

Compositional and Structural Characterization of Three Basic Indigenous Salts Used in Kenya: A Case Study of 'Ebara', 'Magadi' and 'Lebek' Crystalline Salts.

^{1c*}Osano Aloys Mosima, ^{2*}Okong'o Eric Rangondi, ^{1*}Oyaro Nathan and ^{2*}Kiptoo Jackson

^{1*}Department of Chemistry, School of Science, Narok University College P.O. Box 861, Narok. Kenya

^{2*}Department of Chemistry, Faculty of Science, Jomo Kenyatta University Agriculture Technology P.O. Box 62000, Nairobi. Kenya.

^{1c*} Corresponding Author-Aloys Mosima Osano

ABSTRACT

Compositional analysis was carried out on three indigenous basic salts from Lake Magadi, Shores of Lake Victoria and the Hot Springs of the Kerio Valley which are different parts of Kenya. All treatments were done in triplicate in complete randomized block design. Fresh and dry weights were recorded at the end of the experiment and analysed for K, Na, Ca, Mg, Co, Fe, Mn, Cu, Pb, Cd, Zn cations and CO_3^{2-} , and HCO_3^- anions. The three different indigenous basic salts are commonly referred as 'magadi', 'Para', and 'Lebek' respectively from the three areas. pH, quantitative and qualitative analysis was done using Atomic Absorption Spectroscopy, Flame Photometry, FTIR and the wet methods; Gravimetry and titrimetry. A wet digestion procedure was adopted to dissolve the salts. In general, the concentration of heavy metals in the salts followed the order: magadi; $\text{Fe} > \text{Co} > \text{Pb} > \text{Cd} > \text{Mn} > \text{Zn} > \text{Cu}$; Para; $\text{Fe} > \text{Mn} > \text{Co} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cd}$; Lebek; $\text{Fe} > \text{Mn} > \text{Zn} > \text{Co} > \text{Cu} > \text{Pb} > \text{Cd}$. Sodium, Potassium and calcium content was found to be very high in all the samples. Sodium concentration was recorded to be 71.52 mg/g in 'Magadi', Potassium concentration was found to be 2.69 mg/g in 'Para', and calcium concentration was found to be 166.09 mg/g in 'Lebek'. Samples of 'Para' and 'Lebek', contained comparatively higher amounts of Fe as compared to 'magadi'. Lead is present in higher levels in all the samples than minimum levels. The pH values ranged from 9.98 ± 0.01 to 11.26 ± 0.03 , an indication of the alkaline nature of these salts.

Key words: *Indigenous salts; Composition; Characterisation; Heavy metals; Hydrolysis*

INTRODUCTION

Magadi, Para and Lebek are commonly used salts in several countries in East, West, and Central Africa homes [1,2]. The main use of these indigenous salts is cooking tough food materials such as beans and maize utilising their ability to fasten the softening and the digestive property of the food. In addition, the salts are used as prophylactic agents and feed supplements to cattle and goats [1]. In some places, 'magadi' is ground with tobacco in the preparation of snuff [2].

In the alkaline lakes of Eastern Rift Valley, 'magadi' is formed in the crystalline form ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), due to chemical weathering of rock minerals and high evaporation of the lake waters. Magadi is also formed, as the so-called scooped magadi, on the surface soil due to capillary evaporation of soil water [3].

Analyses of both crystalline and scooped magadi from Nigeria and Ghana have shown that crystalline magadi consists essentially of trona mixed with minor contents of halite (NaCl). The scooped magadi is rich in trona but it also contains admixtures of quartz, clays, chlorides, and sulphates [3,4].

The main objective of this study was to determine the differences in metallic ions (Zn, Li, Na, K, Ca, Mg, Pb, Cu, Mn, Copyright © 2013 SciResPub.

Cd, Co) and carbonate (CO_3^{2-} , HCO_3^-) concentration in Magadi, Para and Lebek from the Eastern, Western, North Rift and Kendu-bay parts of Kenya. The differences in the mineralogical composition caused by the differences in structure will also be discussed.

EXPERIMENTAL

Instrumentation and wet chemistry methods of Analysis

Buck Scientific Model 210VGP Atomic Absorption Spectroscopy and Corning Flame 840 photometry were used to analyse the metallic ion composition of the salts. FTIR spectroscopy and potentiometry were used to identify the structure of each salt using carbonates and bicarbonates in them and measure pH respectively. Gravimetry and titrimetry were used for the quantification of CO_3^{2-} , HCO_3^- and pH measurement.

Sample Collection and Analysis

Magadi samples from Lake Magadi, ($n = 15$), Para samples from Kendu-bay at the shores of Lake Victoria ($n = 30$), Lebek samples from Kerio-valley ($n = 30$) and market places ($n=3$)

were collected, packaged dry in paper bags and taken to the laboratory. In the laboratory, each sample was crushed and homogenized in a mortar. About 10.00-20.00 grams of each salt sample was oven dried in a 100.00 mL beaker at a temperature of 110°C for 2.0 hours. A triplicate mass of 2.000 grams of each of the cooled dried salt sample were weighed and dissolved in 100.00 mL beaker with 50.0 mL of de-ionized water. The solution was then filtered using Whatman filter paper No. 42 [5,6].

The pH of the clear filtrate was measured after which the filtrate solution was acidified with 1.0 mL 0.1M HNO₃, placed into a 100.0 mL volumetric flask and filled to the mark with more de-ionized water. The solutions were corked and mixed thoroughly and were ready for metallic ions analysis using AAS and Flame photometry. For quantification of CO₃²⁻ and HCO₃⁻, a triplicate mass of 0.700 grams of each of the cooled dried salt sample was weighed and dissolved in 100.00mL beaker with 50.00mL of de-ionized water. The solution was then filtered using Whatman filter paper No. 42. The end point titration method according to the standard methods where the end point of pH = 4.5 was used. An aliquot of 5.00 ml of the magadi solutions (2.00 g/100.0 ml) was diluted to

50.0 ml and titrated automatically with 0.1 N HCl [3,4]. The samples were categorized as: MS100 series, samples of mineral salts ('Magadi'), PS200 series, samples of mineral salts ('Para'), and LS300 series, samples of mineral salts ('Lebek')

Results and Discussion

From table 1.0, the pH values recorded for MS100, PS200 and LS300 oven dried were 11.26±0.03, 10.88±0.06 and 10.85±0.06 respectively. The pH values of non-oven dried samples were 9.98±0.01, 10.08±0.02 and 10.09±0.02 respectively for the three salt types. Magadi salt recorded the least pH in its raw form because of the acidic hydrogen in the CO-H bicarbonate. The large difference between oven dried and non-oven dried clearly indicates the decomposition and loss of most of acidic hydrogen during the drying stage, increasing the pH proportionately with HCO₃⁻. Magadi salt had the highest amounts of hydrogen carbonates as compared to both para and lebek salts. These findings correlate well with earlier studies [7,8] which recorded similar observations of pH increase wherever HCO₃⁻ decomposed.

Table 1.0: The pH of the salts (1% wt/v solution)

Salt sample	Sample treatment	
	Oven dried (OD)	Non-oven dried
MS100	11.26±0.03	9.98±0.01
PS200	10.88±0.06	10.08±0.02
LS300	10.85±0.06	10.09±0.02

Functional group analysis of the salts using FTIR.

Figures one to three below show the functional group analysis of the salts using FTIR

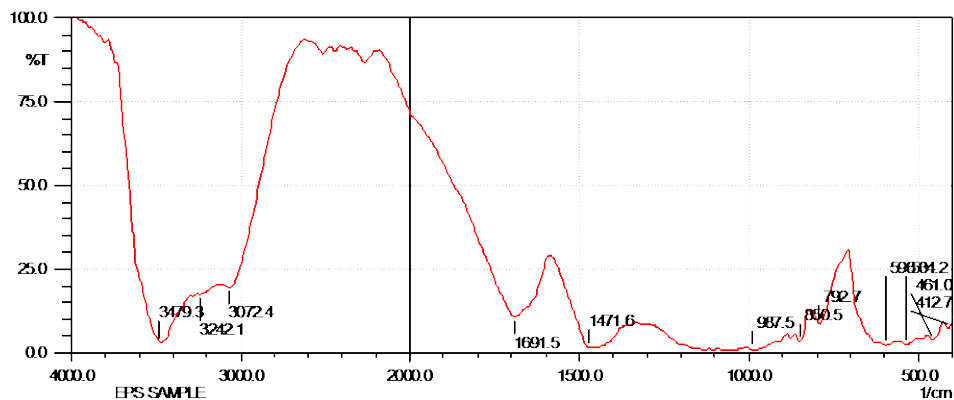


Figure 1: FTIR spectrum of PS200-salt

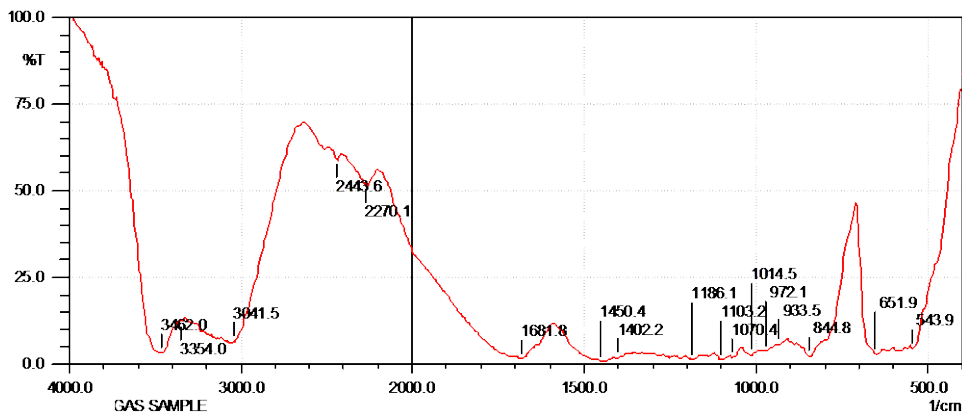


Figure 2: FTIR spectrum of MS100-salt

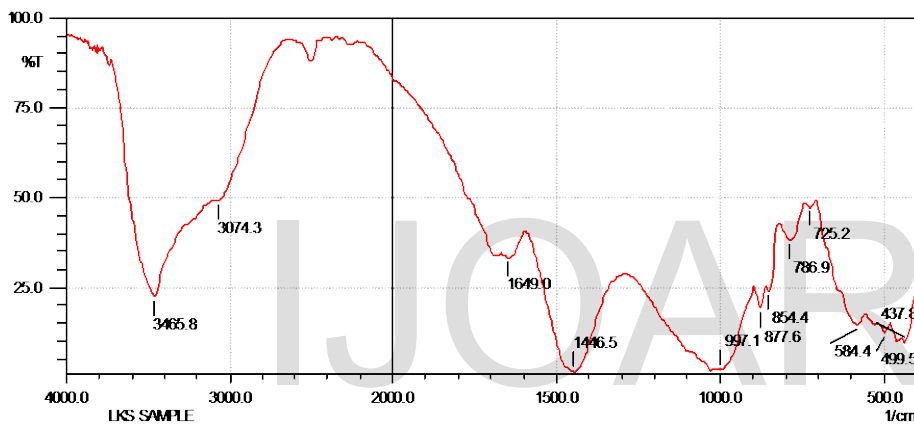


Figure 3: FTIR spectrum of LS300-salt

From figures one to three, it was observed that all the salts showed FTIR major peaks at 3479-3482 cm^{-1} , 1650-1690 cm^{-1} and 950-1000 cm^{-1} ranges due to the -O-H, C=O and C-O stretches respectively. This is an indication of the presence of a carbonate and bicarbonate anions in the salts [9]. The salts contain the two anions. This is in agreement with studies earlier done on metal carbonates and bi-carbonates. In the FTIR transmission spectra of metal bi-carbonate salts, bands for free HCO_3^- ion in aqueous solution were assigned as follows: stretching of C-OH at 1010 cm^{-1} , symmetric stretching of CO_2 at 1360 and 1310 cm^{-1} , asymmetric

stretching of CO_2 at 1668 and 1605 cm^{-1} , and out-of-plane bending of CO_3^{2-} at 843 cm^{-1} . The rest of the fundamental vibration modes, (symmetric in-plane bending of CO_3^{2-}) and (asymmetric in-plane bending of CO_3^{2-}) should appear below 800 cm^{-1} , a spectral region which could not be observed. This is correlates well with earlier studies [7,8,10]

Major elements composition levels

Table 2 below shows the composition of alkali and alkaline earth metals in dry salt samples

Table 2.0: Composition in mg/g of alkali and alkaline earth metallic elements in dry salt

Samples	Alkali and Alkaline earth Metal Composition in mg/g				
	Na	K	Li	Ca	Mg
MS100	71.52±1.96	0.31±0.04	0.21±0.02	0.25±0.12	0.02±0.00

PS200	27.23±0.87	2.69±0.41	0.29±0.02	52.56±8.03	2.89±0.13
LS300	25.83±0.38	1.37±0.05	0.15±0.02	166.09±6.55	0.16±0.00

Sodium concentration in MS100, PS200 and LS300 salts was 71.52±1.96, 27.23±0.87 and 25.83±0.38 respectively. Most of the magadi minerals were sodium based. [11,12]. LS300-salt had the highest Calcium concentration amounts with a mean concentration of 166.09±6.55 mg/g .This could be attributed to the calcite rock source from which the hot spring bines originate. This is in line with other studies done on Lake Brines in Africa [4, 13, 14]. Potassium concentration in PS200-salt had the highest amounts with a mean concentration of 2.69±0.41 mg/g . The concentration of potassium ions in all the three salts was less than 3.00 mg/g. This is in line with studies done in Lake Magadi [11] and Lake Albert [7] which showed that potassium is in low concentration because of leaching during salt precipitations.

Magnesium concentration in PS200-salt was highest amounts with a mean concentration of 2.89±0.13 mg/g .The concentration of magnesium ions in all the three salts was low, as compared to studies done in Lake Magadi [11]. Lithium concentration in PS200-salt had the highest amounts with a mean concentration of 0.29±0.02 mg/g .These results were comparable to those obtained [5,15] and reported that this could be due to the trace nature of lithium in mineral rocks.

Major anions content

Table three below shows the percentage anionic radical content in dry salt samples.

Table 3.0: Percentage (%) Anionic radical Content wt/wt in dry salt sample

Samples	Anionic radicals Content % wt/wt		
	Carbonate CO ₃ ²⁻	Hydrogen carbonate HCO ₃ ⁻	Total Carbonate CO ₃ ²⁻ & HCO ₃ ⁻
MS100	21.9±0.5	25.3±0.3	47.2±0.2
PS200	6.5±0.4	7.3±0.2	13.9±0.3
LS300	5.5±0.1	6.2±0.1	11.8±0.4

The percentage concentration of CO₃²⁻ ranged from 5.5±0.1% to 21.9±0.5%. MS100-salt recorded the highest percentage of total carbonate with a mean percent concentration of 47.2±0.2%, with the mean percent CO₃²⁻ of 21.9±0.5% and hydrogen carbonate (HCO₃⁻) 25.3±0.3%. PS200-salt recorded the second highest percentage of total carbonate (13.9±0.3%) of the salt samples analyzed; with the percent carbonate (CO₃²⁻) being 6.5±0.4% and hydrogen carbonate (HCO₃⁻) 7.3±0.2%. LS300-salt recorded the third highest percentage of total carbonate (11.8±0.4%) of the salt samples analyzed; with the percent carbonate (CO₃²⁻) being

5.5±0.1% and hydrogen carbonate (HCO₃⁻) 6.2±0.1%. This conforms to the earlier studies [11,15] which recorded similar results. This could be due to the fact that, the final major reaction that could influence the HCO₃⁻ contents in the deep aquifer is the addition in the system of CO₂ of deep origin [5,10].

Trace elemental content

Table four below shows the composition of trace metallic elements in dry salt samples.

Table 4.0: Composition in µg/g of trace metallic elements in dry salt samples

Samples	Trace Metallic elements in µg/g						
	Zn	Co	Cu	Pb	Cd	Fe	Mn
MS100	9.06±2.73	20.69±1.02	2.91±0.38	16.16±0.43	11.15±1.20	214.79±16.63	10.21±2.97

PS200	15.33±2.43	15.74±0.60	8.44±0.32	12.83±1.30	2.87±0.27	1650.63±133.89	396.90±35.72
LS300	23.01±3.09	20.49±1.49	10.07±1.04	9.50±1.37	2.24±0.15	5068.59±460.97	346.81±0.47

Iron concentration in LS300-salt had the highest amount with a mean concentration of 5068.6±461.0 µg/g. It was followed by PS200-salt with a mean concentration of 1650.6±133.9 µg/g, while MS100-salt had a mean concentration of 214.8±16.6 µg/g. The salts PS200 and LS300 showed quite significant amounts as compared to MS100. The same trend was reported [5,6], in which it was attributed to the salts rock of origin, clay rock which is rich in iron and manganese .

Manganese concentration in PS200-salt had the highest amount with a mean concentration of 396.90±35.72 µg/g. It was followed by LS300-salt with a mean concentration of 346.81±0.47 µg/g, while MS100-salt had a mean concentration of 10.21±2.97 µg/g. The salts PS200 and LS300 showed quite significant amounts as compared to MS100. These can be attributed to the salts rock of origin, [5,6].

Zinc concentrations in KS300-salt had the highest amount with a mean concentration of 23.01±3.09 µg/g .It was followed by PS200-salt with a mean concentration of 15.33±2.43 µg/g; while MS100-salt had a mean concentration of 9.06±2.73 µg/g. Zinc in the salts generally recorded substantial amounts considering its trace nature. These could be due to the rock source [15].

Lead concentrations in MS100-salt had the highest amount with a mean concentration of 16.16±0.43 µg/g). It was followed by PS200-salt with a mean concentration of 12.83±1.30 µg/g, while LS300-salt had a mean concentration of 9.50±1.37 µg/g. Lead levels in the salts falls beyond the normal minimum levels in residues. This was attributed to the underlying rock source, and the conditions of the underground brine fluids [14].

Copper concentration LS300-salt had the highest amount with a mean concentration of 10.07±1.04 µg/g. It was followed by PS200-salt with a mean concentration of 8.44±0.32 µg/g, while MS100-salt had a mean concentration of 2.91±0.38 µg/g. Copper levels in the salts falls beyond the reported values 4.0-6 µg/g in residues [5,6,15], which was attributed to the underlying rock source, and the conditions of the underground brine fluids.

Cadmium concentration in MS100-salt had the highest amount with a mean concentration of 11.15±1.20 µg/g . It was followed by PS200-salt had a mean concentration of 2.87±0.27 µg/g and LS300-salt had a mean concentration of 2.24±0.15 µg/g. Cadmium concentration levels in the salts falls within the normal

minimum levels of 2-5 µg/g in residues for samples PS200 and LK300 but remained high in MS100 this correlates well by studies done earlier [6,13]. This could be attributed to the underlying rock source, and the conditions of the underground brine fluids [14].

Cobalt concentration in MS100-salt had the highest amounts of Cobalt with a mean concentration of 20.69±1.02 µg/g (table 4.0), while LS300-salt had a mean concentration of 20.49±1.49 µg/g and PS200-salt had a mean concentration of 15.74±0.606 µg/g. Lead levels in the salts falls beyond the normal minimum levels 5-10 µg/g in residues as reported [16]. This could be due to the underlying rock source, and the conditions of the underground brine fluids [14].

Conclusion

The three salts differ in their percent elemental compositional levels greatly (MS100 had 71.53 mg/g Na, and 0.25 mg/g Ca; PS200 had 27.23 mg/g Na and 52.56 mg/g Ca and LS300 had 25.83 mg/g Na and 166.09 mg/g Ca). The salts have the same carbonate and bi-carbonate structure which only differs in percent concentration levels (MS100 had 47.2%; PS200 had 13.9% and LS300 had 11.8% total carbonate).

Magadi salt is basically a sodium carbonate-sodium bi-carbonate. The bicarbonate content is slightly higher than the carbonate. Para and Lebek salts have small amounts of carbonates and bi-carbonate and they are more of calcium and iron salts. All the three salts were found to be alkaline salts with pH values greater than 9.8. FTIR spectra showed that all the three salts had bicarbonate in their structure.

Acknowledgements

The authors gratefully acknowledge the National Council of Science and Technology (NCST) for providing the Research grant for this project, the department of chemistry Jomo Kenyatta University for providing the AAS and FTIR machines and technical assistance and Maasai Mara University for laboratory facilities.

REFERENCES

1. W. J Mavura et al, Vicres Annual Forum 9-13th October, *Chemical composition of indigenous salts consumed in*

2. E.K. Ankrah, F.E. Dovlo, *Journal of Science of Food*

- and Agriculture ,*The properties of Trona Known as Kawe and Its Effect on the Cooking Time of Cowpeas.* 29 ,950-952, (1978).
3. J.M. Nielsen and E Dahi . 2nd International workshop on Fluorosis Prevention and Defluoridation of water , Copenhagen ,Denmark, *Fluoride Contamination And Mineralogical Composition Of East African Magadi (Trona)* (2010).
 4. O.A Sodipo , American Journal of Public Health , , 83,1181 (1993)
 5. A.A.Makanjuola and J.G. Beetlestone , Journal of Mining Geology, 10 ,31-41 (1975).
 6. W.N. Sharp, United States Geological Survey Professional Paper, *Extensive zeolitization associated with Hot Springs in Central Colorado.* 700B, B14-B20 (1970).
 7. N.B.Tatiana et al, American Mineralogist, 95, 1515–1522, (2010)
 8. S.Chunming and D. L. Suarez, Clays and Clay Minerals, 45, No. 6, 814-825 (1997).
 9. C.K Huanc and P F. Konn, The American mineralogist. 4,5 (1960)
 10. S. M . Teleb, E.D Nassr and E. M. Nour , Bulletin Material Science, 27, no. 6, 483–485, (2004).
 11. H.P.Eugster, Mineralogical Society of America, Special Paper 3, 213-235, (1970).
 12. M.F. Hill, *The story of the Magadi Soda Company.* Kynoch Press, Birmingham ,199 (1964).
 13. J.F.Talling and I.B. Talling, Internationale Revue der Gesamten Hydrobiologie, 50, 421-463 ,(1965).
 14. Tata Chemicals Magadi, *Sales Specification CRS.* Reference: SS/CRS.01, Issue No. 2, (2003)
 15. N.J. Guest and J.A Stevens , Geological Survey Tanganyika Mineral Resources Pamphlet. 58,21 (1951).
 16. P. R.Gazis and T. Roush, Journal Geophysics Res., 106(E4), 7765–7773,(2001).

IJOART