

**ANALYSIS OF 'KANWA' SAMPLES  
FOR SOME ANIONS.**

**by**

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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.

  
Palmer A.E. Ako

Date: 15/3/84.....

DEDICATION

To my wife Ruth and my  
Children, Efeturi, Ochuko,  
Ufuoma and Aghogho.

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## ABSTRACT

Thirty eight samples of 'kanwa' were analysed for anions, Carbonate, hydrogen carbonate, chloride and sulphate were detected in most samples and phosphate in only one sample. Quantitative anion analysis was carried out on fourteen water-soluble samples. Separation of carbonate, chloride and sulphate on a column packed with Amberlite resin IRA-401 in the phenate form has also been attempted.

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## CHAPTER 1

### I N T R O D U C T I O N

#### 1.1 Occurrence and formation of 'Kanwa'.

Kanwa is the Hausa name for the lake-salt erroneously referred to as potash. All the samples of the salt for the present study originated from the Chad Basin (Appendix I). For this reason, the geography of this region, with particular reference to the topography, drainage and climate will be described briefly in this introductory chapter. A short account of the mode of formation of saline deposits will also be given. The chapter will also include a description of the sources of the samples within Nigeria.

The Chad Basin (Plate I) has been described as the largest area of inland drainage in Africa, occupying about 230,000 km<sup>2</sup> in the Central Sahara and Central Sudan (1). It lies approximately within Latitude 6°N and 26°N and Longitude 7°E and 25°E. According to Baber (2) the Chad formation includes Kano, Borno and Bauchi States in northern Nigeria with a greater extent in Chad, Cameroun and Niger Republics. He describes the area as a plain which



GEOLOGY OF THE CHAD BASIN

Modified from part of Equatorial Africa by R. Fyson 1958



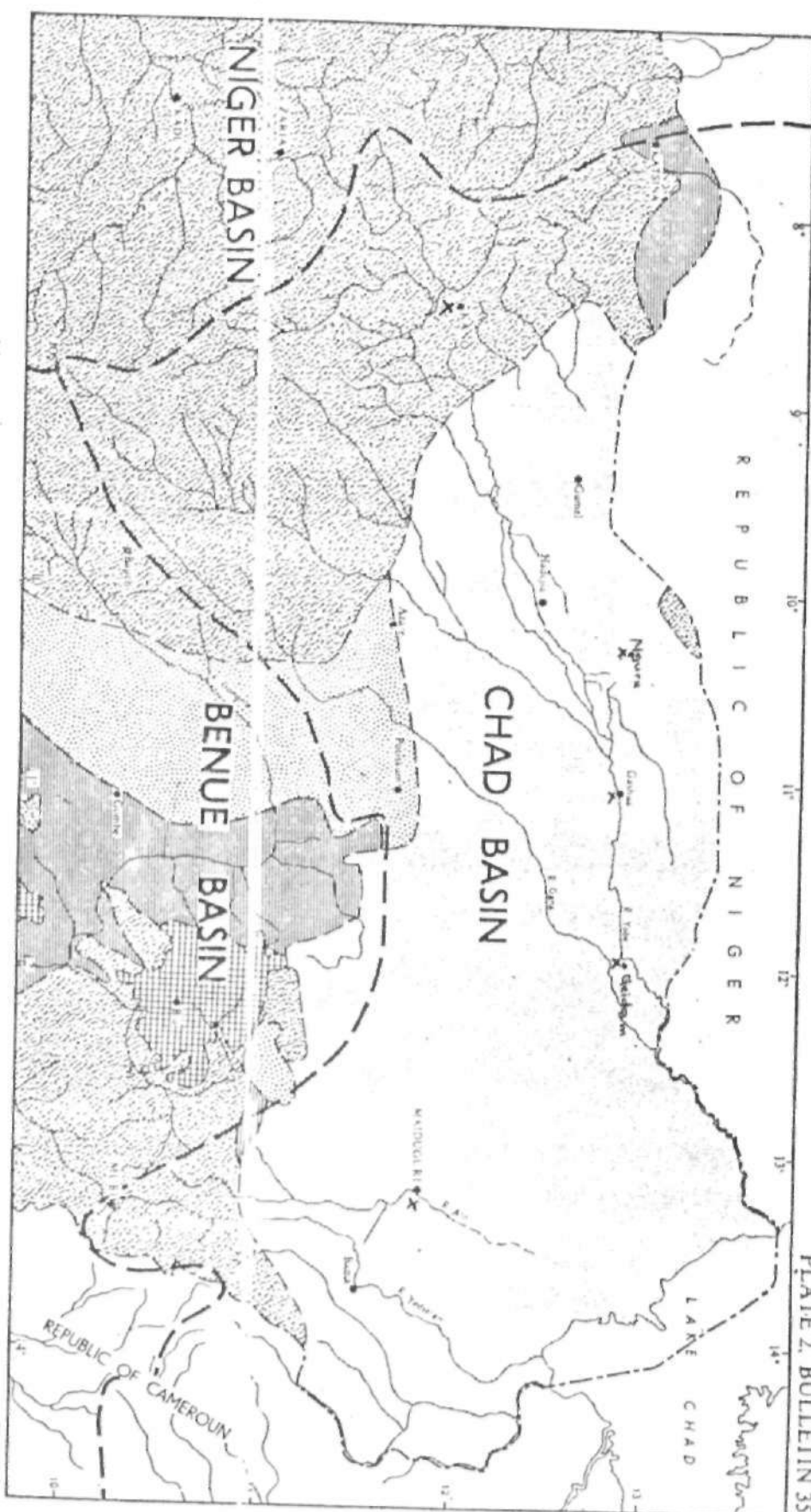
slopes gently towards Lake Chad with no rock outcrops but only superficial coverage of deposits of sand and clay. The basin is composed of rocks which are of sedimentary origin. All drainage is towards Lake Chad but Baber observes that most streams fail to reach it, their water being dissipated in broad swamps and lost by evaporation or transpiration or percolation to the underlying sediments. Some of the important rivers which discharge into the lake include the Komadugu Yobe, the Yedseram, the El-Beid, the Ngadda and the Shari. No river flows out of it and this is mainly because the amount of water the lake receives from rain and rivers is not enough to make up for that lost through evaporation (2). The Nigerian rivers (Hadejia, Yedseram, Gana and Yobe) supply only five percent of the total input into the lake, most of which comes from the Shari-Logone system in Chad and Cameroun Republics (3). The climate is semi-arid.

Where internal drainage exists in arid or semi-arid regions, it is possible for the soluble products of rock weathering to be carried by the infrequent rains to depressions without outlet. As a result of rapid evaporation, a high concentration of the included salts is obtained (4). Raeburn and Jones in

their study of the salt industry of the northern Bornu Province (Borno State) observed that the salts were deposited in depressions between sand dunes and during the rains the depressions contained saline lakes of greater or less concentration. The depressions which usually result from the deflating action of the wind in deserts may become excavated below the water-table, leading to the development of a lake. Excessive evaporation causes the lakes to become salt lakes or playas (5). In regions of interior drainage each lake constitutes a unit by itself and collects into itself the soluble salts of its own drainage area and not of others. Consequently, each lake is different in composition, which is determined by the character of the rocks of its particular drainage basin (4). Saline lakes include the oceanic type, alkali or soda lakes, sodium sulphate lakes and borate, nitrate, magnesium and potash lakes. According to Bateman (4) all contain common salt and most of them contain sulphates. Alkali or soda lakes are common to regions of sparse rainfall and internal drainage where volcanic rocks or sedimentary rocks high in sulphate are undergoing weathering. The saline lakes found around the Chad Basin, including Lake Chad itself, fall into one of the above categories of lakes, but evidence for the particular

type is not immediately available. It has, however, been stated (6) that in the deposition of salts from saline lake waters, trona,  $(\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O})$ , is the first salt to be deposited. This is followed by sodium sulphate, common salt and finally natron  $(\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O})$ . The chief salts deposited from alkali lakes are the sodium hydrogen carbonate or baking soda, sodium carbonate or soda ash, natron and trona. The chlorides, sulphates, carbonates and borates may occur separately or together (6).

The salt occurs as a saline lake residue or as an efflorescence on soil in arid or semi-arid regions. Large deposits occur in Lake Chad. The shores of this lake are rich in salt and potash (3, 7). A wide variety of salts occur in this region but they are all referred to generally by the trade name 'kanwa'. Four types occur in the northern Borno State, in Nguru, Gashua and Geidam areas (8). These include Mongul (common salt), Kilbo kime (red 'flour' potash or natron), Kilbo buktur (white 'flour' potash or natron), and Gwangwarasa (white 'flour' Potash or natron). According to Raeburn and Jones, recovery of the salt is carried out by scrapping it off the surface of the ground with a hoe,



MAP SHOWING THE GEOLOGY  
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or in places where a thick deposit occurs, it is quarried with an axe. The collection of the red variety begins while the water still covers the deposit. The white variant on the other hand is recovered after the pool has completely dried up.

It has been pointed out earlier on that all the samples of the salt for the present study originated from the Chad Basin. The sources of the samples within Nigeria are indicated in Plate II, which shows the extent of the basin in Nigeria. The towns are marked 'X'. The salt is used for various purposes, and they include medicinal and industrial applications. It also serves as a tenderiser in cooking (9, 10). A more detailed information on the various types of the salt found in Central Sudan, the extent of their distribution and uses, is provided by Lovejoy (11) and is shown in Appendix II.

## 1.2 The Chemistry of 'Kanwa'.

Some information is available as regards the chemical nature of the salt. Authors who have studied the chemistry of the salt or those who have carried out a study of the salt industry in general have often referred

to the salt, either as potash, trona or natron. Each of these names suggests the chemical composition of the salt but could be misleading. Nevertheless, they will serve as a guide in the present study.

Two types of 'kanwa', namely, Mongul and Gwangwarasa, obtained from the Chad Basin region have been analysed for their chemical composition (8). The results of the analysis are shown in Table 1.1.

TABLE 1.1

Result of analysis of Chad Basin salts in percent.

| Analyte                         | Salt type |             |
|---------------------------------|-----------|-------------|
|                                 | Mongul    | Gwangwarasa |
| NaCl                            | 68.50     | 0.50        |
| MgCl <sub>2</sub>               | 4.00      | trace       |
| Na <sub>2</sub> CO <sub>3</sub> | 5.20      | 0.69        |
| Na <sub>2</sub> SO <sub>4</sub> | 15.30     | 87.81       |

Makanjuola and Beetlestone (12) analysed eight crude samples of 'kanwa' which were bought from markets located mainly in the southern part of Nigeria.

The metal ions determined include those of aluminium, iron, calcium, magnesium, sodium and potassium. Results indicated that sodium (26 percent) was the predominant ion. The anions carbonate (19 percent), chloride (5 percent) and sulphate (11 percent) were also indicated.

The methods employed for the determination of chloride and sulphate were not clearly stated but the Riley method (13) was used to determine carbonate. The method requires an ignition temperature of  $1100 - 1200^{\circ}\text{C}$ . This ignition temperature is high enough to cause the volatilisation of such constituents as chloride, sulphur and to some extent alkali metals (14). The formation of some acidic or neutral by-products is, therefore, not unlikely. These, on absorption by the barium hydroxide used in trapping the carbon dioxide evolved from the sample may lead to errors (positive or negative) being introduced. Riley has listed two major sources of error in the Penfield's method (14) employed for the determination of total moisture. One of these is the difficulty of ensuring that all the liberated water is condensed, particularly under conditions of low humidity. It may be mentioned that the success of the method depends also on the absence of volatile

constituents and constituents that are readily oxidised or reduced during ignition. Chief among the latter is iron(III).

Makanjuola and Beetlestone have reported an earlier work by Solaja, the result of which showed that 'kanwa' was a susquicarbonate (trona), containing equimolar quantities of sodium carbonate and sodium hydrogen carbonate. This conclusion was reached by titrating an aliquot of a solution of 'kanwa' with standard hydrochloric acid, using the double end point pH titration technique and plotting pH against volume of acid added.

Ekanem (15) unaware of any previous work on 'kanwa', carried out a preliminary analysis of forty three samples and showed that the salt contained sodium (30 percent), and potassium (3 percent). Carbonate, chloride and sulphate were detected and manganese was shown to be present in small amounts (of the order of  $10^{-3}$  percent) in only six samples. He determined sodium and potassium by using both the atomic absorption spectroscopic and flame photometric methods. This enabled him to check the result of one technique against

the result of the other. The result obtained for sodium by Ekanem was comparable with that obtained by Makanjuola and Beetlestone, but while Ekanem recorded appreciable quantities of potassium in all forty three samples, Makanjuola's analysis revealed either traces or complete absence of the ion.

Another analysis was reported by Ankrah and Dovlo (9) who analysed five samples of 'kanwa' obtained in Ghana. The methods of analysis were not indicated but the results showed that 'kanwa' could contain 25 percent sodium; 0.4 percent potassium 0.3 percent calcium, 0.02 percent magnesium, 0.44 percent phosphorus and 25.5 percent moisture.

### 1.3 The aim of the project.

The present work was planned to determine the anion content of 'kanwa' and to relate the results to those already obtained by Ekanem for sodium and potassium. It was also planned to devise an ion-exchange chromatographic technique to separate the anions prior to their chemical or physicochemical determination. The aim was to develop a rapid and more reliable method of anion analysis which would also

check any possible interference by the individual anions in the process of determining one in the presence of the other. The results of the analysis were to be used in establishing the major salts or minerals that are usually associated with 'kanwa'.

## CHAPTER 2

### METHODS OF ANION ANALYSIS

#### 2.1 Detection of anions.

The classical procedure for the qualitative analysis based on the action of group reagents was employed in the detection of anions. Furthermore, the fractional method was preferred to the systematic method whereby the ions are precipitated successively by group reagents in one portion of the test solution. The fractional method enables the ions to be detected in a separate portion of the mixture and prevents the attendant contamination that is usually associated with the systematic method (16). The solubility of the samples was first determined in water, dilute hydrochloric acid, concentrated hydrochloric acid, dilute nitric acid and concentrated nitric acid in that order. Sample solutions were prepared based on the results of the solubility test. The pH of the solution of each sample was also determined by the usual method which employs a pH-meter (16 17). The anions covered in the analysis include borate, carbonate, hydrogen carbonate and chloride. Others were nitrate, phosphate and sulphate.

## 2.2 Determination of anions.

The choice of method for the quantitative analysis of a material is not an easy one but the problem is reduced if some information regarding the composition of the material and its physical properties is available. Some ions interfere with the determination of other ions in several ways, for example, the formation of precipitates or coloured complexes with the reagent. The chemical composition is, therefore, an important factor in the determination of the nature of interferences in analysis. Thus, in making a choice of a method for the determination of each of the ions ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) detected in the samples, due consideration was given to the presence of the other ions, including the metal ions, in solution. The concentration of the analyte, the number of samples to be analysed and the nature of interferences expected were also considered. Ion-exchange chromatography was preferred for the second analytical procedure involving separation, the basis of which was the ease of operation and rapidity. The use of physical method for the detection and determination of the effluents minimises the use of reagents. This is an additional advantage when cost is considered.

The moisture content of the samples was determined gravimetrically since this method has the advantage of simultaneous analysis of several samples. The order of analysis was moisture content first, followed by carbonate and hydrogen carbonate, chloride and finally sulphate.

(i) Determination of chloride.

The Volhard method (18, 19) of chloride determination was employed on account of its being subjected to less interferences among the argentimetric methods. Carbonate and sulphate interfere with the determination by forming the sparingly soluble silver carbonate and silver sulphate, respectively. However, the requirement that the titration be performed in an acidic media ensures that the carbonate is destroyed besides preventing the hydrolysis of the iron(III) indicator to the colourless hexaaquo species,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . Silver sulphate on the other hand is not precipitated since the solubility product is not exceeded in dilute solutions of the ions (16).

(ii) Determination of carbonate and hydrogen carbonate.

The acidimetric method of pH titration was employed in the determination of carbonate and hydrogen carbonate.

The method is most suitable, particularly when these two ions are to be determined simultaneously. It is, however, known that the method suffers from the problem of carbondioxide evolution, which constitutes a major source of error (20, 21). Variable amounts of the gas are evolved near the equivalence point, depending partly on the time elapsed and on the degree of shaking. This leads to a variation in pH at the equivalence point and prevents strict application of the mass-balance equations.

(iii) Determination of sulphate.

Precipitation methods of analysis are commonly employed in the determination of sulphate, and barium chloride has often been used as the precipitating agent. Carbonate is an interfering ion in this procedure, but is readily removed in the acidic medium in which the precipitation is usually carried out. Pataki and Zapp (22), however, observe that the sulphate precipitated in acidic media is often contaminated with barium hydrogen sulphate. Co-precipitation and occlusion of foreign ions or solvent also introduce errors in the determination, particularly in gravimetric and titrimetric analysis (18, 23). As a way of reducing the problem of co-precipitation and occlusion, Fritz and Yamamura (24)

employed barium perchlorate instead of barium chloride as titrant in the direct determination of sulphate. The sulphate was first separated on a column packed with alumina and then passed through a cation exchanger.

Massoumi and Cornfield (25) used a turbidimetric method for the determination of sulphate in water extract of soils. It was a modification of the original method by Butters and Chenery (26) and was found to be suitable for application to as little as 2 ppm of sulphate. Another modification of the method which employed EDTA to overcome precipitate build-up and consequently to improve the precision and development of turbidity has been proposed by Baban et al (27).

Turbidimetry is unsuitable for application to coloured solutions since they also absorb their own amount of radiant energy. Its successful application rests largely on the effective control of the conditions under which turbidity is developed. A fairly uniform size of barium chloride crystals is required and violent shaking at any stage is avoided (28). Lyalikov (29) also lists some areas of special

attention with respect to the development of turbidity. Among them are the following:

- a. Concentration of the ions forming the precipitate.
- b. The ratio of the concentrations of the solutions mixed.
- c. The order of mixing the solutions.
- d. The rate of mixing.
- e. Time required to attain maximum turbidity
- f. Stability of the dispersion.

Other methods of sulphate determination have been reported in literature and they include the indirect determination of excess barium by atomic absorption spectroscopy or conductometry after precipitation of sulphate with barium chloride. The turbidimetric method was employed in the present study, on account of the fact that a filtration process is avoided.

### 2.3 Anion-exchange chromatographic separation of anions.

Small et al (30) achieved a separation of chloride, carbonate and sulphate on a low capacity and small particle size resin. Gjerde et al (31) separated hydrogen carbonate, chloride and sulphate by using a

low capacity resin. The latter investigators also employed fine particle size resin, but while they used XAD-1 resin and potassium hydrogen phthalate as eluent, the former employed Dowex-2 type resin and sodium phenate solution as eluent. Van Os et al (32), in a similar analysis successfully separated chloride, nitrite, bromide, nitrate and sulphate. They employed a small column packed under high pressure with Zipax-SAX pellicular beads and sodium succinate and sodium adipate as eluents at pH 7.

It might be suggested that Small and Gjerde in their choice of eluents considered the presence of the analytes, namely, carbonate and hydrogen carbonate, respectively. The pH of sodium phenate solution is in the upper region where hydrogen carbonate is easily converted to the carbonate in the presence of sodium hydroxide. The pH of potassium hydrogen phthalate on the other hand is at the lower region where carbonate cannot exist in solution. Consequently, in a situation where both carbonate and hydrogen carbonate are present in the mixture to be analysed, it would be more appropriate, for practical considerations, to employ sodium phenate solution as eluent and determine the 'total carbonate' of the material. This would prevent

the decomposition of the carbonate which would be inevitable should the phthalate solution be used as eluent.

An equilibrium reaction for the conversion of sodium hydrogen carbonate to sodium carbonate may be represented as follows.



The equilibrium constant for the above reaction can be written as

$$K = \frac{[\text{CO}_3^{2-}][\text{PhOH}]}{[\text{PhO}^-][\text{HCO}_3^-]}$$

Since the bulk of the mixture is essentially sodium phenate, the equilibrium is to the right. Conversion is, therefore, accomplished.

The determination of distribution coefficient was carried out by using the method described by Strelow (33) and Strelow et al (34) for cations in hydrochloric acid. The resin was first screened to obtain narrower range beads. A combination of the procedure described by Moore and Stein (35) and by Hamilton (36), for the screening and fractionation of resin beads, respectively, was employed.

CHAPTER 3EXPERIMENTAL3.1 Sample treatment and storage.

The samples were obtained already crushed, ground into powder and stored in covered glass bottles from where portions were taken for analysis after thoroughly mixing the bulk sample.

3.2 Qualitative analysis.

Qualitative anion analysis was carried out on the water extract of the water-soluble samples or the sodium carbonate extract of the insoluble samples using the classical method of qualitative analysis.

3.3 pH determination.

Apparatus: Griffin pH-meter (battery operated) fitted with combination glass-calomel electrode.

Sample solutions: 1% (m/v) solution of sample was prepared by dissolving 1g of solid in deionised distilled water and diluting to 100cm<sup>3</sup>.

Buffer solutions (pH 5 and pH 12): pH 5 buffer solution was prepared by mixing 18cm<sup>3</sup> of 0.2M acetic acid and 42cm<sup>3</sup> of 0.2M sodium acetate. pH 12 buffer solution was a 0.01M sodium phosphate solution.

### Procedure:

The electrode was soaked in deionised distilled water in a plastic bottle for about three hours. It was then standardised in buffer solutions of pH 5 and pH 12, respectively, these being the lower and upper limits of the pH range expected as preliminary indicator tests showed that the solutions were either neutral or alkaline. The sample solution was poured into a 150cm<sup>3</sup> conical flask and then stirred by means of a magnetic stirrer. The electrode was immersed after it has been rinsed with deionised distilled water and the meter standardised at pH 7. Care was taken to ensure that the electrode was always rinsed and dried with a soft tissue after every reading has been taken. The electrode and meter were also standardised before use, whenever the apparatus was left unused for some hours. The pH-meter was not adapted to temperature regulation. The results are shown in Table 4.1

### 3.4 Quantitative determination of anions.

For the quantitative analysis of the anions detected, fourteen water-soluble samples were chosen.

(i) Moisture content.

Apparatus: Gallenkamp Oven Size 1; platinum crucibles and desiccator packed with silica gel.

Procedure: The platinum crucible was heated to constant weight at 105°C oven temperature. Some quantity of the powdered sample was placed in the crucible and weighed. The crucible and contents were heated at 105°C to constant weight and the loss in weight was determined. The moisture content, expressed as a percentage, was then calculated from an average of three determinations.

$$\% \text{ Moisture} = \frac{(M_2 - M_3) \times 100}{M_2 - M_1}$$

where  $M_1$  denotes the mass of platinum crucible,  $M_2$  the combined mass of crucible and sample before heating and  $M_3$  represents the mass of crucible and dry sample.

(ii) Chloride.

Reagents: All reagents were of the analytical grade unless otherwise stated.

Water: Deionised distilled water was used for the preparation of all solution.

Standard (0.0995M) silver nitrate solution: Prepared by dissolving 16.992g of dry reagent in water and diluting to 1000cm<sup>3</sup>. The solution was stored in a brown bottle and kept in a dark place.

Standard (0.101217M) potassium thiocyanate solution: Prepared by dissolving 9.8278g of reagent in water and diluting to 1000cm<sup>3</sup>.

Saturated solution of Iron(III) sulphate: Prepared by dissolving some quantity of reagent in water. It was acidified with a few drops of 6M nitric acid.

Standard (6M) nitric acid solution: Prepared by diluting 96cm<sup>3</sup> of reagent to 250cm<sup>3</sup> with water.

Nitrobenzene: Redistilled.

Procedure: The standardisation of potassium thiocyanate was carried out by diluting 25cm<sup>3</sup> aliquot of standard silver nitrate solution to 100cm<sup>3</sup>. 2cm<sup>3</sup> of freshly boiled concentrated nitric acid was added followed by 1cm<sup>3</sup> of iron(III) indicator. The solution was then titrated with potassium thiocyanate solution until the first permanent reddish-brown colour was produced.

A  $25\text{cm}^3$  aliquot of the sample solution was transferred into a  $250\text{cm}^3$  conical flask and  $5\text{cm}^3$  of the standard acid was added and then boiled. After allowing to cool, a measured excess of silver nitrate solution was added and the mixture shaken to mix.  $3\text{cm}^3$  of re-distilled nitrobenzene was added followed by  $1\text{cm}^3$  of iron(III) sulphate indicator. The mixture was again shaken to mix and to coagulate the precipitate of silver chloride. It was then titrated with the standard potassium thiocyanate solution until the first permanent reddish-brown colour appeared. A reagent blank determination was carried out by titrating  $25\text{cm}^3$  of similarly treated water and the corresponding volume of titrant was subtracted from that obtained for the sample aliquot. The chloride content was then calculated as follows:

$$\% \text{Cl}^- = \frac{(AM_1 - BM_2)(35.44)(100)}{w \times 10^3}$$

where A, B are the volumes of silver nitrate solution and potassium thiocyanate solution, respectively;  $M_1$ ,  $M_2$ , are the molarities of silver nitrate solution and potassium thiocyanate, respectively and w is the mass of sample in grammes. The results are as shown in Table 4.2

(iii) Carbonate and hydrogen carbonate.

Apparatus: Griffin pH-meter (battery operated) fitted with a combination glass-calomel electrode.

Reagents: All reagents were of the analytical grade unless otherwise stated.

Water: Deionised distilled water was used for the preparation of all solutions.

Standard (0.098M) hydrochloric acid: Prepared by diluting  $86\text{cm}^3$  concentrated acid to  $1000\text{cm}^3$  with water.

Sample solution: A calculated mass of sample was dissolved in water and diluted to  $100\text{cm}^3$ .

Buffer solutions (pH 10 and 2): The buffer pH values were chosen on the basis of the results of pH determination. pH 10 solution was prepared by adding  $28.5\text{cm}^3$  of concentrated M & B standard reagent ammonia solution to 3.5g of ammonium chloride and diluting to  $50\text{cm}^3$ . pH 2 buffer solution was prepared by mixing 0.05M hydrochloric acid and 0.1M potassium chloride solution.

Procedure: The pH-meter and electrode were standardised at the lower and upper pH range to be measured. An aliquot of the sample solution was transferred into a 150cm<sup>3</sup> conical flask and the pH was measured. Equal volumes (0.1 cm<sup>3</sup>) of the standard acid were added from a 10cm<sup>3</sup> burette and the mixture was shaken after each addition. The pH was then measured. Near the equivalence point smaller volumes (0.05 cm<sup>3</sup>) of the acid were added, so that the end-point was approached more slowly. Addition of acid was continued until changes in pH after the second jump were constant. pH was then plotted against corresponding volume of acid added and the equivalence point of the titration was obtained. Three independent determinations were carried out and the average percent carbonate (hydrogen carbonate) calculated as follows.

$$\% \text{CO}_3^{2-} - \text{HCO}_3^- = \frac{M_a \times V_a \times E \times V_s \times 10^2}{V_t \times m \times 10^5}$$

where  $M_a$  is the molar concentration of acid;  
 $V_a$ , the volume of acid added;  $V_s$  and  $V_t$ , are the volume of sample solution prepared and aliquot titrated, respectively;  $E$  is the equivalence of carbonate (hydrogen carbonate) and  $m$  is the mass of sample. The results are shown in Table 4.2. Typical curves obtained are also shown in figures 2.1 - 2.4.

(iv) Sulphate (37).

Apparatus: Bauch and Lomb Spectronic 20 spectrophotometer and a 0.25mm - Endecott Test Seive.

Reagents: All reagents were of the analytical reagent grade unless otherwise stated.

Water: Deionised distilled water was used for the preparation of all solutions.

25% (v/v) nitric acid solution: Prepared by diluting  $63\text{cm}^3$  of boiled concentrated acid to  $250\text{cm}^3$  with water.

50% (v/v) acetic acid solution: Prepared by diluting  $50\text{cm}^3$  of M & B standard reagent to  $100\text{cm}^3$  with water.

Phosphoric acid: BDH laboratory reagent, specific gravity 1.75.

Barium chloride crystals: The dihydrate salt was ground to pass through a 0.25mm seive.

0.5% (m/v) gum acacia: Prepared by dissolving 0.5g of BDH laboratory reagent in  $100\text{cm}^3$  of warm water.

Standard (0.001652M) magnesium sulphate solution:

Prepared by dissolving about 0.3844g of magnesium sulphate heptahydrate in water and diluting to 1000cm<sup>3</sup>.

Standard (0.001M) EDTA solution: Prepared by dissolving an accurately weighed 0.03723g of the disodium salt in water and diluting to 100cm<sup>3</sup>.

Buffer solution (pH 10): Prepared by adding 28.4cm<sup>3</sup> of M & B standard reagent grade concentrated ammonia solution to 3.5g of ammonium chloride and diluting to 50cm<sup>3</sup> with water.

Solochrome black indicator: Prepared by dissolving 0.25g of BDH laboratory reagent in 50cm<sup>3</sup> of water.

Sample solution: A calculated mass of the solid sample was dissolved in water and diluted to 100cm<sup>3</sup>.

Procedure: 5cm<sup>3</sup> of the sample solution was transferred into a 50cm<sup>3</sup> volumetric flask. 3cm<sup>3</sup> of 25 percent nitric acid was added to each of the flasks containing the sample solutions, followed by 5cm<sup>3</sup> of 50 percent acetic acid and 1cm<sup>3</sup> phosphoric acid. The mixture was swirled to mix and then diluted to the base of the neck of

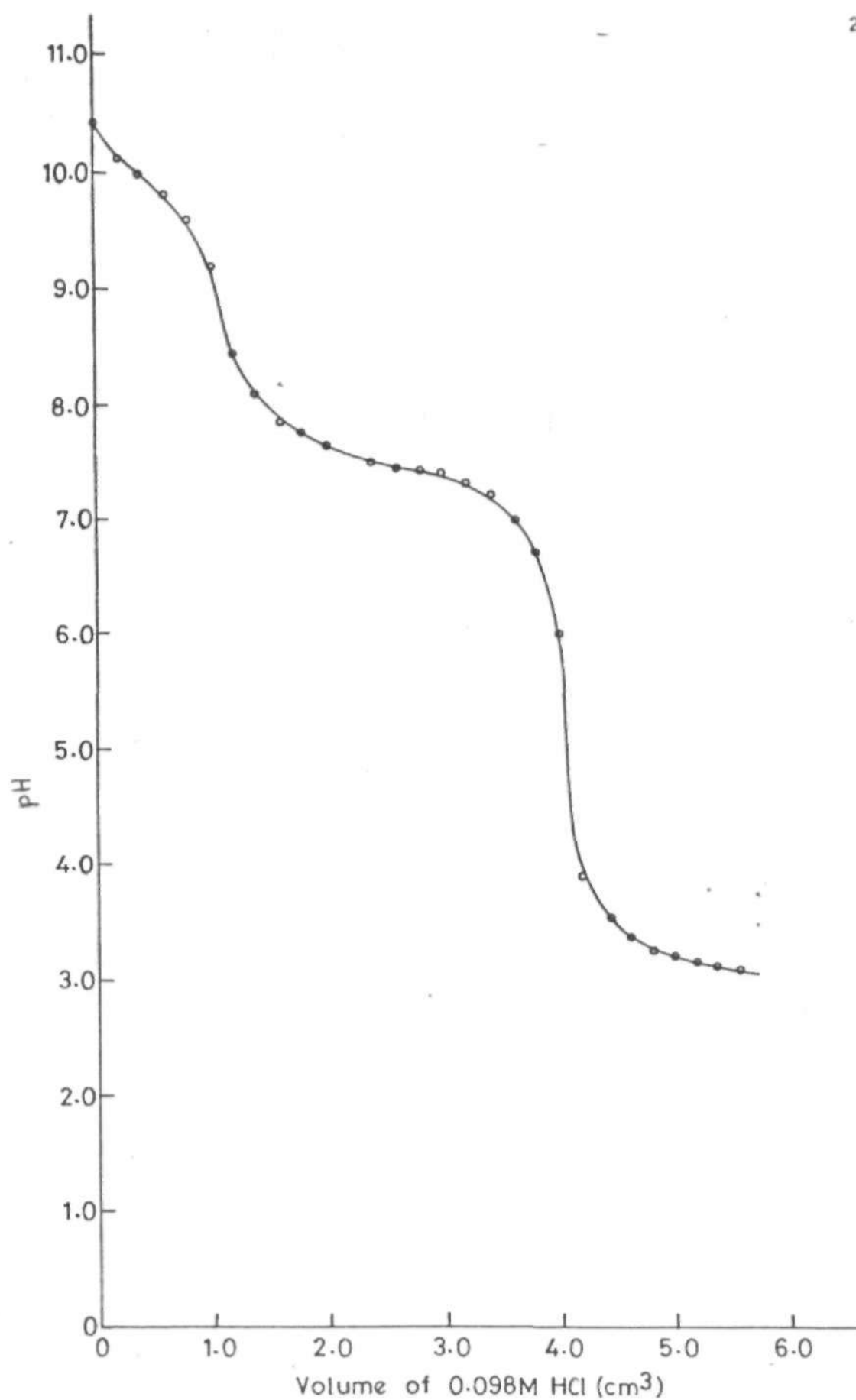


Fig. 2.1 Curve of titration of a mixture of 0.01M  $\text{Na}_2\text{CO}_3$  and 0.019M  $\text{KHCO}_3$  with 0.098M HCl.

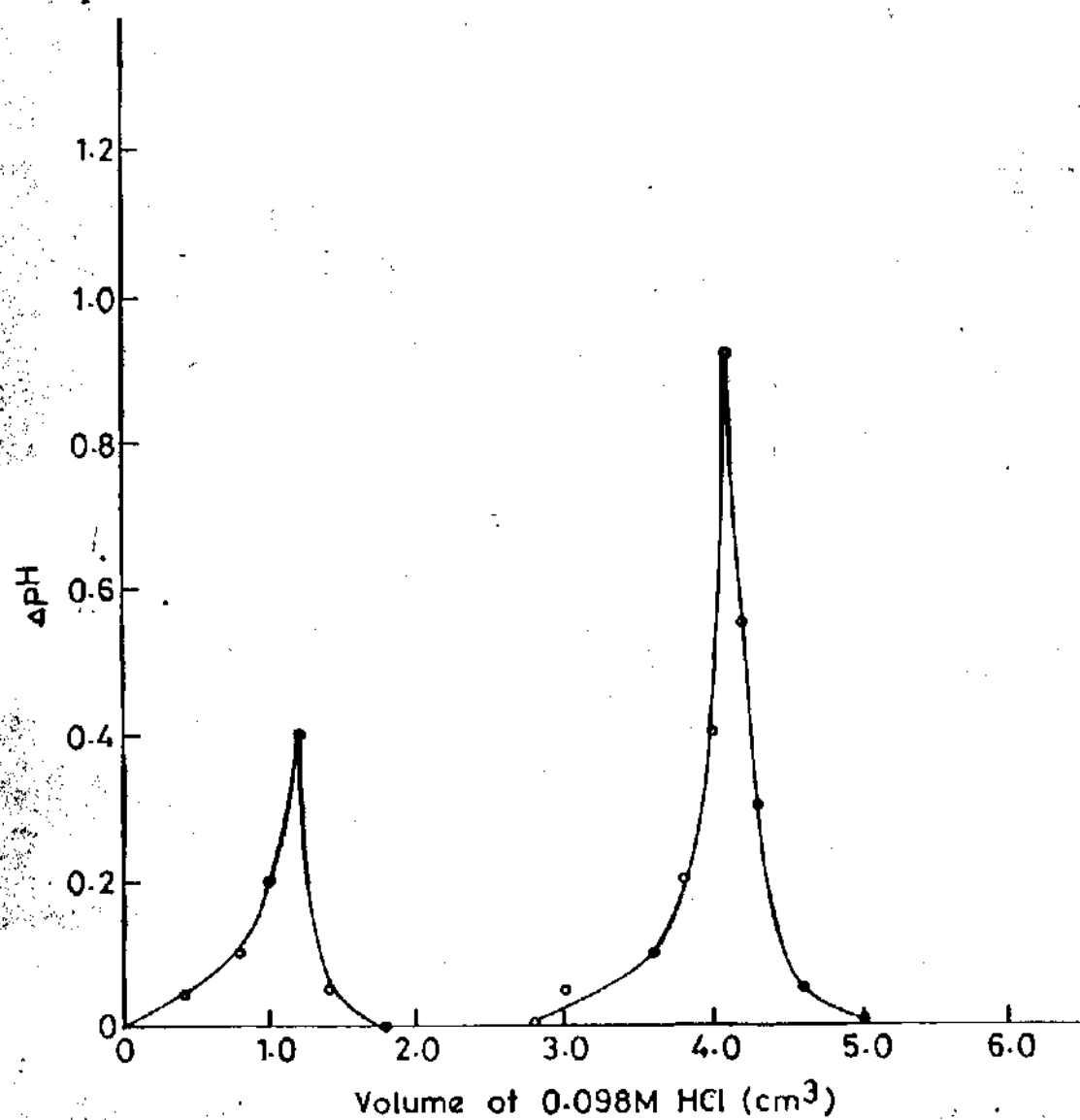


Fig. 2.2 Curve of  $\Delta pH$  against volume of HCl for a mixture of 0.01M  $Na_2CO_3$  and 0.019M  $KHCO_3$ .

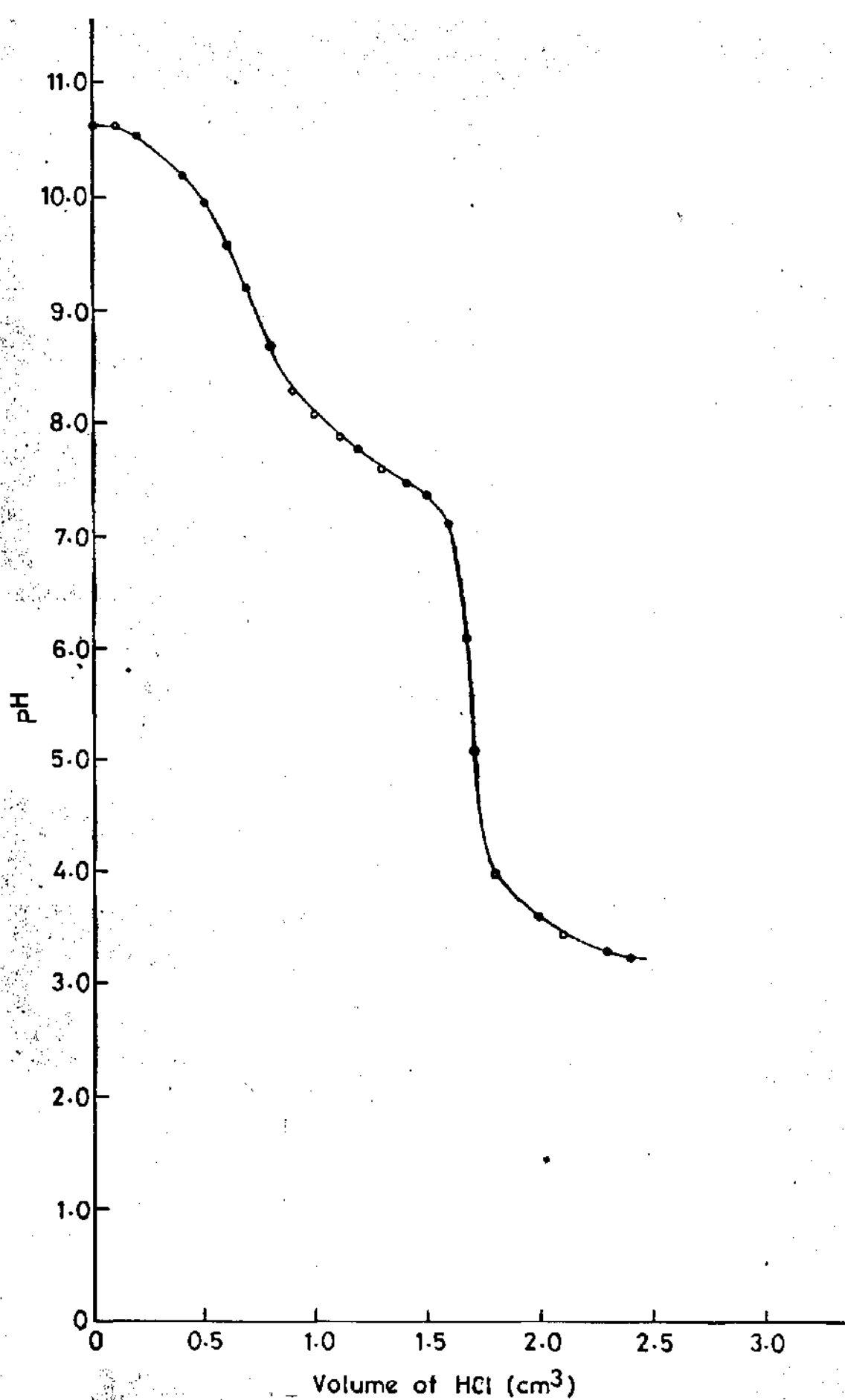


Fig. 2.3 Curve of titration of 0.2 percent solution of Kanwa sample against 0.098M HCl.

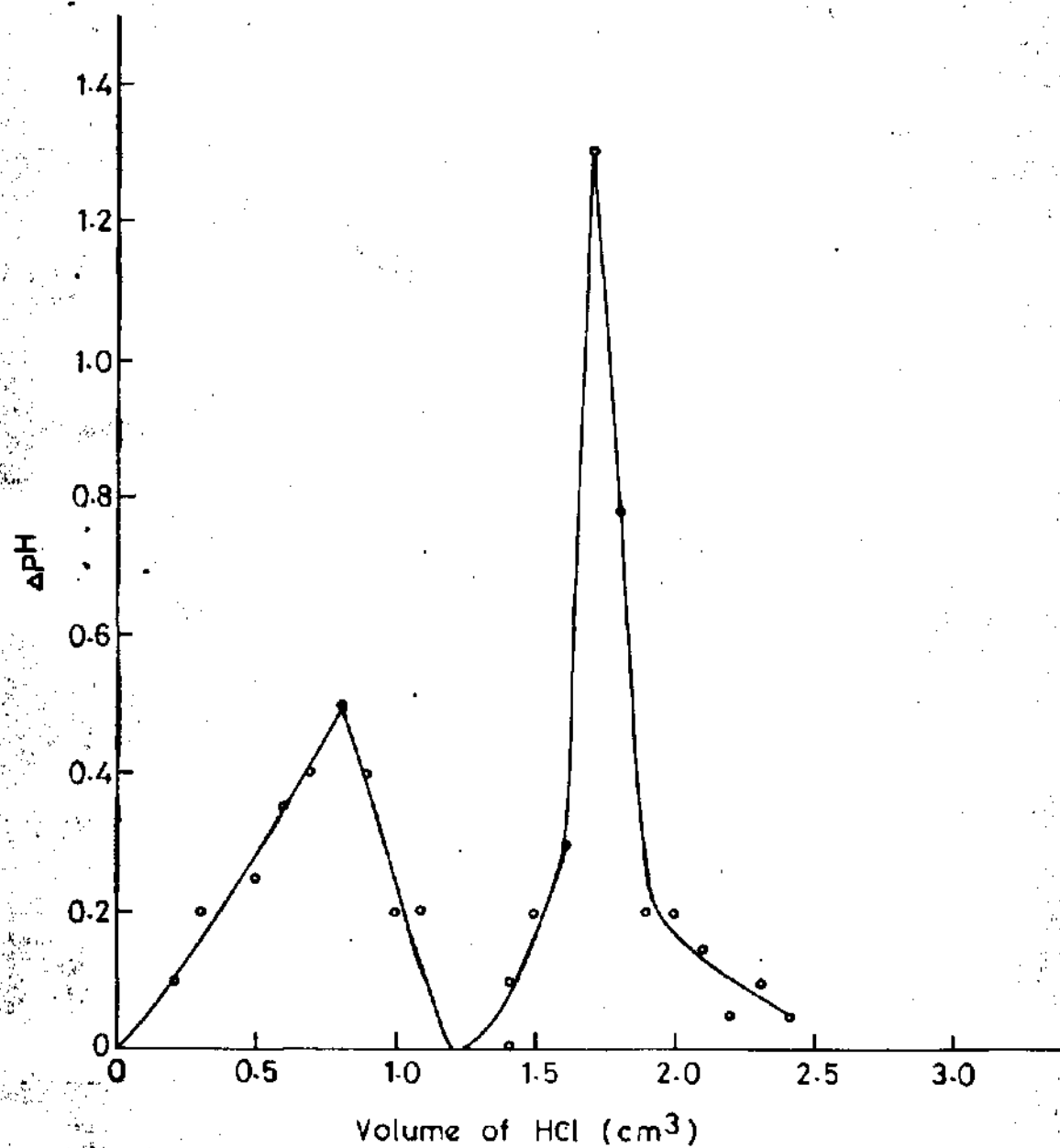


Fig. 2.4 Curve of  $\Delta pH$  against volume of HCl for a 0.2 per cent solution of Kanwa.

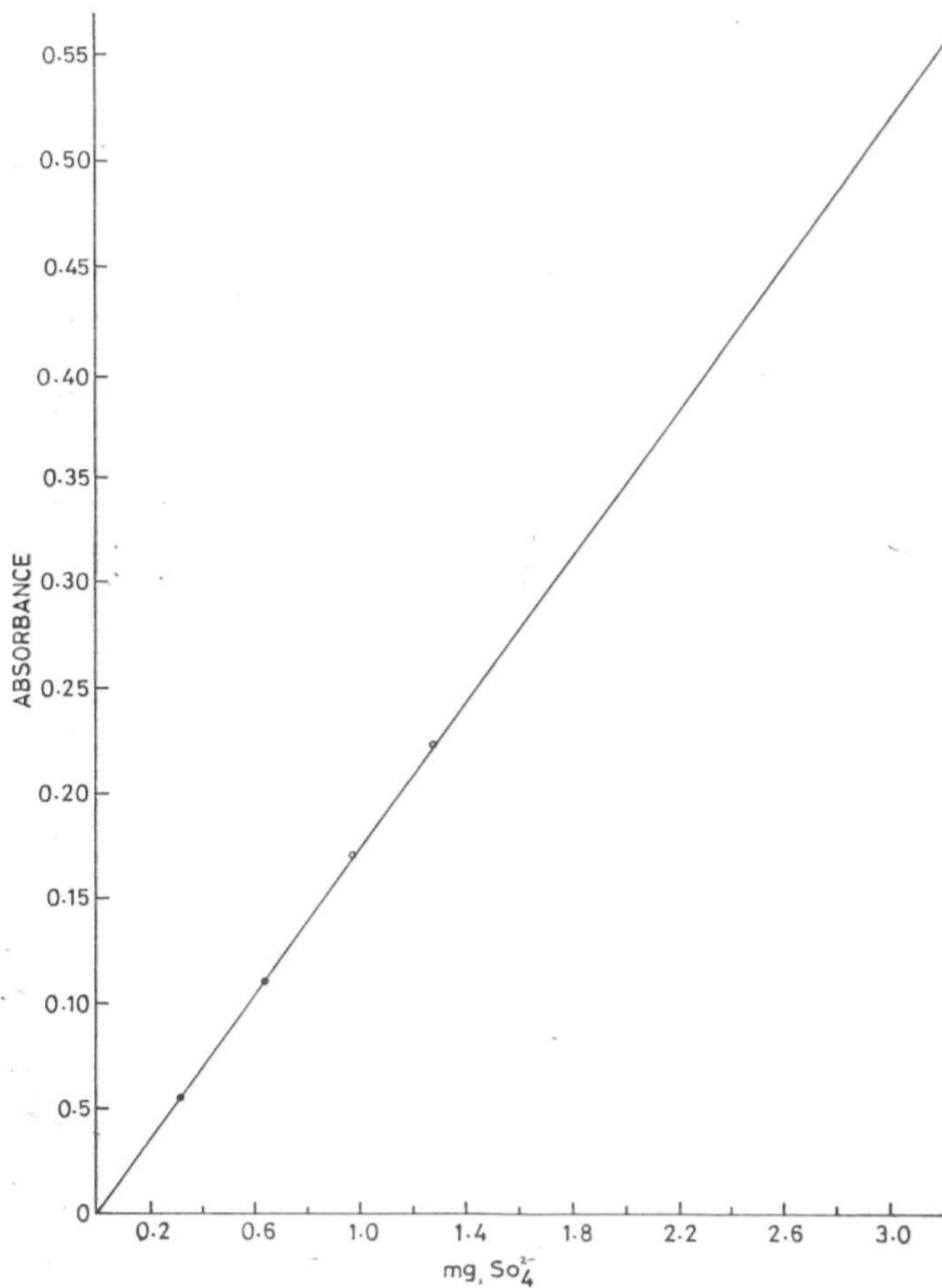


Fig. 2.5 Calibration curve for Sulphate determination.

the flask with water. After mixing, 1g of barium chloride crystals was added and the flasks were left to stand for ten minutes. The flasks were inverted twice and left to stand for five minutes. They were inverted twice again and left to stand for a further five minutes. After this procedure has been repeated ten times, 1 cm<sup>3</sup> of freshly prepared 0.5 percent gum acacia was added and the mixture was made up to the 50cm<sup>3</sup> mark with water. The inversion procedure was repeated for a further five successive inversions. The flasks were left to stand for ninety minutes after which the turbidity was measured at 470nm. Three independent determinations were carried out for each sample.

Five 100cm<sup>3</sup> flasks containing 0, 2, 4, 6 and 8 cm<sup>3</sup> magnesium sulphate standard solution were treated similarly and a calibration curve (Fig 2.5) was plotted. The concentration of the sample solution was then obtained from the graph and the percentage sulphate in each sample calculated as follows:

$$\% \text{SO}_4^{2-} = \frac{C(\text{mg}) \times \text{solution volume (cm}^3) \times 10^2}{10^3 \times \text{aliquot (cm}^3) \times \text{sample mass (g)}}$$

where C represents mg of  $\text{SO}_4^{2-}$  obtained from graph.

### 3.5 Screening of resin for ion-exchange.

Apparatus: (a) 4000cm<sup>3</sup> beaker  
(b) 250cm<sup>3</sup> separatory funnel  
(c) 100mm diameter funnel  
(d) 425 micron - Endecott test seive.

Procedure: The experimental arrangement shown in Figure 2.6 was employed. One end of a rubber tubing was connected to the stem of a separatory funnel and the other end to a water tap. The top of the separatory funnel was closed by means of a rubber stopper. The rubber stopper carried a U-shaped glass tube the other end of which was connected to one end of a rubber tubing. The other end of the rubber tubing was connected to the stem of an inverted funnel.

About one-third of the separatory funnel was filled with wet BDH standard grade Amberlite IRA-401 resin in the chloride form, and the rubber stopper tightly fitted. The stopcock of the separatory funnel and the water tap were opened. The flow rate of water was increased gradually to provide a stirring force to mix the resin, until the level of the slurry was just below the rubber stopper. The stopcock and water tap were closed and the resin allowed to settle. By maintaining

a low and steady rate of flow of water, the floating fine particles were allowed to run to waste. The funnel was then inverted on a seive and the water pressure was increased to the maximum attainable. The resin was forced through the seive by means of the powerful jet emerging from the glass-tube. The flow of water was continued while moving the inverted funnel over the resin retained on the seive, care being taken to avoid pressing the resin against the seive.

The fractions were collected in a 400cm<sup>3</sup> beaker and allowed to settle. The floating fine particles were removed by decantation and after filtration, the beads were washed with 200cm<sup>3</sup> of 10-percent hydrochloric acid and then rinsed with several volumes of deionised distilled water. Finally, the fractions were dried at 50°C and stored in a plastic bottle.

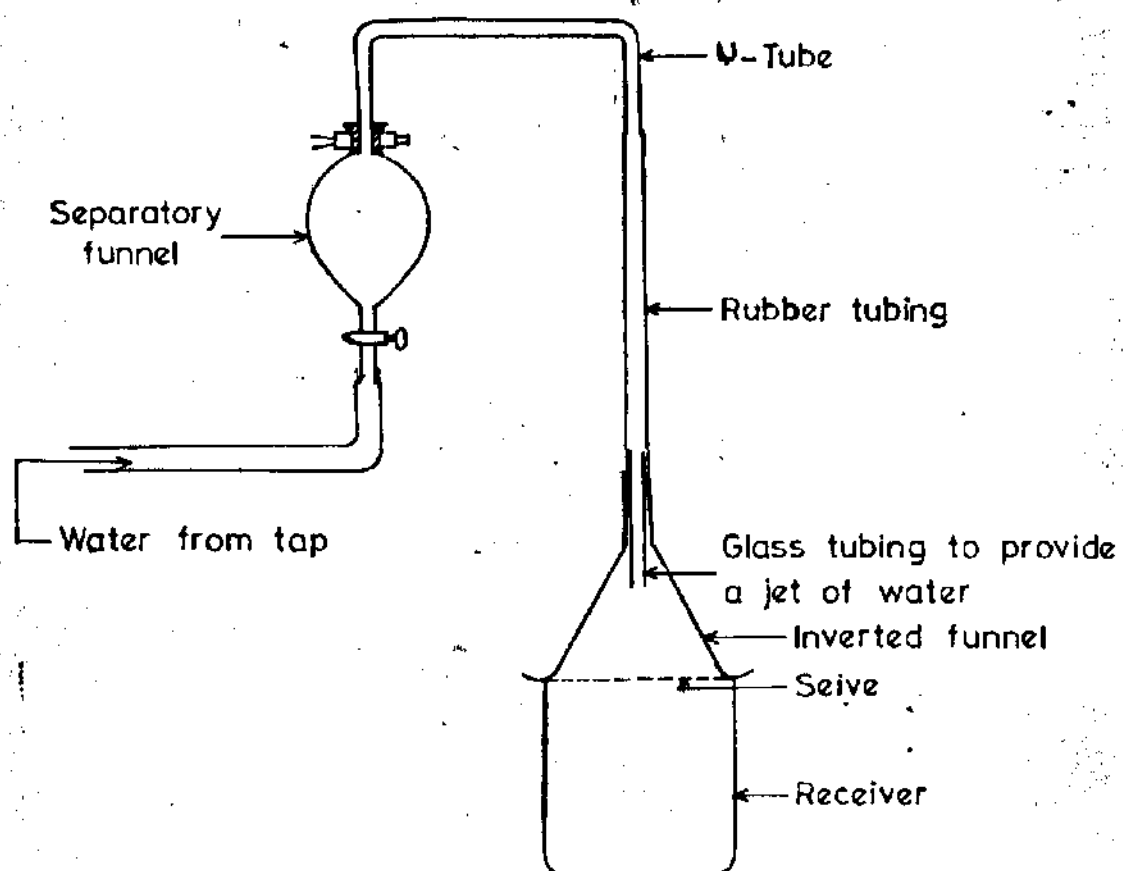


Fig. 2-6 Arrangement for the screening of resin.

### 3.6 Determination of ion-exchange capacity (38).

Apparatus: 120 x 10mm glass column, 100cm<sup>3</sup> separatory funnel, 500cm<sup>3</sup> conical flask.

Reagents: All reagents were of the analytical grade unless otherwise stated.

Water: Deionised distilled water was used for all preparations.

Standard (0.098M) silver nitrate solution: Prepared by dissolving 16.992g of dry silver nitrate in water and diluting to 1000cm<sup>3</sup>. The solution was stored in a brown bottle and kept in the dark.

Potassium chromate - potassium dichromate solution: Prepared by dissolving 4.2g of potassium chromate and 0.7g of potassium dichromate in water and diluting to 100cm<sup>3</sup>.

0.25M sodium nitrate solution: Prepared by dissolving 21.3g of BDH analytical reagent in water and diluting to 1000cm<sup>3</sup>.

Procedure: An accurately weighed 1g of the dry resin was soaked in water for about six hours and the floating particles were removed by decantation. The slurry was then poured into a column which was initially half-filled with water. The column was left to settle and the level of water was reduced to  $1\text{cm}^3$  above the resin top. Standard sodium nitrate solution was allowed to flow through the column from a  $100\text{cm}^3$  separatory funnel and the effluent was collected in a  $500\text{cm}^3$  conical flask. After washing the column with  $100\text{cm}^3$  of water, the pH of the effluent was adjusted to 6 and then titrated with standard silver nitrate solution.  $1\text{cm}^3$  of the potassium chromate - potassium dichromate indicator was used for each determination. Three different determinations were carried out and the average capacity of the resin was obtained. The following expression was used for the calculation of the capacity.

$$\text{Capacity} = \frac{M \times V}{m} \text{ meq. g}^{-1}$$

where  $M$ , is the concentration of silver nitrate solution,  $V$ , is the volume of silver nitrate in  $\text{cm}^3$  and  $m$ , is the mass of resin employed. The exchange capacity of both the screened and unscreened resins were determined and found to be 3.04 and 3.52 milliequivalents per gramme, respectively.

### 3.7 Determination of distribution coefficient.

Apparatus: Gallenkamp flask shaker equipped with a speed regulator and timer.

Reagents: All reagents were of the analytical grade unless otherwise stated.

Water: Deionised distilled water was used for all preparations.

Standard (0.05M) sodium phenate solution: This solution was prepared by diluting  $25\text{cm}^3$  of 0.19M solution to  $100\text{cm}^3$ . The stock solution itself was prepared from purified phenol and sodium hydroxide as described by Todd (39). It was standardised according to the prescribed procedure (40, 41).

Standard (0.0931M) sodium carbonate solution: Prepared by dissolving 1.06g of dry anhydrous sodium carbonate in water and diluting to  $100\text{cm}^3$ .

Standard (0.1M) sodium chloride solution: Prepared by dissolving 0.5844g of dry reagent in water and diluting to  $100\text{cm}^3$ .

Standard (0.0972M) sodium sulphate solution: This was prepared by dissolving 1.4206g of dry anhydrous BDH laboratory reagent in water and diluting to 100cm<sup>3</sup>.

Procedure: 1g of the dry resin in the phenate form was placed in a glass-stoppered bottle. 100cm<sup>3</sup> of 0.05M sodium phenate solution was added and then allowed to stand for three hours. 5cm<sup>3</sup> of a solution of the ion was added and the bottle was stoppered. The bottles were clamped and shaken on the mechanical shaker for six hours. 10cm<sup>3</sup> of an aliquot of the supernatant liquid was withdrawn and analysed by a suitable chemical method. Chloride was determined by the Mohr titration method (18), carbonate by pH-titration and sulphate by precipitation with barium chloride and the titration of the excess barium with potassium sulphate, using sodium rhodizonate as indicator (38). A blank determination was carried out in each case and the value obtained was subtracted where applicable. The distribution coefficient of the ion in sodium phenate solution was calculated as follows.

$$K_d = \frac{\text{Decrease in initial ion concentration (moles)}}{\text{Final ion concentration in supernatant liquid (moles)}}$$

The results are shown in Table 4.3.

### 3.8 Determination of optimum conditions for separation of ions.

The preliminary determinations which include ion - exchange capacity and the distribution coefficients of the relevant anions, were carried out with the aim of using the results in obtaining optimum conditions for separation of chloride, carbonate and sulphate. The total ion-exchange capacity gives an indication of the total number of ion active groups per unit mass of material, and of the maximum sample size that can be handled by the column (38). The distribution coefficient on the other hand enables a calculation of other very useful parameters of the column. These include the theoretical plate number,  $N$ , on which the performance or efficiency of the column in separation of a mixture depends, the total bed volume,  $V_b$ , of the resin required for a good separation and consequently, the mass of resin to be employed.

A distribution ratio,  $a$ , may be calculated from the following expression (42).

$$a = \alpha + (1 - \alpha) \frac{K_d}{C_E} \rho \quad \dots(1)$$

where  $\alpha$  is the void fraction of column,  $C_E$  is the molar concentration of the eluent,  $K_d$  is the distribution coefficient and  $\rho$  is the density in  $\text{g cm}^{-3}$  of dry resin. In calculating  $\alpha$ ,  $\alpha$  was taken to be 0.1.  $\alpha$  was calculated from the relationship between the volume capacity and the mass capacity given as follows (43).

$$C_v = (1 - \beta) \rho C_m (100 - S/100) \quad \dots(2)$$

where  $\beta = V_c/V_b$  is the fractional void volume of the packing ( $V_b$  is bed volume and  $V_o$  is the void or interstitial volume),  $S$  is the water content of the resin in mass percent,  $\rho$  is the density of the swollen resin and  $C_v$  and  $C_m$  are the volume and mass capacities, respectively.

For the separation of chloride and carbonate, for example, which may be designated as A and B, respectively, we let  $\Delta m_2$  be the amount of B eluted with A, then,

$$\Delta m_2 = m_2 \left[ 0.5 - A_e \left( \frac{N - M_2}{\sqrt{M_2}} \right) \right]$$

assuming  $N \gg N_o$

where  $N$  is theoretical plate number,  $M$  is the "theoretical plate elution volume" of solvent and  $A_e$  is the error function (42).

Similarly,

$$\Delta m_1 = m_1 \left[ 0.5 - A_e \left( \frac{N - M_1}{M_1} \right) \right] \quad \dots (4)$$

if  $\Delta m_1 = \Delta m_2$  and  $M_1 = M_2$ , then

$$\frac{N - M_1}{\sqrt{M_1}} = \pm \frac{N - M_2}{\sqrt{M_2}} \quad \dots (5)$$

For a good separation,  $M_1 M_2 = N^2$ , and  $M_1/M_2 = a_2/a_1$ ,

To calculate number of theoretical plates,  $N$ , assuming a degree of purity  $\Delta m/m$ , in separating the two species  $a_2/a_1$  must be known.

Then,

$$-\frac{\Delta m}{m} + 0.5 = A_e \left( \frac{N - M_1}{\sqrt{M_1}} \right) \quad \dots (6)$$

If we take  $\Delta m/m$  as 0.001 and  $A_e$  is obtained from table of error functions.

$$\frac{N - M_1}{\sqrt{M_1}} = \pm 3.08 \quad \dots (7)$$

Substituting for  $N = \sqrt{M_1 M_2}$  and  $M_1/M_2 = a_2/a_1$

$$\sqrt{M_1} \left( \sqrt{\frac{a_1}{a_2}} - 1 \right) = 3.08 \quad \dots(8)$$

If the bands are close together,

$M \approx N$ , then

$$\sqrt{N} \left( \sqrt{\frac{a_1}{a_2}} - 1 \right) = 3.08 \quad \dots(9)$$

$$\text{or } N = \left[ \frac{3.08}{(\sqrt{a_1/a_2} - 1)} \right]^2 \quad \dots(10)$$

The theoretical plate height,  $H$ , was obtained from the following expression (43).

$$H = 1.64r + \frac{D}{(D_v - \beta)^2} \left( \frac{0.142r^2 v}{D_r} \right) + \left( \frac{D_v}{D_v + \beta} \right)^2 \left( \frac{0.266r^2 v}{D_f(1+70)} \right) + \frac{D_f \beta \sqrt{2}}{V} \quad \dots(11)$$

where  $r$  is the radius of the resin beads, (in cm),  $V$ , is the velocity of the mobile (eluent) phase (in  $\text{cm s}^{-1}$ ) and  $D_r$ ,  $D_f$  are diffusion coefficients of the solute within the resin and liquid phases, respectively. Equation (11) shows that the plate height depends on the volume distribution ratio of the ionic

species. Thus, in a separation, the plate height is different for each species. Optimum operating conditions are achieved if the last three terms of the equation for  $H$  are equated to the first and to one another. It is also wise to double the first term to take into account inevitable irregularities in column packing (43). In this way the plate height is

$$H = (1.64r)(2)(3) = 10r \quad \dots(12)$$

The volume of a theoretical plate was calculated from the theoretical plate height and the cross-sectional area of the column tubing.

$$V_T = \pi R^2 H = 10\pi r R^2$$

The bed volume,  $V_b$ , which may be taken as the total volume of  $N$  theoretical plates was then obtained from the expression.

$$V_b = NV_T = 10\pi r R^2 N.$$

The other parameters,  $L$ , the length of column was calculated from  $N = L/H$  and  $M_r$ , the mass of resin required was obtained from the bed volume  $V_b$  and the density of the dry resin. Calculated values are shown in Table 4.4

Apparatus: 450 x 9mm glass column, 200cm<sup>3</sup> beaker, separatory funnel.

Reagents: All reagents were of the analytical grade unless otherwise stated.

Water: Deionised distilled water was used for the preparation of all solutions.

5% (m/v) silver nitrate solution: Prepared by dissolving 2.5g of BDH laboratory reagent in 50cm<sup>3</sup> of water.

5% (m/v) barium chloride solution: Prepared by dissolving 2.5g of reagent in 50cm<sup>3</sup> water.

10% (v/v) ammonia solution: Prepared by diluting 5cm<sup>3</sup> M & B standard reagent to 50cm<sup>3</sup> with water.

10% (v/v) hydrochloric acid: This solution was prepared by diluting 5 cm<sup>3</sup> of M & B standard reagent to 50cm<sup>3</sup> with water.

Synthetic mixture: Prepared by dissolving 1.17g sodium chloride, 1.06g anhydrous sodium carbonate and 1.28g lithium sulphate in water and diluting

to  $250\text{cm}^3$ . This solution contained a total of about 0.06 milliequivalent of the three ions per  $\text{cm}^3$ , calculated such that  $1\text{cm}^3$  of sample solution uses less than 2 percent of replaceable ions per gramme of dry resin.

Procedure: With the data of the calculation of column parameters as a guide, different amounts of the dry resin were soaked in water for six hours and the floating particles were removed by decantation. The slurry was poured into the column which was previously half-filled with water and then left to settle. The level of water above the resin was reduced to  $1\text{cm}^3$  and a calculated volume of the mixture (based on the total ion-exchange capacity of the resin) was transferred into the column. A  $100\text{cm}^3$  separatory funnel was filled with the eluent and was allowed to run through the column. The effluent was monitored by testing for the presence of each of the constituents of the synthetic mixture. The observed retention times with 0.05M sodium phenate solution are shown in Table 4.3.

## CHAPTER 4

## RESULTS AND DISCUSSION

## 4.1 Results:

TABLE 4.1

Results of qualitative analysis of anions.

| Sample Number | Physical Appearance | Solubility        | pH    | Anions indicated                                                             |
|---------------|---------------------|-------------------|-------|------------------------------------------------------------------------------|
| 1             | Grey                | Insoluble         | 10.50 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 2             | Greyish-white       | Insoluble         | 10.10 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ and $\text{CO}_3^{2-}$                    |
| 3             | Greyish-white       | Insoluble         | 10.70 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 4             | Grey                | Insoluble         | 10.80 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 5             | Pinkish-white       | Water             | 10.30 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 6             | Light-grey          | Insoluble         | 10.60 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 7             | Pinkish-grey        | Insoluble         | 6.70  | $\text{Cl}^-$ and $\text{SO}_4^{2-}$                                         |
| 8             | White               | Water             | 7.40  | $\text{Cl}^-$ and $\text{SO}_4^{2-}$                                         |
| 9             | White               | Water             | 6.90  | $\text{Cl}^-$ only                                                           |
| 10            | White               | Water             | 7.50  | $\text{Cl}^-$ and $\text{SO}_4^{2-}$                                         |
| 11            | Yellowish-grey      | Insoluble         | 7.20  | $\text{Cl}^-$ and $\text{SO}_4^{2-}$                                         |
| 12            | Grey                | Insoluble         | 10.60 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 13            | Pinkish-white       | Water             | 10.40 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 14            | Pinkish-white       | Dilute acid       | 7.10  | $\text{SO}_4^{2-}$ only                                                      |
| 15            | Dark-brown          | Insoluble         | 8.20  | $\text{Cl}^-$ and $\text{HCO}_3^-$                                           |
| 16            | Grey                | Concentrated acid | 10.80 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |

Table 4.1 (cont'd)

| Sample Number | Physical Appearance | Solubility  | pH    | Anions indicated                                                             |
|---------------|---------------------|-------------|-------|------------------------------------------------------------------------------|
| 18            | Light pink          | Water       | 7.40  | $\text{Cl}^-$ only                                                           |
| 19            | Brown               | Insoluble   | 10.70 | $\text{Cl}^-$ and $\text{CO}_3^{2-}$                                         |
| 20            | Grey                | Insoluble   | 10.40 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 21            | Grey                | Insoluble   | 10.90 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 22            | Grey                | Water       | 10.00 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ and $\text{HCO}_3^-$                      |
| 23A           | Grey                | Insoluble   | 10.60 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 23B           | Whitish-grey        | Water       | 10.40 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 24            | Whitish-grey        | Insoluble   | 10.50 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 25            | Grey                | Insoluble   | 10.60 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 26            | Dark-grey           | Insoluble   | 10.70 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 27            | Pinkish-white       | Water       | 10.20 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 28            | Pink                | Water       | 10.60 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 29            | Reddish-brown       | Insoluble   | 10.30 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ and $\text{CO}_3^{2-}$                    |
| 30            | White               | Water       | 6.60  | $\text{Cl}^-$ and $\text{SO}_4^{2-}$                                         |
| 31            | Light-grey          | Dilute acid | 10.60 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$                      |
| 33            | Grey                | Insoluble   | 10.70 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 34            | Whitish-grey        | Dilute acid | 10.80 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |
| 36            | Light brown         | Insoluble   | 10.40 | $\text{Cl}^-$ , $\text{CO}_3^{2-}$ and $\text{PO}_4^{3-}$                    |
| 37            | Dirty-white         | Water       | 9.80  | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |

Table 4.1 (cont'd)

| Sample Number | Physical Appearance | Solubility  | pH    | Anions indicated                                                             |
|---------------|---------------------|-------------|-------|------------------------------------------------------------------------------|
| 38            | Dirty white         | Water       | 7.70  | $\text{Cl}^-$ and $\text{SO}_4^{2-}$                                         |
| 40            | White               | Dilute acid | 6.70  | $\text{SO}_4^{2-}$ only                                                      |
| 42            | White               | Water       | 10.20 | $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ |

\*The colours of the salts are those of the ground samples.

TABLE 4.2

Results of quantitative analysis (expressed  
as percentage)

| Sample<br>No. | Carbonate | Hydrogen<br>Carbonate | Chloride | Sulphate | Moisture |
|---------------|-----------|-----------------------|----------|----------|----------|
| 5             | 0.93      | 0.97                  | 0.26     | 57.80    | 1.10     |
| 8             | BD        | BD                    | 0.14     | 67.37    | 0.42     |
| 9             | BD        | BD                    | 58.52    | BD       | 0.21     |
| 10            | BD        | BD                    | 56.97    | 1.45     | 0.64     |
| 13            | 21.22     | 7.76                  | 0.39     | 28.00    | 10.24    |
| 18            | BD        | BD                    | 48.92    | BD       | 4.40     |
| 22            | BD        | 1.08                  | 41.20    | 20.00    | 0.22     |
| 23B           | 22.62     | 18.39                 | 6.71     | BD       | 26.06    |
| 27            | 0.53      | 0.59                  | 0.31     | 64.54    | 0.60     |
| 28            | 19.52     | 9.33                  | 1.63     | 26.06    | 11.34    |
| 30            | BD        | BD                    | 59.45    | 1.12     | 0.34     |
| 37            | 0.72      | 1.09                  | 0.06     | 65.74    | 0.84     |
| 38            | BD        | BD                    | 0.18     | 62.78    | 0.16     |
| 42            | 0.94      | 0.58                  | 44.38    | 19.70    | 0.60     |

TABLE 4.3Observed retention times ( $t_R$ ) of the anions

| Parameter   | Mass of resin(g) | $Cl^-$ | $CO_3^{2-}$ | $SO_4^{2-}$ |
|-------------|------------------|--------|-------------|-------------|
| $K_d$       | 1                | 0.33   | 0.10        | 1.00        |
| $t_R$ (min) | 3*               | 26.00  | 38.00       | 48.00       |
|             | 5 <sup>+</sup>   | 36.00  | $\infty$    | $\infty$    |
|             | 10 <sup>x</sup>  | 65.00  | $\infty$    | $\infty$    |

\*  $CO_3^{2-}$  overlapped with  $Cl^-$  and  $SO_4^{2-}$ +  $CO_3^{2-}$  and  $SO_4^{2-}$  did not emerge after 82 minutes.

x Unscreened resin.

TABLE 4.4

Calculated column parameters

| $C_E$ (moles) | $a_1/a_2^*$ | $m/m$ | N     | H (mm) | $V_T = \pi R_H^2 H$<br>(mm <sup>3</sup> ) | $V_d = NV_T$<br>(cm <sup>3</sup> ) | m (g) |
|---------------|-------------|-------|-------|--------|-------------------------------------------|------------------------------------|-------|
| 0.01          | 0.33        | 0.001 | 52.70 | 1.8    | 114.51                                    | 6.00                               | 2.80  |
| 0.05          | 0.34        | 0.001 | 54.10 | 1.8    | 114.51                                    | 6.20                               | 2.90x |
| 0.10          | 0.35        | 0.001 | 56.60 | 1.8    | 114.51                                    | 6.50                               | 3.00  |
| 0.20          | 0.36        | 0.001 | 59.15 | 1.8    | 114.51                                    | 6.80                               | 3.10  |
| 0.01          | 0.33        | 0.01  | 46.10 | 1.8    | 114.51                                    | 5.30                               | 2.40  |
| 0.05          | 0.34        | 0.01  | 47.30 | 1.8    | 114.51                                    | 5.40                               | 2.50  |
| 0.10          | 0.35        | 0.01  | 49.06 | 1.8    | 114.51                                    | 5.60                               | 2.60  |
| 0.20          | 0.36        | 0.01  | 51.72 | 1.8    | 114.51                                    | 5.90                               | 2.70  |

\* On the basis of Cl(1) and SO<sub>4</sub><sup>2-</sup>(2)

x Chosen on account of the low impurity level and also for the more acceptable retention times produced by 0.05M eluent solutions.

TABLE 4.5

Major salts content of 'Kanwa' samples in percentage.

| Sample No. | *Na <sup>+</sup> | *K <sup>+</sup> | Moisture | HCO <sub>3</sub> <sup>-</sup> | CO <sub>3</sub> <sup>2-</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | Total  |
|------------|------------------|-----------------|----------|-------------------------------|-------------------------------|-----------------|-------------------------------|--------|
| 5          | 31.60            | 1.50            | 1.10     | 0.97                          | 0.93                          | 0.26            | 57.80                         | 94.16  |
| 8          | 31.10            | 0.47            | 0.42     | BD                            | BD                            | 0.14            | 67.37                         | 99.50  |
| 9          | 32.55            | 0.31            | 0.21     | BD                            | BD                            | 58.52           | BD                            | 91.59  |
| 10         | 34.20            | 0.22            | 0.64     | BD                            | BD                            | 56.97           | 1.45                          | 93.48  |
| 13         | 31.35            | 0.35            | 10.24    | 7.76                          | 21.22                         | 0.39            | 28.00                         | 99.31  |
| 18         | 16.15            | 33.50           | 4.40     | BD                            | BD                            | 48.92           | BD                            | 102.97 |
| 22         | 34.05            | 2.30            | 0.22     | 1.08                          | BD                            | 41.20           | 20.00                         | 98.85  |
| 23B        | 18.00            | 1.30            | 26.06    | 18.39                         | 22.62                         | 6.71            | BD                            | 93.08  |
| 27         | 27.05            | 2.45            | 0.60     | 0.59                          | 0.53                          | 0.31            | 64.54                         | 96.07  |
| 28         | 32.00            | 0.70            | 11.34    | 9.33                          | 19.52                         | 1.63            | 20.06                         | 100.58 |
| 30         | 27.65            | 0.65            | 0.34     | BD                            | BD                            | 59.45           | 1.12                          | 89.21  |
| 37         | 11.25            | 1.25            | 0.84     | 1.09                          | 0.72                          | 0.06            | 65.74                         | 80.95  |
| 38         | 30.10            | 0.35            | 0.16     | BD                            | BD                            | 0.18            | 62.78                         | 93.57  |
| 42         | 32.65            | 0.35            | 0.60     | 0.58                          | 0.94                          | 44.38           | 19.70                         | 99.20  |

\* Analysis by Ekanem.

TABLE 4.6

Ratio of carbonate to hydrogen carbonate in samples.

| Sample<br>Number | Concentration(moles/100cm <sup>3</sup><br>sample solution) |                       | Ratio of<br>occurence |
|------------------|------------------------------------------------------------|-----------------------|-----------------------|
|                  | Carbonate                                                  | Hydrogen<br>Carbonate |                       |
| 5                | $2.83 \times 10^{-4}$                                      | $2.92 \times 10^{-4}$ | 1:1                   |
| 13               | $6.82 \times 10^{-4}$                                      | $2.16 \times 10^{-4}$ | 3:1                   |
| 23B              | $5.62 \times 10^{-4}$                                      | $4.52 \times 10^{-4}$ | 1:1                   |
| 27               | $1.36 \times 10^{-4}$                                      | $1.50 \times 10^{-4}$ | 1:1                   |
| 28               | $6.53 \times 10^{-4}$                                      | $3.07 \times 10^{-4}$ | 2:1                   |
| 37               | $1.29 \times 10^{-4}$                                      | $1.92 \times 10^{-4}$ | 1:2                   |
| 42               | $4.80 \times 10^{-5}$                                      | $2.35 \times 10^{-5}$ | 2:1                   |

#### 4.2 Discussion.

It may not be considered strange that only fourteen out of the thirty eight samples analysed were water-soluble, particularly when it is realised that not many carbonate-containing substances are known to be water-soluble. This is not to say, however, that the insolubility of the samples was due solely to the presence of carbonate. Organic matter which was not determined in this study may also be partially responsible, but it must be mentioned nevertheless that qualitative test revealed that carbonate formed part of the insoluble residue of most samples. Although it is clear from Table 4.1 that carbonate and hydrogen carbonate were not regular features of the water-soluble samples, they were present in nearly all the insoluble samples. The two ions ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) generally occurred together in the samples, but it could be seen from Table 4.6 that the ratio of their occurrence is variable. Samples 5 and 27 contained equimolar quantities of carbonate and hydrogen carbonate. Similarly, sample 23B may be considered as containing carbonate and hydrogen carbonate in a 1:1 ratio. The carbonate (11-percent) and hydrogen carbonate (5-percent) are responsible for

the high pH values of the water extracts of the samples. A careful examination of Table 4.1 shows that the neutral samples do not contain these ions.

The ease of precipitate formation observed during the qualitative analysis, could be an indication that the insoluble samples probably contain higher carbonate content than the water-soluble samples indicate.

It has been mentioned in the introductory chapter that common salt is always present in saline lakes and that most of them contain sulphates. A careful examination of Table 4.1 confirms this assertion. The calculated average chloride content was 23-percent while sulphate was found to represent 38 percent.

Table 4.5 is presented to give an indication of the major salts, and hence of the minerals, that may be associated with 'kanwa'. Samples 9, 10 and 30 are obviously sodium chloride (halite) salts 'contaminated' by potassium salts and others not determined. On the other hand, samples 22 and 42 are mixtures of 'contaminated' sodium chloride and sodium sulphate. The results agree with the description of similar salts

in Appendix II. Beza (sample 9), Gallo (Sample 10) and Mangul (Sample 22 and 42) have been described as predominantly sodium chloride salts. Mangul was shown to contain sodium chloride predominantly in Table 1.1. Sample 18 is an interesting case of a pure mixture of sodium and potassium chloride, while samples 5, 8, 27, 37 and 38 may be regarded as 'adulterated' sodium sulphate. It is indicated in Appendix II that 'Jar kanwa' represented by samples 5, 27 and 37 and 'Gwangwarasa' represented by samples 8 and 38 are mainly sodium sulphate salts. The result of the analysis shown in Table 1.1 also showed that the latter variety of the salt is predominantly sodium sulphate.

Mention has been made of the fact that sample 5, 23B and 27 contain equimolar quantities of sodium carbonate and sodium hydrogen carbonate. These samples may, therefore, contain a sesquicarbonate of sodium (trona), occurring as an 'impurity' particularly in samples 5 and 27. Sample 23B may be considered as a mixture of this mineral and some halite.

The water of crystallisation ( $H_2O+$ ) of the salt which would have provided a clearer picture of the mineralogy was not determined. The moisture content ( $H_2O-$ ) alone cannot provide this information, but halite (sodium chloride) is present. Sodium sesquicarbonate (trona) and sodium sulphate decahydrate (Mirabalite) may also be present. The calculated average moisture content was about 4-percent indicating that the salt is not very hygroscopic.

The results of the ion-exchange chromatographic separation of chloride, carbonate and sulphate (Table 4.3) show that the process is not possible on a column packed with screened or unscreened Amberlite IRA-401 resin within reasonable time. Carbonate was found to overlap with either chloride or sulphate or with both chloride and sulphate, depending on the prevailing conditions of the column.

The three anion-chromatographic separations referred to earlier on in the introductory chapter seemed to emphasise the use of both low capacity and small particle size resin to achieve good separation.

Grinding of the resin to give particle size of 100 - 200 mesh or ~~higher~~ mesh may be necessary for the attainment of higher efficiency. It is also important to mention that the 4-percent cross-linkage of the resin employed in the study was insufficient and unsuitable for good separation, since the degree of cross-linkage is considered as one of the important factors which influence selectivity of a resin (44, 45).

The lower value of distribution coefficient obtained for carbonate relative to that of chloride (Table 4.3) may be attributed to the effect of the pH of the eluent (46). The latter had a pH value very close to that of sodium carbonate solution. This perhaps affected the dissociation of the sodium carbonate in a medium containing sodium phenate, leading to a decrease in the electrical charge of carbonate ion. The distribution of the carbonate ion was, therefore, almost completely prevented. In otherwords, the effect of the pH of the eluent almost completely excluded the carbonate ion from the resin. Consequently, it was unwise to use the  $K_d$  value for carbonate in the calculation of the

column parameters shown in Table 4.4. It was also observed that an eluent concentration of 0.05M produced fairly acceptable retention times although the elution peaks still overlapped and this tendency for overlap increased with increase in eluent concentration.

#### SUMMARY AND CONCLUSION

'Kanwa' is a strongly alkaline salt containing 11-percent Carbonate and about 6-percent hydrogen carbonate. Chloride (23-percent) and sulphate (38-percent) are also among the major ions associated with the salt. These ions occur mainly as the sodium salts. It is not very hygroscopic and contains about 4-percent moisture. Carbonate and hydrogen carbonate, when present, generally occur together in a ratio that is not fixed, but occasionally in a 1:1 ratio. 'Kanwa' may, therefore, contain sodium sesquicarbonate (trona) and may be regarded as a 'contaminated' mixture of the minerals, halite ( $\text{NaCl}$ ), trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) and mirabalite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), although evidence for the last mineral is not immediately available.

The separation of chloride, carbonate and sulphate on a chromatographic column packed with Amberlite IRA-401 resin, using sodium phenate solution as eluent may be achieved within reasonable time, provided the resin is first ground to obtain smaller particle size beads. Chloride, carbonate and sulphate are eluted in that order, but the cross-linkage of the resin (4-percent) is insufficient for high selectivity and good separation.

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APPENDIX IORIGIN AND COLLECTION POINT OF SAMPLES.

| Sample Number | Local Name      | Collection point | Origin*                     |
|---------------|-----------------|------------------|-----------------------------|
| 1             | Farar Kanwa     | Kano market      | Gashua or Nguru             |
| 2             | Bilma           | Kano market      | Bilma in Kavar Oasis, Niger |
| 3             | Gari            | Kano market      | Gashua                      |
| 4             | Farar Kanwa     | Geidam market    | Chilluma salt works         |
| 5             | Jar kanwa       | Geidam market    | Kaitawa in Niger Republic   |
| 6             | Ungurnu         | Maidugiri market | Kanem, across Lake Chad.    |
| 7             | Tsumbur tsumbur | Kano market      | Tohoua, Niger Republic      |
| 8             | Gwangwarasa     | Kano market      | Gashua                      |
| 9             | Beza            | Kano market      | Mirria, Niger Republic      |
| 10            | Gallo           | Kano market      | Tahous, Niger Republic      |
| 11            | Kante fa fashi  | Kano market      | Fashi, Niger Republic       |
| 12            | Ungurnu         | Kano market      | Maiduguri                   |
| 13            | Jar Kanwa       | Kano market      | Bilma, Niger Republic       |
| 14            | Gwangwarasa     | Geidam market    | Adebur, Niger Republic      |
| 15            | Mandu Chu       | Maiduguri Market | Geidam                      |
| 17            | Mangul          | Maiduguri market | Gashua or Geidam            |
| 18            | Manda chu       | Geidam market    | Dankindiri, Niger Republic  |
| 19            | Mangul          | Geidam market    | Fanamiram                   |
| 20            | Mangul          | Geidam market    | Wandorem, Niger Republic    |

## Appendix I (cont'd)

| Sample Number | Local Name    | Collection point | Origin*                            |
|---------------|---------------|------------------|------------------------------------|
| 21            | Manguli       | Maiduguri market | Geidam or Gashua                   |
| 22            | Manguli       | Geidam market    | Tatekutu, Niger Republic           |
| 23A           | Ferar kanwa   | Jajimaji market  | Gatilla                            |
| 23B           | Gari          | Nguru            | Thoudeni                           |
| 24            | Ferar kanwa   | Not indicated    | Not Indicated                      |
| 25            | Gari          | Jajimanji market | Karagu in Niger Republic           |
| 26            | Bakin manda   | Nguru market     | Niger Republic                     |
| 27            | Jar kanwa     | Jajimanji market | Karagu, Niger Republic             |
| 28            | Jar kanwa     | Maiduguri market | Geidam                             |
| 29            | Red salt      | Tahoua market    | Dirkou in Kewar Oasis              |
| 30            | Not indicated | Tahoua market    | Tegidda M'Tessoum, Niger Republic. |
| 31            | Ungurnu       | Tahoua market    | Thoudeni, Niger Republic           |
| 33            | Bakin Manda   | Nguru market     | Wacha in Niger Republic            |
| 34            | Balma         | Nguru market     | Karagu, Niger Republic             |
| 36            | Mangul        | Nguru market     | Tsumbar, Niger Republic            |
| 37            | Jar Kanwa     | Geidam market    | Malaka                             |
| 38            | Gur ngwarasa  | Jajimaji market  | Niger                              |
| 40            | Gajimaria     | Kano market      | Geidam                             |
| 42            | Mangul        | Geidam market    | Adebur, Niger Republic             |

\*Information in respect of the origin of the samples was obtained from the traders at the various collection points.

# APPENDIX II

## DISTRIBUTION AND USES OF KANWA.

| Type                                                      | Source                                         | Uses                                                                                   | Extent of Distribution                                                                 |
|-----------------------------------------------------------|------------------------------------------------|----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Farar kanwa<br>(kwaras kwaras)<br>White or gray<br>natron | Muniyo, Man-<br>gari, kanwar,<br>Asben Zaberma | Culinary,<br>Medicinal,<br>Soap-mak-<br>ing, snuff-<br>making,<br>dyeing tex-<br>tiles | Central Sudan, Benue,<br>Cross River areas,<br>Yoruba states<br>Benin Republic, Borgu. |
| Gari (powdered<br>farar kanwa)                            | Same                                           | Livestock<br>feed,<br>medicinal                                                        | Sokoto Caliphate,<br>Borno, Southern<br>Sahara.                                        |
| Jar kanwa (red<br>natron)                                 | Muniyo,<br>Mangari,<br>Kawar.                  | Medicinal,<br>Culinary                                                                 | Sokoto Caliphate<br>Borno.                                                             |
| Ungurnu<br>(natron)                                       | Chad shores<br>Bahr<br>al-Ghazal               | Medicinal,<br>general<br>health, snuff<br>making                                       | Sokoto Caliphate,<br>Asante Borno, Shari<br>basin etc.                                 |
| Gwang warasa<br>(natron)                                  | Mangari                                        | Tanning,<br>animal<br>medicine                                                         | Sokoto Caliphate<br>Borno.                                                             |
| Gallo (sodium<br>chloride pre-<br>dominate)               | Tejuidda                                       | Medicinal,<br>Culinary                                                                 | Kano, Zaria,<br>probably elsewhere.                                                    |

## Appendix II (cont'd)

| Type                                         | Source                        | Uses                            | Extent of Distribution                         |
|----------------------------------------------|-------------------------------|---------------------------------|------------------------------------------------|
| Kige (sodium chloride predominante)          | Chad shores, Mangari          | Culinary                        | Borno, perhaps Mandara.                        |
| Mangul (high sodium chloride content)        | Mangari                       | Culinary, Medicinal             | Borno, Mandara, Sokoto Caliphate.              |
| Beza (best sodium chloride salt)             | Kawar, Agram, Asben, Taoudeni | Medicinal, Culinary, Ink-making | Sahara, Sokoto Caliphate, Borno, elsewhere.    |
| Balma, Kantu (most common Kawar salt)        | Kawar                         | Medicinal, Culinary, Ink-making | Sahara, Sokoto Caliphate, Borno, elsewhere.    |
| Fachi, (like Kantu)                          | Agram                         | Same                            | Same                                           |
| Gishirin Foga (sodium chloride predominante) | Dallol Fogha                  | Culinary                        | Western Sokoto Caliphate, Borgu, Songhay.      |
| Dan awai (sodium chloride and impurities)    | Awe                           | Culinary                        | Bauchi, Kano, Zaria, Jos Plateau, Benue Basin. |
| Dan wase (same)                              | Bomanda                       | Culinary                        | Yola, Benue Basin.                             |

## Appendix II (cont'd)

| Type                                                         | Source                    | Uses                  | Extent of Distribution              |
|--------------------------------------------------------------|---------------------------|-----------------------|-------------------------------------|
| Dan Keana<br>(sodium chloride cent sites.<br>and impurities) | Keana, adja-              | Culinary<br>Medicinal | Plateau, Benue basin.               |
| Kakanda (adul-<br>terated sodium<br>chloride)                | Niger-Benue<br>confluence | Culinary              | Benue-Niger valleys,<br>Kano Zaria. |