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Heavy Metals in Black Tea Samples Produced in Turkey

I. Narin,[1] H. Colak,[2] O. Turkoglu,[2] M. Soylak,[2] M. Dogan[3]

[1] Nigde University, Faculty of Art and Science, Department of Chemistry, 51100 Nigde, Turkey
[2] Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey
[3] Hacettepe University, Faculty of Science, Department of Chemistry, 06532, Ankara, Turkey

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Tea (Camellia sinensis) is one of the world most popular beverages. Because tea contains all kinds of minerals and trace elements, drinking tea is healthy for people. There are various kind teas such as green, oolong, yellow, black. Black tea is fully fermented (Prystai *et al.*, 1999; Matsuura *et al.*, 2001; Costa *et al.*, 2002; Han and Li 2002). The heavy metal contents in tea samples have received great interest because of they are directly related with health and disease. The determinations of heavy metal contents of black tea samples have been performed continuously by using various instrumental methods include atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS) (Csikkel-Szolnoki *et al.*, 1994; Ma *et al.*, 1999; Han and Li 2002). The reliability of heavy metal determination in its complex matrices mainly depends on the dissolution process used. The wet and dry ashing digestion procedures are generally slow and time consuming. Microwave digestion procedures have been developed as a rapid and reproducible sample preparation method for a great variety of complex matrices (McGrath 1998; Mester *et al.*, 1999; Sastre *et al.*, 2002). Microwave extraction using diluted acids is a simple alternative to sample preparation and its use is increasing. Diluted mineral acid solutions can more intensely absorb microwave energy, owing to their water content. The microwave digestion was preferred because this procedure is more proper with respect to both time and recovery than wet digestion. The main disadvantages of the microwave digestion are that it is expensive and requires some experience (Tuzen 2003).

In the present study, fourteen samples of black tea marketed by different companies through out the country were collected end analyzed for manganese, chromium, lead, nickel, cadmium, copper, cobalt and zinc by flame atomic absorption spectrometry (FAAS) after digestion with microwave.

MATERIALS AND METHODS

All reagents were of analytical reagent grade unless otherwise stated. Double deionised water was used in all works. All plastic and glassware were cleaned by soaking in dilute HNO_3 (1+9) and were rinsed with distilled water prior to use. The stock solutions of metals (1000 mg/l) were obtained by dissolving appropriate

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Correspondence to: M. Soylak

salts or the corresponding metals and further diluted prior to use. The dynamic range of metal concentrations required both concentration and dilution of the sample before the analysis. Wherever necessary, samples were diluted with 0.1 M HNO_3. The stream sediment reference material (GBW 07310) was obtained from National Research Centre for Certified Reference Materials (NRCCRM)-China.

The instrumental detection system used was a Perkin Elmer 3110 FAAS. The operating parameters for working elements were set as recommended by the manufacturer. Studies were carried out in the air/acetylene flame without background correction. Bosch HMT 812 C and Milestone Ethos D microwave systems were used for the microwave assisted sample digestion of the samples.

In order to wet digestion of the black tea samples for the determination of traces metals, a sample (1.000 g) was placed into a beaker and leached with mixture of concentrated nitric acid and hydrochloric acid (3:1, V/V). Then the residue was filtered and the filtrate was combined with the leachate and diluted to 25 ml with deionized water. A blank digest was carried out in the same way.

For the microwave digestion of black tea samples, weights of 1.000 g of black tea samples were transferred to 100-ml Teflon beakers. A twelve ml volume of a freshly prepared mixture of concentrated HNO_3–HCl (3:1, /V/V) was added to each teflon beaker. The mixture was submitted to a three-step program: 180 W (3 min), 360 W (5 min) and 180 W (3 min). After digestion, the volume of the sample was made up to 25 ml with distilled water. Blank samples were prepared in the same way as the sample, but omitting the sample.

Manganese, chromium, lead, nickel, cadmium, copper, cobalt and zinc in the digested samples were determined by FAAS. The concentrations of analyte ions were obtained directly from calibration graphs after correction of the absorbance for the signal from an appropriate reagent blank. To validate the wet and microwave digestion procedures for accuracy and precision, stream sediment reference material (GBW 07310) was analyzed for each element by FAAS.

RESULTS AND DISCUSSION

The accuracy of the method was evaluated by means of heavy metals determination in stream sediment standard reference material (GBW 07310). The results were in good agreement with certified values. The results from the analysis of SRM were all within the 95 % confidence limit. The recoveries of the metals in SRM were in the range of 94-103 % in microwave digestion system. The relative standard deviations were less than 10 % for all elements. The results of the present study were found to be in good agreement with earlier observations. The comparison of wet and microwave digestion with the mixture of the hydrochloric acid and nitric acid showed no statistically significant differences in results.

The microwave digestion procedure was examined with the different mixture of hydrochloric acid and nitric acid. Quantitative recoveries of analyte ions were obtained with the mixture of 3 ml of concentrated hydrochloric acid and 9 ml of concentrated nitric acid. In all experiments, this mixture was used. A recovery test of analytical procedure was carried out for some of the metals in selected samples by spiking analyzed samples with aliquots of metal standards and then reanalyzing the samples. Acceptable recoveries (> 95%) were obtained for the analyte ions. Detection limit is defined as the concentration corresponding to three times the standard deviation of ten blanks. Detection limit values for FAAS were found to be as 0.09 mg/l for Mn, 0.11 mg/l for Cr, 0.10 mg/l for Pb, 0.11 mg/l for Ni, 0.05 mg/l for Cd, 0.06 mg/l for Cu, 0.11 mg/l for Co and 0.03 mg/l for Zn.

According to light of the these results, the concentration of manganese, chromium, lead, nickel, cadmium, copper, cobalt and zinc ions in the some black tea samples produced and marketed in our country have been analyzed by flame atomic absorption spectrometry after microwave digestion. Relative standard deviations (RSD) were calculated from pooled data for method. In the precision test, the average RSD % of street dust samples for all metals are in the range of 2-9 % (n=18) for method. The results, which were repeated in triplicate, were given in Table 1. In the investigated ions, manganese is the highest level, while the concentration of cadmium is the lowest.

The levels of manganese were in the range of 563.9-1081.6 μg/g (mean: 788.0±151.8 μg/g). The highest and lowest levels of manganese were found Lipton A and Akfa tea, respectively. The mean level of Mn in tea samples from Pakistan has been reported by Yasmeen *et al.* (2000) as 175 μg/g. The levels of manganese in black teas from Chinese have been reported by Xie *et al.* (1998) as 607±200 μg/g. The mean concentration of chromium in black tea leaves was found 13.0±1.7 μg/g (minimum: <10 μg/g (Caykur Tomurcuk), maximum: 16.9 μg/g (Lipton A)). The level of Cr in the samples was generally in the lower range of other studies. Ferrara *et al.* (2001) have been reported the range of chromium in black tea samples from the various locations of the world as 17.9-115.4 μg/g.

The range for lead concentrations was found as <8-27.3 μg/g (mean: 17.9±7.1). The lowest concentrations of Pb were found in Caykur Kamelya, Caykur Altinbas, Caykur Tomurcuk, Havuz Filiz and Lipton A. The highest Pb concentration was in Harran Altin Basak tea sample (Table 1). The average lead levels in the some Chinese black tea samples were given as 1.42±0.80 (Xie *et al.*, 1998). The highest level of the lead in our samples could have been caused by dust particles in the processing of the black tea.

The lowest nickel level was found in Caykur Altinbas as 10.8 μg/g, while the highest was 38.8 μg/g in Caykur GAP. The mean concentration of nickel was 23.3±9.6 μg/g. Marcos *et al.* (1998) have been reported the range of the nickel concentration in the tea samples as 2.89-22.6 μg/g. Cadmium level of black tea samples produced in Turkey was in the range of <1-3.0 μg/g (lowest in Caykur Tomurcuk, highest in Havuz Filiz). The mean cadmium level was 2.3±0.4 μg/g. In a study, cadmium levels of tea samples have been reported below the detection limit of flame atomic absorption spectrometry by Ferrara *et al.* (2001).

Table 1. The levels of the investigated ions in the black tea samples produced and marketing in Turkey

	Concentration (µg/g)							
Sample	Mn	Cr	Pb	Ni	Cd	Cu	Co	Zn
Altin Yildiz Teras	806.0±34.2	11.7±0.1	8.3±0.1	20.9±1.5	2.0±0.8	11.8±1.0	21.8±1.1	140.9±9.1
Caykur GAP	834.7±51.7	11.2±0.7	17.8±0.1	38.8±6.3	2.6±0.2	20.7±0.8	9.4±1.9	125.1±5.6
Harran Altinbasak	921.6±27.9	14.1±1.4	27.3±0.1	22.5±3.5	2.5±0.1	16.0±1.2	30.2±4.0	127.8±4.8
Akfa	1081.6±25.3	14.8±1.0	27.3±0.1	31.9±2.6	2.2±0.3	17.6±2.0	17.2±2.8	144.4±7.7
Havuz Dogal Filiz	836.8±54.2	12.9±0.7	25.4±3.8	33.1±3.8	1.8±0.7	17.2±1.2	20.4±4.3	146.1±15.5
Caykur Cay Cicegi	971.3±64.8	11.7±0.1	15.4±4.1	29.6±1.6	1.9±0.4	24.8±1.4	19.5±2.9	122.8±8.8
Caykur Rize Turist	857.4±34.0	13.3±1.2	15.9±3.8	32.5±6.5	2.2±0.6	17.0±0.9	21.0±0.9	109.9±10.4
Caykur Kamelya	843.0±59.1	14.6±0.7	< 8	24.2±2.5	2.6±0.2	21.2±0.8	8.9±2.5	113.2±4.4
Havuz Filiz	656.8±16.6	13.3±1.6	< 8	30.4±3.3	3.0±0.3	10.4±1.0	12.4±1.9	123.4±2.4
Lipton A	563.9±52.8	16.9±1.5	< 8	14.7±3.2	2.7±0.2	14.5±1.5	7.7±0.8	140.5±11.8
Caykur Altinbas	659.7±76.4	10.8±1.0	< 8	10.8±2.6	2.2±0.1	18.2±1.7	9.2±0.9	112.7±20.8
Caykur Tomurcuk	614.8±32.1	< 10	< 8	12.6±1.5	< 1	13.2±0.4	9.2±0.9	130.4±7.4
Altin Filiz	599.9±19.9	12.1±2.1	12.1±2.1	11.7±1.8	2.7±0.2	14.8±08.	7.8±1.5	147.5±6.4
Lipton B	784.5±51.9	12.1±0.8	11.8±0.1	12.2±3.2	2.0±0.2	14.2±1.0	7.8±1.5	121.6±12.4

The mean copper contents of the samples was 16.5±3.9 µg/g. The lowest level of copper was found Havuz Filiz tea sample as 10.4 µg/g, while the highest in Caykur Caycicegi as 24.8 µg/g. The range for present study is agreed with the results given for black tea samples by Xie *et al.* (1998) and Ferrara *et al.* (2001). The concentrations of Co and Zn in the samples were in the range of 7.7-30.2 µg/g (lowest in Lipton A, highest in Harran Altinbasak) and 112.7-147.5 µg/g (lowest in Caykur Altinbas and highest in Altin Filiz), respectively. The mean concentrations of cobalt and zinc in the black tea samples were 14.5±7.1 µg/g and 129.0±12.9 µg/g. Marcos *et al.* (1998) have been reported that average cobalt and zinc concentrations in tea samples as 0.2 µg/g and 28.2 µg/g, respectively. The mean level of zinc in black tea were given as 36.6±0.7 µg/g by Matsuura *et al.* (2001).

The study shows that the levels of the investigated heavy metal ions studied are compare well with levels in black tea samples from other parts of the world. The study will be valuable in the appraisal of trace elements in black tea and be helpful for people who like drinking tea.

The whole data were subjected to statistical analysis, and correlation matrices were produced to examine the inter-relationships between the investigated metal concentrations. Correlation coefficients between metal concentrations in black tea samples are given in Table 2. The correlation between manganese-lead, manganese-nickel, manganese-copper, manganese-cobalt, chromium-cadmium, lead-nickel and lead-cobalt were highly significant according to the data given by Poissant *et al.* (1994). The other correlation of metal concentrations of the samples was not significant and zinc ion seems to be independent from all the other elements.

Table 2. Correlation coefficients between investigated metal concentrations (r = 95%)

	Mn	Cr	Pb	Ni	Cd	Cu	Co	Zn
Mn	1.000	0.293	0.746	0.639	0.052	0.541	0.631	0.062
Cr		1.000	0.267	0.292	0.864	0.157	0.203	0.069
Pb			1.000	0.529	0.073	0.284	0.663	0.331
Ni				1.000	0.249	0.387	0.423	0.062
Cd					1.000	0.071	0.000	0.056
Cu						1.000	0.067	0.182
Co							1.000	0.084
Zn								1.000

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