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Determination of trace elements in nutrition materials in Kingdom of Saudi Arabia

Badriah Saad Al-Farhan

Department of Chemistry, Faculty of Girls for Science, King Khalid University, Abha, KSA, Saudi Arabia.

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Four types of edible tubercular roots cultivated in Saudi Arabia are analysed through sequential determination of certain essential and toxic trace elements by inductively coupled plasma atomic emission spectrometry (ICP-AES). Comparable runs carried out using both flame and graphite atomic absorption spectroscopy (AAS). Radish proved to contain the highest concentration level of iron (>21 µg/g), onion contains high concentration of zinc and strontium (~ 6 and 9 µg/g) and potato was found to contain the highest concentration level of copper (~2 µg/g). Samples of carrots, radish and potato collected from different locations are also analysed to study the effect of cultivation area on the concentration levels of trace elements in edible tubercular roots. Variation in the concentration levels of iron, zinc, copper, cobalt, strontium, cadmium and lead in each type of test samples seem not to be significant. Detailed studies seem necessary to throw further light on the effect of different of sample location on the concentration levels of both essential and toxic trace elements in different vegetable materials; especially those cultivated in areas neighboring various industrial and other human activities in Saudi Arabia.

Key words: Tubercular roots, trace elements, inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectroscopy (AAS) analysis.

INTRODUCTION

Human beings are encouraged to consume more food materials such as vegetables and fruits, which are good sources of vitamins and minerals beneficial to human health (Mohamed et al., 2005). Heavy metal contamination in agricultural environments can come from atmospheric fall-out, pesticide formulations, contamination by chemical fertilizer and irrigation with water of poor quality (Marcovecchio et al., 2007).

Trace elements in nutrition materials play significant role in human health. Trace concentration of iron, zinc, copper, manganese, nickel, cobalt, molybdenum, selenium, iodine, and fluorine are considered essential for human life (Clemente et al., 1977; Roberts, 1981). The absence or deficiency of one of these elements in certain body organs leads to physiological abnormalities in a number of biological processes which can be remedied by addition of limited quantities from the deficient element (Cotzias, 1970). Few other elements such as lead, cadmium, tin and mercury are highly toxic for both animal and human lives and may lead to death when ingested with high doses. The presence of different concentration levels of several trace elements (including those with toxic effects) in individual food articles and integrated human diets is mainly due to the uncontrolled release of various types of toxic pollutants in the different environmental compartment from increased industrial and other human activities (Underwood, 1971). It is therefore necessary to monitor the concentration level of toxic and essential elements in common food items for daily intake (Qureshi et al., 1990; Noel et al., 2011). In the present work, four edible tubercular roots including carrots, onion, potato, radish that are mostly consumed by a wide spectrum

E-mail: shahd_bb@hotmail.com

Table 1. Analysed vegetable tubercular roots.

Common name	Family	Botanic name
Carrots	Umbelliferae	*Daucus carota*
Potato	Solanacea	*Solanum tuberosum*
Onion	Amarylilaceae	*Allium cepa*
Radish	Cruciferae	*Raphanus sativum*

of the King of Saudi Arabia population have been analysed to comment on their suitability for human intake.

EXPERIMENTAL

Sampling and sample preparation

The test samples were collected from a number of agricultural areas. A list of test species is given in Table 1, with their botanical names and respective families. To investigate the effect of sample location on the concentration of trace elements in test items; carrots, radish, potato were collected from three areas. From the cultivated part of the southern region in Saudi Arabia, from the northern region, and from eastern region as shown in Figure 1. For sample preparation, collected samples were thoroughly washed and air dried at room temperature. After recording the wet weight, each species was oven- dried at 60°C for 72 h) (Zaidi et al., 1990) and the corresponding dry weight and moisture content determined. Representative dried samples were powdered by using a teflon ball mill, sieved to ≅200 mesh and finally stored in pre-cleaned polyethylene capped bottles. Nitric acid – hydrogen peroxide – perchloric acid mixture was used to digest different test samples.
For (2 to 10 g) of dried matter, the mixture used includes 20 ml of 14.4 mol l^{-1} nitric acid, 10 ml of 30% hydrogen peroxide and 10 ml of 9.9 mol l^{-1} perchloric acid. In addition, 18.0 mol l^{-1} sulphuric acid (for 10 g of dried matter, 2.0 ml of acid was added to prevent losses of metal halides by volatilization (Feinberg and Ducauze, 1980; Erwin and Ivo, 1992). Digestion normally took place in all glass containers under reflux at 170°C until a clear digest was obtained after approximately 3 h (Yaman and Gucer, 1995). The digest was centrifuged to separate the clear solution and the residue washed with bidistilled water and re-centrifuged to prevent any elemental losses. The first washing was added to the original solution before being diluted to known volume.

Instrumentation

(i) Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements were done with a compact tuned – oscillator coupled with high resolution Echelle grating spectrometer, minicomputer control services, peristaltic pump and an automated sample changer. The system includes a plasma spectrometer, type Leeman from USA, 2.5 KW generator, a three -turn copper load coil and a Hidebrand Grid nebulizer. The spectrometric system is of a fixed optics model with a PMT for sequential operation (type f18 Echelle), with a single pass prism / lens used for stray light reduction to cover a wavelength range from 190 to 800 nm.
(ii) The atomic absorption spectroscopy (AAS) measurements were carried out with AA spectrometer, model Z -8100 polarized Zeeman, manufactured by Hitachi, Ltd., from Japan Hitachi single – element hollow cathode lamps were used with air- acetylene flow rate ranging from 0.5 to 4.0 L/min with an auxiliary oxidant gas pressure ranging from 140 to 120 kpa. The instrument is provided with

Figure 1. Samples location

temperature regulation device and automated sampling by a built in auto sampler, type SSC -200. Selection of wavelength ranged from 190 to 900 nm.

Spectroscopic measurements

(i) ICP- measurements were done in sequential multi- element mode. An analytical programme was established both for calibration and routine analysis. The selected analytical wavelengths represent the characteristic lines which are almost free from spectral interference to eliminate any correction at the concentration levels of interest, these are:

(a) Iron - 259.94 (nm)
(b) Copper - 324.75
(c) Zinc - 213.86
(d) Cadmium - 214.44

Measurements were done in triplicates according to the following operating conditions:

(a) Forward r.f. power 1.00 KW (0.5A)
(b) Argon flow rate 12 L/min
(c) Nebulizer gas 0.3-0.5 L/min
(d) Sample uptake rate 1 L/min

(ii) AAS measurements were carried out under a constant air flow rate or (15.0 L/min), according to the following operational condition for each element as in Table 2.

Chemicals and reagents

All chemicals used were of A.R or extra pure grades. A set of standards were prepared from readily made standard solutions provided from Merck, AG, Darmstadt, Germany by dissolution in, or adequate dilution with dilute nitric acid solution. Bidistilled water in all glass apparatus was used for preparation of different solutions, used standards and for final glass ware washing. In the digestion procedure, concentrated nitric acid (65%, 14.4 mol l^{-1}), sulphuric acid (98%, 18 mol l^{-1}), hydrogen peroxide (30%) and perchloric acid (65%, 9.9 mol l^{-1}) were used.

Table 2. Operational conditions for AAS measurements.

Condition	Fe	Zn	Cu	Co	Sr	Cd	Pb
Wavelength, nm	248.3	213.9	324.8	240.7	460.7	228.8	283.3
Lamp current ,mA	15	7.5	7.5	15	10	7.5	10
Slit width	0.2	1.3	1.3	0.2	0.5	1.3	1.3
Acetylene flow rate,$Lmin^{-1}$	1.5	1.5	1.7	1.7	1.7	-----	-----
Heating program drying temp., °C	-----	-----	-----	-----	-----	80-120	80-120
Time/sec	-----	-----	-----	-----	-----	30	30
Ashing temp., °C	-----	-----	-----	-----	-----	300	400
Time/sec	-----	-----	-----	-----	-----	30	30
Atomization temp., °C	-----	-----	-----	-----	-----	1700	2100
Time/sec	-----	-----	-----	-----	-----	7	7
Cleaning temp., °C	-----	-----	-----	-----	-----	2600	3000
Time/sec	-----	-----	-----	-----	-----	30	30

Table 3. Concentration of trace elements in edible tubercular roots*).

Element	Carrots	Onion	Radish	Potato	Intake levels **)
a)Assessment of trace elements by ICP-AES (in µg/g wet weight)					
Iron	4.68±0.1	16.25±0.1	20.84±1.2	6.63±0.1	25-75 mg
Zinc	2.21±0.1	5.74±0.0	2.82±0.2	3.43±0.0	10-20 mg
Copper	1.51±0.2	1.42±0.2	0.31±0.02	1.66±0.05	--------
Cobalt	0.32±0.0	0.54±0.01	0.36±0.0	0.56±0.02	150-580 µg
Cadmium	0.17±0.01	0.34±0.02	0.25±0.01	0.41±0.01	--------
b)Assessment of trace elements by FAAS (in µg/g wet weight)					
Iron	4.79±1.2	16.18±0.4	21.26±0.5	5.82±0.7	25-75 mg
Zinc	2.68±0.2	5.63±0.1	2.67±0.1	3.45±0.2	10-20 mg
Copper	1.39±0.1	1.44±0.3	0.38±0.0	1.92±0.1	--------
Cobalt	0.30±0.0	0.50±0.0	0.38±0.1	0.57±0.02	150-580 µg
Strontium	3.37±0.0	9.19±0.1	4.94±0.05	3.66±0.05	42-1240 µg
c)Assessment of trace elements by GAAs (in µg/g wet weight)					
Cadmium	0.19±0.01	0.34±0.02	0.22±0.01	0.44±0.01	--------
Lead	0.55±0.0	0.68±0.01	0.31±0.04	0.67±0.01	54-500 µg

*) the results are mean of at least triplicate measurements; based on determination of each trace element in aliquot portions of sample solution containing known amounts of respective dried tuber, final concentration levels and the results based on wet weight are calculated from respective dry weight results.**) acceptable levels of daily intake concentration.

RESULTS AND DISCUSSION

Trace elements in tubers

The results in Table 3, show that iron, zinc, copper, cobalt, strontium, cadmium and lead proved to be present in different concentration levels in various types of tubercular roots. The examined species including carrots, onion, radish and potato are among the common vegetables for human nutrition in Saudi Arabia. The choice of these species aims to define the role of different soils, fertilizers and mode of irrigation as possible pathways for trace elements to man through the food chain (Husain et al., 1995; Ozores-Hampton et al., 1997; Millour et al., 2011). To get reliable and comparable results, the assessment of trace elemental concentrations in different samples is based on atomic spectroscopy using ICP-AES, flame and graphite AAS techniques. ICP-AES has the advantage of being rapid in providing analytical data for several elements in a single run. All used techniques proved to give comparable and reliable results. This is clearly illustrated by the results of iron,

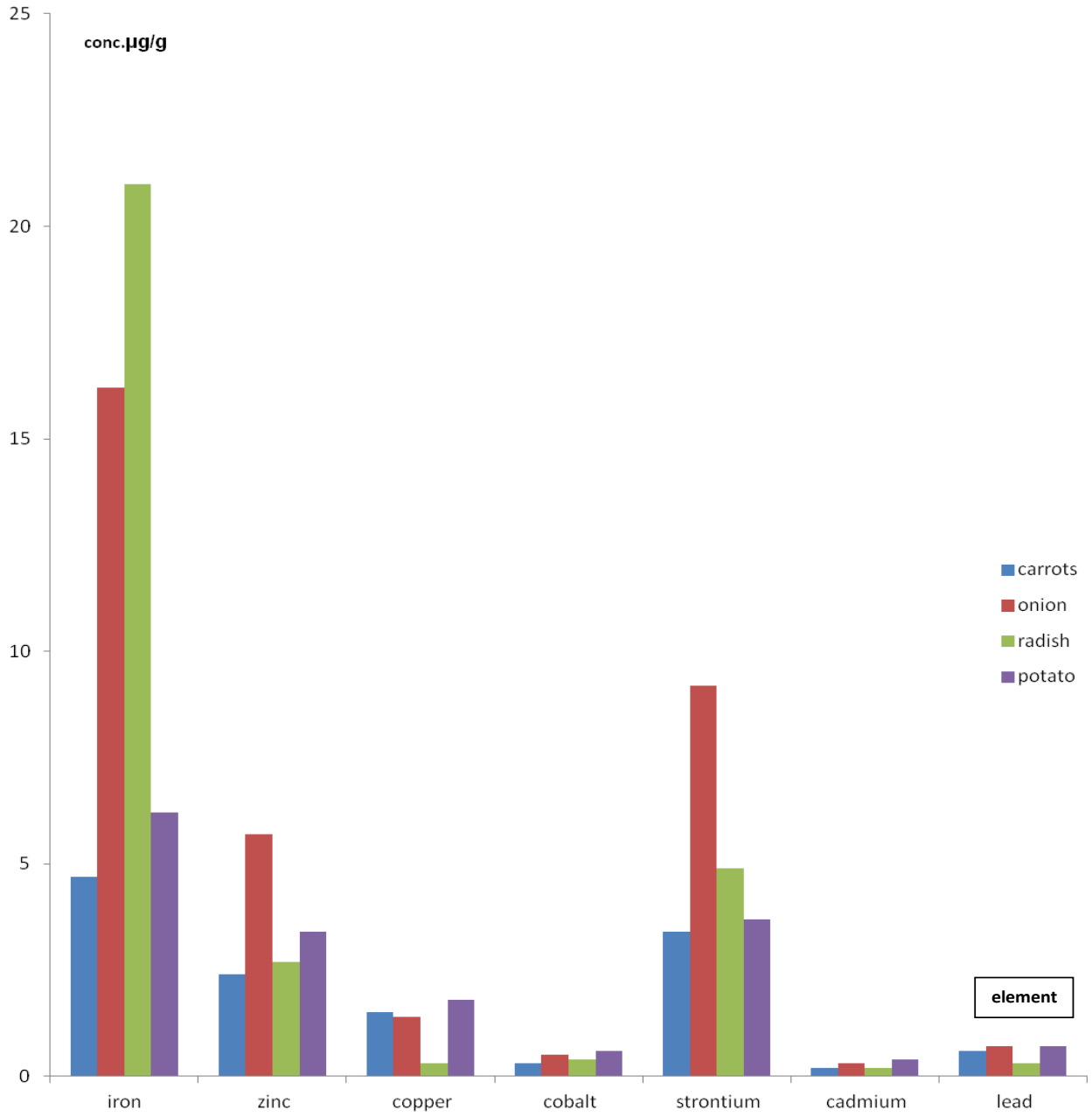

Figure 2. Concentration levels of Trace elements in test samples

zinc, copper, cobalt and cadmium in all types of tested species which proved to be subject to almost the same mean standard deviation for each analyte.

The results (expressed in terms of µg/g of wet weight) showed that radish contains the highest concentration levels of iron (21.26 µg/g), onion proved to contain the highest concentration of zinc (5.74 µg/g) and strontium (9.19 µg/g). Potato contains the highest levels of copper (1.92 µg/g). For toxic elements, it was found that potato contains the highest concentration levels of both cadmium and lead (0.44 and 0.67 µg/g), (Figure 2). The concentration levels of iron, zinc and copper are almost of the same order or even less than those previously reported by several workers (Finch and Monsen, 1974; Thomas et al., 1952). While the concentration of cobalt and strontium is several orders of magnitude higher than the values reported by other workers (Schroeder et al., 1967; Wikelsk et al., 1993).

In general, one assumes that changes in the concentration levels of trace elements in the examined species can be mainly attributed to changes in the chemical composition of water used for irrigation, the type

Table 4. Trace element concentrations in different carrot, radish and potato samples*).

Element	Sarat Ebeda	Alehssa	Algoff	Mean δ_n
		a) Carrots		
Iron	4.6±0.2	5.03±0.1	4.76±0.5	0.2
Zinc	2.33±0.1	3.13±0.1	2.6±0.5	0.2
Copper	0.78±0.1	1.03±0.1	0.806±0.1	0.0
Cobalt	0.28±0.2	0.33±0.1	0.30±0.2	0.05
Strontium	3.16±1.0	3.57±1.0	3.37±1.2	0.1
Cadmium	0.14±0.01	0.21±0.01	0.21±0.01	0.0
Lead	0.50±0.01	0.59±0.01	0.55±0.01	0.0
		b) Radish		
Iron	20.46±1.0	21.8±1.2	21.53±1.0	0.1
Zinc	2.26±0.1	2.90±0.2	2.86±0.1	0.05
Copper	0.33±0.1	0.33±0.05	0.47±0.1	0.02
Cobalt	0.35±0.1	0.42±0.2	0.38±0.1	0.05
Strontium	4.56±1.0	5.50±1.0	4.76±0.5	0.2
Cadmium	0.21±0.01	0.24±0.01	0.22±0.01	0.0
Lead	0.30±0.01	0.32±0.01	0.32±0.01	0.0
		c) Potato		
Iron	5.03±0.2	6.43±0.1	6.00±0.1	0.05
Zinc	2.93±0.1	4.26±0.1	3.16±0.2	0.05
Copper	1.56±0.5	2.36±0.1	1.83±0.2	0.2
Cobalt	0.51±0.1	0.63±0.1	0.58±0.2	0.05
Strontium	3.03±0.5	4.17±1.0	3.77±0.5	0.2
Cadmium	0.40±0.02	0.49±0.02	0.44±0.02	0.0
Lead	0.67±0.01	0.71±0.01	0.67±0.01	0.0

*) concentrations in µg/g, on wet weight basis.

of soil in various agricultural areas, and seasonal changes in ambient temperature.

Under comparable irrigation conditions, however, trace elemental concentrations may be affected by the sorptive capacity of different roots, the physical characteristics of the edible body in different species and the chemical composition of organic compounds in each type that might form different complexes with various metallic species. Thus, the increased concentration levels of cobalt, strontium than the mean values so far reported may be attributed to cultivation in areas rich with different minerals, especially when using water contaminated with industrial waste effluents, including trace concentrations of either or more of these elements. Never the less, the high concentration levels determined in all test samples, do not exceed the acceptable levels for daily intake. These are almost about 150 to 580 µg for cobalt, and 42 to 1240 µg for strontium. For iron, zinc and lead on the other hand, the concentration levels determined are far below those reported for daily intake lying within 25 to 75 mg for iron, 10 to 20 mg for zinc and 54 to 500 µg for lead (Dabeka et al., 1987; Galal-Gorchev, 1991).

Effect of sample location

To study the effect of sample location on the concentration levels of both essential and toxic trace elements in tubercular roots, carrots, radish and potato were collected as test samples from three different areas. These include an agricultural area near the industrial zone of the eastern region of Saudi Arabia (Alehssa), an agricultural area free from any industrial activities at the southern region of Saudi Arabia (Sarat Ebeda), and from the northern region of Saudi Arabia (Algoff). The essential trace elements investigated include iron, zinc, copper, cobalt and strontium, and the toxic elements are represented by cadmium and lead. This was specifically verified by successive triplicate analysis using not only ICP-AES but also, flame and graphite AAS measurements.

In Table 4, the concentration levels of iron, zinc, copper, cobalt, strontium, cadmium and lead in different

samples of carrots, radish and potatoes collected from the three above mentioned areas are presented. It is observed that iron has a mean concentration value of 4.78 µg/g in carrots with a highest concentration level of 5.03 µg/g in samples collected from Alehssa and a lowest concentration level of 4.6 µg/g in those from Sarat Ebeda. For radish and potato, iron proved to have a mean value of 21.26 and 5.82 µg/g respectively. For zinc, the same trend is followed, showing mean concentration levels 2.68, 2.67 and 3.45 µg/g, the highest values of 3.13, 2.90 and 4.26 µg/g for carrots, radish and potato, respectively. On the other hand, copper, cobalt, strontium, cadmium and lead also follow the same trend.

It was found that the concentration levels of the trace elements determined in carrots, radish and potato samples collected from the three different areas are almost of the same order. Samples collected from areas neighboring several industrial activities in (Alehssa) proved to contain slightly higher concentration levels of all the tested elements than those collected from (SaratEbada) and from (Algoff).

Conclusion

The results obtained show that radish contains the highest concentration level of iron, onion contains high concentrations and strontium and potato was found to contain the highest concentration levels of copper. The standard deviations in the results obtained for almost all determined elements are relatively low ranging from 1.5 for strontium determined by FAAS in onion to 0.0 in case of determination of several elements by the different used techniques indicating the reliability of ICP, flame and graphite AAS techniques for the determination of the concerned elements.

In the light of the obtained data, one may conclude that samples cultivated in areas far from industrial and other human activities tend to contain lower concentration levels of both essential and toxic elements than others. This can be noted in particular by considering the change in the concentration levels of the different elements determined in test samples collected from the agricultural area of Sarat Ebeda which seem to be lower than those collected from areas neighboring the industrial zone of Alehssa.

The difference in the concentration levels of all analysed trace elements collected from the different areas give a mean standard deviation not exceeding 0.2 with a percentage difference ≤10%, which lies within the experimental error in optical measurements especially when dealing with low concentration levels of different analytes. It is recommended from the present study that the work needs further investigation referring to soil types and irrigation water that affect on sample location results.

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