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DETERMINATION OF MAJOR IONS CONCENTRATIONS IN KELANTAN WELL WATER USING EDXRF AND ION CHROMATOGRAPHY

(Penentuan Kepekatan Ion-ion Utama Air Telaga di Kelantan, Dengan Menggunakan Pendaflur Serakan Tenaga Sinar-X dan Ion Kromatografi)

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Abstract

Well water is a renewable natural resources and one of the drinking water sources for many areas in Kelantan. The assessment of well water quality is very important in evaluating the suitability of the water for drinking and other domestic purposes. Major ions such as K^+, Ca^{2+} and Na^+ in well water may originated from dissolved mineral composition of the underground rocks and soil mainly granitic in origin. The objective of this study is to determine the concentration of K^+ and Ca^{2+} using Energy Dispersive X-ray Fluorescence (EDXRF), whereas F^-, Cl^- and SO_4^{2-} were determined by ion chromatography (IC) in the well water collected from various districts of Kelantan. The well water samples were collected from Gua Musang, Jeli, and Tanah Merah districts. In situ measurement of water quality parameters such as temperature, pH, salinity, dissolve oxygen (DO), conductivity, turbidity and total dissolved solids (TDS) were conducted using YSI portable multi-probes meter. The concentrations of K+ and Ca^{2+} were measured and found in the range of 227.89 – 691.44 and 0 – 36.71 ppm respectively. The concentration of Cl^-, SO_4^{2-} and F^- were measured and found on the ranged of 2.08-17.0, 0.71-13.10 and 0 – 3.54 ppm respectively.

Keywords: well water, cations, anions, EDXRF, ion chromatography

Abstrak

Air telaga adalah sumber alam yang dapat diperbaharui dan salah satu daripada sumber air minuman untuk beberapa kawasan di negeri Kelantan. Penilaian kualiti air telaga adalah sangat penting dalam menilai kesesuaian air ini sebagai air minuman. Ion-ion utama seperti K^+, Ca^{2+} dan Na^+ dalam air telaga berasal daripada komposisi mineral terlarut dalam batuan bawah tanah dan tanih yang kebanyakannya bercirikan granit. Kajian ini dijalankan untuk menentukan kepekatan K^+, Ca^{2+} dan Na^+ dengan menggunakan Pendaflur Serakan Tenaga Sinar-X, manakala F^-, Cl^- dan SO_4^{2-} telah diukur menggunakan ion kromatografi. Sampel air telaga di dalam kajian ini telah diambil dari daerah Gua Musang, Jeli dan Tanah Merah. Parameter in situ kualiti air telah diukur dengan menggunakan multi probe YSI mudah alih. Julat kepekatan untuk K^+ dan Ca^{2+}, masing-masing adalah dalam lingkungan 227.89 – 691.44 dan 0 – 36.71 ppm. Julat kepekatan untuk Cl^- , SO_4^{2-} dan F^- masing-masing adalah di antara 2.08-17.0 , 0.71-13.10 dan 0 – 3.54 ppm

Kata kunci: air telaga, kation, anion, EDXRF, ion kromatografi

Introduction

Groundwater issues have become great interests among researchers recently due to strong possibility of being anthropogenically contaminated by various types of pollutants. It is a public knowledge that human activities such as mining, agriculture as well as an increase in population may directly affected the groundwater system. Well water categorize as ground water is an important source of domestic, agricultural and industrial activities in some countries and remains one of usable water in fast growing countries [1]. Generally, groundwater is less polluted than surface water because when it flows through soil and rocks, they filters most of the pollutants presents in groundwater [2, 3]. Groundwater also contains higher mineral concentration than surface water since minerals in groundwater come from earth subsurface system. Major ions such as K^{+}, Ca^{2+}, Cl^{-}, and SO_4^{2-} are normally applied in classifying and assessing groundwater quality [3]. It plays a significant component of the total dissolved solids present in groundwater [4]. It is important to have continuously groundwater quality monitoring program especially if the fresh groundwater is used as the major source of urban water supply for domestic and industrial [4]. Continuous monitoring is also needed because the quality of the groundwater may vary due to various factors such as season, climate and other factors which include anthropogenic and domestic activities. This groundwater quality will reflects inputs from the atmosphere and soil, as well as the level of activities that is source of pollutant such as mining, land clearance, agriculture, acid precipitation, domestic and industrial waste [5].

Major and minor ions in drinking water are very crucial to human health. These ions are very important to serve several functions in human body. It can have a significant effect on human health either through deficiency due to inadequate intake or toxicity due to excessive intake of the nutrients [6]. Potassium which present in our daily diet and ground water is vast and widely distributed and is an essential element in human, animal and plant tissues. Potassium and sodium are very important in maintaining normal osmotic pressure in cells. It is a cofactor for many enzymes and is required for the secretion of insulin, carbohydrate metabolism and protein synthesis [6]. Calcium can be found in all natural waters and it can contribute to the water hardness. Calcium is an essential element for human diet as it needed for many body functions such as bone structure, muscle contraction, nerve impulses transmission as well as blood clotting.

Many studies on the determination of major ions in the groundwater had been conducted to assess the concentration of major and minor ions as well as heavy metals. Those studies concluded that these ions are varies from place to place, depending on the chemical composition of the rocks through which the groundwater move and also based on the human activities at that place. The objectives of this study is to determine the concentration of major ions which are, Ca^{2+} and K^{+}, F^{-}, Cl^{-} and SO_4^{2-} in well water collected from different locations in Kelantan and to compare the results with WHO permissible limit.

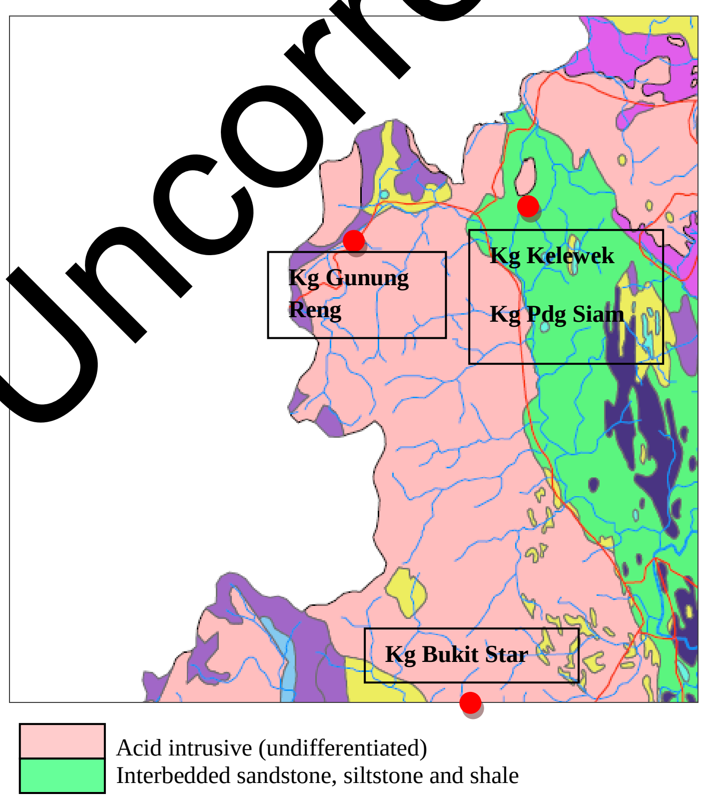

Figure 1: The geological map of the sampling area

Study Area

The State of Kelantan with the total area of 15,099 km^2 still relies on well water and boreholes for drinking and domestic purposes were chosen for this study. It is located in the north-east of Peninsular Malaysia, bordered with Narathiwat Province of Thailand in the north and Terengganu to the south-east, while the west is adjacent to the Perak and Pahang in the south. Figure 1 shows the geological formation of the sampling sites. In general the geology of the sampling sites consists of acid intrusive rock; which is mainly granites and sandstone [7].

Table 1: Sampling points and depth of the well

Location	**Location code**	**Depth of the well (m)**	**Sampling Depth (m)**	**Latitude(N)**	**Longitude(E)**	**Altitude (m)**
Kg Baru Star, Gua Musang	KBS	1.5	1	05°00.009’	101°58.601’	132
Kg Gunung Reng, Jeli	KGR	1.5	1	05°43.056’	101°4[illegible].683’	93
Kg Banggol Jenerih, Tanah Merah	KBJ	5	1,2,3,4,5	05° 49.26[illegible]’	102°08.629’	61
Kampung Kelewek, Tanah Merah	KKL	3.5	1,2,3	05°[illegible]8.38[illegible]’	102°05.888’	44
Kg Padang Siam, Tanah Merah	KPS	1.5	1	05° 4[illegible].175’	102° 07.753’	39

Materials and Methods

Well water samples were collected from five locations in Kelantan. The sampling locations were selected based on the availability of the well in that area. Sampling coordinates and elevation were obtained using Global Positioning System (GPS). Water sampling was performed by taking the samples at every 1 meter interval from water surface. The samples were taken using water sampler and transferred to the polyethylene bottles which were previously washed with nitric acid and thoroughly rinsed with deionized water. YSI portable multi probes water quality equipment were used for in situ measurement of pH, specific conductivity, DO, temperature, salinity, TDS and turbidity. Table 1 shows the sampling points and the depth of the wells.

The water samples were preserved by adding nitric acid 6 M to pH 2 before filtering using 0.45 µm cellulose nitrate membrane filter prior to analysis. The concentration of K^+, Ca^{2+} in both filtered and unfiltered samples were determined using Minipal 4 Energy Dispersive X-ray Fluorescence (EDXRF) and F^-, Cl^- and SO_4^{2-} (for filtered samples) using ion chromatography (IC). For EDXRF measurement, 5 mL of filtered and unfiltered samples were pipette into the sample cups fitted with 1.5 µm thin mylar film beneath the cups. For Ca measurement, helium gas was applied to enhance the stability of air pressure for good precision of measurement. 1000 ppm stock single element standard solutions were used for calibration. It was diluted to several concentrations to obtain linear calibration plot.

In ion chromatography analysis, the filtered samples were injected in the column with running time 12 minutes. Triplicate measurements were done for each sample to ensure constant results obtained. The calibration was done using series of anion concentration 0 to 10 ppm; prepared from stock solution of 1000 ppm to obtain linear calibration with $r^2 = 0.998$, $r^2 = 0.986$ and $r^2 = 0.992$ for Cl, SO_4 and F respectively.

Results and Discussion

Table 2 shows the values of in situ water quality parameters from 5 sampling locations. The values in the table below only differ slightly for different levels of well water samples. There is little variation in the temperature range which is between 26.11 to 27.38°C. The result indicates that the pH of well water samples is slightly acidic which is 4.6 to 5.82. The lower pH is probably due to the acidic type of rock of the well location, in which most of the sampling sites are located on granite rocks which consist of acid intrusive rocks. Generally, it may also be attributed to the interaction of surface water and the carbon dioxide in the atmosphere and gain entry into the well. When the groundwater from open dug well is exposed to the air, the carbon dioxide that present in the air gets dissolved in the water and results in decreasing of pH. This lower pH value is beyond the WHO recommended ranged for drinking purposes which is between 6.5-8 [8]. Conductivity is a numerical expression of ability of an aqueous solution to carry electric current. It also indicates the amount of total dissolved solids (TDS) in water. TDS consist of inorganic salts such as calcium, magnesium, potassium, sodium, bicarbonates, chloride and sulphate [8]. Salinity is an indicator of the concentration of the amount of dissolved salts, including calcium, magnesium, sodium and potassium [9]. KGR water sample has the highest value for TDS, conductivity and salinity which is 0.33 g/L, 523 μS/cm and 0.25 mg/L respectively.

Table 2: Physical and chemical properties of water from the ground water system studied

Loc Code	**Sampling Depth**	**Temp (°C)**	**DO (mg/L)**	**Salinity (mg/L)**	**TDS (mg/L)**	**pH**	**Conductivity (μS/cm)**	**Turbidity (NTU)**
KBS	1 m	26.8	2.40	0.07	0.10	5.5[illegible]	157.0	43.10
KGR	1 m	26.1	2.72	0.25	0.33	4.83	523.0	2.54
KBJ	1 m	27.3	0.81	0.08	0.11	4.65	172.0	2.41
	2 m	27.3	0.86	0.08	0.11	4.60	172.0	2.53
	3 m	27.3	0.75	0.08	0.11	4.70	172.0	2.46
	4 m	27.3	0.68	0.08	0.11	4.80	172.0	2.94
	5 m	27.3	0.67	0.08	0.11	4.87	172.0	97.90
KKL	1 m	26.7	1.66	0.03	0.05	5.08	80.0	0.62
	2 m	26.7	1.62	0.03	0.05	5.17	80.0	1.02
	3 m	26.7	1.60	0.03	0.05	5.58	79.0	2.70
KPS	1 m	27.3	1.44	0.07	0.10	5.82	159.0	1.45

The concentrations of Ca^{2+} and K^{+} for both filtered and unfiltered samples are presented in Figure 2 and 3. These results are the average of triplicate analysis measurement. Table 3 shows a wide variation in the concentration of the major ions. This variation may be closely related to the geological formation and human activities around the wells [10]. The concentrations of calcium for all collected samples are below the permissible limit by WHO which is 75 to 200 mg/L [2]. KGR that were taken from Jeli shows the highest concentration for Ca^{2+} and K^{+}. The concentration of ions in well water is closely related to the specific conductivity and TDS of the samples. From Table 2, we can see that KGR has the highest value for both specific conductivity and TDS. The other reason is it might be due to geological formation of that area. Ca^{2+} is mainly associated with carbonate minerals like calcite ($CaCO_3$) and dolomite $(CaMg)(CaCO_3)_2$ which is occurs in the secondary minerals residual boulders of igneous granite [2]. The concentration could also be attributed by dissolved limestone found in that area, which is Gunung Reng. The concentration of K^{+} for filtered and unfiltered samples are varies between 272.02 to 619.58 ppm respectively. The concentration of K^{+} is higher than the WHO permissible limit 250 mg/L.

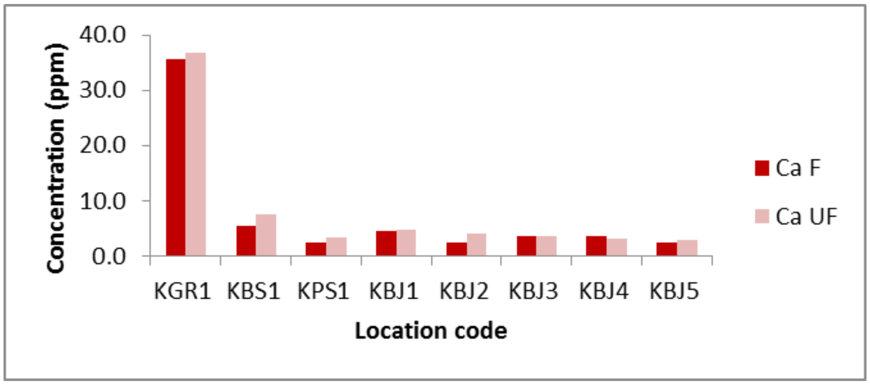

Figure 2: Concentration (ppm) of Ca^{2+} in Kelantan well water

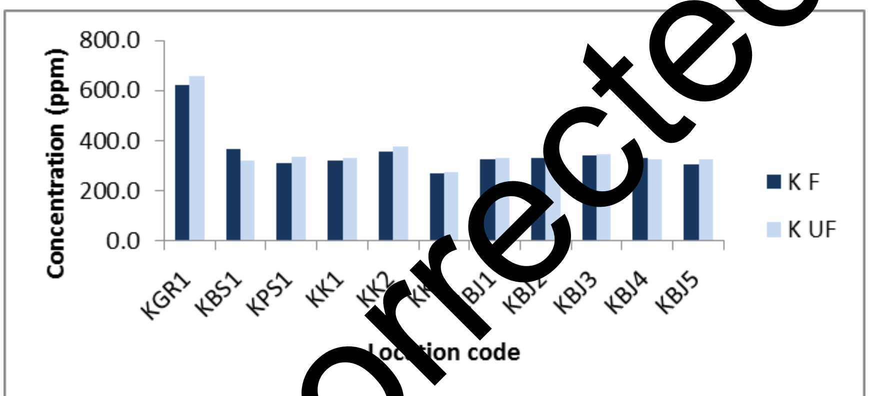

Figure 3: Concentration (ppm) of K^+ in Kelantan well water

Figure 4 shows the concentration of Cl^-, SO_4^{2-}, and F^- for filtered samples. Sulphate is important in groundwater quality assessment because it is part of naturally occurring minerals in some soil and rock formation. Over time, this mineral will dissolve and release into groundwater. Chloride normally present in low concentrations in surface water while groundwater will contain varying amounts of chloride depending on the weathering and leaching of sedimentary rocks and soils and the dissolution of salts deposits. Generally, chloride is not harmful to human beings unless high concentration is reached [11]. Fluoride is an important criterion for groundwater quality with an acceptable limit of 1.5 mg/L [1, 12] [13]. The potential sources of fluoride in the groundwater include various minerals in rocks and the weathering of process of these rocks. It is considered as dominant source of fluoride in groundwater [14]. Fluoride is important for oral health. However high concentration can cause dental and skeletal flourosis [1]. The variations in the results below are mainly due to the different geological formation and anthropogenic sources like agricultural practices. The surrounding area of the wells also plays an important role in determining the concentration of these ions.

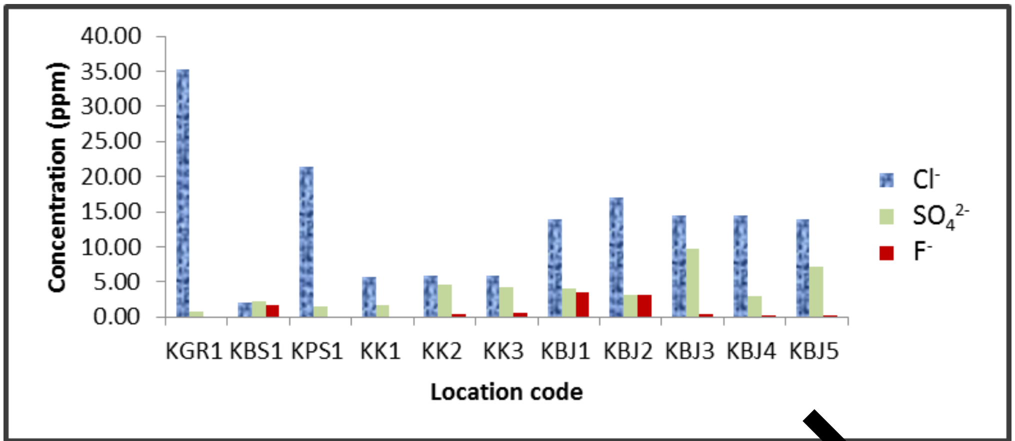

Figure 4: Concentrations of Cl^-, SO_4^{2-} and F^- (ppm) in water from ground water system in Kelantan

Conclusion

The concentrations of K^+ and Ca^{2+} were measured and found in the range of 22[illegible] – 691.44 and 0 – 36.71 ppm respectively, while the concentration of Cl^-, SO_4^{2-} and F^- are ranged of 2.0[illegible]17.0, 0.71-13.10 and 0 – 3.54 ppm respectively. Generally the concentrations of cations and anions in Kelantan well water is not within the WHO permissible levels, consumption of the water for drinking may require treatment. We have found that pH values are slightly acidic and below than with WHO permissible limit which is 6.5 – 8. This is possibly due to acidic type of rock in Kelantan which is acid intrusive rocks.

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