

**ISOLATION OF SODIUM HYDROGEN CARBONATE FROM LAKE SALT FOR
THE FORMULATION OF BAKING POWDER**

BY

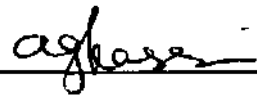
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B.SC. (HONS.) CHEMISTRY**

**A THESIS SUBMITTED TO POSTGRADUATE SCHOOL,
AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE
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ANALYTICAL CHEMISTRY DEPARTMENT OF CHEMISTRY
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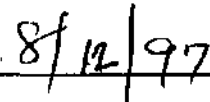
JULY, 1997.

DECLARATION

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.



(A. G. Kassim)



Date:

DEDICATION

To my wife Paulina
and my children Ibrahim and Nuhu

ACKNOWLEDGEMENT ,

Thanks be to God Almighty for His sustenance throughout the period of this work. It was a difficult period. Thank You God for Your faithfulness

I wish to express my sincere gratitude to my supervisor, Dr. E. J. Ekanem, for his kind suggestions and constructive criticisms. He was patient when I was down. Thank you Sir.

To Dr. G.F.S. Harrison I say thank you sir for your keen interest in the work. I also thank my colleagues for maintaining a friendly atmosphere, and all members of staff of the Chemistry Department, Ahmadu Bello University, Zaria.

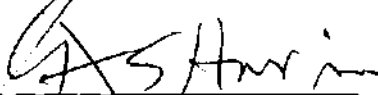
CERTIFICATION

This thesis entitled, ISOLATION OF SODIUM BICARBONATE FROM LAKE SALT FOR THE FORMULATION OF BAKING POWDER, meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University and is approved for its contribution to scientific knowledge and literary presentation.



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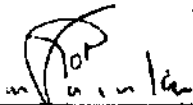
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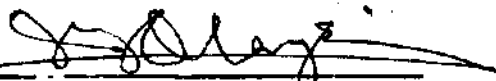
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ABSTRACT

Fractional crystallization of lake salt (kanwa) was carried out by concentrating and cooling its aqueous solution. The crystallized fractions showed higher carbonate-bicarbonate ratio than the raw samples. Controlled acid conversion of the carbonate present in the lake salt to the bicarbonate was carried out in solution and solid product obtained by crystallization. Products containing up to $08.44 \pm 1.05\%$ bicarbonate were obtained when hydrochloric acid was used and up to $74.95 \pm 1.39\%$ when ethanoic acid was used.

Baking powder was formulated using the isolated sodium bicarbonate. The baking powder when in contact with water behaved in a similar manner to a commercial baking powder. The formulated baking powder was also used in baking and the baked products were also found to be very similar to those obtained with the commercial baking powder.

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1.0 INTRODUCTION

Lake salt is a dried substance obtained on evaporation of certain lakes in arid regions (Bateman, 1951). The salt is recovered by scrapping it off the surface of the ground with a hoe or an axe (Ako, 1984). It is taken as medicine for all sorts of minor ailments in Northern Nigeria. It is also used for cooking and in drinking water for cattle (Buchannan and Pugh, 1971).

1.1 Names of the Lake Salt

In Northern Nigeria the salt is locally referred to as 'Kanwa' in Hausa. However, various other names are in common use. These include:

- (i) Potash: This indicates the presence of potassium even though some samples may contain little or no potassium (Buchannan, 1971)
- (ii) Natron: This indicates the presence of sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), even though the natural occurrence may be in the form of thermonitrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). (Palache *et al.*, 1951).
- (iii) Trona: This is the reduced form of the Arabic name for the native salt, natrum. It normally indicates the presence of the sesquicarbonate ($\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). (Palache *et al.*, 1951).

1.2 Varieties of the Lake Salt

Different varieties of the lake salt are known and are in use locally in Nigeria. The most common ones are:

- (i) Red 'Kanwa' ('Jar Kanwa'): This is used for cooking and for medicinal purposes. It is also added to drinking water for cattle (Buchannan and Pugh, 1971). Ekanem (1977) reported that the pinkish colour associated with this variety is due to the presence of Manganese.
- (ii) White 'Kanwa' ('Farar Kanwa'): This is mainly used in cooking as a tenderiser. Information available locally has it that it neutralises the substance that causes the formation of gas and the consequent swelling of the stomach after consumption of beans. Therefore it is popularly added to beans during cooking. Though in some cases the reverse may be true, it is also licked as a remedy for heartburn.
- (iii) Manda: Local information has it that this variety helps in stopping bleeding in women after delivery when taken in the form of porridge made from guinea corn or millet.
- (iv) Ungurnu: This variety consists mainly of sodium carbonate with some sodium chloride (Buchannan and Pugh, 1971). It is used for medicinal purposes.
- (v) Mangul: This consists mainly of sodium chloride and sodium sulphate (Buchannan and Pugh, 1971). It is also used for

medicinal purposes.

1.3 Composition of Lake Salt

The composition of a particular sample of lake salt depends upon the type of lake in which it was formed. The major cation present is that of Sodium (Na^+). Potassium (K^+) is also present. In addition some samples may also contain Calcium (as CaCO_3) and Magnesium ion (Mg^{2+}) (Bachannan and Pugh, 1971). Manganese has also been shown to be present in certain samples (Ekanem, 1977).

The major anion present includes those of carbonate (CO_3^{2-}), Bicarbonate (HCO_3^-) Sulphate (SO_4^{2-}) and Chloride (Cl^-) (Ekanem 1977; Ako 1984). 1% solutions of samples containing Cl^- and/or (SO_4^{2-}) have pH values in the range 6.60 - 7.50 while those of samples also containing (CO_3^{2-}), and (HCO_3^-) have values in the range 8.20 - 10.90 (Ako, 1984)

1.4 Formation of Lake Salt

Different samples of lake salt may have different compositions depending upon the type of lake in which it was formed. Generally, such lakes are found in regions of sparse rainfall and interior drainage where volcanic rocks or sedimentary rocks high in sulphate are undergoing weathering. Volcanic rocks yield much Sodium and potassium. Consequently, the lakes contain Sodium Carbonate, Sodium Sulphate and some Potassium Carbonate and small amounts of other salts (Bateman, 1951). Some Sodium Carbonate also results from slow and complex reactions with other Sodium and Calcium salts, and also

United States, Canada and other countries, (VanThoor, 1968). In Egypt the deposit is excavated and washed to remove sand and sodium chloride. The solid mass is then dried and fiercely heated in a rotary kiln. The trona is converted to sodium carbonate, which can be up to 97% pure.

In the United State of America the natural occurrence is not so pure (VanThoor, 1968). The natural solution is pumped from beneath the hard crust on the surface. The solution contains about 6% sodium carbonate, 2% borax and much sodium chloride, sodium sulphate, potassium chloride and so on. The solution is sent to all steel carbonating towers into which carbon dioxide is pumped. The carbonate is converted to sodium bicarbonate according to the following equation:



The sodium bicarbonate produced is of low solubility and therefore quickly crystallises out. It is allowed to settle out and filtered in rotary filters. The solid is dried and heated to 215°C. At this temperature the sodium bicarbonate is completely converted to the carbonate which is cooled and packed.



1.5.2 Extraction of Sodium Sulphate

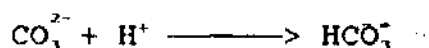
The method employed depends on the composition of the natural source. In Canada where the Canadian salt lake contains up to 50%

sodium sulphate, the solution is simply pumped into large ponds where some water evaporates. As the weather turns colder, the sodium sulphate crystallises out in the form of glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) (VanThoor, 1968). In Texas (U.S.A), the salt lakes contain 7 - 11% sodium sulphate, with some sodium chloride and magnesium sulphate. Sodium chloride is added to the solution until it is saturated with it, making the sodium sulphate far less soluble. Upon cooling to 10°C glauber's salt crystallises out (VanThoor, 1968).

In California the salt lakes are even more complex containing several other salts. Here the solution is treated with carbon dioxide. Sodium carbonate is converted to sodium bicarbonate which precipitates out and is filtered. The remaining solution is cooled in stages. Borax precipitates out first, and at a temperature of $5 - 6^\circ\text{C}$ glauber's salt precipitates out.

1.6 Aim of the Project

The aim of this work was to optimise a method for concentrating and extracting sodium bicarbonate from lake salt by acid conversion of the carbonate present to the bicarbonate and crystallising. The reaction can be represented as



The extracted sodium bicarbonate will be used in formulating baking powder and for other uses where the presence of other salts will not be a disadvantage. Presently, the established methods for

producing sodium bicarbonate all involve the use of carbon dioxide. In the Solvay Process, the general reaction can be represented as (Hicks, 1981).



The sodium bicarbonate precipitates out and is filtered. The ammonia is obtained from the Harber Process and the carbon dioxide from calcium carbonate (limestone). Sodium bicarbonate is also obtained from lake salt by bubbling carbon dioxide through a solution of it as already mentioned in section 1.5.1

All these methods require the use of complex equipment for the generation of the ammonia, carbon dioxide and for the construction of the tall carbonating towers. This is expensive for the level of our technology and for our weak economy.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Qualitative Analysis

Qualitative analysis is the process of determining what elements are present in a sample without regard to metrical quantities (Lambert and Muir, 1987). It must always precede quantitative analysis of an unknown material so that the metallic and acidic radicals in a sample are known.

Sometimes visual observation can give information about the possible composition of a sample; however, more reliable results are obtained by methods of analysis which include decomposition of a sample by heat, reaction with acids and alkalis, a flame test and reactions of solutions of the sample with reagents to give either precipitates or colourations by which elements or groups of elements may readily be recognised (Lambert and Muir, 1987).

2.2 Detection of anions

A sample of the solid material is treated with dilute hydrochloric acid and then, if no result is obtained, a fresh sample is carefully treated with concentrated sulphuric acid (Lambert and Muir, 1987). Different gases are evolved which if carefully identified can indicate the anions present in the sample.

2.3 Test for carbonate and bicarbonate

The success of any carbonate and bicarbonate test depending on the evolution and detection of carbon dioxide is based on the expulsion of the gas dissolved in the reacting liquid. This can be realised by raising the temperature of the reaction to above 60°C (Holness, 1961). A small amount of hydrochloric or sulphuric acid is taken in a test-tube and heated to the required temperature. A little quantity of the test material is dropped into the hot acid. Since carbon dioxide is denser than air much of it from the reaction remains in the atmosphere immediately above the liquid in the test-tube. Its presence there can then be confirmed by sucking the air in the atmosphere just above the solution using a teat pipette. The pipette is then removed and its tip inserted under the surface of a little quantity of lime water held in another test-tube. The gas is then slowly bubbled through the lime water by gently squeezing the teat of the pipette. Milkiness denotes the presence of carbon dioxide and hence carbonate or bicarbonate in the test material.

2.4 Test for bicarbonate in the presence of carbonate

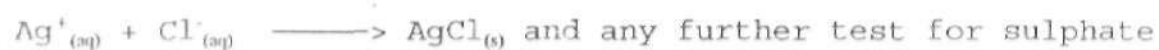
Excess of calcium chloride is added to the solution of material and the mixture is centrifuged. Any carbonate is precipitated as calcium carbonate (Morrison, 1961). The supernatant is removed and may contain soluble bicarbonate. The supernatant is made alkaline with ammonia. Any bicarbonate will now give a further precipitate of calcium carbonate (Morrison, 1961).

2.5 Test for anions in solution

The presence of heavy metals interferes with the test for acid radicals in solution and therefore it is necessary to remove any heavy metals from the original material (Holness, 1961). For example, the test for a sulphate radical in solution is to add dilute hydrochloric acid and barium chloride solution, when a white precipitate of barium sulphate indicates the presence of a sulphate



However if the solution already contains the silver ion (which is a heavy metal), then, on the addition of hydrochloric acid, there would be observed a white precipitate of silver chloride.



would be worthless. Possibilities such as this make it necessary to remove heavy metal radicals before testing for acidic radicals (Lambert and Muir, 1987).

This is done by boiling the solution of the original material with excess anhydrous sodium carbonate. This treatment brings about a substantial amount of double decomposition forming the insoluble carbonates of the heavy metals and the soluble sodium salts of the acid radicals present (Holness, 1961).



After removing the insoluble carbonate the excess sodium carbonate is destroyed with the acid appropriate for each acid radical test. Reagents are then prepared and the classical procedure for the qualitative analysis based on the action of group reagents is then employed in the detection of the anions (Morrison, 1961).

2.6 Test for sulphate radical

A solution of the material freed from heavy metals is used for the test. Excess dilute hydrochloric acid is added and then barium chloride solution. A white precipitate of barium sulphate proves sulphate radical present (Holness, 1961).

2.7 Test for chloride radical

Excess dilute nitric acid is added to the solution of the material followed by silver nitrate solution. A white precipitate of silver chloride, readily soluble in ammonia solution, proves the presence of chloride radical (Lambert and Muir, 1987).

2.8 Crystallisation

Crystallisation is the formation of crystalline substances from solutions or melts (Randolph, 1977). The method is used to recover solutes from solutions

2.8.1 Fractional crystallisation

Fractional crystallisation is the crystallisation of a portion

of one dissolved substance from a solution containing several dissolved substances (Randolph, 1977). All of the dissolved substances in solution can be recovered by complete evaporation of the solvent. However, if a single substance is desired in a pure state complete evaporation cannot be used.

By carefully regulating the conditions of temperature and concentration, it is possible to bring about the crystallisation of individual solutes in fairly pure crystals (Randolph, 1977). This is accomplished more easily when the desired substance is the most abundant material in solution. In fractional crystallisation the crystals formed at a specified temperature from a solution are of fairly well-defined composition, and can be separated into fractions that are of different composition from the crystals formed at other temperatures. Since the first - and last - formed crystals of a particular fraction are the least pure, it is seldom possible to obtain all of any particular solute from a solution containing several solutes. If the originally formed crystals of a particular fraction are not of the desired purity, they can be redissolved in a small amount of the same or a different solvent and recrystallised. By repeated steps of fractional crystallisation and recrystallisation, it is possible to obtain crystalline substances of very high purity.

2.8.2 Methods of fractional crystallisation

The starting materials is dissolved in the smallest possible amount of solvent, usually at elevated temperature, and the solution is filtered to remove foreign matter (Randolph, 1977). Next the

solution is heated to evaporate some of the solvent. The solution is then cooled or further heated to induce the formation of crystals. After crystallisation has proceeded to the desired extent, the crop of crystals is filtered from the mother liquor and washed with fresh solvent to remove adhering mother liquor, which contains impurities. The crystals are then dried.

2.9 Properties of sodium bicarbonate

Sodium bicarbonate is the sodium acid salt of the weak carbonic acid, H_2CO_3 . However, the salt cannot be prepared directly from the acid which is unstable. It can be prepared in the laboratory by passing carbon dioxide through a cold saturated solution of sodium carbonate (Hicks, 1973). It is less soluble than the normal salt and therefore precipitates out and can be filtered.

A solution of sodium bicarbonate is alkaline due to hydrolysis (Hicks, 1973)



Sodium bicarbonate is alkaline to methyl orange but acidic to phenolphthalein (Hicks, 1973). This makes it possible to analyse a mixture of sodium bicarbonate and sodium carbonate. The latter is alkaline to phenolphthalein.

When heated to 215°C sodium bicarbonate loses carbon dioxide (VanThoor, 1968).



When a solution of sodium bicarbonate is boiled decomposition takes place, but the reaction does not proceed to completion in a limited time; in thirty minutes the reaction is as follows (Cox, 1950).

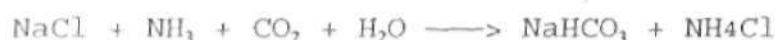


Sodium bicarbonate reacts with acids to produce carbon dioxide, for example



Naturally, sodium bicarbonate exists in the form of the sesquicarbonate, trona, $\text{NaHCO}_3.\text{Na}_2\text{CO}_3.2\text{H}_2\text{O}$.

Industrially it is prepared by the solvay process using sodium chloride, ammonia and carbon dioxide as raw materials. The reaction can be represented as (Hicks, 1981).



2.10 Uses of sodium bicarbonate

Sodium bicarbonate is used in fire extinguishers. It is reacted with acid in the presence of a foaming agent which is spread onto the fire. It is also used in the preservation of butter and for the preparation of some health salts. Mixed with acid ingredients, sodium bicarbonate is widely used as leavening agent in baking powders.

2.11 Determination of a mixture of carbonate and bicarbonate

If sodium carbonate is dissolved in water some of the carbonate ions combine with protons to form bicarbonate ions (Jeffery, 1966).



If an acid is added to the solution, this action will continue until all of the carbonate ions have changed to bicarbonate ions. An indicator such as phenolphthalein can be used to signal this point as it turns colourless in bicarbonate solution.

If methyl orange is then added and the reaction continued, a point is reached when a volume equal to that used previously has been added. (Lambert and Muir, 1947). The total titration for sodium carbonate can, therefore, be arrived at in two ways.

- (i) By using phenolphthalein as indicator and doubling the volume of acid used at the end point.
- (ii) By using phenolphthalein as indicator and noting the volume used at the end point, then methyl orange is added and the extra volume of acid needed to complete the reaction is determined. The two volumes of acid are added together.

When an acid is run into a solution containing sodium carbonate and sodium bicarbonate, using phenolphthalein as indicator, only the carbonate is affected, which is all converted into the bicarbonate at the phenolphthalein end point (Lambert and Muir, 1947). When methyl orange is then added and the titration completed to the end

point of the indicator, the acid used at this stage is a total of two volumes, that is, the second half titration of the carbonate and the acid used by the original bicarbonate.'

In the method employed, a solution of the carbonate and bicarbonate mixture is slowly titrated with standard hydrochloric acid (Vogel, 1975) using phenolphthalein indicator. Let the volume of acid required for this titration be $V_1\text{cm}^3$, which corresponds to half the reaction of the sodium carbonate present in the mixture,

$$\text{CO}_3^{2-} + \text{H}^+ \longrightarrow \text{HCO}_3^-$$

Another sample of equal volume is then titrated with the same standard acid using methyl orange indicator. Let the volume of acid used be $V_2\text{cm}^3$, which corresponds to sodium carbonate plus the sodium bicarbonate. Hence $2V_1$ is the volume of acid required for the complete reaction of sodium carbonate, and $(V_2 - 2V_1)\text{cm}^3$ is the volume of acid required for the complete reaction of the sodium bicarbonate.

2.12 Composition of baking powder

When sodium bicarbonate is heated it breaks down according to the following equation



If it is used alone as a leavening agent, a residue of sodium carbonate in a flour mixture gives a disagreeable flavour. Therefore, a suitable quantity of an acid ingredient is added so

that a more neutral residue is formed (Peckham and Freeland-Graves, 1979). The U.S. Department of Agriculture defines (Peckham and Freeland-Graves, 1979) baking powder as the leavening agent produced by mixing of an acid-reacting material and sodium bicarbonate with or without the addition of starch or flour. The permissible acid ingredients are tartaric acid or its acid salts, monocalcium phosphate and alum. A combination of these acids can also be used.

The rate at which a baking powder gives off carbon dioxide depends on the solubility of its acid-reacting component in water. When the acid component is soluble at room temperature, the baking powder reacts at room temperature. When the acid ingredient is insoluble in cold water, the baking powder will not react completely until elevated temperatures are reached.

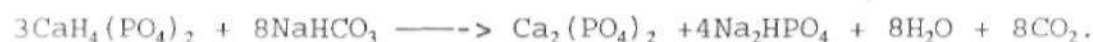
Fast-acting baking powders give off their gas volume during the first few minutes of contact with liquid. When such powders are used in flour mixture, the mixture must be handled quickly to avoid loss of carbon dioxide and volume (Peckham and Freeland-Graves, 1979). Fast-acting baking powders contain tartaric acid and/or its acid salt. The reaction takes place at room temperature in the presence of water as follows



Or



Baking powders containing monocalcium phosphate are also considered as fast-acting though at slightly elevated temperatures.



A slow-acting baking powder gives off its carbon dioxide only at higher temperatures (Peckham and Freeland-Graves, 1979). A slow-acting baking powder contains monocalcium phosphate and alum as the acid ingredient.

The alum reacts with water to produce sulphuric acid as shown



The sulphuric acid reacts with the sodium bicarbonate to produce carbon dioxide. (Peckham and Freeland-Graves, 1979)



The sodium sulphate component gives a bitter-after taste if excess amount of the powder is used.

Baking powder also contains an inert filler which is usually Corn starch. The filler acts as a buffer to standardise the reaction between the acid ingredient and the sodium bicarbonate.

2.13 Analysis of baking powder

2.13.1 Qualitative analysis

A small amount of the baking powder is shaken with carbon tetrachloride in a separatory funnel (Egan, et al., 1981). The starch component floats at the top while the baking chemicals settle. The baking chemicals can be separated and examined qualitatively for the presence of phosphate, calcium, aluminium and other species.

2.13.2 Quantitative examination

Determination of calcium

The titrimetric procedure of Egan, *et al.*, (1981) is popularly used. In this procedure the baking powder is dissolved in hot dilute nitric acid and boiled for thirty minutes. The solution is then filtered, cooled and made just alkaline with ammonia solution. The calcium is then precipitated as the oxalate. The precipitate is filtered and dissolved in dilute acid and the oxalate titrated hot with standard potassium permanganate solution.

Atomic absorption spectrophotometric (AAS) method

The sample is digested with nitric acid and the solution filtered and made up to a known volume (Egan *et al.*, 1981). In the current work the solution was used for the determination of calcium using the AAS method.

Estimation of starch

The baking powder is dissolved in a minimum quantity of cold dilute hydrochloric acid (Egan, *et al.*, 1981). The starchy matter is filtered, dried and weighed. The starch can also be determined polarimetrically or by the diastase method (Egan, *et al.*, 1981).

Determination of aluminium

A number of methods have been described. In the gravimetric method the aluminium is precipitated as the hydroxide using ammonia solution in the presence of ammonium chloride. The gelatinous

precipitate is filtered, washed and converted to the oxide (by ignition) and weighed as Al_2O_3 . (Tikhonov, 1975).

Complexometric method of titration is also widely employed in the determination of aluminium. Aluminium reacts with complexone III in the presence of PAN, 1-(2-Pyridylazo)-2-naphthol.

In the colorimetric method, the aluminum is made to react with coloured reagents. Aluminon is the most frequently employed reagent which forms a complex with aluminium. The complex absorbs at 535nm (Tikhonov, 1973).

CHAPTER THREE

EXPERIMENTAL

3.1 Reagents

All the reagents for qualitative analysis were of the general purpose grade (BDH) unless otherwise stated. Solutions of the reagents were prepared using distilled water and used as described below.

3.2 Choice of samples of lake salt for analysis

The samples of the lake salt chosen were those which looked relatively 'clean' to the eye with minimum amount of earthy impurities. Samples which have high carbonate/bicarbonate content were preferred.

3.3 Sample treatment and storage

The samples obtained were in the form of large lumps of different shapes and sizes. The lumps were ground into powder with a mortar and pestle, thoroughly mixed and stored in a glass bottle.

3.4 Qualitative analysis

3.4.1 Preparation of the sodium carbonate extract of lake salt

1.0g of the lake salt was dissolved in distilled water and the solution filtered. The filtrate was made up to 100cm³ in a volumetric flask. 20cm³ of the solution was taken in a small beaker

and excess anhydrous sodium carbonate added. The mixture was boiled and filtered. The filtrate, referred to as sodium carbonate extract, was kept for qualitative test for chloride and sulphate. (Lambert and Muir, 1987).

3.4.2 Test for chloride

About 2cm³ of the sodium carbonate extract was taken in a test-tube and excess dilute nitric acid (2M) added followed by 3 drops of dilute silver nitrate solution (0.05M). A white precipitate which dissolved in ammonia solution indicated the presence of chloride in the sample (Lambert and Muir, 1987).

3.4.3 Test for sulphate

About 2cm³ of the sodium carbonate extract was taken in a test-tube and excess dilute hydrochloric acid added. This was followed by barium chloride solution (0.5M). A white precipitate indicated the presence of sulphate in the sample. (Lambert and Muir, 1987).

3.4.4 Test for carbonate/bicarbonate

This test was carried out on the solid sample of the lake salt. About 2cm³ of dilute sulphuric acid was taken in a test-tube and warmed. A spatula load of the lake salt was added. The air in the atmosphere just above the solution was carefully withdrawn with a teat pipette. It was then gently bubbled through a little quantity of lime water (saturated Ca(OH)₂ solution) in another test-tube. The appearance of a milky colour indicated the presence of carbon

dioxide and hence carbonate and/or bicarbonate in the lake salt (Holness, 1961).

3.4.5 Test for bicarbonate in the presence of carbonate

The test was carried out on the solution of the lake salt and not on the sodium carbonate extract. Excess calcium chloride solution (5%) was added to the sample solution, a white precipitate was immediately formed which indicated the presence of carbonate. The mixture was centrifuged and the supernatant liquid removed into another test-tube. Dilute ammonia solution (2M) was added to the liquid and this gave a further white precipitate indicating the presence of bicarbonate in the original sample (Morrison, 1961).

3.5 Quantitative analysis of the lake salt

3.5.1 Reagents

All the reagent used were of analytical grade except otherwise indicated.

3.5.2 Fractional crystallisation of the lake salt

100.0g of the sample of lake salt was dissolve in a minimum amount of distilled water and filtered. The filtrate was further concentrated by evaporation over a steambath and then allowed to cool. Crystallisation was allowed to continue overnight. The first crop of crystals were then filtered, washed with ethanol and then dried in air. The product obtained was labelled R₁. The filtrate

was again concentrated by evaporation and crystallised to obtain the second crop of crystals which were labelled R_2 . The procedure was repeated to obtain R_3 , R_4 and R_5 as the third, fourth and fifth crops of crystals respectively. Qualitative analysis was carried out on the various fractions; and the results obtained are shown in Table 4.1.

3.5.3 Estimation of carbonate-bicarbonate content of the various fractions

0.50g of each of the fraction R_1 , R_2 , R_3 , R_4 and R_5 was dissolved separately in water to make 40cm³ of solution. Each of the solutions was titrated with 0.20M HCl using methyl orange indicator. The volume of acid required in each case gave an indication of the level of carbonate-bicarbonate in the fraction. The results obtained are shown in Table 4.1

3.5.4 Recrystallisation of the fractions

R_1 was recrystallised separately using a minimum amount of water. Crystals were obtained and labelled RR_1 . R_2 and R_3 were combined together and recrystallised to obtain RR_2 . R_4 and R_5 were also combined together and recrystallised to obtain RR_3 . Qualitative anion analysis was carried out on the recrystallised fractions. The results are shown in Table 4.2

3.5.5 Estimation of the carbonate-bicarbonate content of the recrystallised fractions

0.20g of each of the recrystallised fractions RR_1 , RR_2 and RR_3

was dissolved separately in water to make 25cm^3 of solution. Each of the solutions was titrated with 0.20M HCl using methyl orange indicator. The volume of the acid required in each case gave an indication of the carbonate-bicarbonate levels in the fractions. The results obtained are shown in Table 4.2

3.5.6 Effect of carbondioxide on crystallisation of lake salt

30.0g of the lake salt was dissolved in distilled water and the solution filtered. The filtrate was divided into two equal portions and concentrated by evaporation over a steambath. The two solutions were allowed to crystallise. Carbon dioxide was continuously bubbled through one of the solutions as crystallisation progressed. The other solution was processed as a control. Crystals obtained from each were analysed for their carbonate and bicarbonate content in a double end point titration. The analysis was carried out in triplicate and average results are shown in Table 4.3.

3.5.7 Bicarbonate: carbonate ratio determination in lake salt and fractions

1.0g of the lake salt was dissolved in distilled water and filtered. The filter paper with any residue was washed thoroughly with water. The filtrate was made up to 100cm^3 in a volumetric flask. 20cm^3 portions of the solution were titrated with 0.20M HCL using phenolphthalein and methyl orange indicators in a double end point titration. The percentages of bicarbonate and carbonate were determined in the lake salt. The analysis was done in triplicate and average results are included in Table 4.4

30.0g of the lake salt was then dissolved in water and the solution filtered. The solution was concentrated by evaporation on a waterbath and allowed to crystallise. The crystals were filtered out and washed with ethanol and allowed to dry.

0.30g of the fraction was dissolved in distilled water. The solution was titrated with 0.20M HCl using phenolphthalein and methyl orange indicators successively in a double end point titration. The percentage of bicarbonate and carbonate in the fraction was calculated. The analysis was done in triplicate and average results are included in Table 4.4.

3.5.8 Acid conversation of the carbonate present in the
crystallised fraction to bicarbonate
Conversion using hydrochloric acid

5.00g of the crystallised fraction was used. This corresponded to 0.0212 moles of the sodium carbonate. 2.10cm³ of the 10.10M HCl was reacted with the 5.00g of the fraction. The volume of the acid used corresponded to 0.0212 moles of the acid. This is the amount of the acid needed to convert the carbonate present in the fraction to bicarbonate, according to the following equation.



The 5.00g of the fraction was dissolved in water to form a saturated solution. The acid was then added carefully with stirring. The mixture was heated over a waterbath to form a clear solution. The solution was heated further to concentrate it and

then allowed to cool. Crystals were formed which were filtered out, washed with ethanol and dried in air before weighing and analysis. The analysis was done in triplicate and average results are shown in Table 4.5.

Conversion using ethanoic acid

5.00g of the fraction was used for the conversion. 1.30cm³ of the 16.67M CH₃COOH was used. This volume contained the equivalent amount of the acid (0.0212 moles) required to convert the sodium carbonate present in the 5.00g of the fraction to bicarbonate, according to the following equation.



The procedure followed was the same as the case of the hydrochloric acid in the previous section. The results obtained are also shown in Table 4.6.

3.5.9 Analysis of the enriched products for bicarbonate and carbonate ratio

In each case the bicarbonate and carbonate ratio of the products was determined by titrating 0.20g of each product against 0.20M HCl using phenolphthalein and methyl orange successively as indicators. The results are shown in Table 4.5

3.6 Analysis of a commercial baking powder

A commercial baking powder was first analysed with the aim of

estimating the relative amounts of the acid ingredient and starch used. This was in order to know how much of these components were to be added per unit mass of the isolated sodium bicarbonate.

The commercial baking powder was obtained from the market. The label on the container stated the acid ingredients as sodium aluminium sulphate and acid calcium phosphate. The sample was stored in the container in which it was purchased.

3.6.1 Estimation of starch

5.00g of the commercial baking powder was dissolved in a small amount of cold dilute hydrochloric acid(2M). The starch matter which remained insoluble was filtered off and washed with water. It was dried in air and finally at 50°C in an oven to constant mass. The analysis was done in triplicate and average results are shown in Table 4.6.

3.6.2 Gravimetric determination of aluminium

In order to determine the amount of sodium aluminium sulphate in the baking powder, the amount of aluminium was determined by the gravimetric method (Tikhonov, 1973; Vogel, 1975). The results were then converted to the amount of sodium aluminium sulphate, $\text{NaAl}(\text{SO}_4)_2$, present in the commercial baking powder.

5.00g of the commercial baking powder was dissolved in dilute hydrochloric acid and boiled to hydrolyse the starch. The solution was then filtered and made up to about 200cm³ with distilled water

in a 600cm³ beaker. 5.0g of pure solid ammonium chloride was added followed by five drops of methyl red indicator solution (2%). The mixture was then boiled. A 1:1 solution of ammonia was added dropwise with constant stirring until the colour of the solution changed to a distinct yellow signalling the completion of the precipitation. The mixture was boiled for two minutes. The precipitate was then filtered out through quantitative filter paper. The precipitate was washed with a 2% solution of ammonium chloride. The precipitate was dissolved in dilute hydrochloric acid and the aluminium reprecipitated following the same procedure.

The precipitate was then ignited to constant weight using a Fisher burner. The aluminium was finally weighed as Al₂O₃. The results and the corresponding amounts of sodium aluminium sulphate (alum) present in the commercial baking powder are included in Table 4.6

3.6.3 Determination of calcium by atomic absorption spectrophotometric method

1.00g of the commercial baking powder was carefully added to 5cm³ of 2M nitric acid in a conical flask. After the reaction subsided, additional 5cm³ of the acid was added. The mixture was then heated carefully. Distilled water was added at intervals to prevent drying up of the mixture. The heating continued until no more brown fumes were produced. The solution was then filtered and the filtrate made up to 100cm³. The level of calcium was determined by atomic absorption spectrophotometry (AAS). The results were related to the amount of monocalcium phosphate present in the baking

powder. The analysis was done in triplicate and average results are included in Table 4.6

3.7 Sourcing and preparation of alum used in the formulation of baking powder

The alum used in the formulation of the baking powder was obtained from the market. It was purified by recrystallisation and dried. It was then thoroughly ground with mortar and pestle and further dried in an oven.

3.8 Formulation of baking powder using the sodium bicarbonate derived from lake salt

From Table 4.6 the percentage of sodium bicarbonate obtained when acetic acid was used is approximately 75%. The composition of the commercial baking powder was adopted and simulated in the formulated one. The following ratios were used.

Sodium bicarbonate obtained from the

Lake salt = 30.00%

Alum = 37.60%

Starch = 32.40%

The constituents were ground together and thoroughly mixed.

3.9 Evaluation and properties of the formulated baking powder

A little of the formulated baking powder was put in a beaker and small amount of water added. There was gentle frothing as a gas

was evolved. The experiment was performed with a commercial baking powder and a very similar gentle frothing was observed.

The formulated and commercial baking powders were used in baking and the products compared by observing various parameters. The volume gain for the product obtained by using the formulated baking powder was about 35% while that using the commercial powder was about 36%. Both products had very similar brownish appearance and they all tasted similarly. The products also retained their shapes and sizes after storage for three days.

This indicated that the product obtained with the formulated baking powder is very similar to that obtained with the commercial baking powder.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Results

The results of the different experiments are shown in Table 4.1
- 4.6.

Table 4.1: Results of fractional crystallisation of lake salt

Fraction	Amount(g)	% of total	Anions indicated	cm ³ HCl consumed
R ₁	38.42	38.42	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻	29.50
R ₂	25.20	25.20	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻	16.60
R ₃	10.45	10.45	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻	20.90
R ₄	8.80	8.80	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻	29.20
R ₅	6.28	6.28	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻	15.90

Table 4.2: Results of the recrystallisation of fractions

Fraction	Percentage Recovered	Anions Indicate	cm ³ of HCl Consumed
RR ₁	27.05	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻	13.20
RR ₂	19.34	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻	12.10
RR ₃	32.49	CO ₃ ²⁻ /HCO ₃ ⁻ , SO ₄ ²⁻	10.90

Table 4.3: Effect of carbondioxide on crystallisation of lake salt

	With CO ₂	Without CO ₂
% CO ₃ ²⁻	20.31 ± 5.50	44.45 ± 0.91
% HCO ₃	68.53 ± 8.44	31.46 ± 3.25

Table 4.4 Percentage of carbonate and bicarbonate in lake salt and first crystallised fraction from lake salt.

	Lake salt	First crystallise fraction
% CO_3^{2-}	38.80 $\pm$ 1.61	44.77 $\pm$ 0.37
% HCO_3^-	24.47 $\pm$ 2.32	35.10 $\pm$ 0.44

Table 4.5: Results of analysis of product obtained after acid conversion of carbonate to bicarbonate

	With HCl	With CH ₃ COOH
Average % yield	34.47 ± 3.95	41.93 ± 2.76
% CO ₃ ²⁻	6.85 ± 3.03	14.85 ± 1.56
% HCO ₃ ⁻	88.44 ± 1.05	74.94 ± 1.39

4.2 Discussion

4.2.1 Fractional crystallisation of lake salt

From Table 4.1 it could be seen that the carbonate bicarbonate content of the lake salt does not come out in a single fraction. Carbonate-bicarbonate and sulphate were detectable in all the fractions. Chloride appeared in the later fractions. The first crystallised fraction (R_1) showed a higher carbonate-bicarbonate content followed by one or two fractions with relatively lower contents, judging by the volume of hydrochloric acid consumed. The carbonate-bicarbonate content then rises after which it again decreases. Bateman (1951) reported the work of Chatard based on which fractional crystallisation attendant upon evaporation yielded trona, sodium sulphate, sodium chloride and normal sodium carbonate in that order. From Table 4.2 it can be seen that a steady decrease in the amount of carbonate-bicarbonate is obtained on recrystallisation of the fractions as against the unsteady change seen in the crystallised fractions of Table 4.1

4.2.2 Bicarbonate and carbonate content of the fractions

In Table 4.4 the average percentage of carbonate was found to be $38.80 \pm 1.61\%$ and the percentage bicarbonate was $24.47 \pm 2.32\%$ in the lake salt. The percentage carbonate in the first crystallised fraction from the lake salt was found to be 44.77 ± 0.37 and the percentage bicarbonate was 35.10 ± 0.44 . It can therefore be seen that crystallisation of the lake salt brings out more of the carbonate and bicarbonate content in the fractions obtained. This was probably due to rejection of other components in

the filtrate. When these results are compared with those obtained in Table 4.3 it can be seen that bubbling carbon dioxide gas through the solution greatly enhanced the crystallisation of bicarbonate as against carbonate. This may be due to the reaction



Though the use of carbon dioxide concentrates the bicarbonate over the carbonate, the method may be more expensive than the acid conversion process because of the need for a second raw material (limestone) for the generation of the carbon dioxide.

4.2.3: Acid conversion of carbonate to bicarbonate

The percentage of carbonate in the first crystallised fraction was found to be $44.77 \pm 0.37\%$ (Table 4.4). This was approximate to 45% when calculating the amount of acid required to convert the carbonate present in the fraction to the bicarbonate. Concentrated acid was used in order to minimise the volume of solution applied for crystallisation.

When hydrochloric acid was used, the average percentage yield of the solid product obtained was 34.47 ± 3.95 (Table 4.5) and the percentage bicarbonate in the product was 88.44 ± 1.05 . This shows that the reaction of the carbonate present in the lake salt with acid can be carefully controlled to allow the concentration and subsequent isolation of a solid product very rich in bicarbonate.

The concentration of the bicarbonate was also attempted using

acetic acid. The average percentage yield of the solid product obtained was $41.93 \pm 2.76\%$ and the bicarbonate content of the product was $74.94 \pm 1.39\%$

Comparing the results, hydrochloric acid gave products richer in bicarbonate than acetic acid. This may be due to the fact that the hydrochloric acid is a stronger acid and therefore the reaction is more complete in a limited time. Acetic acid is a weak acid and sodium carbonate is a weak base, the reaction between them is much less complete in a limited time. However, the yield of the solid product obtained seemed to be generally higher when acetic acid was used.

4.3 Analysis of the commercial baking powder

From Table 4.6 the average starch content of the commercial baking powder was found to be $32.40 \pm 0.20\%$. The proportion of sodium aluminium sulphate (alum) in the baking powder was found as $37.60 \pm 1.80\%$.

From Table 4.6, the percentage of monocalcium phosphate as determined from the amount of calcium found was $0.0183 \pm 0.018\%$.

Though the commercial baking powder analysed mentioned monocalcium phosphate as one of the acid ingredients used, this analysis showed that even if it was present, the amount was very negligible. The actual composition of the baking powder may therefore be;

Starch = 32.40%

Alum = 37.60%

The remaining 30.00% may be taken to be the sodium bicarbonate. This agrees well with the composition of a brand of baking powder reported in the literature (Bennett, 1943), as

Sodium bicarbonate = 31.1%

Monocalcium phosphate = 38.9%

Starch = 30.0%

4.4 Formulation of baking powder from sodium bicarbonate obtained from the lake salt

It can be suggested that for the purpose of making baking powder, acetic acid be used for the concentration of the sodium bicarbonate in the lake salt. This is because the sodium acetate that may be in the product has bactericidal and fungicidal properties and may therefore preserve the baked product (Hanneman, 1980; Ihekoronye, 1985).

4.5 Suggestions

Samples of the lake salt which are relatively clean and of relatively high bicarbonate-carbonate content should be used for the extraction of the bicarbonate. This may improve the yield of the product obtained.

Though the suggested formulation uses sodium aluminium sulphate (alum) as the acid ingredient, minimum amounts should be used

because excess of sulphate leaves a bitter aftertaste in the baked product (Peckham, 1979; Terrell, 1979). This implies that samples of the lake salt low in sulphate should also be used. If the lake salt contains much sulphate, monocalcium phosphate should be used as the acid ingredient in the formulation so as to minimise the amount of sulphate in the product.

4.6 Conclusion

The carbonate-bicarbonate content of lake salt can be enhanced by crystallisation of the salt. Controlled reaction with acid can increase the bicarbonate and a solid product which is essentially bicarbonate can be extracted. This product could be used for making baking powders.

Since the proposed acid conversion process requires simple equipment and since the lake salt used as raw material is available locally, this method would be cheaper.

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