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Studies on the Quality and Heavy Metals in Common Salt Production Using Sea Brine and Sub-Soil Brine in South Tamil Nadu, India

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Abstract - **The manufacture of common salt using sea brine and sub-soil brine contain several chemical and trace metal elements.This study estimated the salt quality parameters like moisture content, insoluble matter, calcium sulphate, magnesium sulphate, magnesium chloride and sodium chloride content of the salt and also estimated the different trace metals like copper, iron, zinc, manganese and chromium in salts harvested from the Salt samples of two selected salt works, Kovalam SW_1 (sea brine) and Puthalam SW_2 (sub-soil brine) in Kanyakumari District and the two selected salt works, Vepalodai SW_3 (sea brine) and Sahupuram SW_4 (sub-soil brine) in Tuticorin District. The salt samples have maximum moisture content in Kanyakumari salt works than Tuticorin District because of the climatic conditions. The salt works using sea brine, harvested salt of the maximum mean sodium chloride content than sub-soil brine using salt works. In both the Districts, sea brine using salt works is having almost similar concentration of heavy metals, likewise sub soil brine using salt works.**
Keywords: **Quality, Common Salt Production, Sea Brine, Sub-Soil Brine**

I. INTRODUCTION

Sea salt contains 92 essential minerals and most all refined adulterated sea salts contain only 2 elements (Na^+ and Cl^-). Biologically, 24 of these elements in real sea salt have already been proven necessary and essential to maintain and recover health (Earl Friden, 1972). The rice eating population requires more salt than others, because rice is deficient in salt. In temperate climate, the annual human requirement of salt is about 5kg/year and it is more in the tropical countries (D.W.Kaufmann, 1960). Sodium and chloride are found in almost all foods. Salt is added to many pet foods, and as we know, can increase the flavour of foods. Sodium and chloride may also be bound to minerals or molecules such as vitamin K or potassium (K). Salt is produced mainly by solar evaporation of sea water, lake and sub soil brines. More than 50% of the countries undergo solar salt production. While the process for solar evaporation of brine is same around the world over, the manufacturing techniques and product quality vary considerably (United Nations Industrial Development Organisation, 1968).

The quality and quantity of the salt depends upon the quality of the brine used, the salt as marketed should not contain more than 6.5% moisture and not more than 1.5 % insoluble matter. The associated salt i.e., magnesium chloride should not exceed 1.2% and no other allied salt may exceed 1% (S.C.Agarwall, 1956). The technique of solar salt production involves fractional crystallization of salts in different ponds to get common salt in the purest form possible (P.Sorgeloos *et al.*, 1990). Common salt is essentially sodium chloride and its quality is determined by its sodium chloride content, the higher the percentage, the purer the salt. Besides human requirement of the salt of good quality, high purity of salt is necessary for all kinds of heavy chemical industries that use salt as their raw material. But, the impurities in the sea salt are unavoidable. In fact the multiplicity of impurities in salt, their relative quantities and how they influence the salt properties are so variable that every salt needs to be considered on its own merits.

Thus the impurities and the various elements present in source water greatly influence the quality of salt. Except for insolubles, the origin of impurities is the sea water. Calcium sulphate is the most persistent companion of sea salt. Magnesium salts are always present in the sea salt, usually in the ratio of approximately one and a half weight units of magnesium chloride and one weight of magnesium sulphate. In America and other advanced countries, salt of as high as 99.9% purity is manufactured and offered for sale. , salt produced in properly designed salt works has a purity of 90 to 95% NaCl, 1% calcium salts, 1to 2% magnesium salts and 5 to 8% water. If the salt is washed and dried, its purity can be improved upto 99%. According to the typical standards adapted in the developing countries the purity required is 99.5% for grade I industrial salt, 98.5% for grade II industrial salt, 97% for table salt and 96% for edible common salt. In the developed countries the specifications are more stringent, the minimum purity prescribed for table salt being 99.5% (G.Leemarose, 2007). Thus high quality of salt is expected not only for human consumption but also for various other uses.

The term ‘trace metal’ may describe a metal found in trace amounts in an organism (eg., less than 0.01%) of the mass of organism or may have a further restriction and apply only to those metals required in metabolism (Rainbow,1986).

Manganese is required for the enzyme needed to synthesize the mucopoly sacharide in cartilage and bone. It also plays a key role in activating enzymes required for carbohydrate and lipid metabolism problems associated with manganese deficiency include weakness, slow growth, shift joints and high birth mortality. Manganese compounds appear to be the most effective scavengers of other trace elements (P.Miramand *et al.*, 2001). Along with iron, copper is also necessary in haemoglobin formation. Zinc is an essential micronutrient in all marine organisms, being a cofactor in nearly 100 enzymes (B.L.Vallee *et al.*,1990). Zinc is required throughout the body to activate enzymes and to form metallo enzymes. These enzymes are required for metabolism and protein synthesis. The daily requirement of manganese for human is about 2-3 mg and zinc is 15 mg.

As salt manufacture is a semi agricultural operation, during monsoon season, the harvest would be stopped. During the study period heavy rain was experienced by all the salt works during the months of November and December 2013 and hence salt samples were not available during these two months and also in the following month January 2014.

II. STUDY AREA

Salt samples from the the two selected salt works, Kovalam and Puthalam (SW_1 and SW_2) of Kanyakumari District and the two selected salt works, Vepalodai and Sahupuram (SW_3 and SW_4) of Tuticorin District.The salt samples were collected and monthly for the period of one year from July 2013 to June 2014.

III. MATERIALS AND METHODS

Salt samples were packed in air tight polythene containers. The different salt quality parameters like, the moisture content, the insoluble matter, calcium sulphate, magnesium sulphate, magnesium chloride and sodium chloride content were analyzed on wet basis as per the PFA ACT using standard methods. The determination of all the chemical parameters was done by the standard procedures (A.I.Vogel, 1961). The heavy metals of copper, iron, zinc, manganese, and chromium were analysed using Atomic Absorption Spectrophotometer (AAS). An average and standard deviation were taken of the data presented monthly during the study period.

IV. RESULTS AND DISCUSSION

Table I provides the mean and standard deviation of salt quality parameters. The mean value of moisture content of the salt samples fluctuated between 4.02±0.16 to 9.26 ± 0.41%, while samples had a maximum mean value of 9.26 ± 0.41% recorded in SW_2 and a minimum mean value of 3.02 ± 0.16 % recorded in SW_3. The fluctuations in the percentage of moisture clearly indicated that the atmospheric climate influenced the moisture content. The comparison between the salt samples from Kanyakumari and Tuticorin Districts, the moisture content was lower in Tuticorin District samples ie (SW_3 and SW_4).

TABLE I THE MEAN AND STANDARD DEVIATION OF VARIOUS SALT QUALITY CONTENT (%) OF THE SALT SAMPLES DURING THE STUDY PERIOD JULY 2013 – JUNE 2014

Salt Works	Moisture Content (%)	Insoluble Impurities (%)	$CaSO_4$ Content (%)	$MgSO_4$ Content (%)	$MgCl_2$ Content (%)	NaCl Content (%)
SW1	7.23±0.77	0.84±0.05	0.38±0.05	1.37±0.07	1.21±0.10	89.25±0.61
SW2	9.26±0.41	0.93±0.38	0.24±0.03	1.54±0.06	1.48±0.19	86.51±0.71
SW3	3.02±0.16	0.24±0.02	0.43±0.03	1.14±0.13	1.22±0.03	94.01±0.38
SW4	5.11±0.62	2.15±0.41	0.88±0.10	1.40±0.16	1.81±0.22	85.90±1.03

The mean insoluble impurities presented in the samples under investigation had a wide range between 0.24 ± 0.02 to 2.15 ± 0.41 %. The maximum amount of insoluble impurities was present in SW_4 and the minimum amount was present in SW_3 throughout the period of investigation. The insoluble impurities in the salt works are due to the bad treatment of the pan floors and also the monsoonal rain, which spoil the salt pan floors at regular interval and also muddy area. In the present study, the insoluble impurities in the salt work SW_3, the value 0.24 ± 0.02% is almost equal to the value 0.1 to 1% reported for sea salt in other parts of India. In SW_3, the pond managements, pan flooring is once done properly.

Calcium sulphate is the most persistent companion of solar sea salt (Food and Nurtition Board, 2004). The mean value of calcium sulpahte present in the samples was ranged from 0.24 ± 0.03 to 0.88 ± 0.10%. The minimum mean value of 0.24 ± 0.03% was estimated in the salt samples of SW_2. The maximum value of 0.88 ± 0.10% was estimated in the salt samples of SW_4. Celtic sea salt had a mean calcium sulphate content of 0.435 %, whereas the earlier report (A.Chidambarathanu, 1997). This value is almost same in the present study. The mean value of calcium sulphate content 0.43% was estimated in SW_3.

The magnesium sulphate and magnesium chloride impurities in the sea salt were within the ratio 1:1:5(L.Crisman *et al.*, 1996). But the salts of the present study magnesium sulphate values are slightly greater or almost equal to the magnesium chloride content. The same observation had been noticed by earlier workers in the salt samples of the study area in Kanyakumari District ie.,(SW_1 & SW_2) where the magnesium sulphate content was higher than magnesium chloride (G.Leemarose,2007). In the present study the mean value of magnesium sulphate content was maximum 1.54 ± 0.06% in SW_2. The magnesium sulphate content was minimum 1.14 ± 0.13% in SW_3.

In the present study mean value of magnesium chloride content in the salt samples ranged from 1. 21 ± 0.10 to 1.81 ± 0.22%. The maximum chloride content 1.81 ± 0.22% was observed in the salt samples of SW_4. The minimum value of 1. 21 ± 0.10% was observed in SW_1.

The accumulation of magnesium sulphate and magnesium chloride in the salt samples was mainly due to the non elimination of bittern in the crystallizer ponds after each scraping of salt. In SW_4, salt work had no proper channel for bittern. The magnesium rich liquor gets stagnated and remains in the crystallizers for a long time. Hence, when sodium chloride crystallizers, they trap more and magnesium salts in the lattice making it impurities.

SW_1 and SW_3 both salt works used pure sea brine, harvested salt of the maximum mean sodium chloride content of 94.01 ± 0.38% was observed in SW_3. The minimum mean sodium chloride content of 85.9 ±1.03% was observed in SW_4. Because of the climatic condition (dry weather) and proper pond management, proper layout and elimination of bittern during the salt production process enhance the maximum mean sodium chloride content in SW_3 i.e., 94.01 ± 0.38%. The mean sodium chloride content of 89.25 ± 0.61% in SW_1, was confirmed by earlier workers (A.Chidambarathanu, 1997). SW_2 and SW_4 both salt works are used subsoil brine for salt production, harvested salt samples with mean sodium chloride content was 86.51 ± 0.71%, 85.9 ± 1.03%. The salt quality parameters revealed that moisture content was maximum during the rainy season while the sodium chloride content was maximum during the other seasons.

An increase in concentration of magnesium salts in sodium chloride crystals resulted in an increase in amount of moisture content resulting in reduction of sodium chloride content (J.G.Walmsley, 1997). The data on the monthly variation in the salt quality parameters revealed that moisture content was maximum during the rainy season while the sodium chloride content was maximum during other seasons. The salt samples having maximum moisture content in Kanyakumari salt works than Tuticorin District because of the climatic conditions.

Table II provides the mean and standard deviation of heavy metal concentration (ppm) of salt samples. The accumulation of copper in the salt harvested ranged from 0.011 ± 0.0049 to 0.079 ± 0.0053 ppm. Among these, the maximum of 0.079 ± 0.0053 ppm and the minimum of 0.011 ± 0.0049 ppm values were recorded at the salt samples from SW_4, SW_3 respectively.

TABLE II THE MEAN AND STANDARD DEVIATION OF HEAVY METAL CONCENTRATION (PPM) OF SALT SAMPLES DURING THE STUDY PERIOD JULY 2013 – JUNE 2014

Salt Works	Copper(ppm)	Iron(ppm)	Zinc(ppm)	Manganese(ppm)	Chromium(ppm)
SW_1	0.028±0.0034	0.048±0.0037	0.049±0.0038	0.15±0.0235	2.5±0.2759
SW_2	0.072±0.0053	0.0316±0.0052	0.12±0.0208	0.19±0.0350	0.79±0.0660
SW_3	0.011±0.0049	0.046±0.0017	0.038±0.0034	0.07±0.0322	1.4±0.2698
SW_4	0.079±0.0029	0.028±0.0037	0.16±0.0255	0.20±0.0135	0.89±0.0899

The accumulation of iron in the salt harvested ranged from 0.028 ± 0.0037 to 0.048 ± 0.0037ppm. Among these, the maximum 0.048 ± 0.0037ppm at SW_1 and the minimum 0.028 ± 0.0037 ppm values were recorded at the salt samples from SW_4.

The accumulation of zinc in the salt harvested ranged from 0.038 ± 0.0034 to 0.16 ± 0.0255 ppm. Among these, the maximum 0.16 ± 0.0255 ppm at SW_4 and the minimum 0.038 ± 0.0034 ppm values were recorded at the salt samples from SW_3.

The accumulation of manganese in the salt harvested ranged from 0.07 ± 0.0322 to 0.20 ± 0.0135ppm. Among these, the maximum 0.20 ± 0.0135ppm at SW_4 and the minimum 0.07 ± 0.0322 ppm values were recorded at the salt samples from SW_3.

The accumulation of chromium in the salt harvested ranged from 0.79 ± 0.0660 to 2.5 ± 0.275 ppm. Among these, the maximum 2.5± 0.275 ppm at SW_1 and the minimum 0.79 ± 0.0660 ppm values were recorded at the salt samples from SW_2.

In the present study, salt sample obtained from subsoil brine (i.e., SW_2, SW_4) accumulated maximum copper content of 0.072ppm and 0.079 ppm, whereas sea salt (SW_1, SW_3) accumulated the minimum copper content of 0.028 ppm and to 0.011 ppm. The mean copper content reported in the commercial sea salt is 0.0014 ppm, which is almost equal to the value recorded for the sea salt 0.011ppm in the present investigation. The amount of zinc accumulated in the salt samples ranged from 0.049 to 0.16 ppm. According to the UK food standards committee report, zinc levels in food should not exceed 50ppm. This shows the zinc content present in the salt samples is below the acceptable limit.

The low iron concentration of 0.020 ppm was reported in the sea waters of the Cadiz Bay (Jose Usero, 2003). In the salt samples, the iron content ranged from 0.028 to 0.048 ppm. The mean iron content recorded in the commercial sea salt was 0.015 ppm, which is slightly higher value to the minimum value reported in the present study.

When compared to other heavy metals, manganese content was present higher in salt samples. In the salt samples, the amount on manganese ranged from 0.07 to 0.20 ppm. The mean value of manganese reported in the commercial salt was 0.038 ppm.

Moreover, the amount of chromium recorded in the salt samples was ranging from 0.79 to 2.5 ppm. This value was agreeable with the earlier report (G. Leemarose, 2007). The amount of chromium in the salt sample was lesser than (3.5 ppm) the recommended by the west Australian food and Drug Regulations List.

V. CONCLUSION

The salt samples have maximum moisture content in Kanyakumari District than Tuticorin District because of the climatic conditions. The salt works used pure sea brine, harvested salt of the maximum sodium chloride content than sub-soil brine used salt works. Because of the climatic condition (dry weather) and proper pond management, proper layout and elimination of bittern during the salt production process enhance the quality of salt. In both the Districts, Kanyakumari and Tuticorin, Salt production using sea brine is having almost similar concentration of heavy metals, likewise salt production using sub soil brine.

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