Research article

Determination of total contents of transition metals in selected granular black teas marketed in Poland

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Abstract: *The total contents of metals in three granulated black tea samples marketed in Poland were determined. Four elements consisting transition metals (Ni, Cu, Zn and Fe) were analyzed using flame atomic absorption spectrophotometry (FAAS). All examined tea brands contain considerable contents of the studied transition metals. Among the tested transition metals Fe (242-589 mg kg^{-1}) was the most abundant one in the granular black tea imported from India. The highest value of Fe was analyzed in the cheapest tea, the smallest in the most expensive. The other metals are less abundant than Fe, their values varied from 8.50-8.90 for Ni, 7.80-10.4 for Cu and 8.13-12.6 for Zn mg kg^{-1}. The accuracy of the proposed method was assessed by determining the recovery of metals from analyzed tea samples using the standard addition method. Recovery assays of nickel, copper, zinc and iron were demonstrated satisfactory, mean recoveries 99.29, 100.31, 99.94 and 99.79 %, respectively.*

Keywords: *transition metal, granular tea, flame atomic absorption spectrometry.*

Introduction

A variety of chemical elements contained in food and beverages are relatively easy absorbed by the human body. Despite the fact that most of them are very important for human health, they can also be toxic, which usually is the result of the presence of contamination in soil, the application of fertilizers and pesticides. Therefore, it is important to study the daily intake of trace elements in the diet [1, 2].

So far, tea has been reported as one of the most widely consumed beverage in the world, taking the second place, after water, in terms of consumption [3, 4]. This represents over 40% of all beverages consumed in winter and 25% in summer. The annual tea consumption *per capita* in Poland is almost 1kg. Most consumers drink this beverage 2-3 times a day, and about 20% even 4-5 times a day [5]. It is estimated that the tea market in Poland is the third largest among all markets in Europe, after Russia and the United Kingdom. In 2011, black tea (including granular one) and herbal tea made out respectively 69.6% and 15.8% of the Polish tea market. Tea is perceived by consumers as a tasty, healthy and safe beverage [6]. Tea drinking has been also claimed to have a large number of

health benefits, including cancer and heart diseases prevention [7]. These advantages are attributed to polyphenolic compounds occurring in tea [3].

Unfortunately, more often, the presence of contaminants in tea leaves may arise as a result of environmental pollution: the air, water and soil [8]. Significant impact on the presence of harmful elements is the quality of drinking water used for tea brewing [9]. The majority of polluting agents (lead, cadmium, arsenic, mercury or nickel) occurring in tea have deleterious effects on human health despite the fact that only about 40% of them goes to the brew. The current European Union legislation on contaminants in foods does not set maximum levels of harmful elements in tea [9].

The content of trace elements, including copper, iron, nickel and zinc, both in raw materials and final products of the food industry should be controlled due to several reasons [10]. Firstly to judge their nutritional value and secondly to guard against any probable ill-effect. For example, copper can be associated with non-Indian childhood cirrhosis [11] and Wilson's disease [12], iron - Parkinson's disease and Alzheimer's disease [13], nickel – carcinogenicity or allergy [14], zinc – nausea, vomiting or epigastric pain (only with extremely high zinc intakes) [15].

The use of rapid methods for the determination of trace elements in food has significant importance [16-20]. These methods should have a high selectivity, a suitable analytical sensitivity and simplicity of performance, as well as reliability, high precision of determinations made, international recognition and facility of validation. These features dominate in atomic spectrometry methods with particular emphasis on atomic absorption spectrometry (AAS). The large popularity of techniques based on the principles of atomic spectrometry results from the fact that these techniques are accurate, precise, flexible and relatively inexpensive. Atomic absorption spectrometry is the most comprehensive method due to a variety of analytical techniques and relatively well recognized interference occurring in different techniques [21].

The aim of this study was the quantitative determination of total zinc, copper, iron and nickel contents using AAS method in teas which are known and generally available on the Polish market. The obtained mean elemental concentrations were compared with the corresponding values of different countries available in the literature.

Experimental

Materials

Atomic absorption standard solution of Ni, Zn, Cu and Fe at a concentration of 1000 mg/L were obtained from Merck Sp. z o.o. Darmstadt, Germany. Nitric acid applied in digestion process was of analytical reagent grade (Lach-Ner, Neratovice, Czech Republic). Ultrapure water from Elix system (Millipore, Bedford, MA, USA) was used for preparation of working reagents and for sample dilutions. The glassware was cleaned and immersed in 4.5 % nitric acid

(J.T. Baker, Deventer, The Netherlands) for 24 h. Teflon beaker was treated with 4.5 % nitric acid and washed with ultrapure water. To prepare the final standard stock solutions, 1 mL of nickel and iron, 0.5 mL of copper and 0.2 mL of zinc standard solution (1000 mg L^{-1}) was diluted with ultrapure water to 100 mL. Standard working solutions were freshly prepared by diluting the obtained final standard stock solution with ultrapure water to an appropriate concentration before analysis.

Samples

Three, black and granulated tea samples from various trade marks were purchased from stores in Lodz. The selected teas were imported from India. They varied in respect of price. The first sample was the most expensive, followed by the second and the third sample, which was the cheapest. The study samples were collected in the first quarter of 2012. Each package of tea weighed 100 g. Three replicate samples of each tea were quantified using flame atomic absorption spectrophotometry (FAAS).

Methods

Preliminary treatment of samples

The tea granules were crushed using pestle and mortar. The powder was stored at room temperature in dry containers for analysis. To avoid metallic contamination, nonmetallic tools were used during sample preparation.

In these studies 10 ± 0,1 g of tea sample was used. It was the most optimal portion of the tea to determining all tested transition metals. Due to industrial safety 1 ± 0,1 g portions of tea samples were used in a microwave digestion system. Each portion of tea was treated 8 mL of 65 %HNO_3. The vessels were heated in a microwave digestion system according to the manufacturer's instructions (Magnum II, Ertec, Wroclaw, Poland). After mineralization, the liquid residues were placed in a final volumetric flask (100 mL) and diluted with distilled water. A blank mineralization was carried out in the same way.

Measurements

For metal analysis, a GBC 932 AA Spectrometer from GBC (Scientific Equipment Pty Ltd., Dandenong, Victoria, Australia) with deuterium background correction was used. The system was operated via GBC Avanta Ver. 1.33 Software Package. Spectrometer was equipped with hollow cathode lamps and an air–acetylene burner. The instrument parameters are shown in Table 1. All samples were prepared in triplicate and injected consecutively in triplicate. The samples were diluted and measured only in case of analysis of iron. The calibration curve was obtained using three standards and blank. To assess the accuracy of the total procedure, the determined samples were enriched with metal standard solutions and re-analysed.

Results and Discussion

Spectrometric analysis of granulated black teas is relatively inexpensive and the operation is simple, it concerns an analytical method for the determination of the transition metal contents in tea [22]. AAS methods require destruction of organic matter by wet mineralization. In our method we have optimized samples mass to 10 ± 0,1 g in order to the detection limits were exceeded. The executed method, which does not require very complicated pre-analytical manipulation, detects the concentration of metals with good accuracy and precision. The analytical curves of the selected metals, obtained by plotting the mean of absorbance at the appropriate wavelengths (Table 1) against the concentration generated the specific parameters which are shown in Table 2.

Table 1. Instrumental conditions of the flame atomic absorption spectrophotometer GBC 932

	Nickel	Copper	Zinc	Iron
Wavelenght (nm)	232.0	324.7	213.9	248.3
Slit width (nm)	0.2	0.2	0.2	0.2
Lamp current (mA)	4.0	3.0	5.0	5.0

Table 2. Linearity parameters for the determination of selected metals

Parameters	Ni	Cu	Zn	Fe
Linearity range [μg mL^{-1}]	2.5 to 10	1.25 to 5.0	0.5 to 2.0	2.5 to 10
Slope	0.0464	0.1056	0.222	0.0409
Intercept	0.033	0.004	0.093	0.0045
Correlation coefficient (r)	0.9991	0.9998	0.9882	0.9998

The accuracy of the proposed method was assessed by determining the recovery of metals from analyzed tea samples using the standard addition method (Table 3). Recovery assays of nickel, copper, zinc and iron demonstrated satisfactory, obtaining mean recoveries of 99.29, 100.31, 99.94 and 99.79 %, respectively.

Table 3. Recovery metals from tea samples

Tea samples	Ni [%]	Cu [%]	Zn [%]	Fe [%]
1	87.02	100	93.27	93.28
2	92.20	97.48	103.64	104.29
3	120.61	103.45	102.46	103.45
Mean recovery	99.29	100.31	99.94	99.79

The results of total contents of the studied trace elements namely nickel(II), copper(II), zinc(II) and iron(III) are presented in Table 4. Determination of transition metals in samples was carried out by FAAS. The values are expressed as mean values (three separate determinations) ± standard deviation of the mean.

The results show the ability of tea as a plant to accumulate transition metals, particularly Fe, to a lower extent Ni, Cu and Zn. Iron as the most abundant metal in granulated tea ranged from 242.33-589.33 mg kg^{-1}. The highest value of Fe was analyzed in the cheapest tea, the smallest in sample No. 2 (the most expensive). The other metals are less abundant than Fe, their values varied from 8.50-8.90 for Ni, 7.80-10.4 for Cu and 8.13-12.6 for Zn mg kg^{-1}.

Table 4. Mean total contents of selected transition metals (Each value is the mean of three samples)

Concentration of metals with standard deviation [mg kg^{-1}] and coefficients of variation (CV) [%]	Tea samples		
	1	2	3
Ni±SD [mg kg^{-1}]	8.50±0.10	8.90±0.53	8.87±0.06
CV [%]	1.2	5.9	0.7
Cu±SD [mg kg^{-1}]	8.47±0.46	7.80±0.95	10.4±1.40
CV [%]	5.4	12.2	13.5
Zn±SD [mg kg^{-1}]	9.43±0.91	8.13±1.02	12.6±0.89
CV [%]	9.6	12.5	7
Fe±SD [mg kg^{-1}]	276.67±6.43	242.33±100.81	589.33±21.59
CV [%]	2.3	41.6	3.6

These metals could be put in a descending order according to their contents in granulated tea as follows:

$$\text{Fe}\ (242.33\text{-}589.33) > \text{Zn}\ (8.13\text{-}12.6) \geq \text{Cu}\ (7.80\text{-}10.4) \geq \text{Ni}\ (8.50\text{-}8.90)$$

The presented order of the total metal content was illustrated graphically in Figure 1. In laboratories precision is expresses as a coefficient of variation, which is nothing more than the standard deviation divided by the mean and expressed as a percentage. In accordance with analytical consideration of World Health Organization the precision determined at each concentration level should not exceed 15% of the coefficient of variation. In this study values of CV for Ni, Cu and Zn do not exceed recommended level. Only in the case of Fe in tea sample No. 2 CV value was significantly higher (41.6%).

Analyzing the contents of four metals in the tested tea samples a variety of results can be concluded (Table 4). Among the tested tea samples, the sample No. 3 as the cheapest one has the highest contents of (Cu, Zn and Fe). The maximum level of Fe (589.33 mg kg^{-1}) in this sample was too high in comparison to teas No. 2 and 3. Such a high iron content in tea the consumers should consider. Generally, Fe showed the highest values in all teas in relation to other metals. The lowest values of Cu and Zn were found in tea sample No. 2 and the highest - in tea sample No. 3. This study shows that the Cu and Zn contents in all the tea samples were less than 13 mg kg^{-1}, which is well below the permissible limit of 20 mg kg^{-1} and 50 mg kg^{-1} respectively, under Polish Regulation of the

Minister of Health and Social Welfare of 27 December, 2000 [23]. According to Falandysz & Kotecka [24] the content of microelements in black tea leaves, including zinc is much higher, compared to green tea. Copper is a component in fungicides applied regularly on the plantations of coffee, tea and cocoa, for protection against the pathogen causing leaf disease.

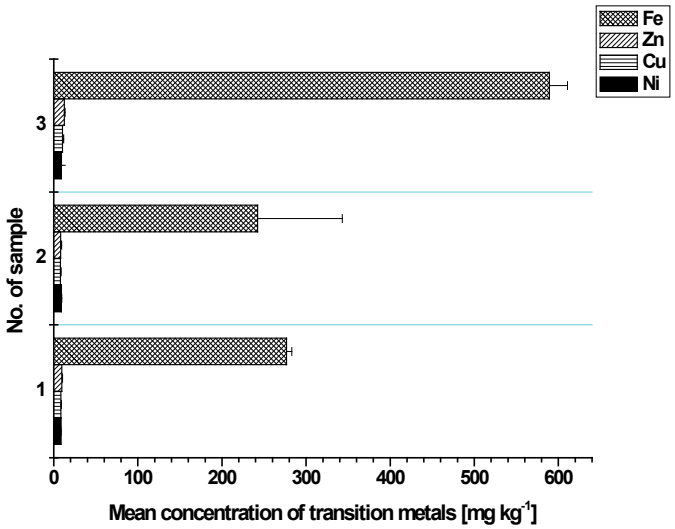

Figure 1. Comparison of data of total contents of metals in black tea samples imported from India

Table 5. The total contents of transition metals in tested tea samples

Tea samples	Used analytical method	Ni [mg kg-1]	Cu [mg kg-1]	Zn [mg kg-1]	Fe [mg kg-1]
Indian teas (own data)	FAAS	8.50-8.90	8.0-10.4	8.13-12.6	242-589
Indian teas [25]	ICP-AES	4.88	23.21	27.26	146.9
Lipton (lose) [26]	ICP	4.8	24.08	31.96	194,.
Lipton® *Yellow label* [27]	ICP-QMS	6,.4	25.3	34.2	344
Indian teas [16]	AAS-GF	24.07	2.53	-	-
Imported teas [24]	FAAS	-	29-34	31-35	230-260

Natural copper content in tea leaves is approximately 28 mg kg^{-1}, and levels above 70 mg kg^{-1} dry weight suggest that copper compounds are regularly used on the plantation [24]. Considering the obtained results, it should be noted that the plant material, used for our analysis, has not been exposed to copper fertilizers. Since Ni and Fe are the toxic elements, not having any tolerance limit in tea, the agro inputs used in tea fields should be analyzed for heavy metal impurities.

Comparing the total content of selected metallic components in analyzed tea samples imported from India with other studies (Table 5) [24-28], values of Cu and Zn from own studies have not exceeded the concentration from literature data. Whereas, the contents of Ni and Fe, and especially the last metal, significantly exceeded the amounts given in the references. Probably, these differences may be due to different working tools, the type of analytical method, measurement error, tea cultivation area or agricultural differences. The granular teas have a lower quality, nevertheless the beverage is popular among the poorer because it is the cheapest. Therefore, monitoring the contents of transition metals in such teas is important and necessary.

The information specifying the rational total contents of transition metals in granular black tea is lacking in literature. The maximum allowed concentration of each metal in granular black tea is needed. Occasional analysis and frequent examination of beverages is advisable to avoid problems that could arise from intake beyond the tolerance limits standards.

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