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Identification and Determination of Metal Elements of Dates Syrup Extracted from Various Varieties Using SEM-EDS Technique

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Abstract: This study has been conducted to determine and identify the metal elements of dates syrup extracted from Khstawy, Zehdy and Shukary using Scanning electron microscope-Energy dispersive Spectrometer (SEM-EDS) technique. The results showed that dates syrup was rich in both metal and non-metals elements. The obtained results showed some different trends in the date syrup content of mineral elements. The results showed the availability of Carbon (C) element in dates syrup extracted via hydraulic pressure from Khstawy (80.73%), Zehdy (65.28 %) and Shukary (68.49%) varieties while in dates syrup produced thermally (80.59%) and dates syrup produced without thermal (72.16%). Oxygen (O) ratio in Khstawy, Zehdy, Shukary, dates syrup produced thermally, and dates syrup produced without thermal were 18.92, 35.27, 15.26, 19.09 and 27.46 respectively. Moreover, the results showed the availability of sodium (Na) (0.17 %), sulphur (S) (0.11 %), potassium (K) (0.05%), silicon (Si) (0.03%) in the dates syrup extracted from Khstawy, while in Zehdy variety there was Aluminum (Al) (0.33%), potassium (K) (0.08%), chloride (Cl) (0.03%), magnesium (Mg) (0.01%). In Shukary variety, Al (5.24%), K (0.05%), nitrogen (N) (10.73%), (S) (0.06%), copper (Cu) (0.18%). Additionally, the results showed that the quantity of metal elements available in dates syrup produced thermally were found as follow as follows: Na (0.22%), S (0.1%) as well as O and C. Yet, the number of the metal elements in the dates syrup produced by hydraulic pressure was more that the dates syrup produced thermally are as follows: Na (0.1%), Al (0.1%), K (0.1%), S (0.02%), Si (0.03%) and phosphor (P) (0.02%).

Keywords: Chemical elements, Date syrup, SEM-EDS, GC/M.

Introduction

Date palm trees and their fruits are used and utilized by Mesopotamian people long time ago, especially to produce dates syrup as well as vinegar (Ibrahim, 2014).

Dates syrup is considered as one of the important transformational industries with high food value especially when produced by using modern method. It is well-known as the intense liquid produced via the extraction of the natural contents of dates, free from fibers, impurities and foreign substances. It is utilized directly or used in making sweets and pastry (Al Sahi, 1986). It has different names for example, In Iraq and Saudi Arabia called "

Dibs", while in Egypt, it is called " Honey of dates", etc. The chemical components of date's syrup are varied where carbohydrates represent the major part of the dry weight 85%. Dates syrup also contains protein, metallic acids and vitamins (Ibrahim, 2015). Furthermore , dates syrup contains (86.6%) of ultimate carbohydrates part of which are reduced carbohydrates (81.7 %) sucrose (4.9%), Dates syrup also contains moister , pH , protein , Ash (metal salts) with the percentage of 24.8%, 0.02%, 2.1%, 6.6% respectively calculated on the basis of dry weight , (Ibrahim , 2015) . It also contains a significant amount of Vitamin A and Vitamin B (Ibrahim, 2014). Ramadan (1998) explains that dates syrup is rich of Na, Ca, K, Mg and Fe with the average of 18.81, 199.31, 780.26, 145.92, 23.38 mg.100 gm^{-1} respectively. Al-Shahib & Marshall (2003) showed that K ratio in dates and seeds reach to 0.9 and 0.5% respectively. They also mentioned that the average of each metal in dried dates reaches around 0.1- 916 mg.100 gm^{-1} depending on the type of metal such as Ca, Co, Cu, F, Fe, Mg, Mn, K, P , Na and Zn. Iron is necessary for brain development and blood haemoglobin in the erythrocytes and its lack leads to alterations in many metabolic processes and anaemia (Murray *et al*., 2000). Zinc is an important for living organisms with a pivotal role in proteins and enzymes (Leigh & Michalczyk, 2006). Manahan (2017) stated that deficiency of zinc is the most common essential trace element in the world. High concentration of Aluminium causes toxic, anaemia and brain damage. The metalloids such as beryllium, arsenic, cadmium, nickel and chromium VI are regard as human carcinogens at wide exposure (U.S. EPA., 2002). High Concentrations of Lead (Pb) in food stuff leads to human's toxic and hazardous air pollutants (Jarüp, 2003). So, the presence of Lead in date fruits above the permissible limit causes extreme health hazards to the human. Hence the determination of leads in dates important to the human health and safety (Kennish, 1992).

Through a study for the effect of various methods of dates syrup extraction from Zahdi variety via rotary evaporator and microwave on the chemical elements existing therein (namely, Na, Ca, K, Mg, Fe and Zn), El-Nagga & El-Tawab (2012) showed such elements values existed in dates are: 90.5, 28.5, 1000, 52, 10, 0.95 mg.100 gm^{-1} respectively. Also, such values amount to 72, 20, 900, 39, 8.7 and 0.7 mg.100 gm^{-1} respectively using a rotary evaporator with water bath and they reach up to 73.8, 21, 925, 41, 8.8 and 0.72 mg.100 gm^{-1} respectively using microwave .

The present study aimed at using SEM-EDS technique to identify and determine the metal elements existing in dates syrup extracted from different varieties of dates.

Materials & Methods

Raw material used in the extraction process

Different varieties of dates are Khstawy, Zehdy and Shukary brought from Babylon Governorate during season of 2016-2017.

Extraction of date's syrup

First, the dates were washed to remove dirt and dusts therefrom. Second, the moisturizing operation was conducted on the dates using water with temperature of 50°C and pH = 7. The moisturizing operation was conducted by spraying water on dates with average of 4 litres.20 Kg^{-1}. Third, dates were packed in enmeshed plastic bags, and the capacity of each was 5 kg with an average of 20 kg per one treatment. Then bags were transformed to

the hydraulic extraction system which is consist of a hydraulic plunger, disk, spring, and thermal heating system within the tank. All such parts are made of stainless-steel.

Identification and Determination of chemical Elements

The chemical elements existing in dates syrup assessed and identified by electronic microscope SEM-EDS, size: Supra 55 VP by way of drying the samples in preparation to conduct an electronic scanning for the elements existing in the substance samples were placed inside the system and it has been firmly locked by using Secondary Electron indicator (SE2) accordingly a high accuracy and clear-contrasted images were obtained and properly system calibration Quantax EDS X flash from Bruker for the purpose of obtaining a quantitative and qualitative identification of elements (Goldstein *et al*., 2017) .

Results & Discussion

SEM-EDS technique has been used to quantify and qualify the metal elements in produced dates syrup. It has been used for the first time in the identification of metal elements existing in dates fruit and their products.

Results of quantitative and qualitative analysis of chemical elements of dates syrup produced out of the three aforesaid varieties as well as natural dates syrup produced via the traditional method in addition to dates syrup produced thermally (commercial type) have been obtained.

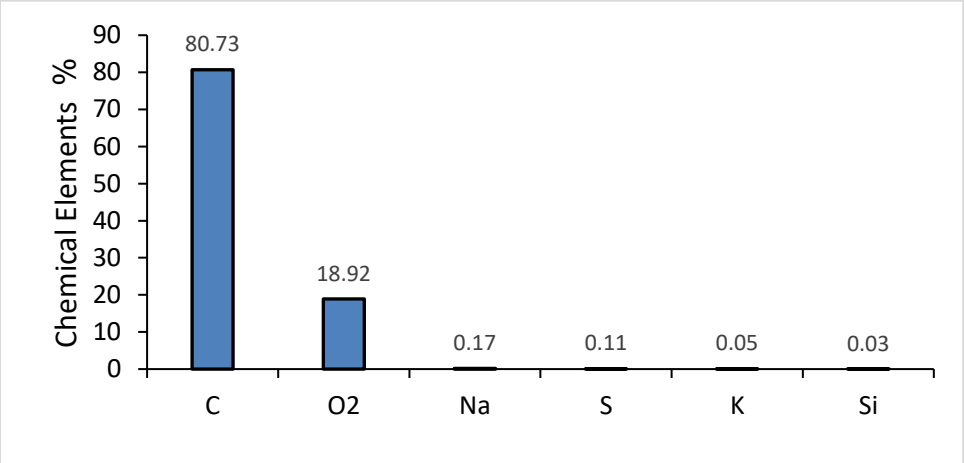

Fig. (1): Metal element of dates syrup content produced out of Khstawy dates variety.

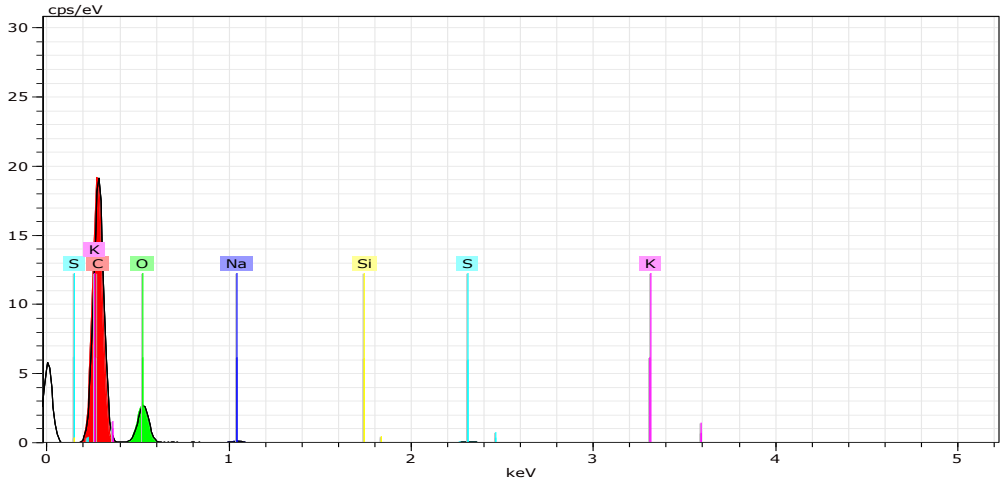

Fig. (2)) EDS Spectrum of date syrup Khstawy variety

The results of analysis of chemical elements of dates syrup produced out of Khstawy date reflects an increase in the carbon content as well as O and Na , S and K as well as Si. The concentrations of elements were recorded as follows 80.73, 18.92, 0. 17, 0.11, 0.05 and 0.03% respectively as shown in figs. (1) and (2).

As to the dates syrup produced from Zehdy dates, it contains carbon with an atomic concentration of 65.28% as well as the preens of O with a ratio 34.27%, while, Aluminium, found with an atomic concentration of 0.33%, K with a concentration of 0.08% while Cl, it occurs with a concentration of 0.03%, Mg with concentration of 0.01% as shown in Figs. (3) and (4). Al-Hooti *et al*. (1995) stated that dates contain noticeable amounts of Mg, K, Ca, Pb, Fe, Zn and Cu. Ahmed *et al*. (1995) reported that the Barhi variety date contains Cu (0.2 mg.100g^{-1}), Fe (0.3 mg.100g^{-1}), Mg (82 mg.100g^{-1}), Ca (12 mg.100g^{-1}), Na (75 mg.100g^{-1}) and K (855 mg.100g^{-1}).

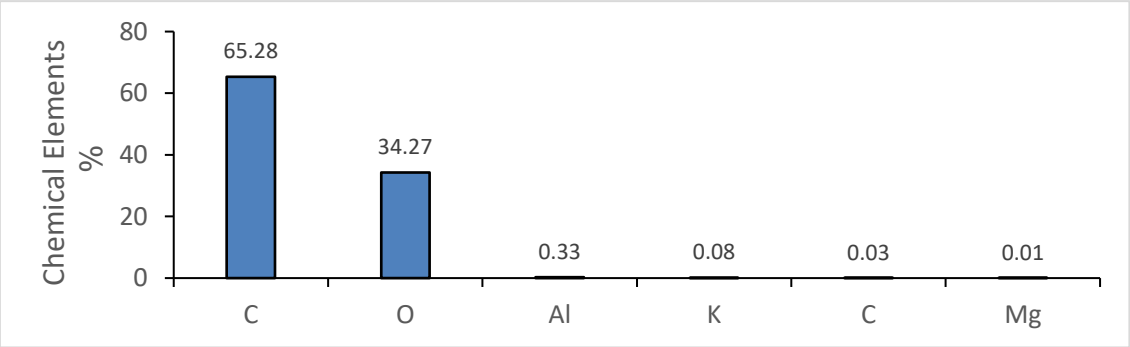

Fig. (3) Chemical elements of Zehdy date syrup variety.

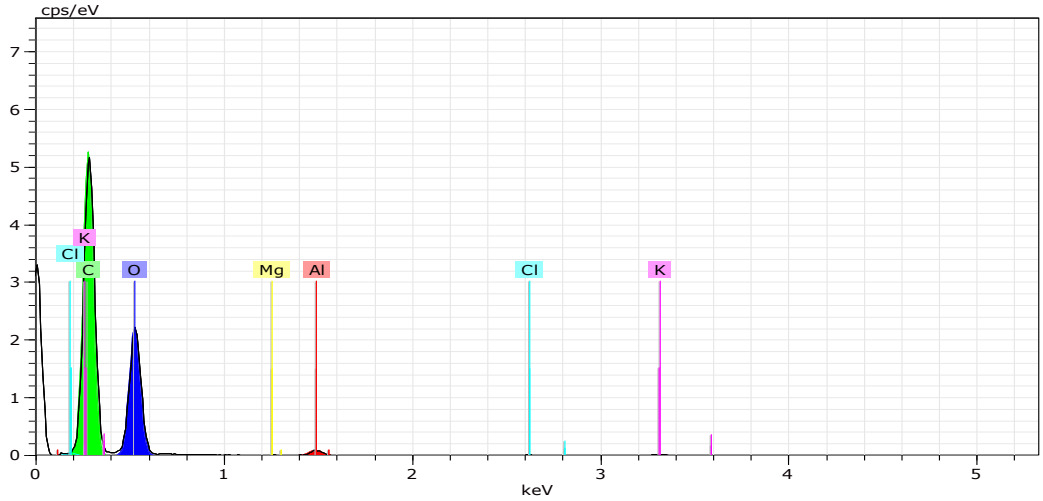

Fig. (4): EDS Spectrum of dates syrup Zehdy variety

While dates syrup produced from Shukary dates, it contains metal elements as shown in Fig. (5) such as C, O and N with the averages of 10.73%, 15.26% and 68.49% respectively. It also contains the following elements with their associated concentrations: K (0.05%), S (0.06%), Al (5.24%). Cu is also existed in dates syrup with a concentration (0.18%). Such concentration is deemed safe that GSO (2012) stated that Cu maximum safe concentration existing in dates syrup is (2 ppm). Fig. (6) shows the course of metal element content. Farahnaky *et al*. (2016) have stated that date syrup contains many mineral

elements such as Na (900 ppm), K (12960 ppm), Fe (33.5 ppm), Ca (444.12 ppm), Cu (0.091 ppm), Zn (2.92 ppm), Mg (1020 ppm) and Mn (0.77 ppm). Assirey (2015) had studied the mineral composition of date in four cultivars (Ajwa, Kodari, Safawy and Burni) and found that the quantity of calcium, phosphorus, potassium, sodium and magnesium reached 187, 27, 476.3, 7.5 and 150 mg.100g^{-1} respectively in Ajwa variety and 133, 16, 289.6, 4.9 and 60 mg.100g^{-1} respectively in Kodari variety. In the case of Safawy, the mineral composition was 123, 12, 512, 8.6 and 56 mg.100g^{-1} respectively and in the Burni variety was 168, 18, 422.5, 8.9 and 100 mg.100g^{-1} respectively.

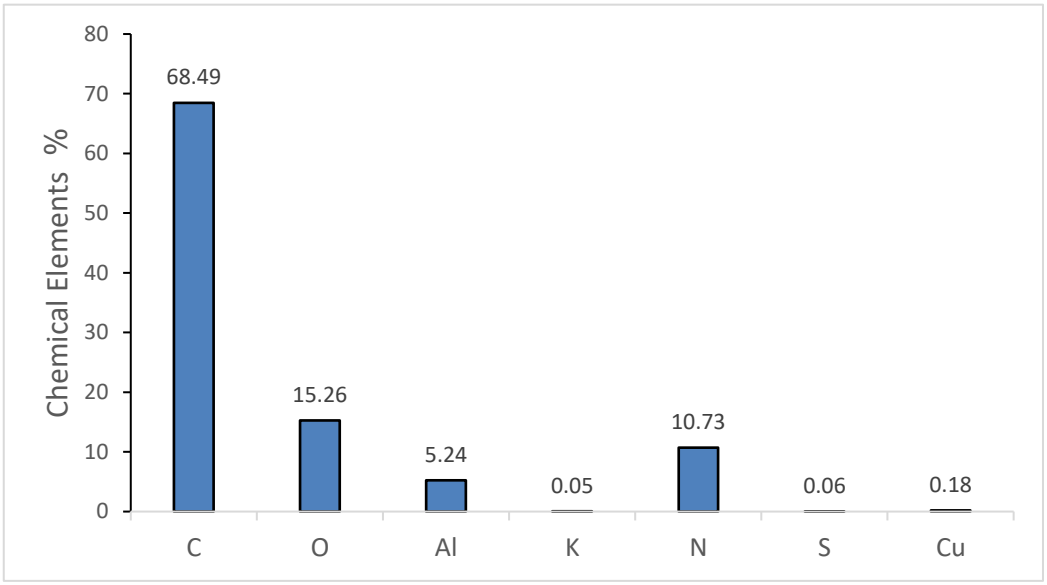

Fig. (5) The content of chemical elements of dates syrup produced out of Shukary dates.

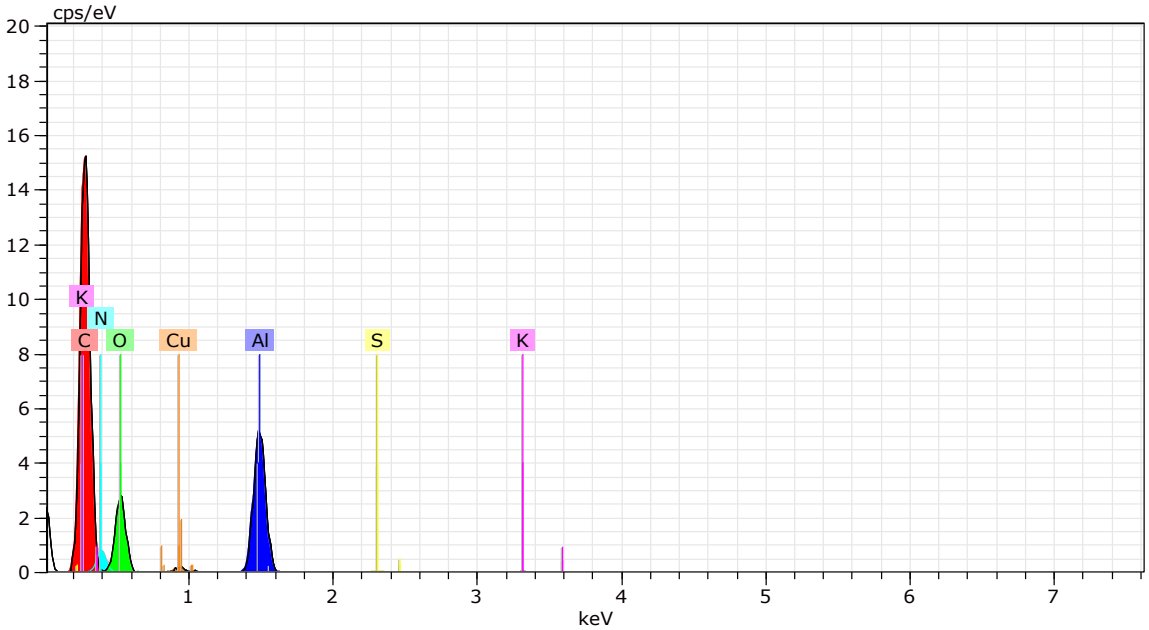

Fig. (6): Spectrum of EDS of dates syrup Shukary variety

Also , the obtained results of dates syrup produced from the three varieties show the presence of major elements in the three varieties with high concentrations such as C, O, K as well as other various and different elements existing in the three varieties. Such variation of elements could be explained by difference of date palm varieties, type of soil, irrigation water and the used fertilization (Bassat, 1971).

The presence of Cl in the dates syrup produced from Zehdy dates may be attributed to the fact that the water used for moisturizing the dates prior the production process may contain a significant amount of Cl.

Concerning the two commercial types of dates syrup, the dates syrup produced via a thermal method contains a high atomic concentration concerning its content of C which amounts to 80.59%, O with a concentration (19.09%), Na with a concentration (0.22%) and S with a concentration (0.10%) as shown in fig. (7) and fig. (8).

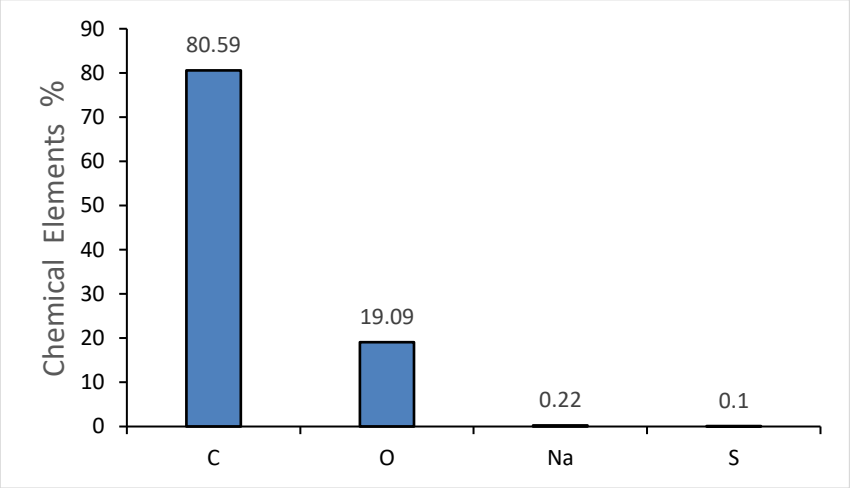

Fig. (7): The content of Chemical elements of commercial dates syrup produced thermally.

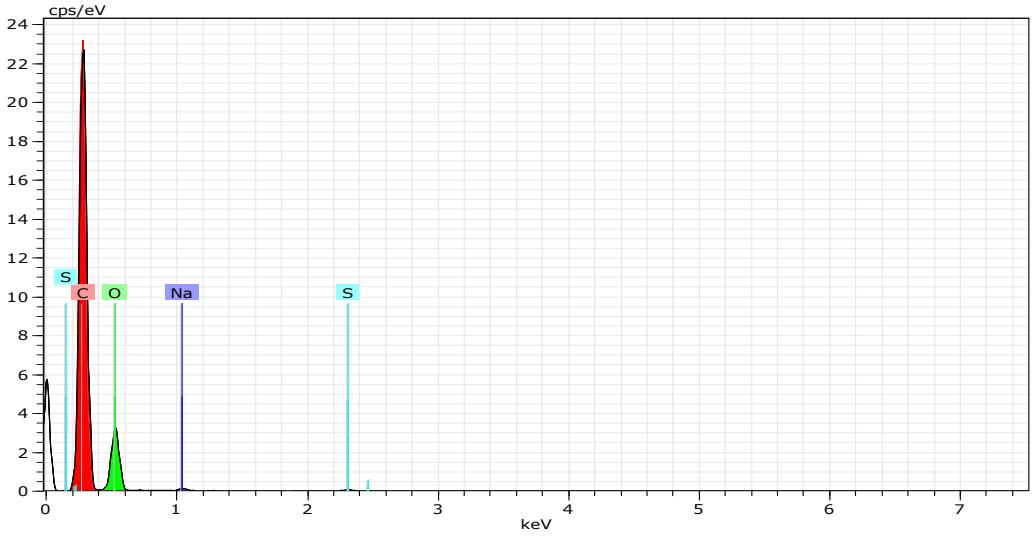

Fig. (8): Spectrum of EDS for commercial date syrup produced thermally.

In terms of the dates syrup produced via the traditional method (dates syrup extracted by natural), such dates syrup contains various metal elements such C, Na, Al, K, S, Si and P with the averages of 0.02%, 0.03%, 0.02%, 0.1% and 0.1% respectively in addition to the presence of O with a ratio of 27.46%.

Fig. (9) showed the content of metal element of dates syrup produced via the traditional method as well as fig. (10). Al-Hooti *et al.* (2002) reported high concentration of sodium followed by potassium, calcium, and magnesium as the second. Date syrup is rich in mineral elements such as Na (31.48 mg.100 g^{-1}), K (218.15 mg.100 g^{-1}), Fe (33.38 mg.100 g^{-1}), Ca (493.2 mg.100g^{-1}), and Mg (242 mg.100g^{-1}) (Ramadan, 1998). Eruvbetine (2003) reported that sodium, phosphorus, potassium and calcium are categorized as macro-elements while potassium, iron, copper, magnesium,

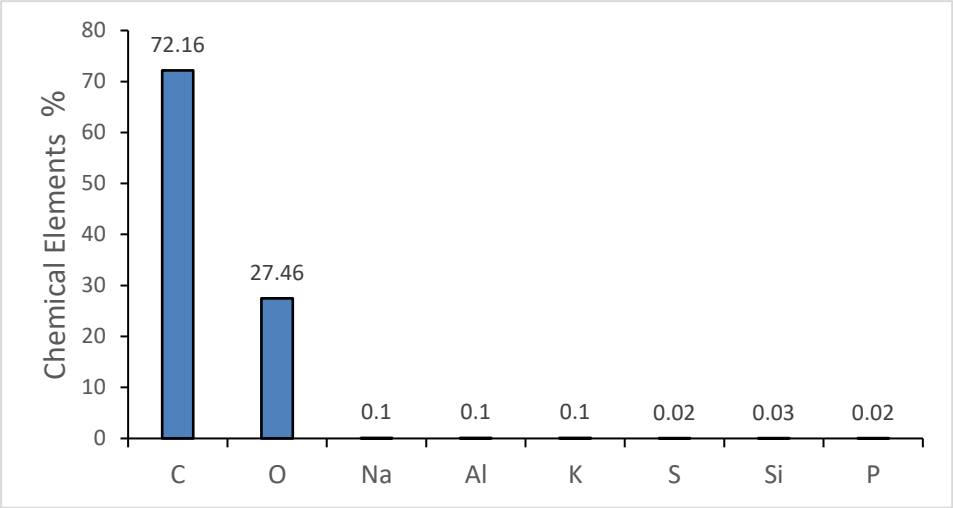

Fig. (9): The content of chemical elements of dates syrup produced traditionally and by using dates syrup.

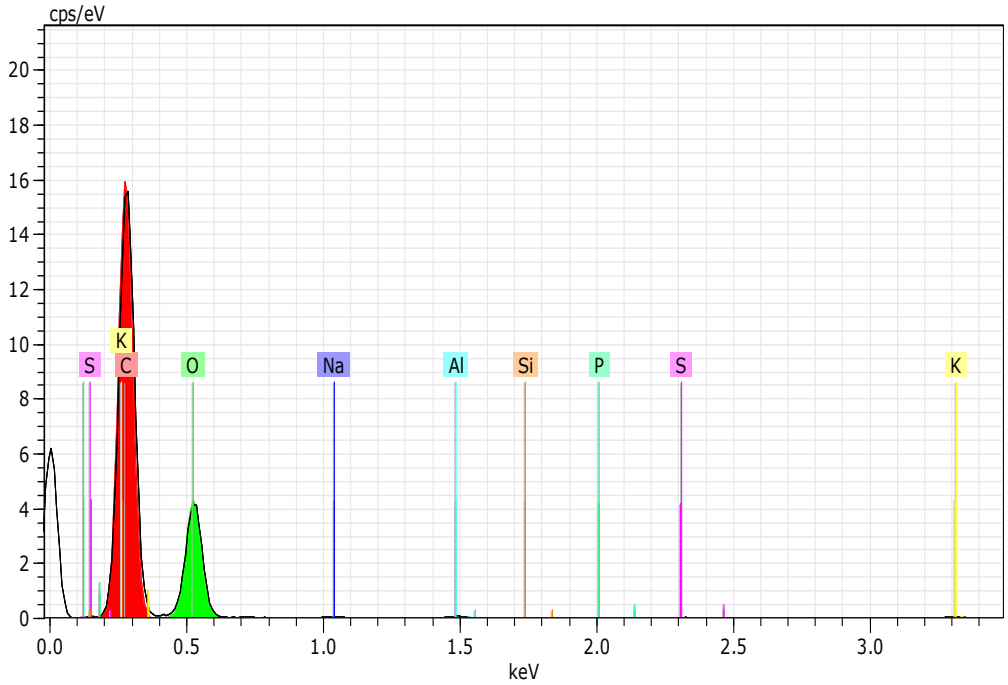

Fig. (10)) Spectrum of EDS of dates syrup produced traditionally.

manganese, cobalt, iodine, zinc, fluoride, molybdenum, chromium, sulphur, and selenium are considered as micro-elements. Both of macro-elements and micro-elements are very important for human health. Human body needs of macro-elements more than 100 $mg.dl^{-1}$, but it needs of micro-elements less than that (Murray *et al*., 2000). On the other hand, the arsenic, cadmium, nickel, and lead are classified as trace elements. In this study the results showed that the iron was not found in the all samples of date syrup.

Conclusions

Through the inspection of metal elements via (SEM-EDS) technique, it has been shown that dates and their products contain a rich content of metal elements useful for human body and the least metal elements occurred in the dates syrup produced thermally. Also, a variation has been recorded in the content of metal elements of dates syrup between the dates varieties.

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Conflicts of interest

The authors declare that they have no conflict of interests.

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