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PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSInet
Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Pakistan Journal of Biological Sciences 11 (2): 285-289, 2008
ISSN 1028-8880

Quantitative Assessment of Metals in Local Brands of Tea in Pakistan

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Abstract: In present study, Mn, Fe, Zn, Cu, Co, Pb, Cr, Ni and Cd were analyzed by FAAS in green and black tea samples of locally available in the Pakistani market. Na and K were also determined by Flame Photometer. Tea leaves can be the source of mineral components and trace elements, as well as some undesirable substances due to exposure to the environment. Among the metals tested, K was the most abundant one followed by Na, Mn and Fe. Fortunately, toxic heavy metals, Pb and Cd, had the lowest contents in tea samples and also in tea aqueous extracts. Concentration of heavy metals in tea aqueous extract was markedly lower than their total contents except that of K. The solubility of studied metals in tea aqueous extract varied widely and ranged from 0.0-95%. The lowest ranges of solubility were listed for toxic heavy metals Pb and Cd. The possible uptake of metals by the human body from tea aqueous extract has also been determined. The amounts of metals that one may take up through consumption of tea aqueous extract were found to match the acceptable daily intake even taking into account exposure from air, food and drinking water.

Key words: Tea, tea extract, *Camellia sinensis*, metals, trace metals, atomic spectroscopy

INTRODUCTION

Tea is one of the most consumed beverages in the world and is prepared from the leaves of the shrub *Camellia sinensis* (Saud and AL-Oud, 2003; Fernandez-Caceres *et al*., 2001; Powell *et al*., 1998). Green and black teas are the two most popular types. Drying and roasting the leaves produces green tea; black tea is obtained after a fermentation process. Considering that an estimated amount of 18-20 billion teacups are consumed daily in the world (Fernandez Caceres *et al*., 2001; Kirk-Othmer, 1995) its economic and social interest is clear. Tea has a recognized therapeutic value. It is important in the prevention and treatment of many diseases (Fernandez- Caceres *et al*., 2001).

Many elements present in food at major, minor and trace levels are reported to be essential to man's well being. However, their ingestion in excessive amount can cause severe health problems (Kumar *et al*., 2005). The optimum concentration needed for this purpose varies widely depending on the kind of element and the age and sex of consumers (Ahmed *et al*., 1989). Human body requires both metallic and non-metallic elements for healthy growth, development and the proper functioning of the body. The determination of these elements in beverages, water, food, plant and soil is thus of utmost importance and is currently the subject of studies by various researchers (Saud and AL-Oud, 2003; WHO, 1998a, b).

Tea leaves (*Camellia sinensis* L.) are source of such mineral elements as essential for health: zinc, manganese, iron, magnesium, copper, titanium, aluminum, bromine, sodium, potassium as well as nickel, chromium and also phosphorus (Fernandez-Caceres *et al*., 2001; Kumar *et al*., 2005; Gramza *et al*., 2005; Chu and Juneja, 1997; Ferrara *et al*., 2001; Tascioglu and Kok, 1998; Anonymous, 1998, 1999a, b, c; Hui, 1992) The study of trace elements in tea has been taken up as trace elements play an important role in the complex metabolic pathways in human system and their deficiency or excess may cause disease (Powell *et al*., 1998; Syed and Qadiruddin, 1993).

Several attempts have been made to assess tea quality by chemical analysis usually with reference to pigmentation and the flavouring characteristics. However, to date little work has been done to identify the metal containing components of tea due to the analytical difficulties associated with both the separation of such components and their quantitative measurement (Saud and AL-Oud, 2003). Metallic constituents of tea leave is normally different according to the type of tea (green or black) and geological sources (Fernandez-Caceres *et al*., 2001; Marcos *et al*., 1996).

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In the present study, the content of Mn, Fe, Zn, Cu, Co, Pb, Cr, Ni and Cd in tea samples and in tea aqueous extract has been determined by using acid digestion followed by FAAS. The content of Na and K were determined by Flame Photometer. Objective of the research was to evaluate the overall metal contents in locally available some brands of tea and tea extracts.

MATERIALS AND METHODS

Instrumentation: A Perkin Elmer Model Analyst 700 with air-acetylene flame Atomic Absorption Spectrophotometer was used for (Mn, Fe, Zn, Cu, Co, Pb, Cr, Ni and Cd) elemental analysis. A flame photometer Sherwood Model 410 was used for (Na and K) analysis.

Chemicals: Almost all of the solvents and reagent were used of Analargrade. HNO_3 and $HClO_4$ were used for digestion of tea leaves. Distilled water was used as solvent for solution preparation.

The samples of tea leaves which are commonly consumed in Pakistan and other countries were collected from local market in 2004-2006. There types and countries of origin, when known, as well as their corresponding codes, are shown in Table 1. Accordingly, an identification code was assigned to each sample. The code consisted of a correlative number followed by a letter (G for green teas, B for black teas). All of the teas varieties beside 5B and 6B belong to the family *Camellia sinensis*. The study was carried out at Environmental Research Laboratory of Chemistry Department, Karachi University. Sample solutions were stored in washed and dried Teflon bottles. Glass wares which were used for experimental work for elemental analysis were washed with distilled water and acids (HNO_3) to remove all impurities. Standards of 500 ppm of all metals were prepared by dissolving specifically weighed quantity of non-hydroscopic, high quality AnalaR grade salts. Working standards were prepared by diluting stock solution from 500 ppm to required concentration.

The two methods are commonly employed for preparations of tea samples were acquired for this study in order for quantification the actual amount of mineral components and trace metals in tea and tea extracts (Saud and AL-Oud, 2003; Syed and Qadiruddin, 1993; Aziz-Al-Rehman, 1985). From these two methods three replicate for each samples were made.

Table 1: Analyzed tea samples

Code	Origin	Class
1B	Unknown	Black
2B	Japan	Black
3B	Japan	Black
4B	China	Black
5B	Unknown	Black (lose)
6B	Unknown	Black (lose)
7G	China	Green (leaves)
8B	China	Black
9B	Kenya	Black
10B	Sri Lanka	Black

Total contents of metals: Portion of one g of each brand was digested using 12 mL of a mixture (3:1 v/v) concentrated HNO_3 and $HClO_4$. The mixture was heated on laboratory send bath until the solution turned white and gave away the white fumes. After the digested sample was cooled, it was filtered and transferred to a 100 mL volumetric flask and the volume was adjusted to the mark with 5% HNO_3 acid. This digestion procedure was validated by using the reference certified material of National Bureau of Standard Certificate of Analysis (NBS). SRM # 1573.

Hot water extract of tea samples: Portion of one g of each brand was boiled with 50 mL of distilled water for 10 min and filtered. The residue obtained was evaporated to near dryness and digested with concentrated HNO_3 and $HClO_4$ as described previously. The final volume of the solution was made up to 100 mL.

Statistical analysis: Statistical analysis of the obtained results was performed according to paired-samples t-test. The results of statistical analysis showed that metal contents in tea and tea extracts (infusion) varied significantly ($p<0.05$).

RESULTS AND DISCUSSION

The concentration of metals in tea samples are shown in Table 2. The concentration of metals transferred to hot water from tea brands are shown in Table 3. In Table 4 metal content of most of the common brands of tea leaves which are used by the 80% of the population in Pakistan have an average value of metals are given (Yasmeen *et al.*, 2000). The solubility and the possible daily uptake and recommended daily allowances are also shown in Table 4.

The obtained result showed that tea plant has ability to accumulate metals particularly K, Mn, Na and Fe and to a lesser extent, Zn and Cu. The most abundant element found in tea has been K. Present result reveals that there is no marked difference between the previous results and out data reported for K (Ahmed *et al.*, 1989). The content of Na in tea samples is relatively lower than K followed by Mn. The maximum quantity of sodium is found in 5B and 6B tea samples and it should be advisable to avoid excess drinking of above mentioned tea samples. The next most

Table 2: Total contents of metal μg g^{-1} (mean±SE) in tea samples

Tea	Cu	Mn	Fe	Zn	Pb	Co	Ni	Cd	Cr	K	Na
1B	20.16±0.20	955±0.20	129.33±2.00	11.43±0.50	0.46±0.01	0.20±0.02	10.67±0.01	0.011±0.01	7.30±0.01	19200±0.01	730±0.02
2B	23.40±1.00	674±1.00	95.47±1.00	10.30±1.00	0.29±0.01	1.10±0.01	8.90±0.01	0.013±0.01	18.90±0.01	18700±0.02	910±0.01
3B	18.40±0.10	845±1.10	84.80±1.00	7.66±0.30	0.31±0.03	0.70±0.02	10.66±0.01	0.009±0.02	10.80±0.03	18500±0.02	980±0.01
4B	23.90±0.20	981±2.00	107.93±2.00	8.60±0.20	0.23±0.02	0.45±0.02	4.86±0.02	0.014±0.02	18.20±0.03	18400±0.02	560±0.03
5B	21.70±0.02	1150±2.00	158.16±3.00	59.40±0.50	0.55±0.02	2.60±0.01	7.63±0.03	0.027±0.01	10.00±0.30	19500±0.10	1100±0.01
6B	20.90±0.02	690±2.00	102.63±2.00	10.96±0.20	0.73±0.01	2.30±0.01	5.23±0.30	0.010±0.01	15.40±0.20	19100±0.01	1300±0.03
7G	21.30±1.00	488±0.50	69.60±1.00	48.60±0.30	0.35±0.05	1.70±0.02	4.90±0.20	0.010±0.03	11.70±0.01	18100±0.03	580±0.01
8B	23.50±1.01	910±2.00	122.73±1.50	36.50±1.00	0.34±0.02	0.30±0.30	7.96±0.03	0.013±0.01	10.30±0.10	18000±0.02	916±0.01
9B	19.86±0.30	1181±0.10	117.40±0.50	48.40±0.60	0.25±0.03	1.10±0.01	1.77±0.20	0.011±0.01	14.80±0.01	20000±0.01	890±0.02
10B	20.80±0.02	758±0.02	196.53±1.00	12.85±0.50	0.21±0.01	0.90±0.01	5.26±0.10	0.003±0.02	8.90±0.20	19500±0.02	870±0.03

Table 3: Metal contents μg g^{-1} (mean±SE) in tea aqueous extract

Tea	Cu	Mn	Fe	Zn	Pb	Co	Ni	Cd	Cr	K	Na
1B	0.36±0.01	417±2.00	13.80±1.00	5.80±1.00	ND	0.04±0.01	9.85±0.01	ND	5.50±0.01	18100±0.01	510±0.01
2B	0.90±0.02	263±3.00	15.27±1.00	3.70±1.00	ND	0.22±0.02	8.50±0.02	ND	7.70±0.01	16300±0.01	750±0.01
3B	3.00±0.01	374±2.00	10.20±1.00	6.76±0.20	ND	0.45±0.03	10.00±0.02	ND	8.20±0.02	17100±0.02	650±0.01
4B	4.50±0.03	383±1.00	63.00±2.00	4.11±0.01	ND	0.19±0.03	3.70±0.01	ND	10.80±0.02	17500±0.02	210±0.01
5B	3.90±0.01	566±2.00	5.26±2.00	27.10±0.20	ND	1.31±0.01	5.66±0.02	ND	6.50±0.01	16900±0.02	770±0.01
6B	3.30±0.03	320±2.00	9.63±1.00	6.30±0.30	ND	1.12±0.03	4.91±0.02	ND	9.60±0.03	17700±0.02	770±0.01
7G	3.90±0.02	174±3.00	2.32±0.20	39.60±1.00	ND	0.75±0.05	4.80±0.20	ND	6.10±0.03	15600±0.02	140±0.02
8B	4.10±0.10	366±1.00	13.93±1.00	7.20±0.20	ND	0.14±0.01	7.00±0.10	ND	7.40±0.02	16100±0.01	690±0.01
9B	2.86±0.20	522±1.50	4.80±2.00	20.90±0.10	ND	0.19±0.02	1.56±0.20	ND	8.50±0.01	18900±0.01	630±0.02
10B	2.10±0.03	325±0.50	1.76±0.20	3.95±0.20	ND	0.32±0.03	4.33±0.01	ND	4.10±0.02	17200±0.01	530±0.02

ND: not detected

Table 4: Overall means (average) of metal contents (μg g^{-1}) in tea samples and tea aqueous extract

Metals	Tea samples (μg g^{-1})	Tea extract (μg g^{-1})	Extracted to hot water (%)	Daily dietary intake (mg day^{-1})	Recommended daily allowances (mg day^{-1})**
K	18900.000	17140.000	90	18-20	500-2000
Na	880.000	565.000	65	0.5-1.5	200-500
Cu	21.390	2.890	13	0.015-0.025	1.5-3.0
Mn	862.960	370.950	45	0.4-1.2	2.0-5.0
Ni	6.780	6.031	88	0.004-0.012	NR
Co	1.140	0.470	41	0.0002-0.0023	NR
Zn	25.470	12.540	50	0.011-0.06	5-15
Fe	118.450	14.030	12	0.08-0.17	5-15
Pb	0.370	0.000	0	0.00	NR
Cd	0.012	0.000	0	0.00	NR
Cr	12.630	7.440	59	0.0041-0.0108	50-200

NR = Not Reported, **: Hui (1992)

abundant element present in tea samples is Iron as already has been reported by Yasmeen *et al*. (2000). Exceptionally low value of Fe has been found in China Green tea which is a special brand of tea family as reported by Yasmeen *et al*. (2000). On the other hand, the content of other metals varied widely among the tested brands and could be arranged in descending order as:

$$Zn > Cu > Cr > Ni > Co > Pb > Cd$$

The concentration of elements transferred to the hot water extract has also been determined in the order of:

$$K > Na > Mn > Zn > Fe > Ni > Cr > Cu > Co$$

General trend on content of metals in tea aqueous extracts shows that the concentration of toxic heavy metals, Pb, Cd as well as other metals such as Co and Cu were too low to be detected by atomic absorption spectroscopy, as reported previously (Saud and AL-Oud, 2003). Comparing with the previous results, the overall values recorded for some metals in tea aqueous extracts were generally higher than those obtained for this study (Ahmed *et al*., 1989).

The daily intake of the studied metals per gram is also estimated and the results show that the tea aqueous extracts have considerable amounts of metals and that could significantly contribute towards daily intake but these values are lower than the daily requirements of the human body as shown in the Table 4.

Studied metals were calculated for their solubility as a ratio between tea beverages and total content, varied widely between studied metals and ranged from 0.0-91%. The obtained result shows that toxic metal Cd and Pb were insoluble in tea aqueous extracts and it is similar to that reported previously (Saud and AL-Oud, 2003). On the other hand solubility of Ni and K ranged from 85-91 and 80-87%. This result shows that K and Ni were the most abundant element which were transferred to hot water extract and shows that K and Ni complexes are more water soluble than the complexes of the other metals present in tea (Ahmed *et al*., 1989). The percentage transfer in hot water of the other elements could be arranged in descending order as follows:

$$Na > Cr > Zn > Mn = Co > Cu > Fe$$

The percent solubility of Fe and Cu reveal that these are in the form of least water soluble complexes, as mention earlier (Ahmed *et al*., 1989).

This result shows that only small part of heavy metal contents of tea sample may get into the tea aqueous extract, while the higher contents remain insoluble in the solid particles during beverage preparation. Thereby, much care should be paid to how to get rid of the residual particles to avoid wide spreading of these metals in the environment. It may be mentioned that the various metallic elements found in beverages are present in the raw material, used to prepare the beverages and are not the result of subsequent processing.

The tea brands selected from the Karachi markets contain considerable contents of the studied metals. Fortunately, the concentration of toxic metals i.e., Pb and Cd, in tea beverage prepared using their leaves are too low. On the other hand, the considerable concentration recorded for other non-toxic metals lie within the acceptably daily intake from air, food and water of these elements.

Due to lack of information specifying the acceptable contents of heavy metals in tea leaves, the maximum allowable and safe concentration of each in tea leaves is urgently needed. Occasionally checked and frequently analyzed foodstuff is also badly needed.

CONCLUSIONS

The analysis results show that tea serves as one of the source of human intake of various metallic elements, which are essential for humans up to certain levels, of course the effects of other compounds present in the beverages have also to be taken into account in order to determine the amount of these beverages that should be taken. It may be concluded that as regards the presence of essential trace elements, tea may be a rich source of some essential and nutritional trace metals

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