

Determination of Trace Elements in Saudi Arabian Dates by Inductively Coupled Plasma-Mass Spectrometry

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ABSTRACT. A rapid and sensitive method for the determination of trace elements (Mn, Pb, Fe, Co, Ni, Cu, Zn and Cd) in the flesh of various date species of Saudi Arabia is described. The optimization of the operating conditions and figures of merit are given. Detection limits are in the range of 0.01-130 ppb. The relative standard deviations range from 0.47 to 4.87% for the flesh in date cultivars. It has been shown that the method has great advantages for the determination of those elements in date cultivars compared to the wet and dry ashing techniques.

Dates have been grown as a staple food for thousands of years in the desert areas of the world. The importance of the date palm tree was appreciated by many nations because of the economic as well as nutritional value of its fruits (Sawaya *et al.* 1982). Date is considered as one of Saudi Arabia's major exports, with an estimated 15 million date trees of which 12 million are fruiting trees with more than 450 different cultivars. Therefore, dates in their various forms are consumed by a large number of Saudi people and considered traditionally an important food (Al-Showiman and BaOsman 1992). The nutritional value of the dates can be seen from the presence of proteins, sugars, amino acids, carbohydrates, vitamins and minerals which should be included in diet for maintenance of proper equilibrium in normal adults (Alwarthan *et al.* 1993).

With increasing tendency for date packaging by both the private and public sectors, a knowledge of the chemical composition of dates for quality control

becomes very essential. The increasing awareness of the importance of trace elements in foods and their speciation, has created a demand for more sensitive determinations.

Inductively coupled plasma mass spectrometry (ICP/MS) is now approaching the end of its first decade of development and is now being considered an established and powerful analytical technique for multi-elemental and isotopic analysis (Date 1983). Applications of ICP/MS in different samples showed many advantages, *e.g.* multi-element capability and low detection limits for most trace elements (Gray 1986, Houk *et al.* 1980). Various types of samples such as alloys, ceramics, oils, food, blood, water, air and dust have been analyzed by ICP/MS for trace elements (Mark and Gray 1987).

In this paper, multi-element analysis for the determination of Cd, Co, Cu, Fe, Mn, Ni, Zn and Pb in the flesh of various date species of Saudi Arabia using ICP/MS is described. The environmental conditions and cultural practices which affect the development of date palm fruits are kept in view (Jones 1984).

Experimental

Instrumentation

The ICP/MS results were obtained using a Sciex Elan model 250. Instrument control, data manipulation and storage were provided by the 15BCO12B computer by Matrox Electronic System Ltd., associated with an Epson printer model LQ1050 and plotter by Houston Instruments. Sample introduction was made with a peristaltic pump, model miniplus 2 by Gilson. Viton pump tubing was connected directly to the concentric glass nebulizer (TR-30-C3). Gas flow was adjusted to position the tongue of the plasma. A muffle furnace by Heraeus Electronics was also used. Full instrument details are given in Table. 1.

Chemicals and Reagents

All Chemicals used for calibration standards were of high purity grade supplied by Spex Industries, Inc. These include $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 2\text{H}_2\text{O}$, Fe metal, $[\text{Co}(\text{en})_3](\text{NO}_3)_3$, $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$, $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$, ZnO, CdO and $\text{Pb}(\text{NO}_3)_2$.

AnalaR nitric and sulphuric acids (BDH Chemicals Ltd., Poole, Dorest, U.K.). All solutions were prepared with deionized distilled water, obtained by using distillation apparatus by Corning Mega-Pure Model MP3-three liters.

A nitric acid solution 4% (v/v) was prepared by the dilution of concentrated nitric acid with distilled deionized water.

Table 1. Instrument details for inductively coupled plasma mass spectrometer

Parameter	Parameter Value
Rf incident power (kw)	1.2
Plasma gas flow (L/min)	13
Auxiliary gas flow (L/min)	1.4
Nebulizer gas pressure (psi)	40
Measurements per peak	5
Repeat per integration	5
Sample flow (ml/min)	1
Resolution	Low
Counting precision	0.1
Threshold (ions/sec)	1
Measurements time (sec)	0.05

Stock solution of the required elements were prepared by dissolving the appropriate weight of the organo-metallic compound into 4% (v/v) nitric acid solution. Working solutions were made by serial dilution to give a linear calibration curve with concentration ranging between 0-220 ppb.

Preparation of Samples

The Sekkeri and Khalas cultivars were obtained from Hotat Bani-Tamime (Central region). The Rezaiz and Sillaj cultivars were obtained from Al-Hassa (Eastern region), while Barhey and Menifi from Madina (Western region) of Saudi Arabia. The collected fruit samples were preliminary cleaned up with distilled deionized water and the flesh with its outermost skin were separated out from the seeds, cleaned up and washed further with deionized distilled water to remove impurities and dried in an oven at 105°C for 20 minutes. Then the flesh were analyzed for the content of trace metals individually.

Procedure

Determination of trace metals

ca. 2 g of the freshly dried flesh sample from each date cultivar were accurately weighed and placed separately in well dried silica dishes. 2 ml of concentrated sulphuric acid were added. The samples were dried in an oven at 110 °C for 30 minutes, carefully volatilized over a hot plate at 200°C for 30 minutes and then the residue was transferred in a muffle furnace (Heraeus Electronic) at 550 °C for an

hour. The samples were cooled to room temperatures, 5 ml of concentrated nitric acid were added; the ash was stirred gently, filtered into 25 ml volumetric flask and diluted by deionized distilled water to the mark. A further dilution also was required to lower the concentration for the determination of iron. Each sample was then aspirated into the Elan ICP/MS using concentration calibration program (concal) supplied by Sciex, and precision studies were made using five replicates.

Results and Discussion

The date palm tree was appreciated by many nations over the centuries, because of the economical as well as the nutritional value of its fruit. Green plants are considered the major selective accumulators of inorganic nutrients upon which other life forms are directly or indirectly dependent. Some metals are essential for animals and human beings.

Because of the biological and toxicological implications of some trace elements consumption, there is a clear need for a sensitive analytical method that can be applied to various biological and environmental samples. The importance of the determination can be seen in the large number of analytical methods that have been developed for the determination of some metals at low level concentrations (Ure and Mitchell 1976, Stieg and Niemann 1977, Grimanis 1978, and Chau *et al.* 1976).

Most of the published work for the determination of macro and trace metals found in the date fruits used atomic absorption spectrometer (AAS) and flame photometry (FP). Therefore, we decided to develop the analysis by using ICP/MS for the determination of the trace metals found in date cultivars. This technique showed improvement in results compared to those obtained by AAS and FP.

The calibration curves were used for the determination of the trace metals of Cd, Co, Cu, Fe, Mn, Ni, Zn and Pb in all the date cultivars. The curves (Fig. 1) were linear with a correlation coefficient of 0.994-0.999 for all determined elements. These elements are observed at 0.01-15.09 ppm levels in the analyzed samples except for Fe where it was observed at a level of 51-130 ppm. Detections of limits for trace metals and their relative standard deviations are shown in Tables 2 and 3.

It can be observed that there is a consistent difference among concentrations of trace metals, particularly, Cu, Fe, Mn and Zn in the various samples. The difference may be rationalized (Clark and Smith 1988) among the properties of the date cultivars due to the changes in regional and seasonal trends for the various elements.

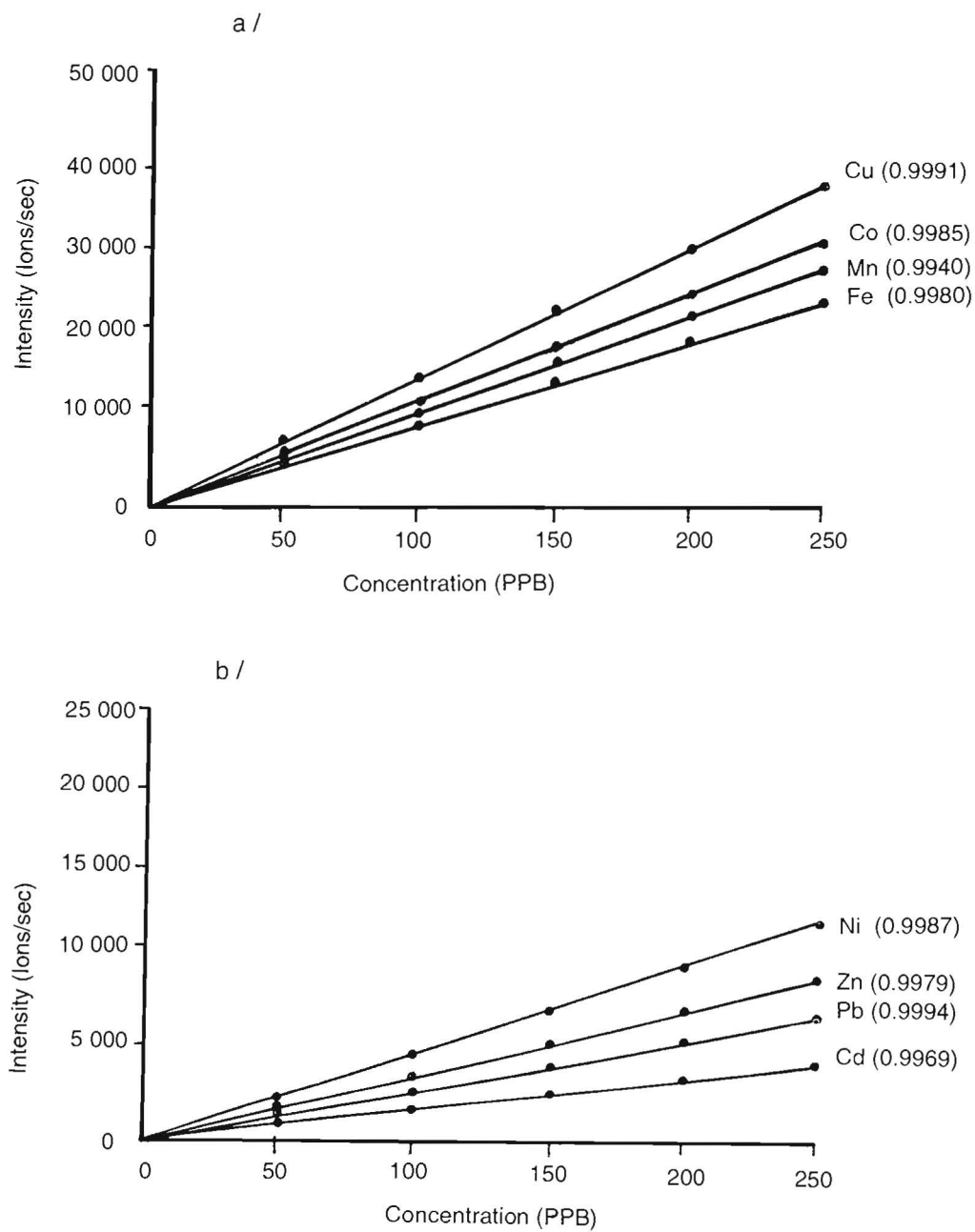


Fig. 1. Typical calibration curves (a and b) obtained for the analysis of trace elements in dates.

Table 2. Results of determination of trace metals in the flesh of some Saudi Arabia date cultivars, based on dry weight

Cultivars	Element Concentration ($\mu\text{g/g}$)*							
	Cd	Co	Cu	Fe	Mn	Ni	Zn	Pb
Barhey	0.02	0.20	1.63	129.9	15.09	0.25	2.37	0.05
Khalas	0.02	0.19	1.99	110.8	11.96	0.23	2.59	0.07
Menifi	0.01	0.11	1.82	46.2	6.92	0.14	2.45	0.01
Rezaiz	0.01	0.19	2.11	105.6	13.85	0.23	3.18	0.04
Sillaj	0.03	0.13	1.19	62.1	9.32	0.18	1.86	0.00
Sekkeri	0.01	0.13	2.42	51.3	9.20	0.18	3.19	0.00

*Average of 5 replicates

Table 3. Relative standard deviation for the determination of trace metals in the flesh of Saudi Arabian date cultivars

Cultivars	Relative Standard Deviation (%) Element							
	Cd	Co	Cu	Fe	Mn	Ni	Zn	Pb
Barhey	4.87	2.22	4.79	0.94	3.50	0.85	3.38	2.76
Khalas	1.99	2.29	4.28	3.09	4.51	0.47	2.39	3.39
Menifi	3.28	1.05	3.82	3.56	3.33	0.59	3.39	4.22
Rezaiz	3.72	1.03	2.11	1.10	1.04	3.26	1.95	1.89
Sillaj	4.51	0.50	4.90	1.54	1.36	1.65	3.09	–
Sekkeri	3.45	3.65	1.18	1.34	4.24	2.04	3.97	–

*Average of 5 replicates

In the date cultivars being studied, the concentration of Cu, Fe, Mn, Ni and Zn were high in the samples of Barhey and Rezaiz, which are popular brands for the Saudi Arabian people, being cultivated in eastern and western regions of the country with semi-arid areas and hot climate, *i.e.* Al-Madina and Al-Hassa.

In conclusion, it is apparent that date cultivars are rich in macro and trace minerals essential for the normal health of mammals. The present procedure proved to be sensitive, less time consuming and easier in sample handling, if compared with the other wet and dry ashing methods.

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تقدير العناصر المتواجدة بكميات ضئيلة في بعض تمور المملكة العربية السعودية بواسطة الحث المزدوج - الكتلة الطيفية

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لقد تم استخدام طريقة سريعة وحساسة لتقدير بعض العناصر المتواجدة بكميات ضئيلة مثل: (Cd, Zn, Cu, Ni, Co, Fe, Pb, Mn) في ستة أصناف من النخيل وهي: برحي، خلاص، منيفي، رزيز، سلج، سكري. واستخدم جهاز بلازما الحث المزدوج - الكتلة الطيفية لتقدير هذه العناصر. لقد دلت النتائج المتحصّل عليها أن هذه الأصناف تحتوي على نسبة عالية من عنصر الحديد خاصة البرحي والخلاص والرزيز حيث يكون متوسط كمية هذا العنصر في هذه الأصناف في حدود 115.4 ميكروجرام لكل جرام. أما أصناف المنيفي والسلج والسكري فتحتوي على كمية من عنصر الحديد في حدود 53.2 ميكروجرام لكل جرام. ويأتي عنصر المنجنيز في المرتبة الثانية بعد عنصر الحديد في تواعده في أصناف النخيل المذكورة أعلاه. ومقدار تواعده في البرحي والخلاص والرزيز في حدود 13.6 ميكروجرام لكل جرام. أما في بقية الأصناف فكميته في حدود 8.5 ميكروجرام لكل جرام. أما بقية العناصر فتواجدها ضئيل جداً في أصناف النخيل المذكورة أعلاه.