# IDENTIFICATION OF BOTTLED ZAM ZAM WATER IN MALAYSIAN MARKET USING HYDROGEN AND OXYGEN STABLE ISOTOPE RATIOS ($\delta^2$H AND $\delta^{18}$O)

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## ABSTRACT

*The water drawn from the well of Zam Zam is believed by the adherents of Islam to be blessed and capable of treating a variety of ailments. The water originates from a well in an alluvium area, located in Mecca, Saudi Arabia, and has been in use since 4000 years ago. Due to the religious significance of the water drawn from this well, bottled versions are very popular among Malaysians. Unfortunately, this disproportionate popularity may entice some unscrupulous dealers to engage in fraudulent behavior, such as selling ordinary water purported to be Zam Zam water. This unethical practice might very well pose a physical and economical hazard to consumers. Therefore, for the purpose of this preliminary study, five samples of Zam Zam bottled water from different brands were purchased and analyzed using Isotope Ratio Mass Spectrometer (IRMS). For comparison purposes, four samples of Zam Zam water from Mecca, and two more types of water samples originating from Malaysia were also analyzed, namely, bottled drinking water and tap water. The sources of these water samples are from groundwater and surface water (river), respectively. Results of hydrogen ($\delta^2H$) and oxygen ($\delta^{18}O$) isotope ratios of Zam Zam water from Mecca are in the range of –13.62‰ to –10.60‰, and –2.17‰ to 0.06‰, respectively, while the hydrogen ($\delta^2H$) and oxygen ($\delta^{18}O$) isotope ratios of five samples from the bottled Zam Zam water are within the range of –12.05‰ to –8.00‰ and –1.60‰ to –0.17‰, respectively. As for the bottled drinking water and tap water, the hydrogen ($\delta^2H$) and oxygen ($\delta^{18}O$) isotope ratios were in the range of –50.74‰ to –40.66‰ and –7.95‰ to –5.39‰, respectively. The results from the measured values of all the water samples demonstrates the ability of the isotope ratios comparison technique in distinguishing different water samples, and might be immensely useful for the purpose of regulatory monitoring of bottled water products.*

## ABSTRAK

*Air yang diambil dari Telaga Zam Zam dipercayai boleh mengubati berbagai penyakit oleh penganut agama Islam. Air tersebut berasal dari sebuah telaga di kawasan alluvium yang terletak di Mekah, Arab Saudi dan telah digunakan sejak 4000 tahun yang lalu. Disebabkan pengaruh penggunaannya yang signifikan dari segi agama, Air Zam Zam jenis berbotol adalah sangat terkenal di kalangan rakyat Malaysia. Malangnya, disebabkan penggunaannya yang popular telah menyebabkan boleh berlaku kemungkinan sesetengah penjual yang tidak bertanggungjawab untuk melakukan penipuan dengan menjual air biasa sebagai Air Zam Zam. Amalan yang tidak beretika ini berkemungkinan boleh memberi kesan fizikal dan ekonomi kepada pengguna. Sehubungan dengan itu, bagi tujuan kajian awal ini, lima sampel Air Zam Zam berbotol dari berbagai jenama telah dibeli dan dianalisa menggunakan Isotope Ratio Mass Spectrometer (IRMS). Untuk tujuan perbandingan, empat sampel Air Zam Zam* *dari Mekah dan dua jenis sampel air yang berasal dari Malaysia juga dianalisa, iaitu air minuman berbotol dan air paip. Sumber-sumber sampel air ini adalah masing-masing dari air bawah tanah dan air permukaan (air sungai). Keputusan nisbah isotop stabil hidrogen ($\delta^2H$) dan oksigen ($\delta^{18}O$) untuk Air Zam Zam dari Mekah adalah masing-masing di dalam julat –13.62‰ hingga –10.60‰, dan –2.17‰ hingga 0.06‰, manakala nisbah isotop stabil hidrogen ($\delta^2H$) dan oksigen ($\delta^{18}O$) untuk lima sampel dari Air Zam Zam berbotol adalah masing-masing di dalam julat –12.05‰ hingga –8.00‰ dan –1.60‰ hingga –0.17‰. Untuk air minuman berbotol dan air paip, nisbah isotop stabil hidrogen ($\delta^2H$) dan oksigen ($\delta^{18}O$) adalah masing-masing di dalam julat –50.74‰ to –40.66‰ and –7.95‰ to –5.39‰. Keputusan daripada pengukuran sampel-sampel air tersebut menunjukkan keupayaan teknik perbandingan nisbah isotop di dalam membezakan sampel-sampel air yang berlainan dan mungkin sangat berguna di dalam pemantauan perundangan produk-produk air minuman berbotol.*

**Keywords :** Zam Zam water, hydrogen, oxygen, stable isotope ratios, distinguish, comparison

## INTRODUCTION

Packaged or bottled drinking water are becoming an increasingly important component of human dietary intake worldwide, as consumers consider it to be a safe, healthy, and conveniently packaged beverage that is comprehensively regulated by the authorities. According to The International Bottled Water Association (IBWA), every person in the United States consumes an average of 110 liters of bottled drinking water in the year 2011 alone (IBWA, 2012).

Zam Zam water, which is drawn from the Zam Zam well in Mecca, Saudi Arabia is often brought back by Malaysian pilgrims from the holy city for personal consumption. Lately however, the import and commercialization of Zam Zam water is carving a niche for itself in the bottled water consumer market. This phenomenon greatly alarms the Ministry of Health (Malaysia), who is responsible for the sale of packaged or bottled water, since some quarters of consumers doubt the genuinity or purity of the bottled Zam Zam water. Moreover, its commercial sale is religiously prohibited for Muslims, with the government of Saudi Arabia forbidding its export and sale as well.

The most salient objective of this study is to identify the naturally occurring light stable isotopes of hydrogen and oxygen as a possible tool for the purpose of authentication of bottled water sources. The development and enhancement of this capability will give way to the creation of a network of databases, which can be accessed and utilized by agencies that monitor and assure the quality, authenticity and the origin of bottled water.

## MATERIALS AND METHODS

The sampling of bottled Zam Zam waters (Z2, Z3, Z5, Z6 and Z7) was performed on samples that are commercially available. Five different brands of bottled Zam Zam water were purchased between 2008 and 2011 in the Klang Valley area. At the same time, four samples of Zam Zam water (Z1, Z4, Z8 and Z9) were brought back from Mecca each year. For comparison purposes, nine brands of bottled drinking water were purchased from the market as well. These bottled drinking waters were sourced from groundwater. The criteria for selection of this bottled drinking water were based on the location of groundwater sources, and their respective producers. The four main locations were from the northern (B1 and B2), eastern (B3), central (B4 and B5) and southern region (B6, B7 and B8) of Peninsular Malaysia. All these water samples (Zam Zam and bottled drinking water) were stored in their original, unopened bottles from the time of purchase until the time of analysis. Local tap water was also analyzed during the course of this study, with most of it being sourced from surface water (river).

All samples were measured for $\delta^2H–H_2O$ and $\delta^{18}O–H_2O$ stable isotopes using SERCON GEO 20–20 Continuous Flow Isotope Ratio Mass Spectrometer (CF–IRMS). Samples for $\delta^2H–H_2O$ and $\delta^{18}O–H_2O$ analyses were treated in the SERCON Water Equilibration System (WES) prior to the analysis via IRMS. A total of 5 ml of water sample, placed in a vial, were used for each analysis. The $\delta^{18}O$–$H_2O$ values were measured via equilibration with $CO_2$ at 50°C for 8 hours, while $\delta^2H$–$H_2O$ values were measured via equilibration with $H_2$ and its reaction with the Platinum stick catalyst at 50°C for 1 hour. In the $\delta^2H$–$H_2O$ analysis, a platinum catalyst stick was used to accelerate the reaction, and the gas exchange equilibrium took place between the introduced pure $H_2$ gas and water vapour. This gas exchange equilibrium caused the water vapour to emit a distinct signature to the introduced pure $H_2$ gas, which represents the isotopic composition of the water prior to the $H_2$ gas analysis by IRMS.

The δ values are calculated by $\delta^2H$ or $\delta^{18}O$ (in ‰) = ($R_{Sample}$ – $R_{Standard}$ x 1000) / $R_{Standard}$, where R represents the ratio of heavy to light isotope ($^2H/^1H$) or ($^{18}O/^{16}O$), and $R_{Sample}$ and $R_{Standard}$ are the isotope ratios in the sample and the standard, respectively. The isotopic ratio of fresh water varies widely and systematically across the globe as a result of the spatially and temporally variable climatic patterns that governs the delivery of precipitated water to designated geographical regions. Strong trends in $\delta^2H$ and $\delta^{18}O$ values occur with increases in altitude, latitude and continentally (Kendall and Caldwell, 1998).

Both $\delta^2H$ and $\delta^{18}O$ values were measured relative to internal/secondary laboratory standard (Puerto Rico 1), with the value of –1.30‰ and –1.52‰, respectively, which has been calibrated using the international standard (VSMOW). For the isotope analysis, each sample was measured in triplicates in each analytical run for an acceptable standard deviation limit (within instrument sensitivity) and better results.

## RESULTS AND DISCUSSION

The results for all of the samples are shown in Table 1. The $\delta^2H$-$H_2O$ and $\delta^{18}O$-$H_2O$ isotopic values for Zam Zam water ranged from –13.62 to –8.00‰, and –2.17 to 0.06‰, respectively, while for the bottled mineral water and tap water, the $\delta^2H$-$H_2O$ and $\delta^{18}O$-$H_2O$ isotope ratios ranged from –50.74‰ to –40.66‰, and –7.95‰ to –5.39‰, respectively.

Isotopic values of Zam Zam water show a unique distinct isotopic signature compared to Malaysian bottled drinking and tap water (Figure 1). These isotopic values of Zam Zam water were highly enriched compared to their Malaysian counterparts. From this study, the Zam Zam water is mirrors the isotopic characteristic of saline water. However, the $Cl^-/HCO_3^-$ ratio of the Zam Zam water was 0.836, where the $Cl^-$ and $HCO_3^-$ values were 163.3mg/l and 195.4mg/l, respectively (Al Zuhair and Khounganian, n.d.). This level of $Cl^-/HCO_3^-$ ratio implies the absence of seawater intrusion. According to Araguás (2003), groundwater samples having $Cl^-/HCO_3^-$ ratio <3.77 represents a freshwater recharge, while $Cl^-/HCO_3^-$ ratio >3.77 reflects seawater influence. There is no significant isotope ratio difference between the Mecca Zam Zam water and bottled Zam Zam water that are available in the Malaysian market.

It was found that from Figure 1 the values for $\delta^2H$ and $\delta^{18}O$ Malaysian bottled drinking water and tap water fall within the GMWL. According to Mook (2000), most groundwater resources are meteoric in origin (meteoric groundwater). There is a strong relationship between the $\delta^2H$ and $\delta^{18}O$ values of precipitation reflected in the Global Meteoric Water Line (GMWL). When the isotopic compositions of precipitation samples from all over the world are plotted relative to each other on $\delta^2H$ versus $\delta^{18}O$ plots, the data form a linear relationship that can be described by the equation, $\delta^2H = 8\ \delta^{18}O + 10$, also known as GMWL (Kendall and Caldwell, 1998). However, the results of $\delta^2H$ and $\delta^{18}O$ for both Zam Zam water (Mecca and bottled) were significantly different from the Malaysian bottled drinking water and tap water and these are due to geographical and temporal variations. The Zam Zam water lies on the Evaporation Line of the $\delta^2H$ versus $\delta^{18}O$ plots. This indicates that the Zam zam water underwent an evaporation process. There are two possible explanations for the occurrence of this evaporation effect; first, excessive pumping of the Zam Zam water, along with the treatment and storage processes. It is generally acknowledged that excessive pumping from the aquifer will inadvertently allow air into the aquifer system, catalysing an exchange between the Zam Zam water and atmospheric water vapour. However, factors such as treatment and storage processes can be eliminated, as the treatment only involves filtration and sterilization, which causes minimal, almost negligible, fractionation. Although the storage of Zam Zam water after the pumping and treatment processes could possibly cause evaporation, the effect is almost negligible, due to the fact that the water is rapidly being replenished almost daily.

Table 1 Stable isotope composition for Zam Zam water, bottled water and tap water (expressed in ‰).

| | Average | | σ | |
|---|---|---|---|---|
| Sample | $\delta^{18}O$ | $\delta^{2}H$ | $\delta^{18}O$ | $\delta^{2}H$ |
| Z1 | 0.06 | -12.35 | 0.18 | 0.44 |
| Z2 | -1.15 | -11.24 | 0.14 | 0.81 |
| Z3 | -0.70 | -8.00 | 0.21 | 0.10 |
| Z4 | -1.09 | -10.60 | 0.39 | 1.11 |
| Z5 | -1.44 | -12.05 | 0.25 | 0.02 |
| Z6 | -1.60 | -9.37 | 0.23 | 0.66 |
| Z7 | -0.17 | -9.22 | 0.27 | 0.53 |
| Z8 | -1.27 | -12.08 | 0.07 | 0.77 |
| Z9 | -2.17 | -13.62 | 0.24 | 0.46 |
| B1 | -6.65 | -45.68 | 0.08 | 0.77 |
| B2 | -6.80 | -42.44 | 0.18 | 2.10 |
| B3 | -7.95 | -49.54 | 0.12 | 2.14 |
| B4 | -7.37 | -44.00 | 0.18 | 0.46 |
| B5 | -7.84 | -50.74 | 0.17 | 2.66 |
| B6 | -6.63 | -42.04 | 0.37 | 0.84 |
| B7 | -7.43 | -44.68 | 0.11 | 1.02 |
| B8 | -6.05 | -40.66 | 0.48 | 1.40 |
| B9 | -6.74 | -43.57 | 0.36 | 1.70 |
| MTW | -7.23 | -45.00 | -* | -* |
| Tap water | -5.39 | -43.27 | 0.02 | 1.27 |

*Internal secondary standard.

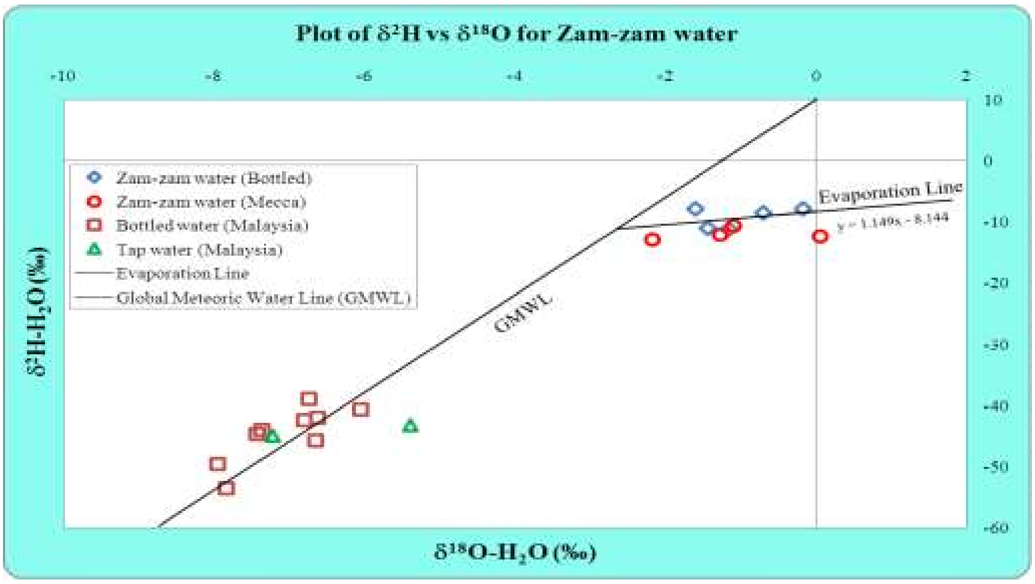


Fig. 1 Plot of $\delta^2H$–$H_2O$ vs $\delta^{18}O$–$H_2O$ for Zam Zam water

## CONCLUSIONS

The use of the stable isotope technique in this study resulted in a distinct isotopic signature for the Zam Zam water samples that were studied, with highly enriched values for $\delta^2H$ and $\delta^{18}O$. The ability to distinguish isotopic value of Zam Zam water demonstrates the possibility of isotope ratios technique as a potential tool in the regulatory monitoring of bottled water products.

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