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Chemical Characterisation of Himalayan Rock Salt

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Abstract. Present study involves the chemical evaluation of rock salt samples collected from the plugging sites of Himalayan salt (Khewra salt mines and Kalabagh salt mines) for their moisture content, water insoluble matter, calcium, magnesium, sulphate content and trace minerals such as Fe,Cu,Cd,Pb,As,Ag and Zn determined by atomic absorption spectroscopy. Moisture content of Khewra and Kalabagh salt samples ranged from 0.03 wt. % to 0.09 wt. % and 0.06 % to 0.08 %, respectively. Water insoluble matter ranged from 0.08 wt. % to 1.4 wt. % and 1.5 wt. % to 2.8wt. % for Khewra and Kalabagh salt samples, respectively. Sulphate content for Khewra salt sample was from 0.39 % to 0.91 % and for Kalabagh salt mines from 0.75 wt. % to 0.95wt. %. For Khewra salt mines calcium ranged 0.15wt. % to 0.32wt. % and for Kalabagh salt samples from 0.1 wt. % to 0.27wt. %. Magnesium ranged from 0.11 wt. % to 0.35wt. % for Khewra salt mines, while for Kalabagh salt samples its range was 0.18wt. % to 0.89wt. %. Trace metals had the concentration ranges between 0.2 to 1.85 mg/kg for copper; between 0.21 to 0.42 mg/kg for manganese; between 0.04 to 0.06 mg/kg for zinc; between 0.12 to 0.18 mg/kg for arsenic and between 0.03 and 0.05 mg/kg for lead while cadmium content was either below the method's detection limits or in very trace amounts. The results show that the concentrations of all the parameters studied are below the limits set by World Health Organization (WHO) and Food and Agriculture Organization (FAO). Therefore, it can be concluded from the paper that the Himalayan salt from the plugging sites of Khewra and Kalabagh salt mines are safe to use.

Keywords: atomic absorption spectrophotometer, minerals, water insoluble matter, sulphate

Introduction

Mining of salt for consumption and food preservation has been practiced for millions of years (Eftakhari *et al*., 2014). Underground mining of salt in Austria and Romania is from new Stone Age (Zarei *et al.,* 2011). Salt is also obtained from the salt lakes. It is found that salt from lakes and seas is with more minerals, less purity and higher water insoluble matter, calcium, magnesium and sulphate content (Pourghesari *et al*., 2014). Table salt is sold in many forms in market such as refined, unrefined and fortified salts. Unrefined rock salt after mining is ready to use after minor mineralogical operations which involve mainly the removal of dust and mud etc. (Heshmati *et al*., 2014). Usage of unrefined salts is in its oldest uses. It is also referred to as the industrial salt. A few mining operations used in mining are packing and its transport (Celik and Oehlenchlar, 2007).Unrefined salts are 96 % pure and have some essential trace minerals such as Mg, Ca, S, N and I etc. Unrefined salt is still the preferable choice of consumers in developing countries despite of the fact that several health agencies have discouraged its usage (Al-Rajhi, 2014). In order to give a whitish look and to increase its shelf life and purity, table salt has undergone through various mineralogical operations. Refined salts are usually 99% pure (Eftekhari *et al.*, 2014). Beside the Na^+ and Cl^-ions in the common salt, some other inorganic trace minerals such as Ca, Mg, Fe and S are also present. Proportion of these minerals is higher in unrefined salts (Tandon and Singh, 2000).

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Himalayan rock salt deposits are among the largest and oldest salt deposits of the world located in Pakistan .Its discovery goes back in 320BC when horses from the troops of Alexander licked the salt. But it became functional for exploration in Mughal reign (Sedivy, 2009). Eighty two billion tonnes (Elsagh and Rabbani, 2010) to 600 billion tonnes (Elsagh, 2012) of rock salt is estimated from these salt deposits. Many researchers have studied mineral characterisation and chemical evaluation of these salt deposits (Hassan and Mohyuddin 2016; Cheraghali *et al*., 2010) but very little is known about their impact on the public health. Parameters used for these evaluations were moisture; water insoluble particles heavy metals, Mg^{2+}, SO_4^{2-}, Cl^-, Na^+, and K (Hassan and Mohyuddin, 2016; Pourgheyshari *et al*., 2014).

Environmental samples like food, salt, water and soil are getting contaminated day by day so a complete chemical evaluation of these environmental samples is very essential (Khaniki *et al*., 2007). Present work involves characterisation of % purity, sulphate, moisture, calcium and magnesium content and minerals (Fe,Cu,Cd, Pb,As, Ag and Zn) in the unrefined table salt samples collected from major Himalayan rock salt plugging sites of Khewra and Kalabagh salt mines in Pakistan to insight their chemical nature. Present work also involved the comparison of unrefined salt samples with the standards regarding human health.

Materials and Methods

Collection of Samples. Salt samples from the plugging sites of Himalayan rock salt (Khewra and Kalabagh) were collected from 25cm below the mining sites. Sample excavation was done with the help of traditional axe used for the mining. Eight samples each of 4kg of weight and rectangular form were collected from the mining site of Khewra salt mines. The same procedure was employed for seven samples collected from the Kalabagh salt mines. After collection they were packed into the Polyethylene bags. In laboratory salt samples were then crushed and sieved to 80 meshes then transferred to air tight glass containers.

Sample preparation. Unrefined salt samples were crushed, sieved to 80 meshes and then stored in the air tight glass containers. One gram of each of sample was taken to dissolve in 100 mL of double distilled water. Residue was separated by filtration. Volume of filtrate was made up to 250 mL to be analysed (ASTM, 2002).

Moisture content. Sample (0.05g) was placed in an oven to calculate its moisture content using a dried and previously tarred moisture dish. This tarred moisture dish was placed in oven at the temperature of 110°C for 2 h. After heating it was cooled in a dessicator. After cooling, this dish was weighed. Percentage of moisture in sample was calculated by the following formula.

$$\text{Weight \% of moisture} = \frac{A}{B} \times 100.$$

Where:

A = weight in grams loss after drying.
B= weight in grams of salt sample.

Atomic absorption analysis. Atomic absorption spectrophotometer (AAS) having Model Hitachi Z8000 with specifications for studied metals enlisted in Table 1 was used for analysis. In 10 mL of HNO_3 and 5 g of sample was dissolved to make slurry. This slurry was then covered with watch glass for 30 min. Volume of the sample was made 1litre by dissolving doubly distilled water in 1000 mL flask. This sample solution was then heated at 110 °C for 15 min and then refluxed for 30 min without boiling. Sample solution was then cooled to add 5 mL of concentrated HNO_3. Sample solution was then again refluxed for 30 min. During refluxing most of the samples gave no brown fumes confirming that HNO_3 had completely reacted. While samples that gave brown fumes were added to 5 mL of concentrated HNO_3 and further stirred for 30 min until no brown fumes.

Table 1. Specifications of metals by atomic absorption spectrophotometer

Metals	$\lambda_{(max)}$	Flame gases	Sensitivity	Maximum lamp current
Cd	228.8	Air-acetylene	1.5	8
Cr	357.9	Nitrous oxide	4	12
Cu	324.8	Air-acetylene	4	10
Fe	248	Air-acetylene	5	30
Mn	279.5	Air-acetylene	2.5	20
Ni	232	Air-acetylene	7	30
Pb	283.3	Air-acetylene	20	15
Zn	213.9	Air-acetylene	1	10

Results and Discussion

Moisture content for Khewra salt mines range from 0.03 to 0.09% (Table 2) and salt samples from Kalabagh salt mines also had the moisture content in the range of 0.06 to 0.08 % (Table 3). Moisture content of both types of salt samples had lower values than the previously reported result by Chen *et al*. (2011) having average content 0.549% and by Usman and Filli (2011) having 0.649% in food grade salt. Sharif *et al*. (2007) reported the content of moisture in unrefined rock salt from Khewra salt mines in the range of 0.9 to 1.2% (Fig. 1). About 1% of moisture is considered as a permissible limit in food grade salt so present results were in this limit and found to be safer to use. Lower moisture content in all rock salt samples suggests them to be free flowing, minimum lump formation and being crystalline. Water insoluble matter was from 0.02 to 1.4% in all salt samples from Khewra salt mines (Table 2). Salt samples from the Kalabagh salt mines had relatively larger values of water insoluble matter ranging from

Table 2. Analytical parameters of Khewra salt

Sodium chloride %	Moisture	water insoluble	(Ca^{++}) (%)	(Mg^{++})	(SO_4^{-2})
96.4	0.08	1.4	0.15	0.23	0.9
97	0.06	1.2	0.2	0.22	0.9
98	0.09	1.2	0.2	0.15	0.9
97.4	0.07	0.02	0.15	0.23	0.91
96.3	0.07	1.06	0.24	0.21	0.77
98.9	0.06	0.09	0.19	0.11	0.36
97.8	0.06	0.87	0.32	0.35	0.54
98.6	0.03	0.06	0.24	0.21	0.39

1.5 to 2.8% (Table 3). When comparing the water insoluble matter of both the salt mines, it is evident that Kalabagh salt mines had a larger value. When the present results were compared with the previously reported results of water insoluble matter in table salt then it was found that the values were obtained by our research were slightly higher than the results reported by Sharif *et al*. (2007); Usman and Filli (2011) and Chen (2011).

Table 3. Analytical parameters of Kalabagh salt

Sodium chloride %	Moisture	Water insoluble	(Ca^{++})% %	(Mg^{++}) %	(SO_4^{-2})
96	0.06	1.5	1.2	0.81	0.77
93.3	0.07	2	1.27	0.89	0.82
92	0.75	2.1	0.26	0.23	0.78
93	0.06	2.4	0.2	0.25	0.75
92	0.07	2.1	0.24	0.2	0.95
95	0.08	2.8	0.26	0.18	0.92
96	0.06	1.6	0.15	0.2	0.94

Table 4. Concentrations of trace minerals in Khewra salt

Sample	Fe	Cr	Zn	Mn (mg/kg)	Cu	Cd	Pb	Se	Ag	As
1	1.2	ND	0.02	ND	0.03	ND	ND	0.03	0.02	ND
2	1	0.42	0.11	0.04	ND	ND	0.1	0.05	ND	0.03
3	1.85	0.22	0.13	ND	0.03	ND	ND	0.04	ND	ND
4	1.2	0.22	0.02	0.06	0.01	ND	ND	0.03	0.01	ND
5	1.8	0.24	0.12	ND	0.03	ND	0.04	0.02	ND	0.04
6	0.2	0.23	0.17	0.05	0.02	ND	ND	0.03	0.02	ND
7	0.4	0.22	0.14	ND	0.03	ND	0.05	0.02	ND	0.05
8	0.2	0.21	0.04	ND	0.05	ND	ND	0.02	ND	ND

ND=not detected

However, all the values of all the salt samples were in the range set by Codex Alimentarius Commission. Sulphate content of Khewra salt sample ranged from 0.36 to 0.91% while for Kalabagh salt mines its range was 0.75 to 0.95%. Present results of research showed that Kalabagh salt mines had relatively higher values of sulphate content. Sharif *et al*. (2007) found the %age of sulphate content in Khewra salt mines in the range from 0.28 to 0.58%.So present results were in accordance with the previously reported literature. According to Codex Food Standard, food grade sodium chloride should be 97% pure. Looking at the %age purity of all the salt samples, it makes clear that out of eight salt samples from Khewra, seven salt samples were above this limit. Only one salt sample had a variation of just 0.6 % (Fig.1). In Kalabagh salt samples however, no salt sample was as pure as 97% (Fig.2). Maximum purity of these salt samples were 96%. These results

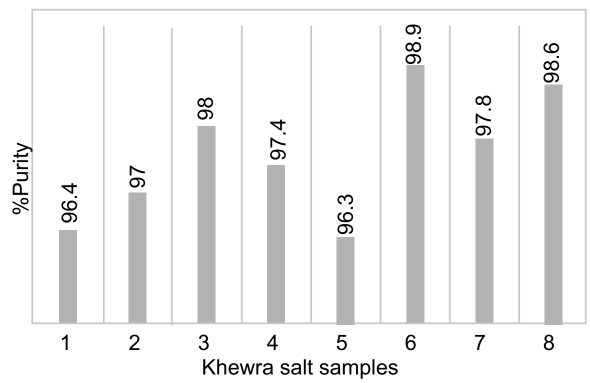

Fig. 1. Weight % purity of salt samples collected from Khewra salt mines.

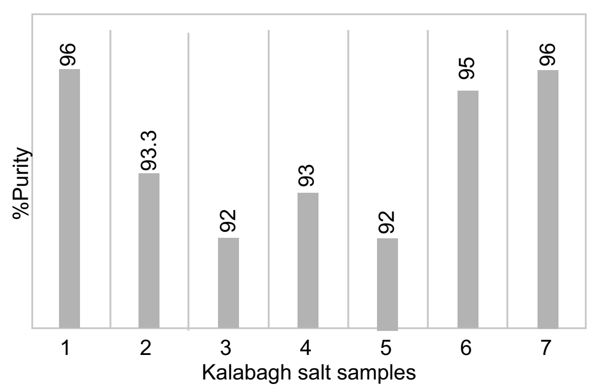

Fig. 2. Weight % purity of salt samples collected from Kalabagh salt mines.

Table 5. Concentrations of trace minerals in Kalabagh salt

sample	Fe	Cr	Zn	Mn	Cu	Cd	Pb	Se	Ag	As
	mg /kg									
1	1.8	0.34	0.1	ND	0.03	ND	0.1	ND	ND	ND
2	1.6	0.34	0.12	0.04	0.04	ND	0.04	ND	0.02	0.01
3	1.9	0.37	ND	0.03	0.04	ND	0.06	ND	ND	ND
4	1.8	0.31	ND	ND	0.02	ND	0.03	ND	ND	0.01
5	1.8	0.34	ND	ND	0.03	ND	ND	0.03	ND	0.02
6	1.75	0.38	ND	ND	0.03	ND	ND	0.04	0.01	0.01
7	1.72	0.22	ND	0.05	0.02	ND	0.1	0.04	ND	ND

ND=not detected

imply that there should be some mineralogical operations in order to improve the purity of Kalabagh salt samples. Unrefined rock salt samples should be undergone through some chemical or physical means to improve its purity level. WHO allows a maximum of 5g/kg of calcium in food grade salts. Results confirmed that the Kalabagh salt samples had a relatively higher concentration of calcium. Blaurockbusch (1996) reported the content of calcium to be 0.349µg/g while Sharif *et al*. (2007) reported the 0. 25mg/kg of sulphate content for Khewra salt mines. So obtained results were in agreement with the values previously reported in literature and also within the legal limits of maximum consumption by WHO. Content of magnesium was in the range of 0.11 to 0.35% for Khewra salt mines while for Kalabagh salt mines its range was in the range of 0.18 to 0.89%. Previously magnesium content was found 0.4% by Bergner (1997) and 0.12 % by Sharif *et al*. (2007). All the values were lower than the maximum human consumption limit of 3g/kg set by WHO. Iron range from 0.2 to 1.85mg/kg for Khewra and from 1.6 to 1.9 mg/kg for Kalabagh samples. Previously iron in Khewra salt mines samples were reported from 0.24 to 0.62 mg/kg by Sharif *et al*. (2007). So obtained results of Khewra and Kalabagh salt mines were within the limit of maximum human consumption and previously reported data. Copper between 0.01 to 0.05mg/kg for Khewra salt mines while for Kalabagh salt mines its range was from 0.02 to 0.04mg/kg in two salt samples. Out of 7 salt samples from the Kalabagh salt samples 5 were without any concentration of copper. Copper in table salt samples has been reported by Soylak *et al*. (2008) in the range of 0.17 to 0.47µg/g and by Usman and Filli (2011) in the range of 0.1 to 2.0 µg/g. Codex Alimentarius Commission recommended that the concentration of copper in food grade salt should be more than 2 mg/kg and recommended that daily allowance for copper is150-600 µg/day (Soylak *et al*., 2008). Thus from the obtained results and permitted level of copper regarding the maximum consumption by human body, it can be concluded that copper in the Khewra and Kalabagh salt samples is below this level. Out of eight salt samples of Khewra salt samples, 3 samples had the manganese concentration ranging from 0.04 to 0.06 mg/kg while in Kalabagh salt samples, out of 7 salt samples, 4 were without manganese and three salt samples had the concentrations 0.03 to 0.05 mg/kg. A maximum of 0.5mg/kg of manganese is reported by Lentech (2004). Present research results have confirmed that manganese is in lower concentrations as recommended daily allowance for the manganese is 20-90µg/day (Sharif *et al*., 2007). Range of chromium was from 0.21 to 0.42 mg/kg in Khewra salt while. Kalabagh salt samples had a slightly higher value of 0.22 to 0.38 mg/kg. All the results were in the limits of maximum human consumption set by Codex Alimentarius Commission. Lead in Khewra salt mines were 0.04 to 0.1mg/kg while it was 0.03 to 0.1 mg/kg for Kalabagh salt mines. Previously reported lead in Khewra salt mines were reported in the range of 0.02 to 0.10 mg/kg so present results were in accordance with the earlier literature. Previously zinc in Khewra salt mines were reported in the range of 0.12 to 0.18 mg/kg.During the present research its concentration was 0.02 to 0.17 mg/kg in Khewra salt mines and 0.1 to 0.12 for Kalabagh salt mines. Out of 7 salt samples of Kalabagh salt mines 5 were without zinc content. Concentration of arsenic in present research was 0.03 to 0.05 mg/kg in Khewra salt mines and 0.01 to 0.02 mg/kg in 4 out of 7 Kalabagh salt samples. Codex Alimentarious Legislation has 0.5 µg/g of arsenic as permissible limit.

Conclusion

Present research was conducted in order to evaluate the unrefined rock salt chemically from two major mining sites of Himalayan Rock salt deposits of Pakistan. During the whole research emphasis has been given on the comparison of results with the international standards regarding their maximum limits of human consumption set by Codex Alimentarius Commission, World Health Organization (WHO) and Food and Agriculture Organization (FAO). As the literature reported contamination of heavy metals with the table salts from Iran, Turkey, Greece, Brazil, Croatia, India, Portugal and Kingdom of Saudi Arabia present research results were also compared with the reported literature.

Analytical parameters had revealed that although the %age purity of all the salt samples for Khewra salt are more than 97% pure set by Codex but there should be some improved mineralogical and refining processes for it to be implied as food grade salt. Kalabagh salt samples are less pure so they must also be undergone through rigorous refining and mineralogy to raise its purity level up to 97%. All essential and non essential minerals were below the maximum limit of human consumption set by Codex Alimentarius Commission. Unrefined rock salts are concluded to be more nutritionally important than the refined ones.

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