ELEMENTAL AND STRUCTURAL CHARACTERIZATION OF SOLAR EVAPORATED SALTS FROM TAMILNADU, INDIA

SANTHANAKRISHNAN T.[1], LAKSHMANAN C.[2] and RADHAKRISHNAN V.[1]

[1] Department of Marine Science, Bharathidasan University, Trichy, India.
[2] Department of Botany, V.O.Chidambaram College, Thoothukudi, India.
E-mail: vrkgeologist@gmail.com, krizshnaa@gmail.com

ABSTRACT

Salt is the most commonly used food additive and preservative. Since most of the salt consumed in India is obtained from solar evaporation, there is variation in the quality of salts which depends upon the chemistry of brine or sea water. It is obvious that one can trace structural incongruencies in the salts consumed in different places of India due to the difference in the amount of minerals in the soils. The moisture, insoluble matter content, elemental analysis of heavy metal composition present in the salt samples has been analyzed by physicochemical studies. A wide analysis by radiation techniques viz, XRD and FTIR results of salt samples from salt producing areas of Tamil Nadu revealed a range of typical anionic and cationic chemical composition of salts. XRD interpretations provide various crystallinity and compositional variation in the salts whereas FTIR helps to identify functional groups and various bonding nature of mineral species. This study fills a significant gap in the salt related research. Salts from Thoothukudi and Vedaranyam are generally or largely accepted for human consumption than the other regions because quality stands up to edible. Hence, this research towards structural and compositional analysis of the salts from these places helps to identify the better places for quality salt consumption.

Keywords: Sodium chloride, solar evaporation, XRD, FTIR, salt consumption

1. Introduction

Salt is a universal mineral commonly used by virtually every person in the world. Although a very common mineral today, at one time, it was considered as precious as gold in certain culture. The term salt has different meaning and definitions according to people in different regions. Chemically, salt is a generic term given to any one of a class of similar compounds formed when all or part of the hydrogen ions of an acid are replaced with a metal or metallic radical. Salt also is the specific chemical name given to sodium chloride (NaCl). Salt or sodium chloride is synonymous and interchangeable term. Salt used for human consumption is composed of 40 % sodium and 60% of chlorine, by weight (Dennis S. Kostick 1992). Solar salterns (saltworks) are man-made systems of interconnected ponds for the production of salt from seawater/ subsoil brine, by means of solar and wind evaporation. Solar salt works are the extreme ecological environments. Solar evaporation is the most common and traditional method for salt production in India. Tamil Nadu is the second largest salt producing state in India, around 40 % of the salt has been produced through solar evaporation. Globally 30 % of the solar salt used for the human consumption. 100 gm of brine was evaporated to produce 27.24 gm of salt crystals which have plenty of NaCl and some amount of other impurities like calcite and sylvite. Remaining brine sample containing lots of chemical compounds like $MgSo_4$, $CaCo_3$, etc. NaCl (halite) is the major mineral for the brine sample. The natural solar salt contains some essential and non-essential minerals and metals. The higher intake of non-essential metals through the salt consumption may create some disorders. The structural characterization of solar salt samples, collected from various salt pans of Tamil Nadu, was done for mineralogical investigations. Content of heavy metals like Cd, Co, Fe, Pb, Ni and Zn in salts are compared. Four solar salt samples analyzed using X-ray Diffractometer (XRD) which confirms that samples mainly consist of halite (NaCl) along with some inclusion of KCl and $CaCl_2$ at much less amount (Saral 2000). The mineral bonding vibrations were investigated with the help of FTIR.

2. Materials and methods

The four samples of raw salt were collected from the major solar salt industries in Tamil Nadu viz, Chennai, Poducherry, Vedaranyam and Thoothukudi during the peak season of salt production. The 500 gm of salt were collected and packed with dry polythene bag that stored in laboratory at room temperature. The moisture content and insoluble matters were analyzed (AOAC 1990). Then, ionic elements of potassium, magnesium, calcium, sulphate as well as sodium and chloride were estimated by titrimetric method (Onwuka 2005) while the heavy metals like copper, iron, lead, cadmium, nickel and zinc were analyzed (Soylak et al. 2008 and Peker et al. 2007) using atomic absorption spectrophotometer. The salts were investigated for their vibration spectra with infrared spectroscopy using Perkin Elmer 1800 model instrument from 450 cm-1to 4400 cm-1 by using KBr tablet. X-ray peak heights were used as gross indicators of the relative proportions of minerals present (Sinha and Raymahashay 2004). X-ray diffraction studies inform about the other crystallite systems that present in the salt samples other than NaCl and their compositions.

3. Results and discussion

3.1. Moisture and Insoluble contents

Table 1shows moisture and insoluble contents of samples. Moisture content varies from 4.27 to 5.94 % which indicates the water molecules are absorbed by the salt. Low moisture content was observed in Thoothukudi salt compared with others because of the atmospheric temperature and wind action is high.

Table 1: Moisture and insoluble matter content in salt samples from major saltpan areas of Tamil Nadu

parameters	Chennai	Poducherry	Vedaranyam	Thoothukudi	Mean
Moisture (%)	5.62	5.94	4.91	4.27	5.19
Water Insoluble matter (%)	0.82	0.81	0.76	0.58	0.74

3.2. Chemical elements

Elemental analyses of six chemical elements such as sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), sulfate (So_4) and chloride (Cl)) are shown in Table 2, for the salt samples obtained from east coast area of Tamil Nadu and poducherry. Elemental analyses inform the considerable similar concentration of Ca, SO_4^{2-} and K, with greater concentration of Na, and Cl along with very low concentration of Mg in all salt. Nearly 35 to 36% of Sodium and 56 % of chloride has been recorded in all salt samples that indicate the good quality of solar salt (Kovac et al, 2013). While Ca and K are equally concentrated with mean values of 0.21 cg/g and 0.25 cg/g respectively. Mg is 0.001 to 0.003cg/g and SO_4 is 0.018 to 0.029 cg/g. Predominant elements of salts ions. Na and Cl range from 34.83 to 36.28cg/g and 56.09 to 56.23 cg/g respectively.

Table: 2: Elemental analyses of salt samples of different saltpan areas of Tamilnadu

Elements (cg/g)	Chennai	Poducherry	Vedaranyam	Thoothukudi	Mean
Na	34.97	34.83	36.28	36.22	35.57
Cl	56.2	56.13	56.09	56.23	56.16
Ca	0.21	0.19	0.18	0.29	0.21
Mg	0.003	0.001	0.002	0.001	0.89
SO_4^{2-}	0.021	0.029	0.024	0.018	0.88
K	0.29	0.31	0.27	0.25	0.25

Table: 3: The heavy metal concentration in solar salts of different saltpan areas of Tamilnadu

Heavy metals (mg/kg)	Area of salt pans				
	Chennai	Poducherry	Vedaranyam	Thoothukudi	Mean
Cadmium	0.04	0.034	0.042	0.04	0.04
Copper	1.86	2.01	1.91	2.16	2.01
Iron	3.84	3.95	3.61	4.01	3.85
Lead	2.06	2.35	1.96	2.01	2.09
Nickel	0.56	0.61	0.52	0.56	0.56
Zinc	0.007	0.007	0.005	0.006	0.005

3.3 Heavy Metals

Cadmium, besides carcinogenic, is detrimental to human health causing bone and renal failure [Ciobanu et al, 2012, and Eftekhari et al, 2014]. Cadmium concentration ranged from 0.034 to 0.042 mg/kg. According to Codex legislation, the maximum permitted level of cadmium in food grade salt is not more than 0.5 mg/kg (Codex Stan 150-1985). The cadmium content of our samples was less than these figures.

Copper ranged from 1.86 to 2.16 mg/kg with mean values of ---. The specific values see table 3. Codex and WHO, limit the level of copper in food grade salt to 2.0 mg/kg. In solar salt samples, copper was 2.16 mg/kg in Thoothukudi, 2.01 in Pondicherry, 1.91 mg/kg in Vedaranyam and 1.86 mg/kg in Chennai. It is slightly more in Thoothukudi saltpan product due to the pollution (INSA 2011). At low concentration, copper is an essential metal for human health, even though more intake of this element is toxic, it leads to liver and kidney damage (Zarei et al, 2011**)** and may cause heamolysis, hepatotoxic and nephrotoxic effects (Watson. 1993, and Sharif et al, 2007).Iron is one of the major essential elements for human being, excessive intake of iron turns toxic (Clark, 2008). In this study, the concentration of Fe found as 3.84 mg/kg, 3.95 mg/kg, 3.61 mg/kg and 4.01 mg/kg in Chennai, puthucherry, Vedaranyam and Thoothukudi respectively in all salt samples of Tamil Nadu. Iron plays an important role in human body metabolisms. And also act as an oxygen carrier for human body (Jacob and Wormwood, 1974).The maximum acceptable limit of lead concentration in food grade salt is 2.0 mg/kg, according to the Codex legislation. In solar salt samples, lead concentration is 2.06 mg/kg, 2.35 mg/kg, 1.96 mg/kg and 2.01 mg/kg in Chennai, Pondicherry, Vedaranyam and Thoothukudi respectively. The lead concentration is higher in all salt samples except in Vedaranyam. This may be attributed to the raise of pollutions as a result of Thermal power plants, ceramics industries, etc, *(*INSA 2011). Lead is also one of the toxic elements to human health affect different functional systems and organs like central and peripheral neural system, gastrointestinal tract, muscles, kidneys and hematopoietic system [Ciobanu, 2012].The toxic effects of Nickel concentration have been reported on the respiratory system, gastrointestinal tract, liver, and kidneys (Codex Stan 150-1985, Aktas Y K, et al, 2005). It also leads to neurological disorders (Zemanova, J .et al, 2007). The nickel concentration in turn of the listed pans of Tamil Nadu salt found to be 0.56 mg/kg, 0.61 mg/kg, 0.52 mg/kg and 0.56 mg/kg. This amount of nickel is very low and in acceptable limit of Codex legislation and WHO. Similarly zinc is also an essential component for human health at low concentrations, but in excessive amount, it is potentially hazard and to both animal and human health [Papagiannis et al, 2004]. The zinc deficiency leads to growth failure, poor in gonaidal function, mental illness and heart diseases (Sharif et al, 2007). It has been found that the concentration of Zinc in all salt samples is very low like 0.007mg/kg, 0.007mg/kg, 0.005mg/kg, and 0.006 mg/kg. This concentration of zinc is in the range of acceptable limit of Codex legislation and WHO.XRD and FTIR results help identify halite, gypsum, calcite, quartz and sylvite minerals in the saltpan samples analyzed. The foresaid minerals are also in accordance with mineralogical observation in different salts (Aral, et al, 2004 and Kovac et al, 2013). Further it helps to determine the structure and its variation with respect to change in the mineralogical composition of raw salts.

3.4. XRD characterization

XRD is used to determine the mineralogical composition of the raw material components as well as qualitative and quantitative phase analysis of multiphase mixtures. X-ray diffraction results show the presence of halite potassian in all the salt, it is the major mineral composing solar salt (Yalçin and Mutl, 2011). The elemental analytical results clearly indicate the dominancy of sodium and chloride along with other elements in all salt. The occurrences of minerals in salt were identified by JCPDF software and compared with Graham Ohmsen 2004. The possible minerals and their 'PDF number' values are presented in the Table 5. The PDF no should be determining the mineral compounds present in the samples. No quantitative estimation phases in these adsorbents have been made but their characterization of XRD patterns indicates the presence of halite potassian, sylvite, gypsum, calcium silicate sulphate as the major phases (Fig 1). Further the occurrence of the above minerals in the aforesaid adsorbents was confirmed by FTIR study.

3.5. FTIR Characterization

FTIR studies of the salts help in the identification of minerals present in the solar raw salts. The coupled vibrations are appreciable due to availability of various constituents in the salt. In Fig. 2, FTIR spectrum of salt is shown. In all salt samples, there are 3864, 3854, 3735, 3635, 1631 peaks.These peaks obtained due to the vibration of water molecules in the structure of salt sample. The absorption band at 1631 cm^{-1} is due to the H-O-H bonding of water molecule. The absorption ~ at 2360 cm^{-1} is because of the C=O molecule vibration which may present as carbon moiety in the salts due to the environmental pollutions which is observed in all samples.

Table 4: XRD result for salt samples

Area	Compound determined	PDF number
Thoothukudi	Halite potassian, syn	75-0305
Vedaranyam	Halite potassian, syn	26-0919
Poducherry	Halite potassian, syn	75-0304
	Gypsum	76-1746
	Calcium silicate sulphate	26-1071
Chennai	Halite potassian, syn	75-0306
	Calcium silicate sulphate	26-1071
	Calcium sulphate	89-1458

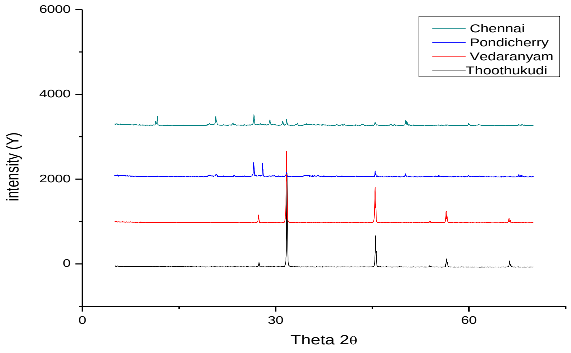

Figure: 1. XRD pattern of salt samples

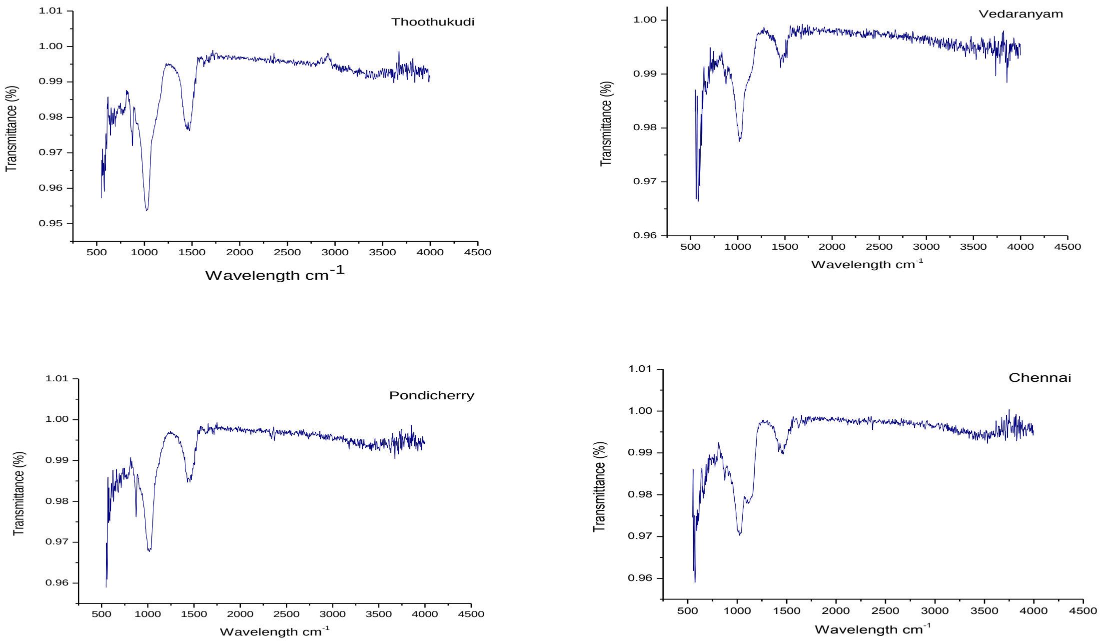

Figure: 2. FTIR spectrum in salt samples

4. Conclusions

Moisture, insoluble matter, elemental and heavy metal composition of various salt samples from various salt samples from selected salt pans of Tamilnadu. Salt pans were analyzed. Moisture and water insoluble matters present in all salt samples are accepted levels by WHO. The chemical analysis of solar salts as the experiment indicated that the chemical compositions vary significantly between Cl-K-Ca-SO4-Mg. The raw salt is dominated by Na and Cl, with lesser quantities of K, SO_4^{2-}, Ca and Mg. it is clear that salts are chiefly composed of halite. The average concentrations of heavy metals (mg/kg) in the solar salt are Fe (3.852), Pb (2.095), Cu (1.985), Ni (0.562), Cd (0.39) and Zn (0.0026) in the order of abundances. These levels of trace metal concentration in salt samples are in the accepted limits by Codex legislation and WHO for human consumption. XRD and FTIR analyses show that all salt samples are mainly constituted with halite potassian, sylvite in major quantities and Calcium silicate sulphate, Calcium sulphate and other elements in minor quantities of all solar salt samples.

REFERENCE

1. Aktas YK. and Ibar H. (2005) Determination of chromium, copper, manganese, nickel and zinc by flame atomic absorption spectrometry after separation of bentonite modified with trioctylamine. J Indian ChemSoc, 82:134–136.
2. AOAC (1990), Official methods of analysis, 15th ed, Washington D.C Association of Analytical,
3. Aral.H, B. D. Hill, G. J. Sparrow G.J., (2004), CSIRO Minerals Report DMR-2378, Value Adding to Salts Recovered from Saline Waters in Disposal Basins in the Murray-Darling Basin, Proof of Concept Study, Appendix 2 – Production of Salts from Brines and Bitterns, MDBC Publication No. 80/04, Murray-Darling Basin Commission 2004, 37 p., http://www2.mdbc.gov.au/data/age/334/Appendix2.pdf, (assessed: October 12, 2011). Chemistry pp1546.
4. Ciobanu C., Slencu BG. and Cuciureanu R. (2012) Estimation of dietary intake of cadmium and lead through food consumption. Rev Med ChirSoc Med Nat Iasi, 116(2):617–623.
5. Clark S F. (2008), Iron deficiency of anemia, Nutr, Clin, Pract, 23 (2): 128-41.
6. Codex Alimentarius Commission: Codex standard for food grade salt. CX STAN 150–1985, Amend. 1-1999, Amend. 2-2001, Amend. 3-2006. 2006:1–7. URL: http://www.docstoc. Com/?DocId=155745518&download=1.

7. Watson. D., (1993) Safety of chemicals in food chemical contaminants, published by Ellis.New York, p 109.
8. Dennis S. Kostick. (1992), The material flow of salt. United States, bureau of mines; 9343 september 1992.
9. Graham Ohmsen. (2004), Quantitative X-Ray Diffraction And Chemical Analysis of Tsp And Pm10 Filters Collected From Ummock Hill, Walls Street And Civic Park, Whyalla. Environmental Health Service, Department Of Health, South Australian.
10. Indian National Science Academy (2011), Hazardous Metals and Minerals Pollution in India. BahadurshahZafarMarg, A Position Paper August 2011New Delhi and printed at Angkor Publishers (P) Ltd., Noida.
11. Jacob A and WormwoodM, (1974), Blood and its disorder, R.M Hardest and D. J Weatherall.P 135.
12. Mohammad Hassan Eftekhari, Seyed Mohammad Mazloomi, MarziehAkbarzadeh and MojdehRanjbar, (2014) Content of toxic and essential metals in recrystallized and washed table salt in Shiraz, Iran. Journal of Environmental Health Sciences & Engineering, 12:10.
13. NivesKovac, NeliGlavasMatejDolenec, Nastja Rogan smuc and Zdenkaslejkovec, (2013) Chemical composition of natural sea salt from the secovljesalina(gulf of Trieste, northern Adriatic. ActaChim.Slov, 60: 706–714.
14. Onwuka, G.I. (2005) Food analysis and instrumentation (Theory and Practice). 1st edition. Naphtali prints, Surulere, Lagos.pp.50-58.
15. Papagiannis I, Kagalou I, Leonardos J, Petridis D, Kalfakakou V. (2004) Copper and zinc in four freshwater fish species from Lake Pamvotis (Greece). EnzvironInt, 30:357–362.
16. Peker DSK, Turkoglu O, Soylak M. (2007) Dysprosium (III) hydroxide coprecipitation system for the separation and preconcentration of heavy metal contents of table salts and natural waters. Journal of Hazardous Materials. 143: 555-560.
17. Qazi Muhammad Sharif, MumtazHussian and Muhammad TahirHussain(2007) chemical evaluation of major salt deposits of Pakistan, jour, chem. Soc. Pak vol. 29, no. 6, 569
18. Saral.R, M.Sc. Thesis, Gebze Institute of Technology, Kocaeli (Turkey).
19. Soylak M., Peker D. andTurkoglu O. (2008) Heavy metal contents of refined and unrefined table salts from Turkey, Egypt and Greece. Environ Monit Assess. 143(1-3):267-72.
20. Yalçin S. and MutluI.H, (2011) Structural Characterization of Some Table Salt Samples by XRD, ICP, FTIR and XRF Techniques. Proceedings of the International Congress on Advances in Applied Physics and Materials Science, Antalya 2011. ActaPhysicaPolonica A, Vol. 121.
21. Zarei M., Eskandari MH. andPakfetrat S, (2011) Determination of heavy metals content of refined table salts. American-Eurasian Journal of Toxicological Sciences, 3(2):59–62.
22. Zemanova J., Lukac N., Massanyi P., Trandzik J., Burocziova M.and Nad P. (2007), Nickel seminal concentrations in various animals and correlation to spermatozoa quality. J Vet Med A 2007, 54:281–286.