

METHOD DEVELOPMENT FOR DETERMINATION OF SODIUM, POTASSIUM AND CALCIUM IONS CONCENTRATIONS IN HOT SPRINGS WATER USING EDXRF

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ABSTRACT

Measurement of major cation such as Na^+ , K^+ , and Ca^{2+} in water are normally carried out using AAS, ICP-OES or flame photometry. In this study, an attempt was made to measure these cations using Energy Dispersive X-ray Fluorescent Spectrometry (EDXRF). Hot springs water was taken from varies hot spring in Selangor and divided into two portions that is filtered and unfiltered. 5 mL of water samples were pipette into a special liquid cups (sample holders) which has a thin mylar film underneath. The MiniPal4 XRF instrument was used in this study. The resolution for the instrument use is 145 keV with energy resolution at 5.9 keV. The spectrum of cations were analysed by using MiniPal/MiniMate software to determine the cations concentration. For K^+ and Ca^{2+} , Al-thin filter was used and default filter was used for Na^+ . The concentration of Na^+ obtained for filtered and unfiltered samples were ranged from 38.00 to 66.05 and 43.26 to 76.95 ppm. Meanwhile, concentrations of K^+ for filtered and unfiltered samples were ranged from 2.42 to 8.07 and 6.18 to 29.28 ppm. Concentrations of Ca^{2+} for filtered and unfiltered samples were ranged from 2.59 to 10.94 and 3.18 to 12.99 ppm.

Keywords: Na^+ , K^+ , Ca^{2+} , X-ray Fluorescent Spectrometer (EDXRF), Selangor, Hot springs water

ABSTRAK

Ukuran kation utama seperti Na^+ , K^+ , Ca^{2+} di dalam air biasanya menggunakan AAS, ICP-OES atau nyalaan pengukuran cahaya. Dalam kajian ini, percubaan telah dibuat bagi mengukur kation dengan menggunakan Pendaflur Serakan Tenaga Sinar X (EDXRF). Air panas telah diambil daripada pelbagai kolam air panas di Selangor dan telah dibahagikan kepada dua bahagian yang mana dituras dan tidak dituras. 5mL sampel air dipipet ke dalam cawan cecair khas (pemegang sampel) yang mana mempunyai filem mylar nipis dibawah. Dalam kajian ini, instrumen MiniPal4 XRF telah digunakan. Resolusi untuk instrumen yang digunakan adalah 145 keV dengan tenaga resolusi pada 5.9 keV. Spektrum kation telah dianalisis dengan menggunakan perisian MiniPal /MiniMate untuk menentukan kepekatan kation. Bagi K^+ dan Ca^{2+} penuras 'Al-thin' dan bagi Na^+ tiada penuras digunakan. Kepekatan Na^+ yang diperolehi bagi sampel dituras dan tidak dituras adalah dari 38.00 hingga 66.05 dan 43.26 hingga 76.95 ppm. Sementara itu, kepekatan K^+ untuk sampel yang dituras adalah diantara 2.42 hingga 8.07 dan 6.18 hingga 29.28 ppm. Kepekatan Ca^{2+} untuk sampel dituras dan tidak dituras adalah dari 2.59 hingga 10.94 dan 3.18 hingga 12.99 ppm.

Kata kunci: Na^+ , K^+ , Ca^{2+} , Pendaflur Serakan Tenaga Sinar X (EDXRF), Selangor, Air panas

INTRODUCTION

Malaysia has about 45 known hot springs (Samsudin *et al.*, 1997). Nowadays, hot springs water become one of the attractive spot for local and international either for tourism or for curing various types of skin diseases. According to Matz *et al.*, (2003), hot springs water have abilities for curing eczema and atopic dermatitis because of salty, sulfurous, bicarbonated, sulfate, carbonic, arsenic on the basis of their chemical content. Hot springs water had been formed when groundwater seeping through the fracture consequently from the magmatic heat and pressure that had being heated by contact with hot granitic rocks (Samsudin *et al.*, 1997). In the process of groundwater seeping through the fracture, waters had been penetrated layers of rocks and had been dissolved various salts and most of them are sodium, potassium and calcium (Kot *et al.*, 2000).

Previously, inductively coupled plasma optical emission spectrometries (ICP-OES), atomic absorption spectroscopy (AAS) and flame photometry were used to determine the concentration of these major cations in water (sodium, potassium and calcium). The objective of this work is to develop a method for the analysis of sodium, potassium and calcium by using the Energy Dispersive X-ray fluorescence Spectrometer (EDXRF). EDXRF had become a versatile technique for the materials analysis. This instrument can differentiate elements present in a sample based on the characteristics X-ray energies emitted. Besides, it also can helps in determining elemental concentration in the samples.

Theoretically, X-rays are part of the electromagnetic spectrum with energies ranging from 0.1 to 100 keV. According to Khalid *et al.*, (2011), it can be produced from the mechanisms of deceleration of high velocity electrons in the vicinity of a target nucleus, atomic transitions between discrete energy levels and radioactive decay of some atomic nuclei. Meanwhile, X-ray fluorescence is the emission of secondary X-rays from a material that has been excited by bombarding with high energy electrons. EDXRF commonly fitted with a side window X-ray tube. This (9W) X-ray tube has a Rhodium anode with minimum voltage from 4 kV to 30 kV and current from 1 μ A to 1 mA (PANanalytical, 2009). According to Ferrero *et al.*, (2001) the excitation source is come from an X-ray tube that produces an X-ray beam coming from an anode of Rhodium and X-ray tube is a commonly device used for the generation for X-rays (Khalid *et al.*, 2011).

This X-Ray Fluorescence (XRF) technique has advantages such as multi-elemental capability, possibility to perform qualitative and quantitative determinations, simple sample preparation prior to analysis, a wide dynamic range, high throughput and low cost predetermination (Abdullah *et al.*, 2011). Besides, EDXRF requires time less than two minutes for a sample analysis (Lipscomb *et al.*, 2007).

METHODOLOGY

Sampling and samples preparation

Samples of hot springs water were collected from various hot springs in Selangor. The positions of hot springs water (sampling points) were determined using Global Positioning System (GPS) (Table 1). Temperature of the hot springs water also measured in-situ by using high temperature thermometer. 20 L of hot springs water then were collected and transferred into the polyethylene plastic container. Water samples were then acidified to pH less than 2 using 6 M nitric acid. This is done to prevent any loss of radionuclides fractions by adsorptions on the wall of containers (Jobbagy *et al.*, 2010). After acidify, water samples were divided into two portions which is filtered and unfiltered. The water samples were filtered through the 0.45 μ m cellulose nitrate membrane filter paper. It is used to separate suspended from dissolved portions of the analyte. 5 mL of filtered and unfiltered samples were pipette into special cups (sample holders) which has a 1.5 μ thin mylar film underneath.

Instrumentation

In this study, the samples were measured by using Rh target Minipal4 PANalytical bench-top EDXRF and the tube ratings were set to 14 kV, 0.150 mA (Hamzah *et al.*, 2011). The detector for this instrument is a silicon drift detector. Each sample was analysed at every 100 s and the spectrum of cations were analyzed by using MiniPal/MiniMate software to determine the cations concentration. The MiniPal4 XRF instrument consists of sample spinner which is designed to reduce effects caused by non-homogenous samples (PANalytical, 2009). The X-ray beam is filtered through an Al-thin filter for determination of K^+ and Ca^{2+} cations and default for Na^+ . According to Anjos *et al.*, (2002) the angle of incident X-ray beam is 16° to the sample surface and the detector was placed perpendicular to the sample surface.

RESULTS AND DISCUSSION

Table 1 shows the latitude, longitude and altitude of study areas

Table 1: The latitude, longitude and altitude of study areas

Locations	Latitude	Longitude	Altitude (m)
Kerling	03 ⁰ 36.603'	101 ⁰ 36.539'	69
Kuala Kubu Baru	03 ⁰ 33.910'	101 ⁰ 38.753'	68
Sg. Tamu	03 ⁰ 27.838'	101 ⁰ 41.814'	75
Hulu Yam	03 ⁰ 25.549'	101 ⁰ 40.991'	99
Selayang	03 ⁰ 15.542'	101 ⁰ 38.766'	82
Batu 9,Gombak	03 ⁰ 15.246'	101 ⁰ 43.430'	73
Setapak	03 ⁰ 11.384'	101 ⁰ 42.816'	81
IKBN, Hulu Langat	03 ⁰ 08.215'	101 ⁰ 50.072'	59
Semenyih	03 ⁰ 02.532'	101 ⁰ 52.348'	67

The EDXRF results for Ca^{2+} , Na^+ and K^+ concentrations were plotted against the measured concentrations determined by ICP-OES are shown in Figure 1 (a)-(c). Minimum variation between levels of concentration were observed when comparing the results in Table 2. Of these cations correlation between measured concentrations determined by EDXRF and ICP-OES, Ca^{2+} cation shows the highest correlation ($R^2 = 0.9964$), which suggest that the values correlate between EDXRF and ICP-OES are comparable. Na^+ and K^+ cations correlation between measured concentrations determined by EDXRF and ICP-OES also shows high correlation with value of

correlation coefficient (R) are 0.8751 and 0.9452. This EDXRF method is comparable to well-known method (ICP-OES) to determine cations in water

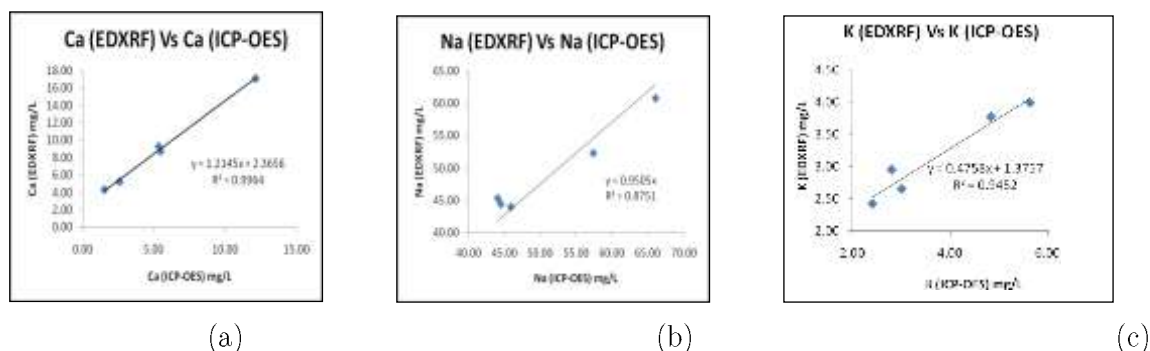


Figure 1 : Correlation between EDXRF and ICP-OES results for Ca^{2+} , Na^{+} and K^{+}

Table 2 shows the comparison value obtained between measured concentrations of water determine by EDXRF and ICP-OES for certain locations of hot springs water at Selangor state. All these three elements (Ca^{2+} , Na^{+} and K^{+}) show the variation concentration for different location but the value obtain for EDXRF and ICP-OES are closed. Study indicated that different concentrations of elements present probably because of location variation based on geological factor such as rocks. According to Homma & Tsukahara, (2008), major cations of Na^{+} , K^{+} and Ca^{2+} generally are originated from mother rocks (igneous rocks) of the hot springs. In Malaysia, most of hot springs are located close or in granitic masses (Samsudin *et al.*, 1997) and mostly all the hot springs at Selangor are located close to igneous rocks and have high tendency to the presence of major cations (Na^{+} , K^{+} and Ca^{2+}) in hot springs water. From the results, there are little amount of Ca^{2+} present. According to Homma & Tsukahara (2008), rocks such as granitic rocks contain little amount of Ca^{2+} .

Table 2: Comparison between EDXRF and ICP-OES results for Ca^{2+} , K^{+} and Na^{+}

Locations	Ca^{2+} (mg/L)		K^{+} (mg/L)		Na^{+} (mg/L)	
	EDXRF	ICP-OES	EDXRF	ICP-OES	EDXRF	ICP-OES
KKB(F)	5.47 ± 0.27	8.73 ± 0.03	3.01 ± 0.15	2.65 ± 0.01	44.06 ± 2.20	45.32 ± 0.18
Ulu Yam(F)	2.59 ± 0.13	5.25 ± 0.03	2.42 ± 0.12	2.41 ± 0.02	44.49 ± 2.22	44.44 ± 0.44
Selayang (F)	12.15 ± 0.61	17.09 ± 0.26	2.81 ± 0.14	2.95 ± 0.04	45.89 ± 2.29	44 ± 0.44
Batu 9,Gombak (F)	5.33 ± 0.27	9.29 ± 0.10	4.84 ± 0.24	3.77 ± 0.07	57.37 ± 2.87	52.27 ± 0.59
Hulu Langat IKBN(F)	< 2.58	4.32 ± 0.02	5.64 ± 0.28	3.99 ± 0.03	66.05 ± 3.30	60.74 ± 0.39

Table 3 shows the value obtained for analysis of Ca^{2+} , Na^{+} and K^{+} (filtered and unfiltered samples) using EDXRF. There are variations of values obtained but values of unfiltered samples for each element consistently higher than filtered. This might due to the cations that attach to the suspended solids. For filtration process, 0.45 μm cellulose nitrate membrane filter paper was used and this make some of the suspended solids which has size greater than

0.45 μm retained on filter paper. Besides, some of the values obtained are below limit of detection (LOD) as LOD for Na^+ , K^+ and Ca^{2+} are 37.34, 2.06 and 2.58 mg/L.

Table 3: Concentration of Ca^{2+} , Na^+ and K^+ obtained from EDXRF analysis

Locations	Ca^{2+}	Ca^{2+}	K^+	K^+	Na^+	Na^+
	(mg/L) Filtered	(mg/L) Unfiltered	(mg/L) Filtered	(mg/L) Unfiltered	(mg/L) Filtered	(mg/L) Unfiltered
Kerling	9.93 ± 0.50	11.83 ± 0.59	4.84 ± 0.24	12.64 ± 0.63	38.00 ± 1.90	48.70 ± 2.44
Kuala Kubu Baru	5.47 ± 0.27	5.71 ± 0.29	3.01 ± 0.15	8.33 ± 0.42	44.06 ± 2.20	66.95 ± 3.35
Sg. Tamu	< 2.58	< 2.58	8.07 ± 0.40	29.28 ± 1.46	< 37.34	43.26 ± 2.16
Hulu Yam	2.59 ± 0.13	3.18 ± 0.16	2.42 ± 0.12	9.78 ± 0.49	44.49 ± 2.22	46.51 ± 2.33
Selayang	12.15 ± 0.61	12.99 ± 0.65	2.81 ± 0.14	6.18 ± 0.31	45.89 ± 2.29	46.51 ± 2.33
Batu 9, Gombak	5.33 ± 0.27	6.36 ± 0.32	4.84 ± 0.24	9.03 ± 0.45	57.37 ± 2.87	66.37 ± 3.32
Setapak	3.43 ± 0.17	3.64 ± 0.18	3.87 ± 0.19	10.21 ± 0.51	61.68 ± 3.08	76.42 ± 3.82
IKBN, Hulu Langat	< 2.58	3.21 ± 0.16	5.64 ± 0.28	16.45 ± 0.82	66.05 ± 3.30	68.66 ± 3.43
Semenyih	10.94 ± 0.55	10.10 ± 0.51	5.91 ± 0.30	20.16 ± 1.01	38.88 ± 1.94	76.95 ± 3.85

Three aliquots of a sample were analysis by EDXRF spectrometry. The measured concentrations are shown in Table 4. The percentage difference of EDXRF was 3.47%. The accuracy for K is 6 %.

Table 4: Average percentage difference of EDXRF

	Elements	EDXRF	% Diff
10 ppm	Ca	10.28 ± 0.38	0.28(2.8%)
100 ppm	Na	98.32 ± 0.9	1.68(1.68%)
60 ppm	K	56.45 ± 2.17	3.55(5.92%)
Average % Diff			3.47%

CONCLUSION

The study had shown that EDXRF able to determine the concentration of Ca^{2+} , K^{+} and Na^{+} ions in hot springs water. Besides, the results of this study show that samples measured by EDXRF are comparable with ICP-OES. A simple, low cost method has been developed.

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