A COMPARATIVE STUDY OF PHYSICO-CHEMICAL PARAMETERS AND TRACE METAL CONTENTS OF HOLY WATER ZAMZAM AND LOCAL POTABLE AS WELL AS HOT SPRING WATERS

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Using standard analytical methods and the atomic absorption technique, certain physico-chemical parameters and trace metal levels are estimated for the water samples from holy water Zamzam, collected from Mecca, Saudi Arabia, during Haj period from 1983 through 1985. The estimated parameters include pH chloride, sulphate, hydrogen carbonate hardness ($CaCO_3$) conductance, nitrate, Total Dissolved Solids (TDS) and silica. At optimized atomic absorption conditions the trace metal analysis is conducted for sodium, potassium, iron, zinc, calcium, megnesium, lead, cadmium, strontium, copper, cobalt, manganese mercury and chromium. Averaged results for replicate measurements are reported at ± 2S confidence level. The data obtained are compared with those for local, non-treated surface potable water, hot spring water and sea water. The interrelationship is examined from seasonal and/or regional viewpoints.

Key words. Parameter, Tracemetal, Water

INTRODUCTION

Mineral waters with variable chemical compositions are available throughout the world for various usages. Generally, these waters are potable, but not liked as drinking waters due to high concentrations of certain cations and anions which impart these waters their distinct taste The cations present are normally calcium, magnesium and sodium, while the major anions include chloride, sulphate and hydrogencarbonate. However, lower concentrations of phosphate, nitrate and silica are also invariably present in addition to organic matter at micro-and submicro gram level. The normal concentrations of the above mentioned cations/anions in mineral waters are high and vary considerably as compared with ordinary surface/ground or sea waters.

Earlier studies have shown that waters occuring in regions of unusual rock formation may differ considerably in terms of their chemical composition and they closely resemble in this respect with sedimentary rocks [1,2]. It is also indicated that development trends of natural waters can be deduced from analytical data for waters belonging to areas falling under various climatic zones [3]. In arid areas, the process of salt enrichment in water has been studied based on data obtained from evaporation, precipitation and absorption processes [4,5]. Studies on the uptake and excretion of trace metals from saline environ-

ment have also been undertaken [6,7]. The distribution of heavy metals as a function of river and sea-induced mixing processes has also been examined previously]8[. Studies based on solubilization, coagulation and complexation especially with respect to heavy trace metals, have also been carried out [9]. The importance of these investigations, especially when temporal, regional and seasonal aspects are included, cannot be overemphasized.

Currently active research attention has been focussed on the preparation of fresh drinking water from mineral waters. In addition to this primary requirement, fresh water so prepared finds numerous applications in agriculture, industry, chemical processing and fuel (hydrogen) production. People living in arid areas do require large supplies of fresh potable water. It is only in recent years that desalination has emerged as a viable physico-chemical process to obtain water of desired purity from saline waters. In fact, this has been made possible through an in-depth study of the physico-chemical characteristics of individual saline waters.

In line with various objectives described above, an attempt has been made in the present investigation to provide, in the first place, basic data on the physico-chemical character of the holy water Zamzam, for which thermal neutron activation data for some trace metals are previously available [10]. The atomic absorption data are obtained to augment a comparison between trace metal contents of local drinking/spring waters and the sea water with Zamzam. The characteristics of these in terms of the

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variation of their chemical compositions are compared with those of sea water are described in terms of geology, climatic conditions and soil/rock composition. A year-wise study is undertaken to check the possibility whether any seasonal and/or regional veriables are attendant on the composition of the Zamzam.

EXPERIMENTAL

Plastic cans (2.5 L capacity) were used for sampling. These cans were prewashed first with chromic acid and then with ample distilled water to remove any sticking organic matter. Blank checks on these cans were made using deionized water as the leaching solvent. The objective behind this was to verify whether the cans were contaminated at the detection level of the individual trace metals, especially with respect to chromium. The investigation revealed that the cans were not contaminated with respect to any of the metals estimated quantitatively. Also, the cans were found to be capable or retaining a given water sample for a period of seven to ten days without causing a detectable change in the trace metal level or major anionic/cationic concentrations. Three samples were air-lifted each year directly from Mecca, Saudi Arabia, through pilgrims during the Haj period. The analyses were completed within 72 hours after sampling. No preservatives were used.

The trace metal analysis was conducted at optimized operational conditions achieved for each metal separately. A Hitachi Atomic Absorption Spectrophotometer, model 170-10, was used in this investigation. Absorption signals were recorded on and X-Y chart recorder. Quantification was done through the calibration method.

Merck GR chemicals (min. purity 99.8%) were used for the preparation of standards. Metal stock solutions were made in dionized water at 100 mg/1 metal concentrations. Appropriate aliquots were taken from these standards for subsequent dilution to the desired level. The standards were checked against FAO standards for intercalibration and exact quantification. The experimental procedures for the estimation of physico-chemical parameters and most trace metals were adopted from literature [11]. Lead and cadmium were estimated by the chelation/solvent extraction method based on APDC-MIBK [12]. Mercury was estimated by the flameless atomic absorption technique. Rest of the trace metals were estimated by the direct aqueous phase aspiration of the samples.

DISCUSSION

The estimated physico-chemical parameters for the water Zamzam appear in Table 1. In Table 2 are listed the estimated concentrations of trace metals reported at ± 2S confidence level. The average overall precision in the estimation of physico-chemical paramaters is within ± 2.0% while for trace metals it is within ± 1.5%. The listed values appear as average values computed for replicate measurements involving at least five independent estimations for each water sample collected during a year.

As examination of Table 1 reveals that the major anionic constituents present in Zamzam are the chloride, sulphate and hydrogencarbonate. The water possesses 'bicarbonate' type of alkalinity with a pH value within a range of 7.3-7.5. The water is genuinely hard. It has been observed that the hardness may be effectively reduced by 50-70 mg/1 CaCO$_3$ through simple boiling. However, this process does not warrant a viable conversion of the water into a 'soft' form. The upper allowed limit laid down internationally for hardness stands at 150 mg/1 CaCO$_3$ for drinking waters.

Total dissolved salts (TDS) in the water are comparable with any mineral water with the same chemical composition. However, natural drinking waters, such as S-4 (a local water sample having a 60-feet deep origin) have a far less TDS content. The TDS content in Zamzam is higher by a factor of about 1.7 compared with S-4. This shows the presence of a high mineral content in the water. It may be seem from the figures given in Table 1 that the contents of the major ions mentioned above give independently a fair idea of the total dissolved solids in the water. The year-wide study confirms the fact that no unusual rock formations are involved in the bedment of this water for, otherwise, there was bound to occur a substantial variation in the estimated magnitudes of various parameters as a function of time. Although samples were collected over the same period of the year under unknown circumstances, yet the observed variation spread over three years is only marginal within ± 5% of the extremum values in each case.

The macronutrients, sodium and potassium, as present in sample S-1 at 108.0 mg/1 and 11.0 mg/1 levels respectively. These levels are higher by a factor of about 10 and 2.5 as compared with those for their counterparts in local sample S-4. The iron, zinc, magnesium, lead, copper, cobalt and mercury levels in Zamzam are found to be higher than the corresponding levels in the local waters. The distinct taste of Zamzam may, therefore, be attributed to this variation in the amounts of the minerals present. Also, the

data reveal that the cobalt, copper, cadmium, lead and iron levels in Zamzam are higher than the corresponding levels in sea water. This indicates that Zamzam does not have a sea derived origin as supported by the fact that the base ment rocks bearing the water in Zamzam area are bout 100 Km away from the sea coast and about 285 meters above the sea level The only resemblence between the two is in terms of sodium to mangesium ratio that lies within 7.7 - 9.0.

The contents of sodium, chloride, sulphate and calcium are found to be significantly enriched as compared with the local, underground water sample S-4, thereby indicating the presence of a saline environment of Zamzam. In general, the salt content is relatively constant as a function of time, and has little effect on heavy metal concentrations. Also, the salt content is not high enough to alter the pH and, for that matter, the solubility of the metals in general.

Table 1. Estimated physico-chemical parameters for the water zamzam, at ±2S confidence level, and other waters

Parameter Sample/Year	pH ±0.1	Chloride mg/1 ±0.5	Sulphate mg/1 ±0.6	Hydrogen- carbonate ± 5	Hardness mg/1 CaCO$_3$ ±5	Conductance μS/Cu ±0.2	Silica mg/1 ±0.2	Nitrate mg/1 ±0.005	TDS mg/1 ±6
S-1 (1983) September 20	7.5	47.1	45.5	198.5	300	600	9.4	0.201	415
S-2 (1984) September 11	7.3	43.2	47.2	189.0	310	650	9.1	0.283	420
S-3 (1985) August 29	7.4	45.1	48.8	196.0	288	630	9.8	0.210	398
S-4*	7.2	13.7	14.3	94.7	185	390	2.1	0.010	245
S-5**	7.5	45.9	35.9	180.3	258	510	4.5	0.183	375

*local, non-treated water sample from Islamabad (location: 33.7°; 73°)
**local, hot spring water (location: 33.8°, 73.1°)

Table 2. Estimated concentrations (at ± 2S confidence level) of various trace metals in water zamzam and other waters

Trace metal sample	Na mg/1 ±1.0	K mg/1 ±0.2	Fe mg/1 ±0.001	Zn mg/1 ±0.001	Ca mg/1 ±0.6	Mg mg/1 ±0.1	Pb μg/1 ±0.2	Cd μg/1 ±0.1	Sr μg/1 ±0.9	Cu μg/1 ±0.1	Co μg/1 ±0.3	Hg ng/1 ±0.1	Mn mg/1 ±0.1	Cr μg/1 ±0.1
S-1	108.0	11.0	0.103	0.088	40.0	12.0	7.1	4.0	7.6	13.1	12.9	15.6	0.85	3.4
S-2	106.0	11.8	0.110	1.848	42.0	12.8	8.2	4.3	8.1	9.7	14.1	15.4	0.90	4.1
S-3	103.0	11.2	0.091	0.082	47.5	12.1	7.9	4.9	7.9	9.4	13.7	5.0	0.81	3.9
S-4*	10.5	4.8	0.020	0.009	41.7	8.9	3.2	11.3	13.5	1.3	10.4	10.1	1.10	13.1
S-5**	95.1	8.3	0.097	0.073	38.7	15.7	10.0	3.9	8.5	12.3	9.3	13.7	1.20	4.1
Sea Water***	10.5 x10^3	385	0.0034	0.011	405	1.35 x10^3	0.030	0.11	8.1 x10^3	3	0.3	30	2.0	0.2

*local, non-treated water sample from Islamabad (location: 33.7°; 73°)
**Local, hot spring water (location 33.8°, 73.1°)
***data based on reference 13.

It is seen in the case of physico-chemical parameters that the individual dispersion in estimated values does not vary appreciably as a function of time; the same is true for trace metals. The only exception in the latter case is that of zinc in sample S-2. The estimated zinc concentration in this sample of 1984 is about 20 times as great as that found in samples S-1 and S-3. Again, a substantial decrease in mercury concentration is also observed in Sample S-3 compared with S-1 and S-2. Since rest of the levels of the trace metals are comparable in samples S-1, S-2 and S-3, there is little possibility for the contamination with respect to zinc alone. As a result of a query to this effect, it turned out that the sample S-2 was drawn from a newly installed Zamzam distribution system. It is highly likely that the new pipeline might have contributed towards high zinc content in Sample S-2. The fact finds support from the lead content of the same sample, which in relation to S-1 and S-3, is higher. Plumbosolvancy may be considered to be the operative process in this instance.

A direct comparison of the estimated values of various trace metals in samples S-1, S-2 and S-3, together with S-4, with those of sea water indicated that the mineral enrichment in Zamzam is not derived from sea water. It, thus, appears that the process chiefly influencing the distribution of dissolved metals in the water emerges from local rock/soil composition. In addition, climatic conditions (rainfall, temperature, etc.), morphology and anthropogenic influences might have contributed over centuries to the characteristic development trend met with today in this water. It may, thus, be concluded that high rate of evaporation and sorption should have played the important role towards initial salt enrichment in the water. The data also reveal that the composition of the Zamzam is, rather, close to that found in mineral spring waters (S-5).

In conclusion, the water Zamzam poses as such no physiological impact on the consumer. The only excessive concentration met with is that of sodium; the rest of trace metal levels are well within internationally laid down range for safe use of waters.

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