Assessment of Minerals in Phoenix Dactylifera L. as Determined by Inductively Coupled Plasma Optical Emission Spectrometry using ANOVA and PCA

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ABSTRACT--- Dates (Phoenix dactylifera L.) is one of mankind's oldest cultivated plants. It is known to be the most important fruit tree particularly in the Middle Eastern and Asian countries due to its natural sources of nutrition. The element composition of 10 commercially available dates and its pit samples purchased from local market were determined and evaluated using multivariate analysis technique. Samples were digested using nitric acid and hydrochloric acid and analyzed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Potassium, magnesium, calcium and sodium were found to be the major elements in both flesh and pit samples. Comparison between minor elements in both samples showed that the flesh samples contained higher levels of aluminium, barium and selenium while other minor elements were higher in the pit samples. Principal Components Analysis (PCA) and Analysis of Variance (ANOVA) were performed on multivariate dataset of the flesh and the pit samples separately to observe the relationship between samples.

Index Terms: ANOVA, date fruit, inductively coupled plasma optical emission spectroscopy (ICP-OES), mineral elements, principal components analysis (PCA)..

I. INTRODUCTION

Phoenix dactyliferaL. or commonly known as the date palm is a tropical and subtropical tree that belongs to *Palmae (Arecaceae)* family and is one of the earliest plants cultivated by humans [1], [2]. Date palms are also called *Sugar Palm* (English), *Nakhal* (Arabic), *Hurmaağacı* (Turkish), *khrma*(Persian), *Khajur* (Hindi and Urdu), *Karchuram* (Tamil, Malayalam) and *Karjura* (Kannada). Dates are reported to contain essential minerals such as sodium (Na), potassium (K), phosphorus (P), calcium (Ca), magnesium (Mg) and vitamins, for example, vitamin C and vitamin E [3], [4]. Some of the minerals are essential in bone metabolism and enzymatic activity [5]. Minerals in food can be grouped into macro (major) or micro (minor) minerals, the macro-minerals include calcium (Ca), phosphorus (P), potassium (K), magnesium (Mg), sodium (Na) and chlorine (Cl), while the micro-minerals include iron (Fe), copper (Cu), cobalt (Co), iodine (I), zinc (Zn), manganese (Mn), molybdenum (Mo), fluoride (F), chromium (Cr), selenium (Se), nickel (Ni) and sulfur (S) [6]. The macro-minerals are required in amounts greater than 100 mg/dl and the micro-minerals are required in amounts less than 100 mg/dl [7]. Mg, Cu, Se, Zn, Fe, Mn and Mo are important co-factors found in the structure of certain enzymes and are indispensable in numerous biochemical pathways. Na, K and Cl play a crucial role in the maintenance of osmotic balance between cells and the interstitial fluid [5], [8]. The minor elements like Cu, Fe, Se, and Zn have shown immunity in HIV-1 patients by lowering the rate of progression to AIDS. The quantity of micronutrients intake is also important for energy and protein sources [9].

The macro and micro minerals contents in date flesh have been reported previously by [10]-[12] with different varieties of dates samples and the instrument used. Inductively coupled plasma is one of the analytical technique that is more frequently reported [13]-[16] to analyze metals in the plant materials and food samples. In this study, Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was used instead of atomic absorption spectroscopy (AAS) technique that is used previously by several researchers in determining metals concentration. ICP-OES has a very good detection limit for most elements, small sample usage and many samples can be run at a time compared to AAS. In addition, ICP-OES has characteristics such as high reliability, high sensitivity and relatively less affected by chemical interference [17], [18]. In [19] measured the concentrations of K, Fe and Mg in date fruit using ICP-OES, while in [20], [21] employed

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ICP-OES to determine the mineral profile of date fruits and seeds, respectively in Saudi Arabia. Different techniques and methods were used in mineral determination with different dates samples, however, only a few varieties have been investigated so far and very little information has been published particularly on dates which are available in Malaysia markets.

In elemental analysis, the results obtained are in multivariate dataset which are huge and complex. Previous works on date samples used basic statistic to analyze their data, whereas in this study, one way-Analysis of Variance (ANOVA) and Principal Components Analysis (PCA) were used to evaluate the obtained data. PCA is a multivariate data analysis technique for evaluation and characterization of complex analytical data [22]. In [23] applied PCA to evaluate the minerals content of 50 Chinese medicinal herbs after acid digestion using flame AAS. In [24] determined the differences between the minerals of Zhongning wolfberry among the regions using PCA and Linear Discriminant Analysis (LDA). Furthermore, PCA combined with cluster analysis are useful tools to classify mineral content as shown by [25] for fruit juices and nectars according to fruit type and the geographical origin; and in [26] for minerals and heavy metals contents in raw honeys from four different bee species to distinguish the honeys by its species using AAS and inductively coupled plasma-mass spectrometry (ICP-MS), respectively. PCA has also been successfully used in differentiating different grape cultivars [27] and the peel, pulp and seed of *Passifloraedulis f. flavicarpa*and *Passifloracincinnata* cultivated in Bahia state, Brazil based on their mineral contents [28].

In Malaysia, dates are more desired fruit during the Ramadan month when Muslim performing their fast. The fruit also consumed by many people regardless of race and religion. Prices differ by the types and grades of dates. Suppliers in Malaysia usually import dates in bulk, repack into small packaging and market them under different names and prices. Unfortunately, the contents of only several elements such as K, Ca, Mg and Fe are labeled while information of other major and minor elements in dates is not included. Hence, this study was conducted to measure the elements composition in a variety of dates (and their pits) available in Malaysia markets using ICP-OES. ANOVA and PCA analyses provide information that will reveal the differences between the varieties of dates and thus allow a more informed decision among Malaysian consumers in their selection of dates based on the quality. The dates pits were also included in this study since they are used as mineral sources in animal feeds or turned into non caffeinated coffee.

II. MATERIALS AND METHODS

Chemical Reagents and Solutions

All chemical reagents were of analytical grade. Ultrapure water (18.2 MΩ.cm^{-1}) from a Milli-Q system (Millipore, MA, USA) was used to prepare all the solutions. Stock solutions of the elements; Aluminium (Al), Barium (Ba), Calcium (Ca), Copper (Cu), Iron (Fe), Potassium (K), Magnesium (Mg), Manganese (Mn), Sodium(Na), Nickel (Ni), Lead (Pb), Zinc (Zn), Selenium (Se) (1000 mg.L^{-1}, Merck, Darmstadt, Germany) were used to prepare working standard solutions by dilution with 1% (v/v) nitric acid. All laboratories glassware used were immersed in 10% v/v of nitric acid solution for 12hr for decontamination prior to use and then rinsed several times with deionized water. Nitric acid (65% v/v, Merck, Darmstadt, Germany) and hydrochloric acid (65% v/v), were used for acid digestion.

Instrumentation

ICP-OES model Optima 4300DV (PerkinElmer Inc., USA) was used with axial viewing for determination of elemental composition. The ICP-OES was set-up with the following conditions:

RF Power	: 1300 Watt
Plasma gas rate (Ar)	: 8.0 Lmin^{-1}
Auxiliary gas rate	: 0.2 L min^{-1}
Nebulizer gas rate	: 0.55 L min^{-1}
Pump flow rate	: 1.5 mL min^{-1}

Sample Preparation

Ten samples of imported date fruits (Ajwa, Medjool, Mariami, Sunsweet, Nourina, Mabroom, Khudry, Sunseed, Degletnour and Mesir) were purchased from a local supermarket. The samples were stored in refrigerated bags to prevent the proliferation of fungi and bacteria. Samples were washed several times with deionized water to remove any impurities and then oven dried at 50^{o}C for 1 hour. All the samples were blended using a, 2 speed, 230V/50Hz, 1L of Waring blender (National, Japan) to homogenize the samples.

Ash and Elements Determination

The samples (approximately 2.0 g) were dried in the oven (Binder, FisherScientific, Malaysia) at 115°C for 1 hour. They were placed in a muffle furnace (Carbolite, England) at 550°C for 24 hours. The ash samples were taken from the furnace and allowed to cool in desiccators provided with a desiccant agent. After cooling, the samples were weighed and replaced in the oven until the differences between two successive weightings were not exceeded ± 0.001 g. Acid digestion method was used to determine elements constituents. Each sample (2.0 g) was digested with a mixture of HNO_3 (0.1 M, 20 mL) and HCl (6 M, 5 mL) at the room temperature (25°C) [29], [30]. The solution was subsequently transferred to a 50 mL volumetric flask and diluted with deionized water. The amounts of elements were analyzed using an ICP-OES. The analysis was performed in triplicate and the results were presented in mean value ± standard deviation.

The concentration (C) of the metal in the test sample was then calculated using the following formula:

$$C = \frac{(a-b)x\,V}{m}.df \qquad (1)$$

where *C* means concentration of elements in the test sample (mg/kg), *a* = concentration in the experiment solution (mg/mL), *b* = mean concentration in the blank solutions (mg/mL), *V* = volume of the experiment solution (mL), *m* = weight of the test portion (g) and *df* = dilution factor.

Data Analysis

Significance between elements was tested with one way ANOVA using Minitab statistical software (Version 16, Minitab Inc., USA). Differences among means were considered significant at $p < 0.05$. Multivariate data of major and minor elements in dates-flesh and dates-pits (triplicates samples) were mean-normalized using Microsoft Excel 2007. Exploratory analysis technique using PCA was performed on the normalized data matrix using Unscrambler 10.3 (CAMO software AS, Oslo, Norway) to identify the relationship between samples studied and its elements content in scores and loadings plots.

III. RESULTS AND DISCUSSION

A. Analysis of Variance (ANOVA)

ANOVA by one way technique on dataset of ICP-OES showed significant differences among samples in dates-flesh and dates-pits.

B. Dates-Flesh

The major and minor elements of ten varieties of date-flesh samples are presented in Table 1. The results showed significant ($p< 0.05$) differences among several of the 10 varieties.

C. Major Elements

The content of each sample in Table 1 showed that K, Ca, Mg and Na are higher (95 mg/kg-5623 mg/kg) than other components hence considered as the major elements while Al, Ba, Cu, Fe, Mn, Ni, Pb, Zn and Se were grouped as minor elements (less than 52 mg/kg), except for Al where the maximum value was 105.8 mg/kg in Ajwa date. Pb and Cd were the main heavy metals in dates due to rapidly increasing population in urban areas led to anthropogenic activities and fossil fuel combustion. Emissions from road traffic that uses fossil fuel, industry, agriculture, sewage sludge, and waste incineration are the chief sources of air pollution [31], [32]. The maximum permitted metals contaminant in fruit products in Malaysian Food Act 1983 are Pb (2 mg/kg), Cd (1 mg/kg), As (1 mg/kg), Hg (0.05 mg/kg) and Sb (1 mg/kg) and therefore the levels of Pb in date-flesh (0.090 mg/kg-0.534 mg/kg) is within the permissible limit. K content of the samples was between 2823 mg/kg to 5623 mg/kg, with the highest value recorded for Mabroom, and the lowest was observed in Medjool. The wide range of K was similar to those reported by [33] in the range of 3500 mg/kg to 7500 mg/kg in dates from different varieties. K is known as an essential nutrient in maintaining the nervous system [29]. Lack of K in body may lead to hypokalemia and causes elevation in blood pressure [34]. Mg concentration of Nourina, Mesir, Mariami and Medjool was in the range of 507 mg/kg to 530 mg/kg higher than those recorded for other samples that ranged from 336 mg/kg to 493 mg/kg. Sunsweet dates registered the lowest content of Mg (336 mg/kg). The evaluated Mg concentration of the date samples was within the range and comparable to the Mg content in date fruits from different origins as reported by others. In [29] reported the concentration of Mg in dates was 480 mg/kg to 530 mg/kg; in [33] mentioned that the Mg concentration of their date samples was 262 mg/kg to 2250 mg/kg, while in [35] reported Mg concentration of 560 mg/kg to 600 mg/kg. Variability in Ca concentration among the date samples was recorded with values ranging from 343 mg/kg to 870 mg/kg. Ajwa dates recorded highest Ca concentration (870 mg/kg) followed by Mariami dates (707 mg/kg). The lowest Ca content was recorded for Mesir date (343 mg/kg). The Ca concentration of the studied dates was comparable to the dates from previous studies. In [33] reported Ca concentration of 249 mg/kg to 1100 mg/kg. In 29] reported Ca concentration of 480 mg/kg to 530 mg/kg, while in [36] reported Ca concentration of 12 mg/kg to 800 mg/kg. In contrast, higher concentration of Ca in dates was recorded by [19] with values 1230 mg/kg to 1870 mg/kg and in [35] reported Ca concentration of 1330 mg/kg to 2070 mg/kg for dates from different countries. Ca works together with Mg and help in bone development and energy metabolism [19]. Na concentration of 10 samples was in the range between 95 mg/kg for Khudry to 473 mg/kg for Ajwa dates. People who are suffering from hypertension are advisable to consume dates due to its high K and low Na content.

D. Minor Elements

Limited information reported on the Al content in date fruit, which it can be described as a heavy metal. Trace elements and heavy metals have certain health benefits at lower concentrations, but at higher levels, they can be toxic and pose health risks [14]. The European Food Safety Authority (EFSA) has established for the lifelong intake of Al at a tolerable weekly intake (TWI) of 1 mg/kg body weight [36]. Al was detected present in the samples in the range of 16.5 mg/kg to 106 mg/kg. Ajwa dates were recorded to contain 106 mg/kg and significantly ($p<0.05$) higher than other dates samples. Medjool dates contain 51 mg/kg and Mariami contain 48 mg/kg of Al. Low Al concentration was recorded for Khudry (16.5 mg/kg) similar to that reported by [37] which was in the range of 15.2 mg/kg to 16.7 mg/kg. The Ba concentration of date samples ranged between 0.115 mg/kg to 0.86 mg/kg and Ajwa dates recorded significantly ($p<0.05$) high Ba content (0.86 mg/kg), while other samples were in the range between 0.115 mg/kg to 0.45 mg/kg. Ba compound is widely used in industrial application such as in the production of plastics, textile and rubber [38]. Ba can be found naturally in drinking water and food, usually at low levels but it is not considered to be an essential element for human health. In [39] reported maximum daily dietary intake of barium for adults as 0.72 mg/person. The concentration of Ba in date samples is within the permitted range as humans consume small amount of dates per day, example Ba content in 200 g of Ajwa dates is only 0.172 mg. Cu is vital for human body,

especially for the nervous and cardiovascular systems. The obtained results was in the range value of 0.7 mg/kg-7.7 mg/kg and 2.7 mg/kg-7.9 mg/kg as reported by [33], [40] respectively, but higher levels was reported by [41] (12 mg/kg-727 mg/kg) and in [42] (8.9 mg/kg-18.6 mg/kg). Maximum concentration values in Cu were obtained in Medjool (6.23 mg/kg) and Khudry (5.88 mg/kg) samples, while minimum concentrations of Cu were noted in DegletNour (1.86 mg/kg) and Mabroom (2.98 mg/kg) samples. The tolerable upper intake level for adults is 10 mg/day [43]. The concentration of Cu in date samples is within the permissible range. Iron deficiency is considered as the number one nutritional disorder in the world by the World Health Organization (WHO).

Table 1: The elements concentration of dates-flesh and pits

Sample	Concentration of Dates (mg/kg)																									
	Al		Ba		Ca		Cu		Fe		Mg		Mn		Na		Ni		Pb		Zn		Se		K	
	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pit	Flesh	Pits	Flesh	Pit	Flesh	PPit
Sunsweet	26.5^{d} ± 1.27	6.96^{b} ± 0.80	0.259^{c} ± 0.05	0.139^{b} ± 0.01	488de ± 23.65	186^{f} ± 1.96	4.47^{b} ± 1.03	22.57^{c} ± 1.15	8.08^{e} ± 0.17	13.18^{b} ± 0.53	336^{e} ± 11.73	557de ± 16.13	3.36^{b} ± 0.87	8.90^{b} ± 0.13	123^{ef} ± 0.60	137^{d} ± 5.52	0.194^{fg} ±0.03	3.10^{b} ± 0.50	0.484^{a} ± 0.06	1.27^{b} ± 0.07	3.28^{c} ± 0.18	22.30^{d} ± 0.74	0.138^{a} ± 0.02	ND	3612^{d} ± 57.8	1249de ± 74.5
Nourina	43.3^{bc} ± 4.50	3.05^{cd} ± 0.46	0.356^{b} ± 0.04	0.131^{b} ± 0.03	554^{cd} ± 0.69	208de ± 5.75	4.31^{b} ± 0.17	12.39^{e} ± 1.48	10.56^{cd} ± 1.25	12.32^{b} ± 1.23	507^{ab} ± 41.50	629^{b} ± 35.02	3.32^{b} ± 0.27	9.66^{b} ± 0.57	247^{c} ± 26.77	113^{e} ± 4.76	0.273^{de} ± 0.02	1.83^{de} ± 0.27	0.488^{a} ± 0.04	0.67^{d} ± 0.002	3.28^{c} ± 0.17	13.41^{e} ± 0.82	ND	ND	5185^{a} ± 29.6	1149^{e} ± 40.2
Mabroom	24.1^{de} ± 3.08	4.19^{cd} ± 0.09	0.172^{d} ± 0.001	0.138^{b} ± 0.01	483de ± 2.55	260^{b} ± 2.17	2.98^{c} ± 0.36	20.89^{d} ± 1.11	9.76^{de} ± 0.91	11.17^{b} ± 0.19	423^{cd} ± 1.60	586^{cd} ± 7.01	1.37^{d} ± 0.02	6.87^{c} ± 0.14	139^{e} ± 4.37	133^{d} ± 5.42	0.500^{a} ± 0.04	2.25^{bc} ± 0.18	0.534^{a} ± 0.12	1.05^{c} ± 0.07	3.79^{b} ± 0.19	21.09^{d} ± 0.36	0.065^{a} ± 0.09	ND	5623^{a} ± 342.2	1235^{e} ± 14.1
Khudry	16.5^{e} ± 0.90	4.32^{c} ± 0.847	0.115^{e} ± 0.01	0.116^{b} ± 0.01	474de ± 5.86	216^{d} ± 2.66	5.88^{a} ± 0.32	33.82^{b} ± 1.42	7.68^{e} ± 0.23	12.05^{b} ± 0.35	383de ± 9.52	538^{e} ± 2.68	2.85^{b} ± 0.16	9.04^{b} ± 0.10	95^{f} ± 1.81	130^{d} ± 1.87	0.418^{b} ± 0.03	6.15^{a} ± 0.31	0.418^{a} ± 0.06	1.55^{a} ± 0.03	4.27^{b} ± 0.28	31.13^{b} ± 0.45	0.107^{a} ± 0.14	ND	4594^{b} ± 266.2	1908^{a} ± 44.5
Sunseed	41.2^{c} ± 4.85	3.57^{cd} ± 0.44	0.403^{b} ± 0.07	0.151^{b} ± 0.003	419^{ef} ± 10.88	226^{d} ± 1.41	4.18^{b} ± 0.11	25.82^{c} ± 2.20	8.12^{e} ± 0.84	13.72^{b} ± 0.36	392de ± 15.65	565de ± 9.38	2.69^{b} ± 0.53	7.12^{c} ± 0.23	219^{cd} ± 7.55	127^{d} ± 1.70	0.354^{bc} ± 0.03	3.22^{b} ± 0.18	0.370^{a} ± 0.04	1.27^{b} ± 0.002	3.74^{b} ± 0.25	25.02^{c} ± 0.598	0.066^{a} ± 0.17	ND	4441^{b} ± 366.9	1392^{bc} ± 67.1
Degletnour	17.8^{e} ± 0.89	4.10^{cd} ± 0.33	0.147^{d} ± 0.03	0.125^{b} ± 0.0003	558^{cd} ± 27.63	188^{f} ± 2.47	1.86^{d} ± 0.32	21.20^{d} ± 0.70	7.52^{e} ± 0.28	13.93^{b} ± 0.43	454^{bc} ± 10.00	647^{b} ± 10.74	3.08^{b} ± 0.18	7.71^{c} ± 0.13	189^{d} ± 23.30	130^{d} ± 3.91	0.206^{ef} ± 0.01	2.37^{bc} ± 0.36	0.354^{b} ± 0.06	1.25^{b} ± 0.02	2.42^{d} ± 0.14	20.39^{d} ± 1.06	0.074^{a} ± 0.04	ND	4298^{c} ± 287.3	1389^{bc} ± 71.3
Mesir	42.6^{bc} ± 0.38	3.58^{cd} ± 0.04	0.344^{b} ± 0.02	0.108^{bc} ± 0.03	343^{f} ± 3.91	236^{c} ± 3.02	5.16^{a} ± 0.10	6.67^{f} ± 0.28	17.61^{a} ± 0.34	17.22^{a} ± 0.29	517^{a} ± 25.90	623^{b} ± 6.10	5.02^{a} ± 0.29	10.87^{a} ± 0.45	390^{b} ± 9.03	154^{c} ± 2.95	0.312^{cd} ± 0.01	1.50^{e} ± 0.04	0.328^{b} ± 0.02	ND	6.70^{a} ± 0.33	13.25^{e} ± 0.38	ND	0.037^{a} ± 0.02	3060^{ef} ± 359.2	1284^{cd} ± 32.9
Ajwa	105.8^{a} ± 1.10	15.13^{a} ± 0.49	0.859^{a} ± 0.09	0.233^{a} ± 0.03	870^{a} ± 69.27	284^{a} ± 4.83	4.99^{a} ± 0.39	8.04^{f} ± 0.44	16.43^{ab} ± 1.40	79.96^{a} ± 1.18	493^{ab} ± 16.19	717^{a} ± 5.70	2.95^{b} ± 0.11	9.03^{b} ± 0.27	473^{a} ± 6.37	332^{a} ± 4.36	0.190^{fg} ± 0.01	0.34^{f} ± 0.05	0.140^{c} ± 0.05	0.10^{e} ± 0.00	3.94^{b} ± 0.50	11.84^{e} ± 0.12	0.223^{a} ± 0.24	ND	3873^{c} ± 46.3	1432^{bc} ± 42.7
Medjool	51.2^{b} ± 3.26	2.62^{d} ± 0.49	0.406^{b} ± 0.05	0.050^{c} ± 0.00007	582^{c} ± 38.66	273^{a} ± 14.4	6.23^{a} ± 0.18	39.91^{a} ± 1.21	11.89^{cd} ± 0.45	11.41^{b} ± 0.29	530^{a} ± 18.39	614^{bc} ± 3.04	2.97^{b} ± 0.37	5.88^{d} ± 0.15	240^{c} ± 2.79	203^{b} ± 4.97	0.236^{de} ± 0.02	6.62^{a} ± 0.32	0.090^{c} ± 0.03	1.59^{a} ± 0.21	3.84^{b} ± 0.20	36.33^{a} ± 1.35	0.215^{a} ± 0.03	0.100^{a} ± 0.07	2823^{f} ± 150.6	1492^{b} ± 53.2
Mariami	48.3^{bc} ± 2.84	6.61^{b} ± 0.21	0.455^{b} ± 0.03	0.077^{bc} ± 0.000	707^{b} ± 55.86	204^{ef} ± 9.13	5.04^{a} ± 0.38	7.33^{f} ± 0.52	13.48^{bc} ± 2.49	11.97^{b} ±0.61	522^{a} ± 24.01	543^{e} ± 11.68	1.62^{c} ± 0.005	9.57^{b} ± 0.51	248^{c} ± 25.07	125^{d} ± 4.25	0.149^{g} ± 0.03	2.00^{cd} ± 0.22	0.099^{c} ± 0.04	ND	3.41^{b} ± 0.17	11.58^{e} ± 0.23	0.333^{a} ± 0.05	0.125^{a} ± 0.04	5457^{a} ± 348.5	1440^{b} ± 57.3

The Fe concentration of Mesir and Ajwa were 17.61 mg/kg and 16.42 mg/kg, respectively and higher than the Fe content of Sunseed (8.12 mg/kg), Sunsweet (8.08 mg/kg), Khudry (7.68 mg/kg) and DegletNour (7.52 mg/kg). The results of Fe concentration were within the range reported by others. In [33] reported the Fe content of 2.1 mg/kg-16.2 mg/kg, while in [34] reported the Fe content of 8.5 mg/kg-72 mg/kg. In contrast, higher Fe content of 40.6 mg/kg-69.1 mg/kg [41] and 32.1 mg/kg-52.6 mg/kg [35] were observed in dates from different countries. Mn concentrations of date samples ranged between 1.37 mg/kg and 5.02 mg/kg. High Mn content was recorded for Egypt dates, and the lowest Mn concentration was observed in Mabroom dates. The Mn concentration in the studied samples was comparable with the previous reports. Mn concentration in ranges of 1.0 mg/kg-7.0 mg/kg and 3 mg/kg-59 mg/kg were reported by [33], [43] respectively. In contrast, other studies reported higher concentrations of Mn in dates from various countries [10], [35], [40]. Mn is a crucial trace element for brain function and metabolism of protein and carbohydrates [10], [30]. High value of Ni in dates fruit was reported by [11] with the values in the range between 16.27 mg/kg and 17.85 mg/kg. In contrast, the result obtained in this study showed that Ni was present in very low concentrations in all the date varieties with values in range from 0.149 mg/kg (Mariami) to 0.499 mg/kg (Mabroom). The results are within the range of 0.071 mg/kg to 0.7 mg/kg as reported by [33]. The highest value of Zn was determined in Mesir dates with the concentration of 6.70 mg/kg and insignificant different noted between other samples in the range between 3.28 mg/kg and 4.27 mg/kg. Values of Zn obtained in this study were in agreement with the previous studies [33], [40], [42]. Zn is classified as an essential component which plays a vital role in sustaining proper immune function. Level of Se in all date samples were insignificantly different between ranges 0.065 mg/kg to 0.333 mg/kg and no Se was detected for Mesir and Nourina dates. According to [44] in their finding, Se is one of the elements found in dates and has a potential as anti-cancer and important in immune function.

E. Dates-Pit

1. Major Elements

The result from ICP-OES has revealed the concentration of minerals in dates-pit, as shown in Table 1. The major elements in dates-pit are same as flesh, but the values are less; K (1149 mg/kg-1908 mg/kg), Ca (186 mg/kg-284 mg/kg), Mg (538 mg/kg-717 mg/kg) and Na (113 mg/kg - 203 mg/kg). Mg was found to be higher than the dates-flesh. Khudry dates contained 1908 mg/kg of K and significantly ($p<0.05$) higher than other dates samples. Both Medjool and Mariami contain 1492 mg/kg and 1440 mg/kg of K, respectively and insignificantly different. The K was noted lower in both Mabroom (1235 mg/kg) and Nourina (1149 mg/kg) samples. Variability in Mg concentration among dates samples were recorded with values ranging from 538 mg/kg to 717 mg/kg. Ajwa dates recorded highest Mg concentration (717 mg/kg) followed by DegletNour (647 mg/kg), Nourina (629 mg/kg) and Mesir samples (623 mg/kg). Meanwhile, the lowest Mg content was recorded for Khudry date (538 mg/kg). Na in dates-pit is usually slightly higher than Ca, Ajwa has proven to have the maximum concentrations in both Na (332 mg/kg) and Ca (284 mg/kg). Nourina sample showed the lowest level of Na (113 mg/kg), while Sunsweet and Deglet Nour were proven to have lower concentration Ca (186 mg/kg). There is lack of information on the elemental compositions in other literature for dates-pit. In the United States, date pits have been a problem to the date industry as a waste stream. Pulverized ground date pits are being used on a small scale, on dirt roads as a type of road base gravel. However, finding a way to make a profit on the pits would benefit date farmers substantially [45].

2. Minor Elements

The minor elements such as Fe, Cu, Zn, Mn, Pb, Ni and Se of dates pit for the 10 varieties are presented in Table 1. Fe value was the highest, followed by Cu, Zn, Mn, Pb and Ni. Fe concentration ranges between 11.17 mg/kg and 79.96 mg/kg with the highest value observed in sample Ajwa, while no significant difference was observed in the others sample. Cu ranged between 6.67 mg/kg and 39.93 mg/kg; Mesir had the lowest level of Cu while Medjool showed the highest level of Cu. There is no significant difference in Cu content between Sunseed, Sunsweet, DegletNour and Mabroom. Ajwa, Mariami and Mesir are among the samples with the lower Cu content. The analysis showed highest level of Zn (36.3 mg/kg) was present in sample Medjool and lowest level (11.58 mg/kg) was found in sample Mariami. ANOVA revealed insignificant difference in Zn content between samples Nourina, Mesir, Ajwa and Mariami which is in the range between 11.58 mg/kg and 13.41 mg/kg. Ajwa showed the highest level of Mn (10.87 mg/kg) and Medjool had the lowest content (5.89 mg/kg) while other samples were proven to have insignificant difference in the range of 6.87 mg/kg-7.71 mg/kg (Mabroom, Sunseed and DegletNour) and 8.9 mg/kg-9.66 mg/kg (Sunsweet, Ajwa, Khudry, Mariami and Nourina). Se was detected to be insignificantly different between concentration 0.037 mg/kg to 0.125 mg/kg for samples Mesir, Medjool and Marimi while the presence of Se was not detected in other samples.

Other minor elements that were observed higher in decreasing order are Al, Pb, Ni and Ba. Al ranged between 2.62 mg/kg and 15.13 mg/kg; Ajwa sample showed the highest level of Al (15.13 mg/kg) and significantly different compared to other samples while the lowest value of Al was observed in Medjool sample (2.62 mg/kg). Ba levels ranged between 0.05 mg/kg and 0.23 mg/kg with Ajwa contains the highest level and other samples were proven to be insignificantly different with range 0.05 mg/kg to 0.15 mg/kg. The content of Pb in dates-pit was in the range of 0.10 mg/kg to 1.58 mg/kg, which is within the permissible level. The highest level of Pb was found in Medjool while Ajwa shown the lowest value. Pb was not detected in Mariami and Mesir samples. Ni level was found to be highest in Medjool (6.62 mg/kg) and lowest in Ajwa (0.34 mg/kg).

3. Principal Components Analysis (PCA)

The similarities of dates-flesh and dates-pit for major and minor elements in Table 1 were well observed using Principal Components Analysis (PCA).

F. Dates-Flesh

1. Major Elements

The first principal component (PC1) and second principal component (PC2) accounted 90% and 7% of variance, respectively, was obtained after PCA was performed on the data matrix for major elements in dates-flesh samples (Table 1). The scores and loadings matrices obtained from PCA were used to create scores and loading plots of PC1 versus PC2 of the major elements in dates-flesh as shown in Fig. 1. Scores plot explains the distribution among the samples whereas the loadings plot explains the effect of elements on the distribution of samples. Samples that are closed together in scores plot have the similarities. The scores plot shows that Ajwa, Medjool and Mesir are located between 0.6-1.6 on the right side of PC1 while in loadings plot, the element of Ca, Mg and Na are located around 0.25 on the right side of PC1. Thus, this indicates that Ajwa, Medjool and Mesir are significantly different from other samples which contained high level of Ca, Mg and Na. The confirmation was made by referring the value (mg/kg) of each element in Table 1 where Ajwa (870, 493, 473), Medjool (583, 530, 240) and Mesir (343, 517,390) for Ca, Mg and Na, respectively. The same way can be used to determine the composition of other samples for K. It can be seen that other samples are located on the left side of PC1 in the scores plot especially Mabroom (-1.2) where it can be correlated with the high level of K in the loadings plot. Mabroom and Sunsweet contained 5623 mg/kg and 3612 mg/kg of K, respectively. Composition of K in Medjool and Mesir were found to be lower than Sunsweet but not for Ajwa where it recorded 3873 mg/kg which is slightly higher than Sunsweet. Mariami has high values of Ca (707 mg/kg) and Mg (522 mg/kg), however it is classified in the group which contain highest amount of K (5457 mg/kg).

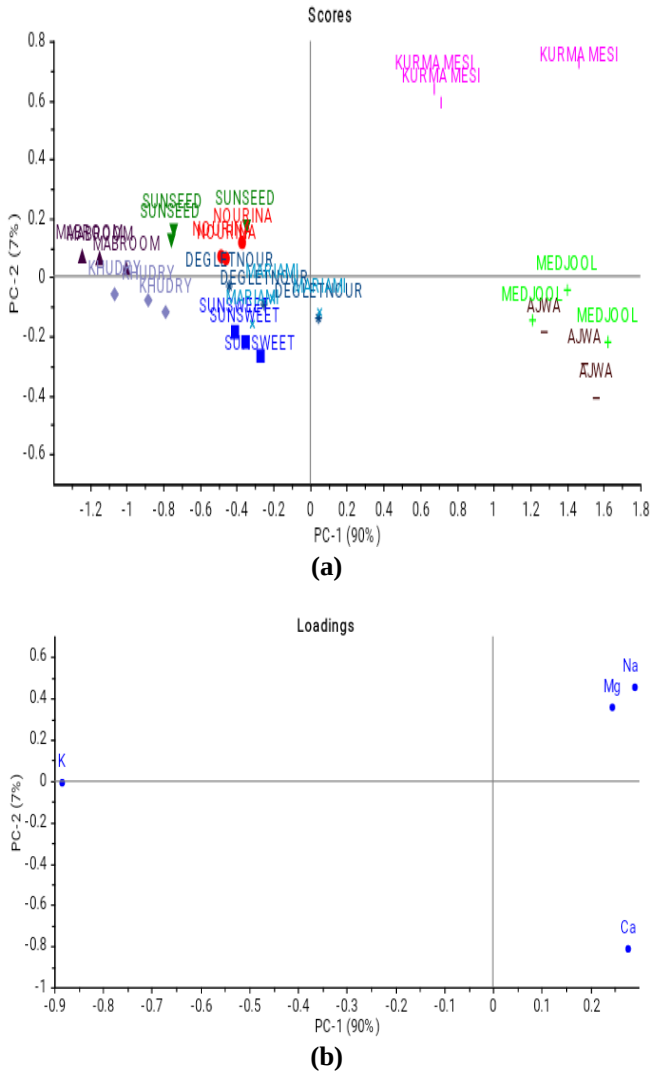


Fig. 1: Major elements plot of the first principal components (PC1) versus the second principal component (PC2) for the triplicate of 10 dates –flesh samples: (a) scores plot and (b) loadings plot

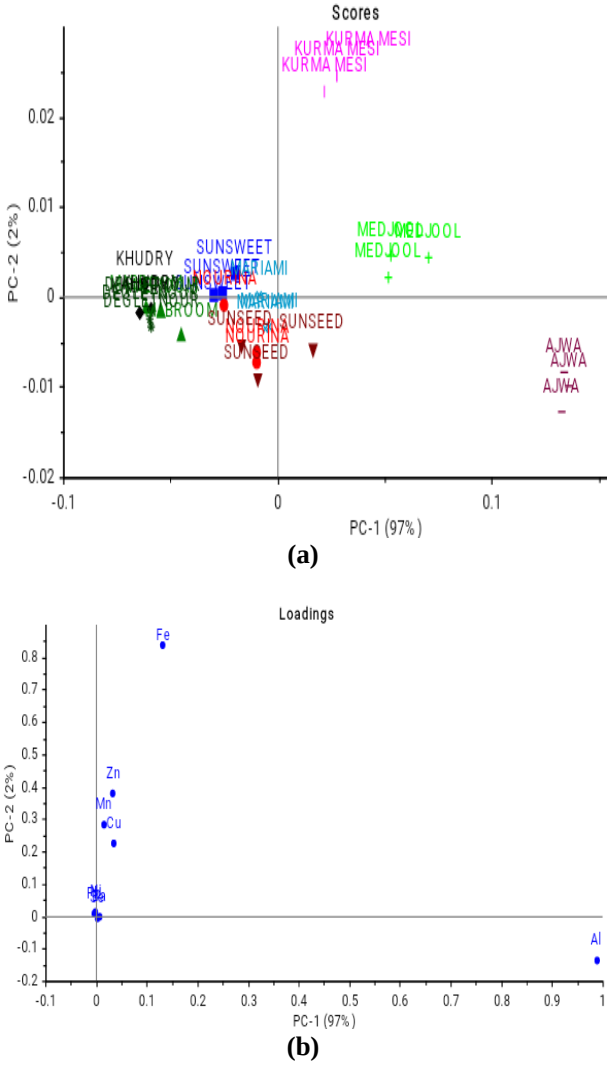


Fig. 2: Minor elements plot of the first principal components (PC1) versus the second principal component (PC2) for the triplicate of 10 dates –flesh samples: (a) scores plot and (b) loadings plot

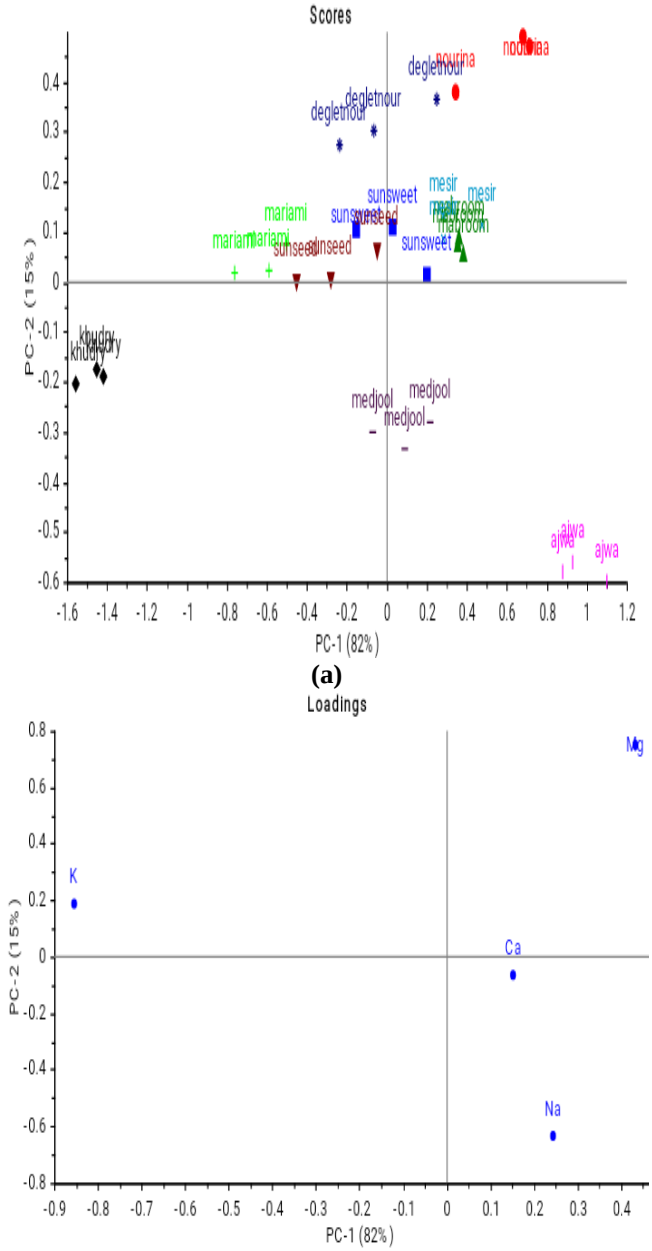
2. *Minor Elements*

Similarly, the scores and loadings matrices obtained from PCA were used to create scores and loading plots of PC1 (97% variance) versus PC2 (2% variance) of the minor elements in dates-flesh as shown in Fig. 2. Ajwa, Medjool, Mesir and Sunseed are distributed on the positive values of PC1 in the scores plot. Loadings plot shows that Al and Fe located at approximately 1 and 0.15, respectively on PC1. Thus, it can be concluded that the samples contained high values (mg/kg) of Al and Fe; Ajwa (105.8, 16.43), Medjool (51.2, 11.89), Mesir (42.6, 17.61) and Sunseed (41.2, 8.12) respectively. However, it was observed that Sunseed is closely located with other samples due to its lowest value of Fe compared with Ajwa, Medjool and Mesir. Sunseed and other samples located at the center in the scores plot indicate that the contents of Cu, Zn and Mn; and followed by Ba, Ni, Pb and Se are closely similar. These were confirmed by referring to their values in Table 1.

G. *Dates-Pit*

1. *Major Elements*

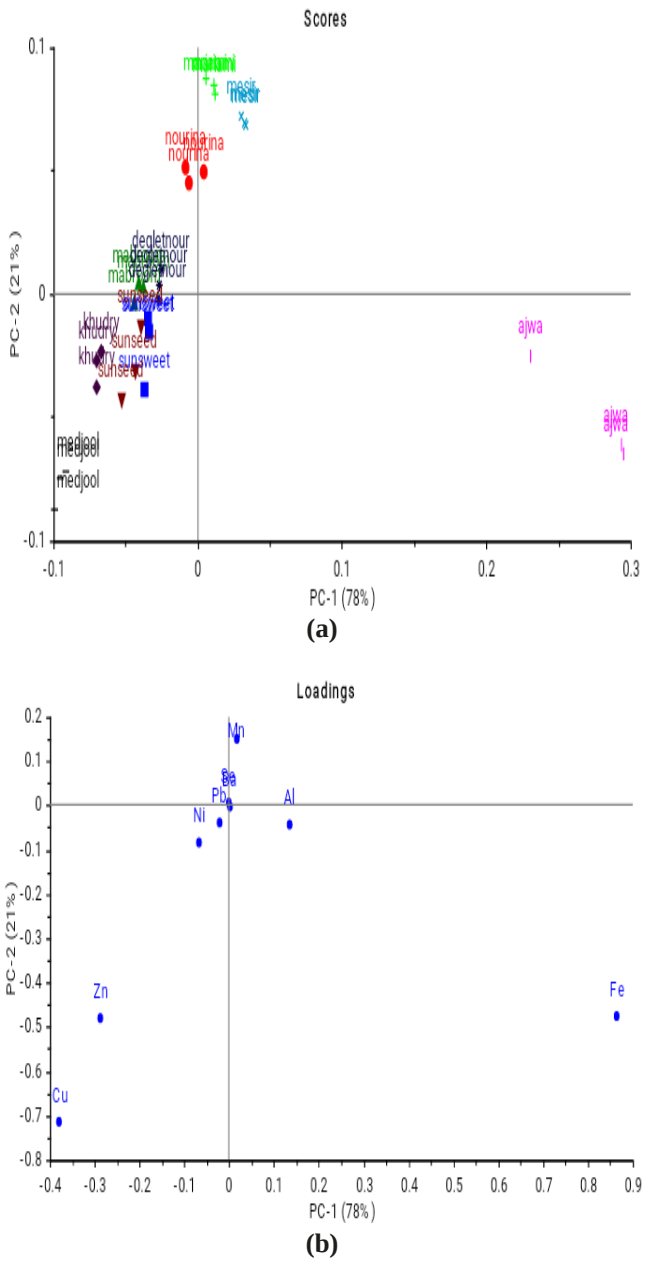
The relationship between samples with major elements was observed by mapping the position of Mg, Na, Ca and K on PC1 of loadings plots with distribution of samples in scores plots as shown in Fig. 3, where PC1 and PC2 accounted 82% and 15% variance respectively in PCA model. The high content of those elements can be related to samples such as Ajwa to Na; Medjool and Ajwa to Ca; and Nourina to Mg. Thus, it can be seen that the values (mg/kg) of Mg, Na and Ca were high in Ajwa (717, 332, 284), Medjool (614, 203, 273) and Nourina (629, 113, 208) respectively. While, K was observed high level in Khurdy (1908 mg/kg).



(a)

(b)

Fig. 3: Major elements plot of the first principal components (PC1) versus the second principal component (PC2) for the triplicate of 10 dates –pits samples: (a) scores plot and (b) loadings plot



(a)

(b)

Fig. 4: Minor elements plot of the first principal components (PC1) versus the second principal component (PC2) for the triplicate of 10 dates –pits samples: (a) scores plot and (b) loadings plot

2. Minor Elements

The relationship of samples and minor elements in dates-pit was observed in scores and x-loadings plots as shown in Fig. 4. Ajwa was found high in Fe (79.96 mg/kg) and Al (15.13 mg/kg) whereas Medjool contained high levels of Cu (39.91 mg/kg) and Zn (36.33 mg/kg). It was found that Khudry located close to Medjool as its Cu and Zn levels were 33.82 mg/kg and 31.13 mg/kg respectively, which are not much different with Medjool. Mariami, Mesir and Nourina were found closely located in the upper part of scores plots which is related with Mn in x-loadings plot. The content of Mn in respective samples was 9.57 mg/kg, 10.87 mg/kg and 9.66 mg/kg. Other samples such as Mabroom, Negletnour, Sunsweet and Sunseed located in the middle of scores plot were found related with Ni, Pb, Ba and Se in x-loadings plot where their values were closely similar.

IV. CONCLUSION

Hence, this study provides the elemental composition of dates fruit according to different varieties, purchased from Malaysia's supermarket. Both flesh and pits were determined for their minerals content and results revealed that K was the most abundant element (5223 mg/kg for flesh and 1908 mg/kg for the pit). Based on the PCA plot, elements contained different varieties of dates sample was able to evaluate. The major elements content in dates are K, Mg, Na and Ca while other elements were observed in minor concentrations. Both Ajwa pits and flesh contained high concentration of Ca, Na and Mg. Ajwa, Medjool and Mesir dates-flesh proven to be different from other samples

in both major and minor elements. While for dates-pit, the differences were showed in Ajwa, Medjool and Khudry.

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REFERENCES

1. I. A. Ahmed, A. W. Ahmed, and R. K. Robinson, "Chemical composition of date varieties as influenced by the stage of ripening," Food Chemistry, 54(3), 1995, pp. 305-309.
2. F. Guido, S. E. Behija, I. Manel, Z. Nesrine, F. Ali, H. Mohamed, H. A. Noureddine, and A. Lotfi, "Chemical and aroma volatile compositions of date palm (Phoenix dactylifera L.) fruits at three maturation stages," Food Chemistry, 127(4), 2011, pp. 1744-1754.
3. W. Braide, S. U. Oranusi, and C. C. Otali, "Nutritional, antinutritional, minerals and vitamin compositions of fourteen brands of fruit juice sold in Onitsha main market," FS J Res Basic and App Sci., 1(3), 2012, pp. 4-6.
4. I. J. Salma, M. A. Sajib, M. Motalab, B. Mumtaz, S. Jahan, M. M. Hoque, and B. K. Saha, "Comparative evaluation of macro and micro-nutrient element and heavy metal contents of commercial fruit juices available in Bangladesh," American Journal of Food and Nutrition, 3(2), 2015, pp. 56-63.
5. F. A. Fazli, and N. A. Fazli, "Evaluation and determination of minerals content in fruits," International Journal of Plant, Animal and Environmental Sciences, 4(2), 2014, pp. 160-166.
6. D. Eruvbetine, "Canine nutrition and health," Seminar of Kensington Pharmaceuticals Nig. Ltd., 2003.
7. R. K. Murray, D. K. Granner, P. A. Mayes, and V. W. Rodwell, Harper's Biochemistry. New York: McGraw-Hill, 2000.
8. K. O. Soetan, C.O. Olaiya, and O. E. Oyewole, "The importance of mineral elements for humans, domestic animals and plants-A review," African Journal of Food Science, 4(5), 2010, pp. 200-222.
9. World Health Organization (WHO), The World Health Report 2001: Mental health: New understanding, new hope. Geneva: WHO, 2001.
10. M. S. Jamil, R. Nadeem, M. A. Hanif, M. A. Ali, and K. Akhtar, "Proximate composition and mineral profile of eight different unstudied date (Phoenix dactylifera L.) varieties from Pakistan," African Journal of Biotechnology, 9(22), 2010, pp. 3252-3259.
11. M. N. Al-Seeni, "Minerals content and antimicrobial efficacy of date extracts against some pathogenic bacteria," Life Science Journal, 19(2), 2012, pp. 504-508.
12. O. S. Agboola, and A. L. Adejumo, "Nutritional composition of the fruit of the Nigerian wild date palm, Phoenix dactylifera," World Journal of Dairy and Food Sciences, 8(2), 2013, pp. 196-200.
13. M. A. Sahari, M. Barzegar, and R. Radfar, "Effect of varieties on the composition of dates (Phoenix dactylifera L.)—note," Food Science and Technology International, 13(4), 2007, pp. 269-275.
14. R. Bhat, K. Kiran, A. B. Arun, and A. A Karim, "Determination of mineral composition and heavy metal content of some nutraceutically valued plant products," Food Analytical Methods, 3(3), 2010, pp. 181-187.
15. H. Altundag, and M. Tuzen, "Comparison of dry, wet and microwave digestion methods for the multi element determination in some dried fruit samples by ICP-OES," Food and Chemical Toxicology, 49(11), 2011, pp. 2800-2807.
16. K. K. Taha, and F. M. Al Ghtani, "Determination of the elemental contents of date palm (Phoenix dactylifera L.) from Kharj Saudi Arabia," World Scientific News, 12, 2015, pp. 125-135.
17. G. Tyler, and S. J. Yvon, ICP-OES, ICP-MS and AAS techniques compared. ICP Optical Emission Spectroscopy Technical Note, New Jersey: Kyoto: Horiba Group, 1995.
18. G. Baskaran, N. A. Masdor, M. A. Syed, and M. Y. Shukor, "An inhibitive enzyme assay to detect mercury and zinc using protease from Coriandrum sativum," Scientific World Journal, 2013, 2013, pp. 1-7.
19. E. A. Assirey, "Nutritional composition of fruit of 10 date palm (Phoenix dactylifera L.) cultivars grown in Saudi Arabia," Journal of Taibah University for Science, 9(1), 2015, pp. 75-79.
20. F. Y. Al-Juhaimi, S. H. Hamad, I. S. Al-Ahaideb, M. M. Al-Otaibi, K. Ghafoor, T. Abbasi, and S. A. Abbasi, "Biogas production through the anaerobic digestion of date palm tree wastes-process optimization," BioResources, 9(2), 2014, pp. 3323-3333.
21. F. A. Juhaimi, K. Ghafoor, and M. M. Özcan, "Physical and chemical properties, antioxidant activity, total phenol and mineral profile of seeds of seven different date fruit (Phoenix dactylifera L.) varieties," International Journal of Food Sciences and Nutrition, 63(1), 2012, pp. 84-89.
22. R. G. Brereton, Chemometrics: Data Analysis for the Laboratory and Chemical Plant. New Jersey: John Wiley and Sons, 2003.
23. A. Kolasani, H. Xu, and M. Millikan, "Evaluation of mineral content of Chinese medicinal herbs used to improve kidney function with chemometrics," Food Chemistry, 127(4), 2011, pp. 1465-1471.
24. S. Zhang, Y. Wei, S. Wei, H. Liu, and B. Guo, "Authentication of Zhongning wolfberry with geographical indication by mineral profile," International Journal of Food Science and Technology, 52(2), 2017, pp. 457-463.
25. I. Coelho, A. Rego, S. Gueifão, A. C. Nascimento, and I. Castanheira, "Application of chemometric methods for multi-elemental characterization of fruit juices and nectars analysed in the Portuguese Total Diet Studies pilot study," Journal of Chemometrics, 31(2), 2017, pp. 1-11.
26. S. P. Kek, N. L. Chin, S. W. Tan, Y. A. Yusof, and L. S. Chua, "Classification of honey from its bee origin via chemical profiles and mineral content," Food Analytical Methods, 10(1), 2017, pp. 19-30.
27. A. G. Potortí, V. L. Turco, M. Saitta, G. D. Bua, A. Tropea, G. Dugo, and G. D. Bella, "Chemometric analysis of minerals and trace elements in Sicilian wines from two different grape cultivars," Natural Product Research, 31(9), 2017, pp. 1000-1005.
28. C. G. Novaes, I. L. da Silva Romão, B. G. Santos, J. P. Ribeiro, M. A. Bezerra, and E. G. da Silva, "Screening of Passiflora L. mineral content using principal component analysis and Kohonen self-organizing maps," Food Chemistry, 233, 2017, pp. 507-513.
29. S. Parvin, D. Easmin, A. Sheikh, M. Biswas, S. C. Sharma, M. G. Jahan, M. A. Islam, M. S. Shovon, and N. Roy, "Nutritional analysis of date fruits (Phoenix dactylifera L.) in perspective of Bangladesh," American Journal of Life Sciences, 3(4), 2015, pp. 274-278.

30. A. Uba, M. I. Abdullahi, A. J. Yusuf, Z. Y. Ibrahim, M. Lawal, I. Nasir, and F. T. Abdullahi, "Mineral profile, proximate and amino acid composition of three date's varieties (Phoenix dactylifera L.)," Derpharma, 7(5), 2015, pp. 3-48.
31. V. B. Vouk, and W. T. Piver, "Metallic elements in fossil fuel combustion products: Amounts and form of emissions and evaluation of carcinogenicity and mutagenicity," Environmental Health Perspectives, 47, 1983, pp. 201-225.
32. A. Celik, A. A. Kartal, A. Akdoğan, and Y. Kaska, "Determining the heavy metal pollution in Denizli (Turkey) by using Robinio pseudo-acacia L.," Environment International, 31(1), 2005, pp. 105-112.
33. S. S. Abdrabo, G. Grindlay, L. Gras, and J. Mora, "Multi-element analysis of Spanish date palm (Phoenix dactylifera L.) by inductively coupled plasma-based techniques. Discrimination using multivariate statistical analysis," Food Analytical Methods, 8(5), 2015, pp. 1268-1278.
34. P. Mariyam, and V. Mary, "Nutritional analysis (macronutrients, potassium and iron content) of four palm date varieties (phoenix dactylifera l.) and study of consumption pattern among muslim and maharashtrian community," Journal of Food Processing and Beverages, 3(1), 2015, pp. 1–9.
35. B. Al-Gboori, and V. Krepl, "Importance of date palms as a source of nutrition," Agric. Trop. Subtrop., 43(4), 2010, pp. 348-351.
36. BfR, BfR Health Assessment No. 034: Aluminium in apple juice: No storing of fruit juice in aluminium tanks. Available: http://www.bfr.bund.de/cm/349/aluminium_in_apple_juice_no_storing_of_fruit_juice_in_aluminium_tanks.pdf.
37. D. M. Trabzuni, S. E. Ahmed, and H. M. Abu-Tarboush, "Chemical composition, minerals and antioxidants of the heart of Date Palm from three Saudi cultivars," Food and Nutrition Sciences, 5(14), 2014, pp. 1379-1386.
38. H. A. Schroeder, I. H. Tipton, and A. P. Nason, "Trace metals in man: Strontium and barium," Journal of Chronic Diseases, 25(9), 1972, pp. 491-517.
39. World Health Organization (WHO), Cancer pain relief: With a guide to opioid availability. Geneva: WHO, 1996.
40. S. Al-Hooti, J. S. Sidhu, and H. Qabazard, "Physicochemical characteristics of five date fruit cultivars grown in the United Arab Emirates," Plant Foods for Human Nutrition, 50(2), 1997, pp. 101-113.
41. N. H. Jamil, I. Izzuddin, Z. Zainuddin, and M. H. Jumali, "Microstructural studies of nanocrystalline barium zirconium titanate (BZT) for piezoelectric applications," AIP Conference Proceedings, 1678(1), 2015, pp. 1-5.
42. R. M. Mohamed, A. S. Fageer, M. M. Eltayeb, and I. A. M. Ahmed, "Chemical composition, antioxidant capacity, and mineral extractability of S udanese date palm (P hoenix dactylifera L.) fruits," Food Science and Nutrition, 2(5), 2014, pp. 478-489.
43. Food and Nutrition Board, 2001.
44. W. Al-Shahib, and R. J. Marshall, "Fatty acid content of the seeds from 14 varieties of date palm Phoenix dactylifera L.," International Journal of Food Science and Technology, 38(6), 2003, pp. 709-712.
45. J. S. Hamada, I. B. Hashim, and F. A. Sharif, "Preliminary analysis and potential uses of date pits in foods," Food Chemistry, 76(2), 2002, pp. 135-137.