Levels of Selected Heavy Metals in Black Tea Varieties Consumed in Saudi Arabia

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Abstract The metal contents (Fe, Cu, Zn, Mn, Cr, Pb, Ni, Cd, Co) of 17 black tea samples were analyzed by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Among the investigated metals Mn was the highest (1,071.7 µg/g), whereas Pb showed minimum levels (0.30 µg/g). Iron was the second highest element found in black tea samples. Lowest Pb concentration (0.30 µg/g) was found in Abu Jabal tea; whereas maximum (2.2 µg/g) was found in Manasul tea. Lowest Cd concentration was found in Lipton whereas maximum level was observed for Al-Diafa tea. The concentrations of Co and Zn in the analyzed samples were in the range of 4.5–17.4 and 23.7–122.4 µg/g, respectively. Metal-to-metal correlation studies showed strong correlations between iron–chromium, iron–cadmium and lead–copper pairs. The data obtained in the present work compared well with the counterpart data reported internationally. Based upon the present safety standards, the tea versions selected in the present study were found to be safe for human consumption.

Keywords Heavy metals · ICP · Black tea · Saudi Arabia

Tea is one of the heavily consumed beverages in the world which is prepared from the leaves of a shrub *camellia sinensis*. It is also regarded as the most served beverage in the world. Black and green teas are the popular versions. Drying and roasting produces green tea whereas black tea is obtained after a fermentation process. Economic and social interest in tea is clear from the fact that about 18–20 billion tea cups are consumed daily in the world (Pedro et al. 2001; Marcos et al. 1998). The medicinal value of tea for prevention and treatment of many health problems has become more and more commonly known (Naithani and Kakkar 2005). Tea contains flavonoids, minerals and trace elements that are essential to human health. Current studies show that tea contains specific antioxidants and health promoting ingredients, lowering the risk of heart diseases, stroke and certain types of cancer like oral, pancreatic and prostate. The main source of trace metals intake by the shrubs is their growth media, consequently, some differences in the metal contents are expected. Therefore, tea drinking could be an important source of some essential minerals such as manganese, which activates numerous enzymes. The levels of manganese in other foods/beverages are relatively small (Pedro et al. 2001). Owing to the great importance of the minerals present in tea, many studies have been carried out to determine their levels in tea leaves and their infusions. Various analytical techniques that have been used for this purpose include atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and total reflection X-ray fluorescence spectrometry (TR-XRF) (Narin et al. 2004; Han and Li 2002; Matsuura et al. 2001; Xie et al. 1998).

With a long tradition of drinking tea, Saudi Arabia boasts the second largest retail tea market in the Middle East. Along with other popular hot beverages, tea continues to play an integral part in family and social occasions in Saudi Arabia. Drinking tea is a traditional habit amongst

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Saudi people. It is consumed throughout the day and at all social occasions. Given the prohibition of alcohol, tea and coffee are seen as socializing tools in the Kingdom. Determination of heavy metals in tea samples is important from two aspects; to judge their nutritional value and to guard against any probable ill-effect, they may cause to human health. In the present paper the contents of heavy metals Fe, Cu, Zn, Cd, Ni, Pb, Co, Mn and Cr in black tea samples has been determined by using acid digestion followed by ICP-AES technique.

Materials and Methods

A Thermo ICP-AES was used for metal determinations. The operating parameters are shown in Table 1. Nitric and perchloric acids (E.Merck) were of ultrapure grade. Working standard solutions were prepared by serial dilutions of the stock solutions. All aqueous solutions and dilutions were prepared with ultrapure water (Milli-Q, Millipore).

Seventeen commercial tea samples were selected for this study. All of them were procured from local markets and hypermarkets.

All glassware was cleaned by soaking in dilute nitric acid and was rinsed with milli-Q water. Each tea sample of 0.50 g was accurately weighed into a clean 100 mL beaker. Concentrated nitric acid (10.0 mL) was added, the

beaker was covered with a watch glass and material was boiled gently on a hot plate provided with a tunable thermostat until digestion was complete. The complete digestion took about 1 h. A 1.0 mL portion of 70% perchloric acid was then added and gentle heating was continued for another 1 h. Small aliquots of milli-Q purified water were added to prevent dryness due to evaporation. After the digest was cooled, it was filtered and transferred to a 100 mL volumetric flask that has been rinsed with ultrapure water. Three replicate digestions were made for each sample. The average of blank signals was subtracted from analytical signals of digested samples. All necessary precautions were adopted to avoid any possible contamination of the sample as per AOAC guidelines (1998). To express the results on a dry weight basis the moisture of the samples was removed by keeping them at 60°C for 6 h.

The accuracy of the digestion procedure was evaluated by heavy metal determination in the SRM NIES #7. The results were in good agreement with certified values and lied within the 95% confidence limit. The recoveries of the metals in the SRM were in the range of 95%–103%. The relative standard deviations were less than 10% for all metals determined. A recovery test of the analytical procedure was carried out for some of the metals in selected samples by spiking with aliquots of metal standards and then analyzing them as usual. Acceptable recoveries, >96%, were obtained for the analyzed metals.

Table 1 The operating conditions for ICP-AES instrument

ICP-AES	IRIS Itrepid II XDL
Plasma conditions	
Rf frequency	30 MHz
Rf power	1.0 kW
Gas flow rate	
Carrier gas	Ar 0.5 L/min
Auxiliary gas	Ar 1.0 L/min
Coolant gas	Ar 20 L/min
Sampling conditions	
Observation height	18 mm above coil
Nebulizer	Cross-flow type
Sample uptake rate	1.2 mL/min
Spectrometer conditions	
Polychromator	Paschen-Runge mounting
Focal Length	75 cm
Entrance slit	25 μm
Exit slit	50 μm
Data acquisition	
Integration time	10 s
Repetition	3 times

Table 2 Levels (μg/g) of selected metals in black tea samples consumed in KSA

Brand	Fe	Cu	Zn	Mn	Cr	Pb	Ni	Cd	Co
Deemah	251.7	16.8	26.9	976.3	2.3	0.4	22.5	0.9	4.5
Al-Rabea	246.2	24	29.6	853.7	6.8	1.7	18.9	1.3	9.7
Panda	239.5	9.4	31.2	564.6	11.5	0.8	14.5	1.4	8.3
Dilmah	115.8	18.9	23.7	750.3	3.2	0.5	17.5	0.7	14.5
Al-Diafa	946.7	29.8	36.8	865.3	17.5	1.3	11.4	2.2	11.3
HiTea	388.2	12.7	76.3	651.7	16.8	0.7	25.3	0.4	17.4
Red label	351.6	19.3	46.7	932.6	5.3	1.8	19.7	1.8	15.3
Tata Tea A	175.3	12.5	88.2	1007.8	6.5	1.5	13.5	0.6	12.4
Tata Tea D	122.5	13.8	112.7	664.4	9.7	0.6	9.2	1.2	9.3
Orlanda	183.7	18.6	67.8	738.8	8.8	0.5	14	1.5	7.8
Lord	285.3	12.4	56.3	527	12.5	0.8	10.6	0.7	10.6
Lipton	108.5	22.5	77.2	1071.7	17.2	0.7	16.8	0.3	9.7
Ahmad	176.5	31	122.4	550.5	11.5	1.3	15.8	1.0	15
Manasul	247.8	27.8	102.7	447.8	9.7	2.2	22.3	1.2	6.8
Unicom	90.3	17.2	97.8	791.5	8.5	0.6	20.5	1.9	13.9
Abu Jabal	88.7	11.7	63.4	565.2	8	0.3	13.7	1.3	8.7
Kanan Devan	239.6	9.6	57.3	806.5	11.3	1.3	18.8	0.9	11.5

Results and Discussion

The results of tested metals in 17 tea versions are given in Table 2. Among the investigated metals, manganese was the highest whereas cadmium showed minimum levels. The levels of manganese were in the range of 447.8–1,071.7 µg/g ($X = 750.9$). The highest and the lowest levels of manganese were found in Tata Tea A and Manasul, respectively. Yasmeen et al. (2000) have reported 175 µg/g manganese in tea samples from Pakistan. The levels of Mn in black tea samples from China have been reported by Xie et al. (1998) as 607 ± 200 µg/g. Iron was the second highest element found in black tea samples. The range being 88.7–946.7 µg/g with an average value of 250.5 µg/g. Pedro et al. (2001) have shown Fe to be in the range of 74–1,000 µg/g for black tea samples. Average concentration of Cr in our samples was found to be 9.8 µg/g; minimum being for Deemah (2.3 µg/g) and maximum being for Al-Diafa (17.5 µg/g). Ferrara et al. (2001) have reported the levels of Cr in black tea samples from different parts of the world as 17.9–115.4 µg/g.

Levels of Pb in the tea samples analyzed ranges between 0.3 and 2.2 µg/g. Lowest concentrations of Pb were found in Abu Jabal, Deemah and Dilmah. The highest Pb concentration was encountered in Manasul (2.2 µg/g) (Table 2). Xie et al. (1998) have reported average Pb contents in some Chinese black tea samples as 1.42 ± 0.8 µg/g. Narin et al. (2004) has found maximum lead in Turkish tea samples at the levels of 27.3 ± 0.1 µg/g. The higher levels of Pb in tea samples could be attributed to dust particles during tea processing and solder being used in packaging. The lowest Ni level was found in Tata Tea D as 9.2 µg/g, while the highest was 25.3 µg/g in HiTea. The mean concentration of Ni was 16.8 µg/g. Narin et al. (2004) have reported 38.8 ± 6.3 µg/g Ni in Turkish black tea Caykar GAP. Marcos et al. (1998) have reported Ni levels in tea samples as 2.89–22.6 µg/g.

Cadmium levels in black tea samples included in the present study were in the range of 0.32–2.17 µg/g (lowest in Lipton; highest in Al-Diafa). The mean cadmium levels were 1.1 µg/g. In a study by Ferrara et al. (2001), cadmium levels were found below detection limit by using flame

Table 3 International comparison of the data

	This work	Turkey (Narin et al. 2004)	Spain (Pedro et al. 2001)	Japan (Matsuura et al. 2001)	China (Han and Li 2002)	India (Naithani and Kakkar 2005)
Fe	250.5 ± 199	NA	946.2	134 ± 48	32.5	446.6 ± 22.8
Cu	18.1 ± 6.9	24.8 ± 1.4	31	27.7 ± 0.7	NA	13.2 ± 0.96
Zn	65.7 ± 31.3	140.9 ± 9.1	43.2	36.6 ± 0.7	25.5	39.5 ± 0.75
Mn	750.9 ± 185	806.0 ± 34.2	1004.1	503 ± 7	1519	140.0 ± 5.29
					607 (Xie et al. 1998)	
Cr	9.8 ± 4.5	11.7 ± 0.1	NA	NA	NA	NA
Pb	1.7 ± 0.8	8.3 ± 0.1	NA	0.71 ± 0.02	3.30; 1.42	NA
					1.42 (Xie et al. 1998)	
Ni	16.8 ± 4.5	20.9 ± 1.5	NA	8.06 ± 0.19	NA	NA
Cd	1.1 ± 0.5	2.0 ± 0.8	NA	NA	NA	NA
Co	11.0 ± 3.4	21.8 ± 1.1	NA	NA	NA	NA

All levels in µg/g

NA, Not available

Table 4 Metal-to-metal correlation coefficient matrix for tea samples ($r = 95\%$)

	Fe	Cu	Zn	Mn	Cr	Pb	Ni	Cd	Co
Fe	1.000	0.359	−0.332	0.108	0.450	0.304	−0.085	0.420	0.109
Cu		1.000	0.177	0.038	0.152	0.463	0.090	0.288	0.038
Zn			1.000	−0.297	0.255	0.129	−0.079	−0.120	0.187
Mn				1.000	−0.145	0.008	0.119	−0.046	0.033
Cr					1.000	0.010	−0.164	−0.093	0.199
Pb						1.000	0.224	0.176	0.128
Ni							1.000	−0.156	0.184
Cd								1.000	−0.070
Co									1.000

atomic absorption spectroscopy. However, Narin et al. (2004) have found 2.0 ± 0.2 µg/g Cd in Turkish Lipton tea sample. The mean copper contents of the analyzed samples were 18.1 µg/g. The lowest level of copper was found in Panda tea as 9.4 µg/g, whereas highest in Ahmad tea as 31.0 µg/g. Similar results for copper have been reported by other workers (Narin et al. 2004; Ferrara et al. 2001; Xie et al. 1998). The concentrations of Co and Zn in the samples were in the range of 4.5–17.4 µg/g and 23.7–122.4 µg/g, respectively. Marcos et al. (1998) have reported average Co and Zn concentrations in black tea samples as 0.2 and 28.2 µg/g, respectively. On the other hand, much higher levels have been reported by Narin et al. (2004) as 30.2 and 147.5 µg/g for Co and Zn, respectively. Matsuura et al. (2001) have reported mean Zn level in black tea as 36.6 ± 0.7 µg/g (Table 3).

The whole data was subjected to statistical analysis and correlation coefficients were determined. Metal-to-metal correlation coefficient matrix is given in Table 4. The correlation between iron–chromium, iron–cadmium and lead–copper were significant whereas all other correlations of metal concentrations were not significant (>0.400).

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