, the content in each conical flask was carefully transferred into 5 different volumetric flask and labelled them. 5mL of ammonium acetate buffer and 2mL of o-phenanthroline was added into each volumetric flask and they were diluted upto marked level with distilled water. Solutions were left for about 10 min. for colour development.

2.2.2 Determination of λ_{max}

The λmax was determined by measuring absorbance of any one calibration standard solution (solution of 3ppm) at various wavelengths from 400nm to 600nm.

2.2.3 Preparation of calibration curve

At first absorbance of each standard solution was measured. A calibration curve was then obtained by plotting absorbance as a function of concentration of Fe^{++} in ppm.

2.2.4 Method validation

Calibration standard solutions were first labelled as A, B, C D and E for 0.5ppm, 1ppm, 2ppm, 3ppm and 4ppm respectively. 2mL of solution A was then taken in a conical flask and 1mL of HCl and 0.5mL of hydroxylamine solution was added. This was boiled till the content in conical flask was reduced to half. After cooling, it was carefully transferred into 50mL volumetric flask. In this solution 5mL of buffer and 1mL of o-phenanthroline were added and was diluted upto marked level. It was allowed to stand for about 10min for maximum color development. Then absorbance was measured.

The same process was done for rest of standard solutions (B, C, D and E). The amount of iron was then calculated using calibration curve.

2.2.5 Estimation of total iron in salt sample

2mL of one of the salt sample solution was taken in a conical flask. 1mL of HCl and 0.5mL of hydroxylamine solution was added. The content in conical flask was boiled till volume reduced to half. After cooling it was carefully transferred in a 50mL volumetric flask. 5mL of ammonium acetate buffer and 2mL of o-phenanthroline was added and it was diluted upto marked level. It was allowed to stand for about 10min for maximum colour development. Then absorbance was measured.

The same process was done for rest if the salt samples. The amount of iron was then calculated using the calibration curve.

2.3 Determination of Magnesium and Calcium

The determination of the amount of magnesium and calcium in salt sample was carried out by following a standard method for determination of total calcium and magnesium ion concentration described by Sobel *et al.* [30], which is described as follow:

2.3.1 Reagent preparation

a. Preparation of 500mL solution of 0.05M EDTA

9.306g of EDTA was weighted using an analytical balance and it was transferred into a 500mL volumetric flask using a funnel. It was then diluted upto marked level.

b. Preparation of ammonium chloride (NH_2Cl) buffer

17.4g of ammonium chloride was weighted in an analytical balance and was carefully transferred into a 250mL volumetric flask. 142mL concentrated NH_3 was added into it using a measuring cylinder and it was diluted upto marked level.

c. Preparation of 500mL solution of 0.025M $MgCl_2.6H_2O$

2.541g of $MgCl_2.6H_2O$ was weighted using an analytical balance and transferred into a 500mL volumetric flask using a funnel. It was then diluted upto marked level.

d. Preparation of Erichrome black T. indicator

0.200g of Erichrome black T indicator was weighted in an analytical balance and it was carefully transferred in a beaker containing 15mL of concentrated ammonia and 5mL of ethanol.

e. Preparation of 100mL solution of 50ppm $CaCO_3$ and $MgCO_3$ mixture (stock solution)

2.497g of $CaCO_3$ was taken and it was transferred into a 100mL volumetric flask. About 5mL of water was added and shaken well till the content dissolved then diluted upto marked level to get 100ppm $CaCO_3$ solution.

Similarly, 3.469g of $MgCO_3$ was taken and was transferred into a 100mL volumetric flask. About 5mL of water was added and shaken well till the content dissolved then diluted upto marked level to get 100ppm $MgCO_3$ solution.

Finally, 50mL of each of the solution were mixed in a 100mL volumetric flask to get 50ppm of $CaCO_3$ and $MgCO_3$ mixture.

f. Preparation of a series of standard solution of $CaCO_3$ and $MgCO_3$ mixture

Five sets of standard solution i.e. 2ppm, 4ppm, 6ppm, 8ppm and 10ppm were prepared using stock solution, by following dilution technique.

2.3.2 Standardization of EDTA solution

10mL sample of the EDTA solution was pipetted into a conical flask. 10mL of ammonia buffer and 1mL of Erichrome Black T indicator solution was added into it. It was titrated against magnesium chloride solution until an end point appeared; a permanent color changed from blue to pink, as in figure 2.1.

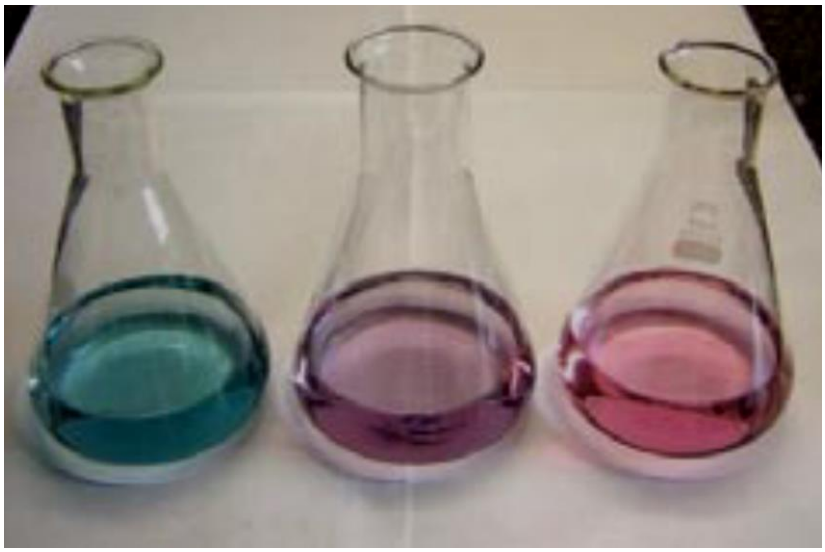

Figure 2.1. Color of solution during EDTA titration in presence of Erichrome Black T indicator.

At first, Mg^{2+} forms a complex with EDTA molecules till all the excess EDTA has been complexed. After this Mg^{2+} ion starts to complex with indicator changing its color from blue to pink.

2.3.3 Method validation

In order to know the validity of this method, at first amount of calcium and magnesium in standard solution of calcium and magnesium was measured. For this, 10mL of each of standard solution was pipetted into five different conical flask. 10mL of 0.05M EDTA solution 10mL of ammonia buffer and 1mL of Erichrome Black T indicator and 20mL of water was added in all conical flask containing standard solution. It was then titrated against 0.05M $MgCl_2.6H_2O$ solution. Pink color appeared at end point, which gives total moles of Ca^{++} and Mg^{++} in each of the standard samples.

At first, the blue color of solution is well before end point in which all Ca^{2+}/Mg^{2+} ions complexed by excess EDTA and all indicator molecules are free. Last trace of blue/purple color which appeared during titration is just before endpoint in which excess EDTA almost totally complexed by added Mg^{2+}. Lastly, Pink/red color of

solution is the endpoint in which all EDTA complexed by added Mg^{2+} and indicator also complexed.

The main reaction occurring in this method are

$Ca^{2+} + EDTA^{4-} \rightarrow [Ca\text{-}EDTA]^{2-}$

$Mg^{2+} + EDTA^{4-} \rightarrow [Mg\text{-}EDTA]^{2-}$

During titration the excess EDTA, that left in flask after complexing with calcium and magnesium ions in the solution, forms complex with Mg^{2+} added from burette.

$EDTA^{4-} + Mg^{2+} \rightarrow [Mg\text{-}EDTA]^{2-}$

After excess EDTA used up the indicator ErioT, which is blue in color, reacts with Mg^{2+} cshanging its color to pink, as in figure 2.1.

$ErioT + Mg^{2+} \rightarrow ErioT\text{-}Mg$

Calcium can be determined by EDTA titration in solution of 0.1 M sodium hydroxide (pH 12-13) using murexide as an indicator. Magnesium in that high pH precipitates as $Mg(OH)_2$ and is not complexed by EDTA, thus its presence can be ignored.

To calculate moles of Ca++ only, 10mL of standard solution was pipetted into a conical flask 2-3 granules of solid NaOH and a pinch of murexide was added into it and it was titrated against EDTA. Color changed from red to violet at the end point, as shown in following figure 2.2.

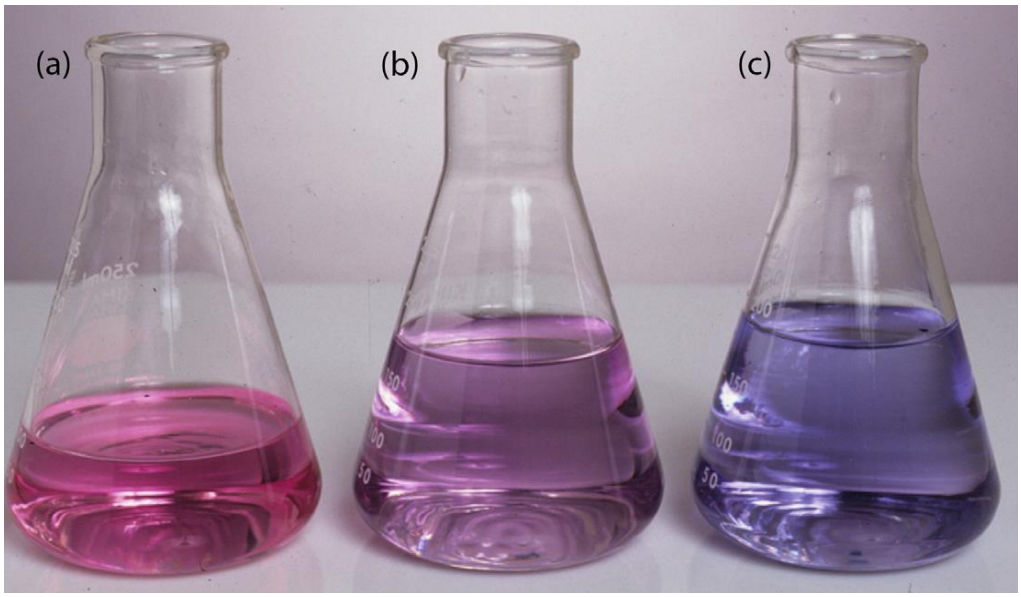

Figure 2.2. Color of solution during EDTA titration of calcium using Murexide indicator.

Reaction taking place during titration is:

$$Ca^{2+} + EDTA^{4-} \rightarrow [Ca\text{-}EDTA]^{2-}$$

2.3.4 Estimation of Ca^{++} and Mg^{++} in salt sample

At first step, total amount of Ca^{++} and Mg^{++} present in all salt sample was estimated by EDTA titration in presence of Erio T indicator as described above.

After determination of Ca^{++} and Mg^{++} content, amount of calcium only in the same sample was determined by EDTA titration in the presence of murexide.

2.4 Determination of Hg, As and Pb

Hg, As and Pb in some selected salt samples were measured with the help of atomic absorbance spectroscopy. Atomic absorbance spectrometer from lab of Water Engineering and Training Centre (P) Ltd., Dillibazar Kathmandu was used for the purpose.

CHAPTER-III

RESULTS AND DISCUSSION

3.1 Determination of % purity and amount of sodium

3.1.1 Method validation

Potentiometric titration of known amount of sodium chloride against standard AgCl solution was carried out. The result of percentage recovery experiment for method validation is shown in table 3.

Table 3. Percentage recovery study

SN	NaCl added (mg)	NaCl measured (mg)	% recovery mean ±σ
1	12.437	13.123	94.49±6.788
2	24.875	24.862	100.05±3.394
3	37.312	39.487	94.49±2.262
4	49.750	51.187	97.19±1.697
5	62.187	64.350	96.63±1.337
6	74.625	73.125	102.05±1.131

From this study, excellent % recovery in the range of 94-102% is obtained for estimation of NaCl. The % recovery reported here fall within the acceptable limit as reported by WHO standard. This observation nicely validates the potentiometric titration method for the estimation of % purity and sodium chloride.

3.1.2 Estimation of amount of sodium chloride in salt sample

Amount of sodium estimated, using potentiometric titration method, in each of the collected salt samples is shown in following table 4.

Table 4. Amount of Na and % purity in salt samples reported as **mean ±σ**

Black salt sample			White salt sample		
Sample ID	Sodium mg/100mg	% purity	**Sample ID**	Sodium mg/100mg	% purity
BS1	33.12± 3.19	84.24±8.11	**WS1**	23.30± 2.12	59.28±5.40
BS2	36.49± 2.12	92.82±5.4	**WS2**	34.65± 2.65	88.14±6.75
BS3	30.05± 5.31	76.44±13.5	**WS3**	35.57± 1.06	90.48±2.70
BS4	36.19± 1.06	92.04±2.7	**WS4**	34.34± 1.06	87.36±2.70
BS5	36.19± 1.06	92.04±2.7	**WS5**	32.50±2.81	82.68±7.14
BS6	34.35± 1.06	87.36±2.7	**WS6**	34.96± 1.84	88.92±4.68
BS7	35.57± 1.06	90.48±2.7	**WS7**	35.57± 2.12	90.48±5.40
BS8	37.11± 1.06	94.38±2.7	**WS8**	34.34± 1.06	87.36±2.70
BS9	35.88± 0	91.26±0	**WS9**	34.34± 1.06	87.36±2.70
BS10	37.11± 1.06	94.38±2.7	**WS10**	33.73± 1.66	85.80±2.70

It is clear that the amount of Na in black rock salt sample is reported in the range of 30 to 37 mg/100mg whereas that in white rock salt sample is reported in the range of 23-35 mg/100mg of salt sample (see table 4). There is no significant difference in % purity of white rock salt and black rock salt as shown in table 4. Among the collected black salt samples of different origin, BS3 is reported to have lower amount of Na, i.e. 30.05± 5.31 mg/100mg, which was of Indian origin and Na in other black salt sample of Indian origin BS2, BS4, BS6, BS7, BS8 and BS10 is in the range of 33-37 mg/100mg.Whereas white rock salt samples except WS1 (23.30± 2.12mg/100mg) contain Na in the range of 32-35mg/100mg.

3.2 Determination of total iron

3.2.1 Determination of λ_{max}

The plot absorbance versus wavelength plot for the Fe complex is given in figure 3.1.Form the plot, λ_{max} was found to be 510 nm. The measurement was made by selecting this wavelength.

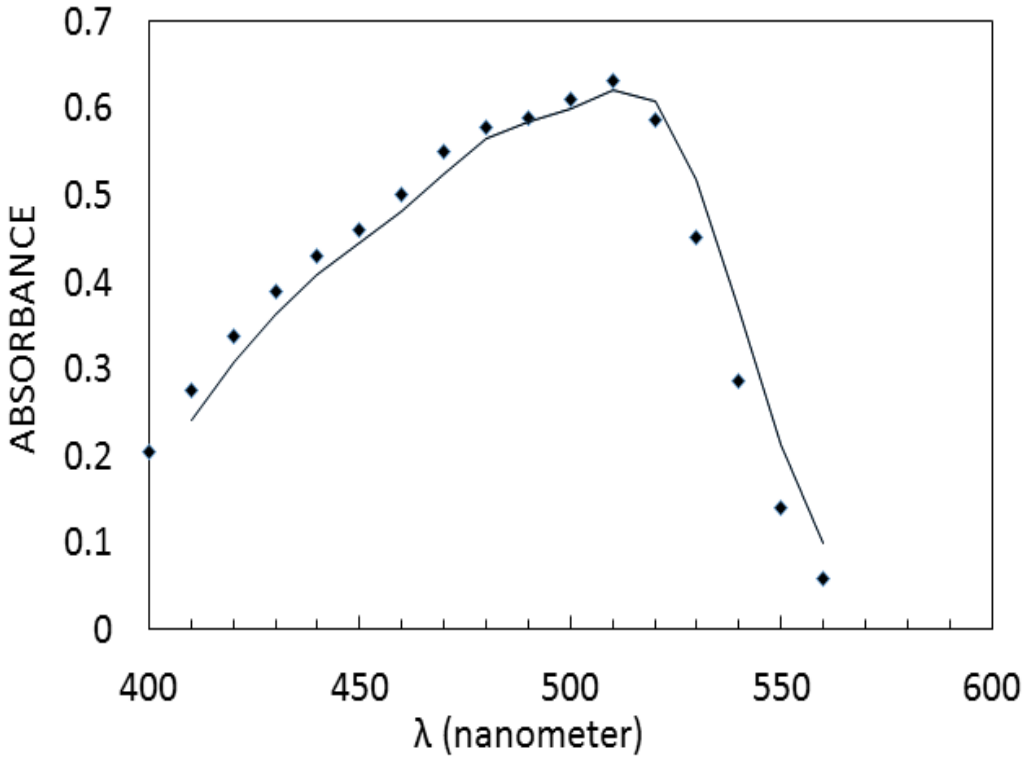

Figure 3.1. Determination of λ_{max}

3.2.2 Calibration curve for the determination of iron

The plot of absorbance as a function of concentration of standard solution is shown in following figure 3.1. In this figure, it is clear that the linearity (R^2=0.9935) is obtained up to 4 ppm of solution.

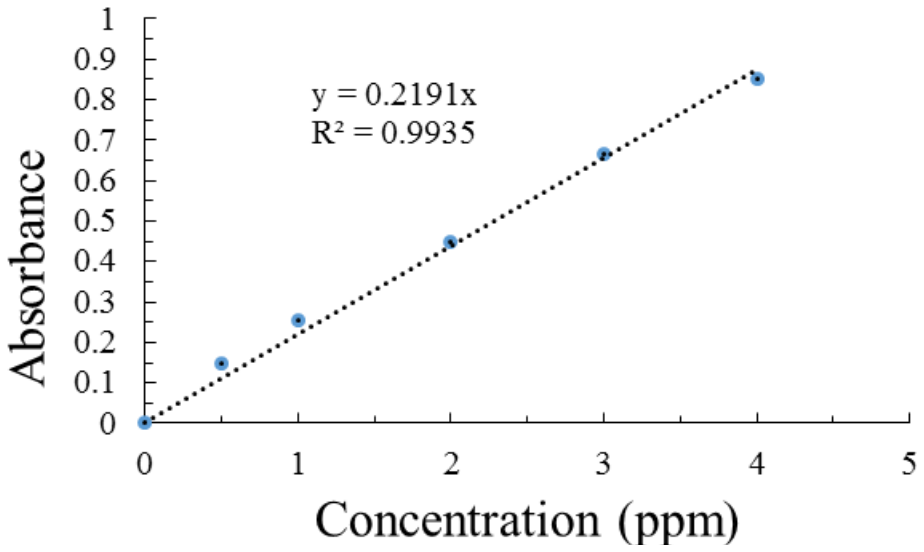

Fig 3.2. Calibration curve for the determination of iron.

The determination of the amount of the iron in different samples was made by using the above calibration curve.

3.2.3 Method validation

Excellent % recovery is observed on experimentally measuring the concentration of solution with already known concentration, by using the calibration curve explained above. This provides the validity for this method. Hence this same method is used to calculate the concentration of iron in all the collected salt samples.

Table 5. Method validation for spectrophotometry

SN	Added ppm	Measured ppm(mean±σ)	%Recovery (mean±σ)
A	1	1.17±0.011	115.37 ± 1.149
B	1.5	1.54±0.005	104.83 ± 0.345
C	2.5	2.37±0.013	105.75± 0.547
D	3.5	3.49±0.013	99.51 ± 0.389
E	4.5	3.97±0.006	87.83 ± 0.145

3.2.4 Determination of iron in salt sample

Amount of iron in collected salt sample has determined with the help of calibration curve, which is shown in table 6.

Table 6. Amount of iron in salt samples

Black salt	ppm (mean±σ)	**White salt**	ppm (mean±σ)
BS1	17.57±0.35	**WS1**	13.38±0.26
BS2	24.49±0.48	**WS2**	14.45±0.28
BS3	16.43±0.32	**WS3**	10.49±0.20
BS4	20.99±0.41	**WS4**	9.81±0.19
BS5	14.98±0.21	**WS5**	7.37±0.14
BS6	14.90±0.29	**WS6**	7.75±0.15
BS7	19.09±0.38	**WS7**	7.75±0.15
BS8	27.38±0.54	**WS8**	11.10±0.22
BS9	12.77±0.55	**WS9**	8.29±0.16
BS10	18.78±0.37	**WS10**	7.60±0.15

Significant amount of iron has found in both types of rock salt. Iron is more in black salt in comparison to white salt. White rock salt sample of Nepali origin i.e. WS9 and WS10 contain 8.29ppm and 7.60ppm of iron respectively. Among the collected white salt sample amount of iron is highest in WS2 i.e.14.45ppm which is of Indian origin according to retailer. The obtained result shows that the salt of Tibetan origin i.e. WS3 and WS5 contain 10.49±0.20ppm and 7.37±0.14ppm of iron. This result shows that, there is no vast different in amount of iron of Indian, Tibetan and Nepali origin.

3.3 Determination of magnesium and calcium

3.3.1 Standardization of EDTA solution

Table 7. Standardization of EDTA solution

SN	Volume of EDTA(ml)	Volume of $MgCl_2$ consumed(ml)			Concurrent reading
		Initial	Final	Difference	
1	10.0	0.0	20.5	20.5	20.5
2	10.0	20.5	41.0	20.5	
3	10.0	0.0	20.5	20.5	

Calculation:

Volume of EDTA (V_1) = 10ml

Volume of $MgCl_2$ consumed (V_2) = 20.5ml

Concentration of $MgCl_2$ (N_2) = 0.025N

Concentration of EDTA (N_1) =?

$$N_1 = \frac{20.5\text{ml} \times 0{,}025\text{N}}{10\text{ml}}$$

N_1 = 0.5125N

3.3.2 Method validation

Low % error has obtained in the calculation of amount of magnesium in standard solution by EDTA titration method. This result provides validity of the method used. Hence the same method is used for the determination of magnesium in all the salt samples.

Table 8. Method validation of EDTA titration

SN	Actual weight of Mg (g/L)	Experimental weight of Mg (g/L)	% Recovery (mean±σ)
A,	4.9	4.59	106.326±0.683
B	9.8	8.874	109.440 ±0.097
C	14.7	13.46	108.400 ±0.154
D	19.6	18.97	103.200± 0.391

3.3.3 Determination of Mg and Ca

At first, we get the amount of total magnesium and calcium by the EDTA titration method in presence of Erio T indicator. The salt sample solution has not changes to red color on addition of 2-3 granules of NaOH and a pinch of murexide whereas the standard solution has changed to red color. So, it shows that calcium is not present in collected salt samples or it can be said that it may be present beyond detectable limit by this method.

Hence, the total amount of magnesium and calcium determined by EDTA titration in presence of Erio T indicator is equivalent to the amount of magnesium only. The amount of magnesium determined in salt sample is shown in following table 9.

Table 9: Amount of magnesium in salt sample

Black salt	ppm (mean±σ)	White salt	ppm (mean±σ)
BS1	-	**WS1**	1.55 ± 0.03
BS2	-	**WS2**	0.4 ± 0.020
BS3	-	**WS3**	1.3±0.017
BS4	-	**WS4**	-
BS5	-	**WS5**	0.15 ± 0.005
BS6	-	**WS6**	5.45 ± 0.028
BS7	-	**WS7**	0.2 ± 0.061
BS8	0.1±0.002	**WS8**	0.25 ± 0.073
BS9	-	**WS9**	3.25 ±0.094
BS10	0.3±0.017	**WS10**	0.1 ±0.002

Data reported in table 9 shows that magnesium was found to be present in low levels in black salt sample BS8 and BS10. In the white salt samples, it is reported in all samples except in WS4. The highest amount of magnesium is reported in WS6.

3.4 Determination of heavy metals by AAS

The amount of Pb, As and Hg was measured in few selected samples. The data is provided in table 10. The measurement was made on the basis of the calibration curve provide in figures 3.2, 3.3 and 3.4. The standard sample of $PbCl_2$, $HgCl_2$, and As_2O_3 was used to make the calibration curve of Pb, Hg, and As, respectively.

Table 10: Amount of Hg, As and Pb in selected samples.

	Mercury (mg/kg)	**Arsenic(mg/kg)**	**Lead(mg/kg)**
WHO safe limit	0.1	0.5	2
WS9	1.03	2.49	0.72
WS10	0.14	0.45	0.89
BS5	0.08	0.17	0.05

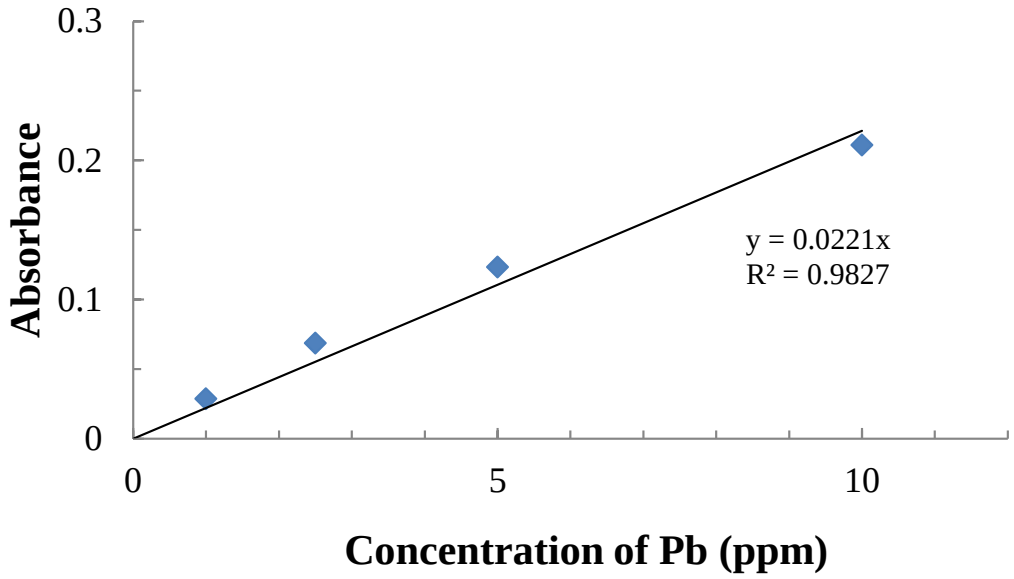

Figure 3.3. Calibration curve for the determination of Pb.

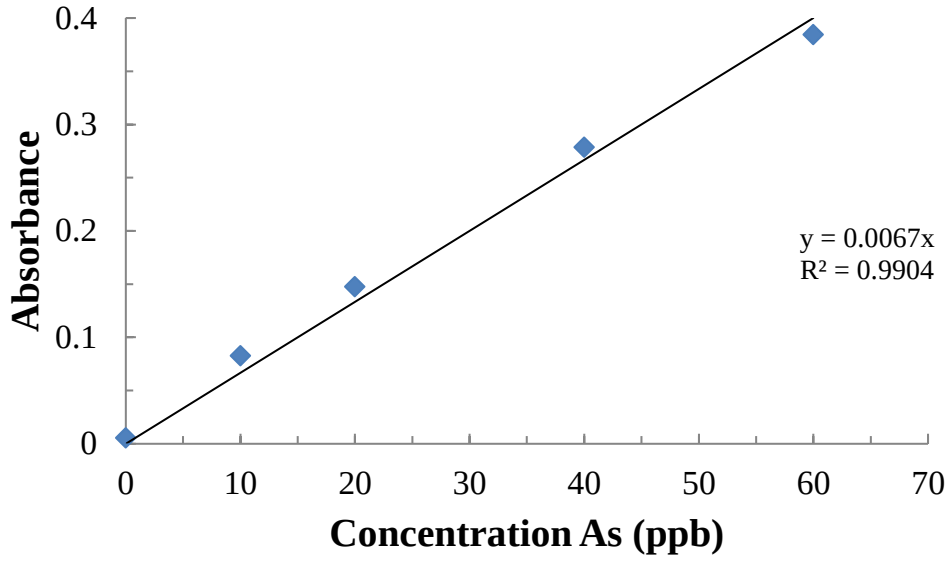

Figure 3.4. Calibration curve for the determination of As.

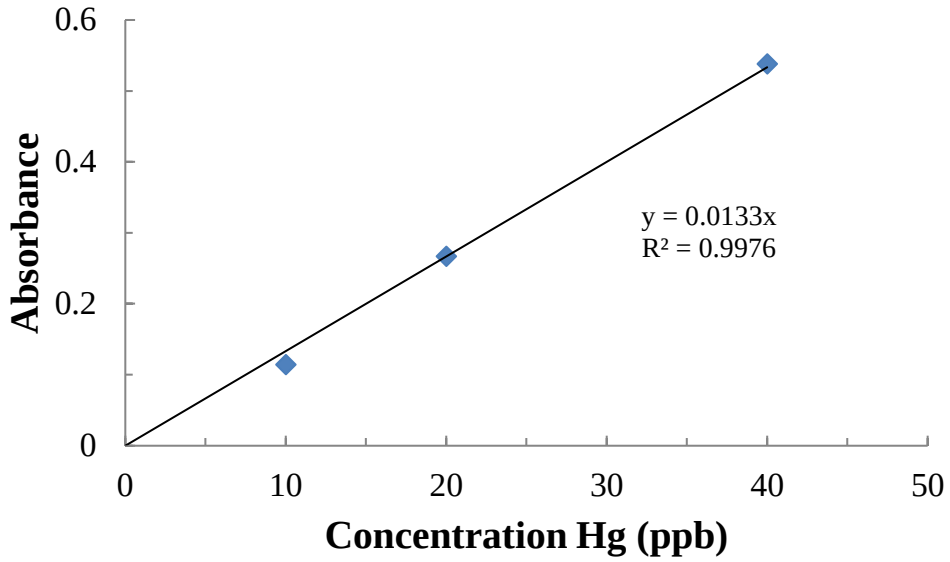

Figure 3.5. Calibration curve for the determination of Hg.

Data reported in table 10 show that white rock salt sample WS9 is reported to have amount of mercury and arsenic beyond the safe limit for consumption of salt according to WHO. Whereas, the amount of mercury and arsenic in rest of the tested salt sample i.e. WS10 and BS5 lies within the safe limit for consumption by human beings. The amount of lead also falls within the safe limit for consumption in all three selected salt samples.

The data reported in table 10 are very preliminary and it to be verified by other methods such ICS-OES and ICP-MS.

Chapter IV

Conclusions and Future Work

4.1 Conclusions

The amount of sodium in the black salt samples determined potentiometrically was found to be in the range of 30 to 37 mg/100mg of salt sample. In white salt sample, relatively lower amount of sodium in the range of 23-35 mg/100g was detected.

Iron was detected in all white and black sample studied. The amount of iron in the black and white salt samples was found to be in the range 12-24 and 7-14 ppm, respectively. This tells that black salt is better source of iron than white salt. The low level of magnesium was detected only in two black salt samples. On the other hand, in white salt samples magnesium was detected in nine samples in the range of 0.1-5 ppm.

Calcium was not detected in all the white and black salt samples.

The AAS measurement in few selected samples showed that Hg and As beyond the WHO safe limit.

This study showed that white and black salt better good source of sodium and iron than white salt. On the other hand, white salt is a source of magnesium. Comparatively there is no significant difference in amount of essential elements *i.e.* Na, Fe, Mg and Ca in black and white rock salts of different origin.

4.2 Future Work

The AAS measurement made in this work is preliminary and further confirmation is required by other methods such as ICP-OES and ICP-MS.

It is also important to make a complete elemental analysis in all the samples studied.

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