Simple and Fast Sample Preparation Procedure Prior to Multi-element Analysis of Slim Teas by ICP OES

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Abstract The knowledge about mineral content of slim teas is of great importance since the consumption of these beverages has rapidly increased for the past several years. An increasing popularity of these tea products is mainly attributed to their nutritional properties, flavor, taste and health effects. Therefore, the main goal of the present work was to develop a precise and accurate method of the multi-element analysis of slim teas by inductively coupled plasma optical emission spectrometry (ICP OES) without the need for a laborious and tedious sample treatment preceding spectrometric measurements. Five sample preparation procedures, i.e., the total decomposition in a mixture of HNO_3 and H_2O_2 solutions using closed vessel microwave-assisted or open vessel hot-plate systems, the solubilisation in aqua regia or a tetramethyl ammonium hydroxide solution and the extraction in a diluted HNO_3 solution, were compared. The performance of the compared procedures was determined in terms of the precision and the accuracy of results achieved and limits of detection of elements. It was found that the solubilisation in aqua regia gave the best results, i.e., limits of detection between 0.15 and 98.4 ng l^{-1}, the precision within 0.6−3.0 % and the accuracy better than 5 %. The developed method of the analysis, being a useful alternative to time-consuming wet digestion procedures, was successfully applied to the analysis of five slim tea products.

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Introduction

Nowadays, an interest in the consumption of specific teas (e.g., slim teas) can be observed. These particular teas, being mixtures of different types of teas (black, green or Pu-erh), herbs and various additional bioactive components, are preferred by the people who wish to reduce their body weight. So far, there have been no reports at all on the analysis of such products, specifically on the total content of different elements. Recently, however, an extended literature review devoted to sample preparation strategies and the elemental analysis of tea made from leaves *Camellia sinensis* was presented by Welna et al. 2013.

Generally, the determination of total concentrations of various macro- and micro-elements in different teas as well as medicinal plants is carried out with the use of flame atomic absorption spectrometry (FAAS) (Aksuner et al. 2012; Colak et al. 2005; Kumar et al. 2005; Li et al. 2006; Malik et al. 2008; Narin et al. 2004a,b; Seenivasan et al. 2008; Soylak et al. 2007), graphite furnace atomic absorption spectrometry (GF AAS) (Dash et al. 2008; Seenivasan et al. 2008), inductively coupled plasma optical emission spectrometry (ICP OES) (Chen et al. 2009; Dash et al. 2008; Kara 2009; Malik et al. 2008; Matsuura et al. 2001; McKenzie et al. 2010; Mierzwa et al. 1998; Özcan et al. 2008), inductively coupled plasma mass spectrometry (ICP MS) (Kara 2009; Matsuura et al. 2001; Nookabkaew et al. 2006; Shen and Chen 2008) and X-ray fluorescence spectrometry (XRFS) (Salvador et al. 2002; Xie et al. 1998). As a rule, the decomposition of the matrix of tea samples is an indispensable and mandatory step before their elemental analysis by the majority of these spectrometric methods. Typically, the digestion is carried out by a conventional hot-plate or microwave-assisted heating of tea samples with oxidizing reagents, including HNO_3, $HNO_3 + H_2O_2$, $HNO_3 + H_2SO_4 + H_2O_2$, $HNO_3 + H_2O_2 + HF$, $HNO_3 + HClO_4$, $HNO_3 + HCl$, $HNO_3 + HCl + HF$, (Aksuner et al.

2012; Colak et al. 2005; Kumar et al. 2005; Narin et al. 2004a,b; Dash et al. 2008; Matsuura et al. 2001; McKenzie et al. 2010; Mierzwa et al. 1998; Nookabkaew et al. 2006; Salahinejad and Aflaki 2010; Shen and Chen 2008; Soylak et al. 2007). Except for the mentioned wet ashing procedures, dry-ashing procedures, as described by the Association of Analytical Chemistry (Seenivasan et al. 2008) or modifications of this official method (Chen et al. 2009; Li et al. 2006; Malik et al. 2008; Narin et al. 2004b), are also used at the stage of the sample preparation of tea before its spectrochemical analysis.

Wet acid digestion and dry-ashing procedures reported in the literature are tedious and time-consuming, require the use of hazardous reagents and often lead to systematic errors and failures (Welna et al. 2011). Therefore, an interest in improving and simplifying sample preparation procedures prior to the elemental analysis has lately been observed. The most common approach to achieve this is to reduce the processing time and amounts of reagents used or completely eliminating the sample matrix destruction step. The detailed information about conventional and alternative procedures, including their advantages and disadvantages, aimed at preparing different tea samples prior to their elemental analysis by atomic spectrometry methods is given in Table 1.

So far, only few studies have been carried out to compare the different procedures for the sample preparation of teas before their elemental analysis by spectrochemical methods. Narin et al. (2004a) compared two different digestion procedures, i.e., hot-plate heating and microwave-assisted decompositions with a mixture of concentrated HNO_3 and HCl solutions (3:1, v/v), to determine concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in black teas by FAAS and ICP OES. Aksuner et al. (2012) examined a microwave-assisted digestion procedure in a mixture of concentrated HNO_3 and H_2O_2 solutions (3+1 ml) and a hot-plate heating digestion procedure in a mixture of concentrated HNO_3 and $HClO_4$ solutions (7+8 ml) for the determination of Cu, Fe, K, Mn, Ni and Zn in black, green, white and herbal tea samples by FAAS. In both cited reports, it was shown that there were no significant differences in results obtained using compared procedures. Mierzwa et al. (1998) evaluated the suitability of different microwave-assisted digestion procedures of oolong teas for the determination of Ba, Cu, Fe, Pb, Zn by ICP OES. For this purpose, a concentrated HNO_3 solution only and its combinations with other acids were tested, i.e., HNO_3+HF (9+1 ml), HNO_3+HCl (9+1, 9+2 and 9+3 ml), HNO_3+HCl+HF (9+1+1, 8+2+1 and 7.5+2.5+1 ml). Furthermore, a microwave oven heating program was optimized to be as short as possible. It was found that a 10-min digestion at 180 °C was optimal for sample portions of 0.3 g. Poor recoveries (based on the analysis of a tea GBW 07605 CRM) were obtained if only HNO_3 was used. The mixture of HNO_3 with HCl and HF was more efficient than mixtures of HNO_3 with

HF or HNO_3 with HCl. In the same work, the direct analysis of teas using the slurry sampling (SS) technique was also tested to avoid the complete sample digestion. In this procedure, finally ground tea samples were diluted in a HNO_3 solution (0.4 % or 4 % v/v) containing 0.005 % (v/v) Triton X-100 and ultrasonicated to form suitable sample slurries. Dash et al. (2008) developed an efficient alternative procedure of the decomposition of tea and tulsi samples based on the UV photolysis before the determination of Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Rb by GF AAS and ICP OES. Accuracy was verified with a certified reference material of Cabage (GBW 08504) and in-house spinach standard. It was established that the UV photolysis of analyzed samples resulted in obtaining reliable results.

The main purpose of the present work was to develop a simple, precise and accurate method of the multi-element analysis of slim teas by ICP OES. To the best of our knowledge, this work is the first to report on the analysis of such tea products in reference to their elemental composition (macro-, micro- and trace elements) as well as the comparison of three alternative to open and closed vessel system wet digestions sample preparation procedures of slim teas prior to the determination of total concentrations of 13 elements, i.e., Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr and Zn, by ICP OES. Five different slim teas, commercially available in Poland, were analyzed using the new sample preparation procedure providing the best precision and accuracy of results.

Materials and Methods

Samples

Five slim bag teas, i.e., *Slim Figure age 30+*, *Slim Figure age 45+*, *Slim Figure age 55+*, *Slim Figure fat burning* and *Figure 1*, were purchased at a local market (Wrocław, Poland). Detailed ingredients of the analyzed products are as follows:

1. Slim Figure age 30+: *Yerba mate* leaves, apple fruits, black tea, cinnamon bark, cloves, flavors, *Garcina cambogia* extract containing hydroxycitric acid
2. Slim Figure age 45+: *Y. mate* leaves, *Hibiscus* flowers, soybean aroma, fennel fruits, focus
3. Slim Figure age 55+: *Hibiscus* flowers, green tea, strawberry fruits, flavors, focus
4. Slim Figure fat-burning: Pu-erh tea, *Y. mate* leaves, guarana seeds, chamomile flowers, peppermint leaves, fennel fruits, anise fruits, *G. cambogia* extract containing hydroxycitric acid
5. Figure 1: Pu-erh tea, *Hibiscus* flowers, elder fruits, apple peels, rosehip fruits, *G. cambogia* extract containing hydroxycitric acid

Table 1 Sample preparation procedures of teas prior to their elemental analysis by spectrometry methods

Conventional methods

Dry ashing

Sample	Analyte	Methodology	Detection	Reference	Advantages	Disadvantages
Tea (Camellia sinensis)	Al, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Pb, Zn	5.0 g, 500 °C, 6 h; Ash: 2 ml HCl (6 mol l⁻¹); Final volume: 25 ml	ICP OES	Chen et al. 2009	- Large sample amounts - Complete destruction of organic matter	- Slow - Labourious - Time-consuming - Loss of volatile analytes - Possible contaminations of samples - High temperature treatments - Lower precision
Green tea	Al, F, K	5.0 g, 300 °C, 1 h, 550 °C, 4 h; Ash: extraction 5x2 ml HCl (2 mol l⁻¹), 4 h pH 5.5 (2 mol l⁻¹ NaOH); final volume: 50 ml	ICP OES	Li et al. 2006	- Simplification to a variety samples - Application to a variety samples	
Tea (black, green, oolong, white)	Al, B, Cu, Fe, Mn, P, Zn	1.0 g, 500 °C, 16 h; Ash: 3 ml aqua regia (100 °C), 5-10 min, Final volume: 20 ml	ICP OES	Malik et al. 2008		
Herbal tea	Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	0.25 g, 450 °C, 8 h; Ash: 5 ml HNO₃ (25 %); Final volume: 10 ml	FAAS	Narin et al. 2004b		
Black tea	Cd, Cr, Cu, Ni, Pb	0.5 g, 450 °C, 3 h; Ash: 5 ml HCl (6 mol l⁻¹); Final volume: 50 ml	FAAS	Seenivasan et al. 2008		

Open vessel hot-plate wet digestion

Sample	Analyte	Methodology	Detection	Reference	Advantages	Disadvantages
Tea (black, green, white)	Cu, Fe, K, Mn, Na, Ni, Zn	HNO_3 (7),[a] pre-digestion, + $HClO_4$ (8)[a] (1.0 g+15 ml); Final volume: 25 ml	FAAS	Aksuner et al. 2012	- Large sample amounts - Lower temperatures as compared to dry ashing - Application to a variety samples	- Slow - Time-consuming - Laborious - Loss of volatile analytes - Contaminations of samples - Use of large amounts of strong oxidizing reagents - Pre-concentration of reagent impurities - Incomplete solubilisation of sample constituents - High temperature treatments - Lower precision
Black tea	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	HNO_3 (10),[a] 1 h, + $HClO_4$ (1),[a] 1 h (0.5 g+11 ml); Final volume: 100 ml	FAAS	Ashraf and Mian 2008		
Tea (herbal, fruit)	Cu, Fe, Mn, Ni, Zn	$HCl+HNO_3$ (3:1),[b] 3 h (1.0 g+8 ml); Final volume: 25 ml	FAAS	Colak et al. 2005		
Tea (black, green, herbal)	Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr, Zn	HNO_3 (10),[a] 3 h (0.25 g+10 ml); Final volume: 25 ml	ICP OES ICP MS	Kara 2009		
Tea	Co, Ce, Cr, La, Br, Cu, K, Mn, Na	HNO_3+HClO_4 (5:1)[b] (1.0 g+10 ml); Final volume: 50 ml	INAA, FAAS	Kumar et al. 2005		
Black tea		HNO_3 (5),[a] pre-digestion, + HNO_3 (5)[a], 3 h + HF (2),[a] 2 h (0.5 g+12 ml); Final volume: 100 ml	ICP OES ICP MS	Matsuura et al. 2001		
Tea (black, green)	Ba, Ca, Mg, Mn, Zn	HNO_3 (10),[a] 1 h (0.25 g+10 ml)	ICP OES	Mokgalaka et al. 2004		

Table 1 (continued)

Conventional methods

Dry ashing

Sample	Analyte	Methodology	Detection	Reference	Advantages	Disadvantages
Black tea	Cd, Co, Cr, Cu, Mg, Ni, Pb, Zn	Final volume: 50 ml HNO_3+HCl (3:1)[b] (1.0 g)	FAAS	Narin et al. 2004a		
Herbal tea	Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	Final volume: 25 ml HNO_3+H_2SO_4+H_2O_2 (2:2:2),[b] 4 h (0.25 g+6 ml)	FAAS	Narin et al. 2004b		
Black tea	Al, As, Ca, Cd, Cr, Cu, Fe, Mn, Mg, Ni, Pb, Zn	Final volume: 10 ml HNO_3 (5),[a] pre-digestion, + HNO_3+$HClO_4$ (1+4),[a] 1 h (1.0 g+10 ml) Final volume: 25 ml	ICP OES	Salahinejad and Aflaki 2010		

Closed vessel microwave-assisted wet digestion

Sample	Analyte	Methodology	Detection	Reference	Advantages	Disadvantages
Teas (black, green, white)	Cu, Fe, K, Mn, Na, Ni, Zn	HNO_3+H_2O_2 (3+1),[a] 11 min (0.3 g+4 ml) Final volume: 10 ml	FAAS	Aksuner et al. 2012	- Closed system - Reduce volume of aggressive reagents	- High cost of equipment - Small sample amounts - Time required for cooling vessel
Tea (oolong, green, white pu-erh, black)	Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, Zn	HNO_3+H_2O_2 (6+1),[a] 23 min (0.25 g+7 ml) Final volume: 25 ml	ICP OES	McKenzie et al. 2010	- Minimal contamination - Lack of loss volatile analytes - Minimal contaminations of samples	- Control of process - Food matrix may require a different microwave program
Oolong tea	Ba, Ca, Fe, Pb, Zn	HNO_3+HF (9+1)[a] HNO_3+HCl (9+1, 9+2, 9+3)[a] HNO_3+HCl+HF (9+1+1, 8+2+1, 7.5+2.5+1)[a] 30 min	ICP OES	Mierzwa et al. 1998	Better precision and accuracy	Contaminations of samples
Black tea	Cd, Co, Cr, Cu, Mg, Ni, Pb, Zn	HNO_3+HCl (3:1),[b] 11 min (1.0 g+12 ml) Final volume: 25 ml	FAAS	Narin et al. 2004a		
Herbal tea	Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	HNO_3+H_2SO_4+H_2O_2 (2:2:2),[b] 32 min (0.25 g+6 ml) Final volume: 10 ml	FAAS	Narin et al. 2004b		
Herbal tea	Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Sr, V, Zn	HNO_3+H_2O_2 (6+2),[a] 70 min (0.25 g+8 ml) Final volume: 50 ml	ICP MS	Nookabkaew et al. 2006		
Black tea	Al, B, Ba, Bi, Ca, Cd, Co, Cr, Fe, Ga, Ln, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Sr, Ti, V, Zn	HNO_3 (15)[a] (0.5 g+15 ml) Final volume: 100 ml	ICP OES	Özcan et al. 2008		
Tea (black, green)	As, Cd, Co, Cu, Cr, Fe, Mg, Pb, Se, Zn	HNO_3 (20),[a] 70 min (2.0 g+20 ml) Final volume: 50 ml	ICP MS	Shen and Chen 2008		
Tea (black, green, herbal)	Cu, Ni, Zn	HNO_3+H_2O_2 (6+2),[a] 28 min (0.2 g+8 ml)	FAAS	Soylak et al. 2007		

ALTERNATIVE METHODS

Table 1 (continued)

Conventional methods

Dry ashing

Sample	Analyte	Methodology	Detection	Reference	Advantages	Disadvantages
Sample	Analyte	Methodology	Detection	Reference	Advantages	Disadvantages
Tea (*Camellia sinensis*)	Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, Rb	UV photolysis-assisted digestion HNO$_3$ (3),[a] 30 min, + H$_2$O$_2$ (0.5),[a] 30 min (0.25 g+3.5 ml) Final volume: 25 ml	ICP OES GF AAS	Dash et al. 2008	- Complete destruction of organic matter	- Time-consuming - specific equipment
Oolong tea	Ba, Cu, Fe, Pb, Zn	Slurry sampling Sample: <60 μm Slurry: HNO$_3$ (0.04 and/or 0.4 %, v/v) + Triton X-100 (0.005 %, m/v) Ultrasonic bath: 15 s	ET AAS	Mierzwa et al. 1998	- Elimination of tedious step of sample digestion - Avoidance of use concentrated reagents - Minimalisation of analytes losses	- Stabilisation of the slurry - Homogeneity of the slurry - Sedimentation must be carefully considered - Time-consuming
Tea (black, green)	Al, Ba, Ca, Mg, Mn, Zn	Slurry sampling Sample: <4 μm (0.25–1.0 g) Slurry: HNO$_3$ (5 %, v/v)+Triton X-100 (1 %, m/v) Ultrasonic bath: 15 min Final volume: 100 ml	ICP OES	Mokgalaka et al. 2004	- Safety Possibility of use small amounts of samples	
Slim tea	Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr, Zn	Solubilisation in aqua regia (0.5 g+2 ml) Ultrasonic bath: 15 min Centrifugation:10 min, 12,000 rpm Final volume: 25 ml	ICP OES	this study	- Simple - Fast - Higher precision - Enables the accurate determination of very low concentrations of analytes - Not require high temperature treatments - Reduce risk of contamination - Loss of volatile analytes can be eliminated	- specific equipment

[a] Volumes of reagents (in ml)

[b] The ratio of reagent volumes (ml/ml)

Before the analysis, the tea material was removed from bags, mixed, ground and stored at room temperature in polyethylene (PE) containers.

Reagents

All chemicals were of analytical grade purity. Concentrated HNO_3 (Merck, Darmstadt, Germany) and HCl (POCh, Gliwice, Poland) solutions, in addition to a 30 % (v/v) H_2O_2 solution (POCh) and solid tetramethyl ammonium hydroxide (TMAH) (Sigma-Aldrich, Saint Louis, MO, USA) were used for the sample preparation. Working standard solutions were prepared by appropriate dilutions of a multi-element (1,000 μg ml^{-1}) ICP standard (Merck). De-ionized water (18.3 MΩ cm) was obtained from an EASYpure™ water purification system (Barnstead, Thermolyne Corporation, Dubuque, IA, USA). Glassware and plastic bottles were cleaned with a 10 % (v/v) HNO_3 solution and next, rinsed several times with de-ionized water.

Sample Preparation Procedures

The following sample preparation procedures were tested.

Closed Vessel Microwave-Assisted Wet Digestion (P1)

Tea samples (0.5 g) were weighed into Teflon digestion vessels, and 6 ml of a concentrated HNO_3 solution with 1 ml of a 30 % (v/v) H_2O_2 solution was added. Vessels were closed and reaction mixtures were immediately subjected to the microwave heating at a maximum power of 600 W and for 45 min. After cooling, colorless sample solutions were quantitatively transferred into 25-ml volumetric flasks and made up to the volume with de-ionized water prior to the multi-element analysis by ICP-OES.

Open Vessel Hot-Plate Wet Digestion (P2)

Tea samples (0.5 g) were weighted into 150-ml Pyrex beakers and 10 ml of a concentrated HNO_3 was added. Beakers were covered with watch glasses and reaction mixtures were heated on a hot plate at 85 ° C and for 3 h. Then, sample solutions were cooled and 5 ml of a 30 % (v/v) H_2O_2 was subsequently added. The heating was continued until sample solutions were clear and their volumes were reduced to about 2 ml (~30 min). Finally, aliquots left were quantitatively transferred into 25-ml volumetric flasks and made up to the volume with de-ionized water prior to the multi-element analysis by ICP OES.

Solubilisation in Aqua Regia (P3)

Tea samples (0.5 g) were weighed into 30-ml polypropylene (PP) centrifuge tubes and 2 ml of aqua regia was added. Tubes were stoppered and reaction mixtures were sonicated in an ultrasonic bath for 15 min. Then, they were filled up to 25 ml with de-ionized water and finally, resulting sample solutions were centrifuged for 10 min at 12,000 rpm. Supernatants were taken for the determination of elements by ICP OES. This procedure was finally used for the preparation of slim teas samples prior to multi-element determination by ICP OES.

Solubilisation in TMAH (P4)

Tea samples (0.5 g) were weighed into 30-ml PP centrifuge tubes and 0.75 ml of a 25 % (m/v) TMAH aqueous solution was added. Tubes were stoperred and shaken at 80 ° C and for 30 min. Next, reaction mixtures were cooled, made up to 25 ml with de-ionized water and then centrifuged for 10 min at 12,000 rpm. Supernatants were stored in PE containers at 4 ° C before the determination of elements by ICP OES.

Extraction in HNO3 (P5)

Tea samples (1.0 g) were weighted into 30-ml PP centrifuge tubes and 10 ml of a 1.0 mol l^{-1} (m/v) HNO_3 solution was added. Tubes were stoppered and reaction mixtures were sonicated in an ultrasonic bath at 50 °C and for 20 min. Next, mixtures were cooled, made up to 25 ml with de-ionized water and finally centrifuged for 10 min at 12,000 rpm to remove any solid particles. Supernatants were saved for the multi-element analysis by ICP OES.

Slim Figure age 30+ was used for the comparison of different sample preparation procedures. For each sample preparation procedure tested (P1–P5), three parallel sample solutions were prepared in addition to respective blank solutions that were used to correct the final results. Then, the sample preparation procedure that provided the best precision and the accuracy of results was applied to prepare other tea products before their analysis on total concentrations of 13 elements by ICP OES against the external calibration with simple working standard solutions.

Apparatus

A JY38S (Jobin Yvon, Longjumeau, France) ICP OES instrument was used to measure total concentrations of Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr, Zn in all sample and blank solutions. Operating parameters were as follows: 1.0 kW of RF power, 13 l min^{-1} of a plasma-gas flow rate, 0.2 l min^{-1} of a sheath-gas flow rate and 0.25 l min^{-1} of a nebulizer-gas flow rate. Solutions were introduced into the plasma torch using a Burgener (MiraMist, Mississauga, Ontario, Canada) nebulizer and a cyclonic type spray chamber at a flow rate of 0.75 ml min^{-1}. The most prominent analytical lines of Ba 233.53 nm, Ca 317.93 nm, Cd 228.80 nm, Cr 267.72 nm, Cu 324.75 nm, Fe 259.94 nm, Mg 285.21 nm, Mn 259.37 nm, Ni

221.65 nm, P 214.65 nm, Pb 220.35 nm, Sr 407.77 nm and Zn 213.86 nm were selected for measurements.

A Milestone (Sorisole, Bergamo, Italy) high-pressure microwave digestion system (MLS-1200 MEGA), equipped with a rotor MDR 300/10, was used for the closed-vessel microwave-assisted sample decomposition of samples. An Elpin (Katowice, Poland) thermostatic water bath shaker (type 357) and a JP Selecta (Barcelona, Spain) ultrasonic cleaning bath with a thermostat for heating (UltrasonsH) were used for experiments in which samples of slim teas were treated with aqua regia and TMAH solutions. An MPW-350 centrifuge (MPW Med. Instruments, Warsaw, Poland) was used to accelerate the separation of sample solutions from solid particles.

Statistical Methods

Differences between concentrations of elements measured in solutions of Slim Figure age 30+, prepared with the aid of compared sample preparation procedures, were tested using the t-test at the 95 % significance level (Ellison et al. 2009). The tightness of the relationship between concentrations of these elements in all analyzed slim teas was evaluated by calculating Pearson's correlation coefficients (r) (Ellison et al. 2009).

Results and Discussion

Comparison of Sample Preparation Procedures

Five different sample preparation procedures of slim tea products, including two wet digestions (P1, P2) and three alternatives to the complete destruction of sample matrices, that precede the ICP OES analysis of these samples on the total concentrations of Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr and Zn were investigated. For the reasonable comparison of the suitability of different sample preparation procedures in ICP OES measurements of resulting sample solutions, basic chemometric parameters such as precision and accuracy of results achieved were evaluated. The relative standard deviation (RSD) was used to express the precision of measurements of elements' concentrations. The accuracy of the results was assessed by comparing total concentrations of elements obtained using the hot-plate wet digestion (P2), the solubilisation in aqua regia (P3) or TMAH (P4) solutions and the extraction in a diluted HNO_3 solution (P5) with those achieved using the microwave-assisted digestion procedure (P1). Among the digestion procedures reported for plant matrices, including teas, the microwave-assisted digestion in HNO_3/H_2O_2 is usually suggested. It is recognized as a well-established tool that provides the total sample decomposition without losses of analytes and treated as a reference method (Kingston and

Jassie 1988). Accordingly, this procedure (P1) was taken as a reference treatment in this work.

Precision

Total concentrations of elements (arithmetic means with RSD values) determined by ICP OES in Slim Figure age 30+ samples treated with compared sample preparation procedures are shown in Table 2.

The precision of concentrations of all elements obtained after the use of microwave-assisted and hot-plate wet digestions (P1, P2) and the solubilisation in aqua regia (P3) varies from 0.88 % (Ba) to 3.8 % (Cd, P), 1.8 % (Cu, P) to 4.1 % (Cd) and 0.64 % (Sr) to 3.0 % (Cd, P), respectively, for procedures P1, P2 and P3. The precision of measurements obtained with both wet digestion procedures, i.e., P1 and P2, is slightly worse than that achieved after the application of the procedure P3. In the case of procedure P4, RSD values were below 5 % for nine out of 13 elements determined, i.e., Ba, Ca, Cu, Fe, Mg, Mn, Ni, Sr and Zn. For procedure P5, only in four out of 13 elements determined (Ba, Ca, Cu and Mg) was the precision better than 5 %. For the remaining elements, the precision assessed, in cases where both latter procedures were used, was much lower. Accordingly, RSDs up to 7.1 % and 9.1 % for the solubilisation in TMAH (P4) and the extraction in diluted HNO_3 (P5), respectively, were obtained.

Table 2 Concentrations (in µg g^{-1}) of elements determined by ICP-OES in samples of Slim Figure age 30+ prepared using the microwave-assisted digestion in HNO_3 with H_2O_2 (P1), the hot-plate digestion in HNO_3 with H_2O_2 (P2), the solubilisation in aqua regia (P3) and TMAH (P4) and the dissolution in HNO_3 (P5)

	P1	P2	P3	P4	P5
Ba	30.1 (0.88)	29.9 (3.5)	30.2 (3.0)	8.93 (3.4)	13.3 (4.2)
Ca[a]	27.8 (1.2)	28.3 (3.7)	28.1 (1.7)	20.6 (4.8)	12.3 (2.9)
Cd	0.225 (3.8)	0.228 (4.1)	0.223 (3.0)	0.196 (7.1)	0.118 (8.8)
Cr	1.86 (2.3)	1.80 (2.6)	1.82 (2.2)	0.832 (6.8)	0.273 (8.5)
Cu	7.56 (1.2)	7.75 (1.8)	7.54 (0.45)	7.53 (1.8)	3.85 (1.8)
Fe	202 (2.6)	210 (3.4)	195 (2.8)	30.6 (4.2)	50.2 (6.9)
Mg[a]	3.02 (2.9)	2.98 (2.6)	3.02 (2.7)	2.42 (4.8)	1.34 (3.1)
Mn	920 (1.5)	911 (2.3)	916 (0.96)	304 (3.3)	295 (5.8)
Ni	3.90 (2.6)	4.00 (3.5)	3.89 (2.0)	3.87 (4.4)	2.14 (5.3)
P[a]	1.12 (3.8)	1.12 (1.8)	1.12 (3.0)	0.939 (5.1)	0.305 (9.1)
Pb	3.61 (1.8)	3.70 (3.0)	3.63 (2.0)	2.31 (5.5)	<LOD[b]
Sr	31.8 (1.1)	32.2 (2.0)	31.5 (0.64)	13.2 (3.5)	13.8 (6.3)
Zn	62.6 (2.6)	61.5 (2.9)	62.2 (2.6)	30.8 (2.3)	28.2 (6.2)

Average values ($n=3$) with relative standard deviations (RSDs) in brackets

[a] Concentrations in mg g^{-1}

[b] Below the limit of detection

Accuracy

Comparing concentrations of elements measured in samples of Slim Figure age 30+, it was found that the use of the open vessel wet digestion in a HNO_3 and H_2O_2 mixture (P2) and the solubilisation in aqua regia (P3) leads to obtaining results comparable to those obtained after the application of the closed vessel microwave-assisted wet digestion (P1). Using the t-test at the 95 % level of the significance, we determined that differences between results obtained using the reference procedure (P1) and those achieved using the second (P2) or the third procedure (P3) are statistically insignificant. As shown in Table 3, values of the calculated parameter t for both compared procedures (P2, P3) are lower than the critical value of this test ($t_{critical}$=4.303). Therefore, it was concluded that the solubilisation of slim tea samples in aqua regia (P3) could be an excellent alternative to time-consuming and laborious wet digestion procedures. Importantly, before the application of the t-test, the F test was used to compare the standard deviations. This is mandatory because two mean values can be compared using the t-test only if irrelevant differences in variance for comparing sets of results (F test) are present.

For the two remaining procedures (P4 and P5), a significant decrease in concentrations of most elements can be observed. This is particularly noticeable in thhe case of the extraction in diluted HNO_3 (P5). This sample preparation procedure is certainly not suitable for the reliable determination of studied elements by ICP OES because it does not provide the quantitative release of elements from the sample matrix and, in consequence, leads to serious systematic errors during the whole analysis. It seems that procedure P4 (the solubilisation in TMAH) can alternatively be used instead of the complete destruction of samples by wet digestion procedures (P1, P2), but only in the case of some selected elements, i.e., Cd, Cu and Ni.

The accuracy of the examined sample preparation procedures was also verified by the recovery test. Samples of Slime Figure age 30+ were spiked with a multi-element standard solution at two different concentrations (0.5 and 1.0 $\mu g\ ml^{-1}$) and prepared following all compared procedures. Experiments were performed in triplicate and resulting sample solutions were analyzed by ICP OES against simple working standard solutions to assess recoveries of elements added. As shown in Table 4, obtained recoveries are within 95.8−108%, 88.5 −118%, 98.7−105%, 76.7−137% and 71.3−121%, respectively, for procedures P1, P2, P3, P4 and P5. Results achieved for only two procedures, i.e., the microwave-assisted digestion in HNO_3 with H_2O_2 (P1) and the solubilisation in aqua regia (P3), provide the best quantitatively recoveries for all elements studied. Additionally, for these two procedures, slopes of standard additions' calibration curves (a_{Sadd}) were established to be comparable to those found for the external calibration curves ($a_{Ext.}$) with simple working standard solutions. By comparing the slopes (a) of calibrations curves, the following values of $a_{Sadd}/a_{Ext.}$ ratios were obtained: 0.94– 1.05 and 0.97–1.04 for microwave-assisted digestion procedure (P1) and solubilisation in aqua regia (P3), respectively. Therefore, it can be concluded that matrix effects are not observed for these two sample preparation procedures. Recovery values for other procedures indicate that they are not suitable for the determination of elements in resulting sample solutions by ICP OES.

Considering the precision and the accuracy, procedure P3 (the solubilisation in aqua regia) was chosen as a simple, fast and reliable means of the preparation of slim tea samples prior to their multi-element analysis by ICP OES.

Limits of Detection

Limits of detection (LODs) of elements achieved with ICP OES were calculated as concentrations corresponding to signals equal to 3 times standard deviations of ten replicates of respective blank solutions (3σ criterion), which were prepared in the same way as those of tea sample solutions. LOD values for all five sample preparation procedures are listed in Table 5.

As shown, the detectability of ICP OES for studied elements measured in solutions resulted from the application of both wet digestion procedures (P1, P2) and the solubilisation in aqua regia (P3) is better than that obtained after the use of the solubilisation in TMAH (P4) or the extraction in diluted HNO_3 (P5). The application of wet digestion procedures (P1, P2) provide quite comparable LODs of elements with the exception of Ba, Ca, Cr and Fe for which higher LOD values

Table 3 Calculated values of the t-test ($t_{calculated}$) for the comparison of average concentrations of elements determined in Slim Figure age 30+ by ICP OES using the reference procedure (P1) and other alternative procedures: the hot-plate digestion in HNO_3 with H_2O_2 (P2), the solubilisation in aqua regia (P3) and TMAH (P4) and the dissolution in HNO_3 (P5)

	P2	P3	P4	P5
Ba	0.320	0.183	90.55	46.89
Ca	0.780	0.826	12.06	54.81
Cd	0.408	0.319	3.069	13.72
Cr	1.643	1.180	25.06	56.29
Cu	1.948	0.345	0.320	54.52
Fe	1.565	1.606	55.88	42.26
Mg	0.681	0.029	7.085	29.80
Mn	0.614	0.423	62.34	49.14
Ni	1.000	0.133	0.261	19.84
P	0.074	0.032	4.883	27.87
Pb	1.226	0.361	15.86	–
Sr	0.953	1.287	55.59	33.22
Zn	0.781	0.302	30.73	24.75

The critical value of the t-test ($t_{critical}$): 4.303 (p=0.05, n=3)

Table 4 Recoveries of elements in samples of Slim Figure age 30+ prepared with the microwave-assisted digestion in HNO₃ with H₂O₂ (P1), the hot-plate digestion in HNO₃ with H₂O₂ (P2), the solubilisation in aqua regia (P3) and TMAH (P4) and the dissolution in HNO₃ (P5)

	Addition[a]	P1	P2	P3	P4	P5
Ba	0.5	101±1.18	96.3±5.11	98.9±1.20	86.0±8.72	115±11.5
	1.0	99.6±0.92	101±4.58	100±1.10	103±6.57	96.2±9.21
Cd	0.5	96.7±5.47	107±5.66	103±3.20	112±5.95	121±10.1
	1.0	101±4.06	98.2±5.03	99.2±1.01	97.1±5.12	94.6±8.83
Cr	0.5	104±3.29	100±2.75	101±2.12	82.6±9.02	112±9.45
	1.0	99.0±0.22	99.9±1.52	99.7±0.17	104±6.38	96.9±7.69
Cu	0.5	102±4.77	105±5.69	99.1±1.10	97.0±6.21	92.2±7.72
	1.0	99.5±4.00	98.7±4.83	100±0.50	101±4.35	102±5.66
Fe	0.5	108±7.55	118±9.80	105±5.20	83.3±10.6	72.2±13.0
	1.0	98.1±5.60	95.4±7.40	98.7±3.01	104±7.15	107±8.93
Mn	0.5	95.8±6.26	101±3.84	100±3.06	76.7±9.52	71.3±11.2
	1.0	101±5.82	99.8±2.19	99.9±1.50	106±7.15	107±8.24
Ni	0.5	101±2.62	98.0±3.78	102±1.50	105±4.92	111±6.33
	1.0	99.7±2.15	101±3.12	99.6±0.36	98.9±3.87	97.3±5.68
Pb	0.5	103±3.54	108±4.71	99.1±2.96	137±10.2	117±8.46
	1.0	99.2±2.81	98.0±3.31	100±2.35	90.6±7.93	95.8±6.38
Sr	0.5	98.6±5.63	103±6.08	100±4.40	89.3±9.48	93.1±7.82
	1.0	100±4.99	99.2±5.12	99.9±3.90	106±7.20	102±6.31
Zn	0.5	99.0±2.34	88.5±5.10	102±2.30	82.7±5.40	78.0±6.89
	1.0	100±3.56	103±4.74	99.3±1.80	104±5.02	105±5.63

Average values (n=3)

[a] In µg ml⁻¹

are established for the hot-plate wet digestion procedure (P2). LODs of Ba, Ca, Cd, Fe, Mg, P, Pb and Zn assessed when the procedure P3 was used are similar to those determined when the microwave-assisted digestion procedure (P1) was applied. In the case of other elements, even lower LOD values were achieved when procedure P3 was used. LODs resulting from the application of the solubilisation in TMAH (P4) and

Table 5 Limits of detection (in ng ml⁻¹) of elements for ICP OES achieved with different sample preparation procedures: the microwave-assisted digestion in HNO₃ with H₂O₂ (P1), the hot-plate digestion in HNO₃ with H₂O₂ (P2), the solubilisation in aqua regia (P3) and TMAH (P4) and the dissolution in HNO₃ (P5)

	P1	P2	P3	P4	P5
Ba	0.82	1.64	0.80	0.86	1.04
Ca	14.0	15.6	13.5	16.9	16.0
Cd	0.61	0.64	0.55	1.63	1.20
Cr	1.05	1.34	0.62	0.65	1.59
Cu	1.35	1.41	0.97	1.34	1.45
Fe	1.52	1.86	1.59	1.99	3.20
Mg	3.25	3.25	3.15	5.29	16.5
Mn	0.52	0.49	0.42	0.59	0.75
Ni	2.85	2.96	2.53	3.54	3.25
P	102	108	98.4	98.7	111
Pb	31.1	33.1	31.4	38.4	38.3
Sr	0.14	0.16	0.15	0.19	0.38
Zn	0.79	0.86	0.70	1.45	0.96

extraction in diluted HNO₃ (P5) are for most elements up to 3 times higher than those assessed for the procedure P1. In the case of Mg (P5), an increase in the LOD of this element by 1 order of magnitude was even observed. Only for Ba (P4), Cu (P4, P5), Ni (P5) and P (P4, P5) LOD values comparable to those obtained for the procedure P1 were achieved.

Analytical Application

Slim Teas

Considering the analytical characteristic of sample preparation procedures investigated here, the solubilisation in aqua regia (P3) was selected as the most suitable sample treatment prior to the multi-element analysis of slim tea products by ICP OES. This procedure was demonstrated to be a much faster, straightforward and more precise alternative to wet digestion procedures. Concentrations of 13 elements were determined in five different herbal teas and results of this analysis are presented in Table 6. They are mean values for three replicates (n=3) with RSDs.

As can be seen, in all cases, the precision of measurements is very good and varies from 0.21 % (for Ca in Slim Figure age 55+) to 4.7 % (for Mg in Slim Figure fat-burning). It was found that the highest concentrations of elements are in Silm Figure age 45+ (Ba, Mg, Mn, Sr, Zn), while the lowest in Figure 1 (Ba, Cd, Cr, Mn). In general, Ca, Mg and P are the major mineral constituents of slim teas. Concentrations of

Table 6 Concentrations of elements in analyzed slim teas: Slim Figure age 30+ (SFA 30+), Slim Figure age 45+ (SFA 45+), Slim Figure age 55+ (SFA 55+), Slim Figure fat-burning (SFFb) and Figure 1 (F1)

	Concentration[a] ($\mu g\ g^{-1}$)					Release into infusion (%)[b]				
	SFA 30+	SFA 45+	SFA 55+	SFFb	F1	SFA 30+	SFA 45+	SFA 55+	SFFb	F1
Ba	30.2 (3.0)	53.5 (3.2)	42.7 (2.7)	28.0 (4.4)	26.5 (2.5)	31.1	36.3	45.7	8.7	26.9
Ca[c]	28.1 (1.7)	8.75 (1.6)	7.89 (0.21)	18.6 (4.4)	17.9 (1.8)	54.5	47.8	50.3	21.5	40.2
Cd	0.223 (4.0)	0.251 (2.7)	<LOD[d]	0.262 (2.5)	0.222 (3.4)	56.5	–[e]	–[e]	–[e]	54.0
Cr	1.82 (2.2)	1.10 (3.7)	1.16 (3.7)	0.992 (2.8)	0.879 (4.0)	30.3	21.7	20.0	7.46	–[e]
Cu	7.54 (0.45)	7.19 (2.0)	12.8 (3.0)	9.36 (2.6)	9.50 (2.7)	66.2	60.1	30.0	33.0	20.4
Fe	195 (2.8)	204 (4.4)	228 (3.3)	276 (3.3)	237 (2.9)	9.03	10.6	11.2	4.02	7.59
Mg[c]	3.02 (3.3)	3.89 (3.7)	2.24 (1.3)	2.89 (4.7)	2.35 (4.4)	83.4	77.1	85.2	88.4	72.9
Mn	916 (0.96)	1090 (3.2)	546 (2.0)	654 (1.7)	459 (1.2)	48.0	52.0	71.4	31.2	47.3
Ni	3.89 (2.0)	4.82 (2.3)	6.07 (1.6)	5.59 (4.7)	4.55 (3.6)	94.1	83.2	92.8	87.3	81.4
P[c]	1.12 (3.0)	1.04 (4.2)	1.42 (0.56)	2.47 (3.9)	2.07 (2.7)	61.8	58.1	69.6	48.2	58.2
Pb	3.63 (2.0)	4.44 (3.9)	4.22 (0.31)	4.75 (0.91)	6.16 (2.4)	74.7	80.2	67.3	78.7	72.3
Sr	31.5 (0.64)	55.7 (2.7)	51.2 (2.9)	27.0 (0.77)	28.5 (1.6)	63.2	56.1	49.8	20.6	41.4
Zn	62.2 (2.6)	70.6 (2.3)	32.6 (2.6)	56.3 (1.6)	34.2 (0.75)	63.0	54.2	62.3	26.5	51.1

[a] Average values (n=3) with relative standard deviations (RSDs) in brackets

[b] One cup infusion was prepared from one bag of tea poured with 200 ml of hot de-ionized water

[c] Below the limit of detection

[d] Concentrations in $mg\ g^{-1}$

[e] Not possible to evaluate percentages of release due to concentrations of Cd and Co below their respective limits of detection in samples or infusions

these elements decrease in the order: Ca>Mg>P. The highest concentrations of Ca, Mg and P were determined in Silm Figure age 30+ (Ca), Silm Figure age 45+ (Mg) and Slim Figure fat-burning (P), while their lowest concentrations were found in Silm Figure age 55+ (Ca, Mg) and Figure 1 (P). The level of Ca is about 1 order of magnitude higher than that of Mg and P. The concentration of P is by 12 % (Slim Figure fat-burning, Figure 1) to 300 % (Silm Figure age 45+) lower than that of Mg. These results are in a good agreement with those reported in other studies (Chen et al. 2009; Malik et al. 2008; Nookabkaew et al. 2006; Szymczycha-Madeja et al. 2013), indicating that the aforementioned elements are the most abundant in many herbal medicines and teas.

Teas and herbs can be an important source of such essential elements as Mn, Fe, Zn and Cu, which are crucial for bio-chemical reactions in the human body. Manganese activates numerous essential enzymes; Fe is within the hemoglobin molecule, Zn is necessary for an enzymatic activity among humans, while Cu is essential for the hemoglobin synthesis (Biego et al. 1998; Colak et al. 2005; Xie et al. 1998). Concentrations of these micro-elements fulfill the following order: Mn>Fe>Zn>Cu. The content of Mn (459−1.09×10^3 $\mu g\ g^{-1}$) is about 2–4 times higher than that of Fe (195−276 $\mu g\ g^{-1}$), 2 orders of the magnitude higher than that of Zn (32.6–70.6 $\mu g\ g^{-1}$) and even 3 orders of the magnitude higher than that of Cu (7.19−12.8 $\mu g\ g^{-1}$). Results for Mn presented in our study are generally comparable to those reported by Chen et al. (2009), Colak et al. (2005), Dash et al. (2008), Narin

et al. (2004a,b), Malik et al. (2008), McKenzie et al. (2010) and Nookabkaew et al. (2006). Concentrations of Fe in slim teas are very similar to those obtained by Aksuner et al. (2012), Colak et al. (2005), Kara (2009) and McKenzie et al. (2010), but higher than those determined by Chen et al. (2009), Matsuura et al. (2001) and Narin et al. (2004b). Contents of Zn found in this work are consistent with the findings of Matsuura et al. (2001) and Xie et al. (1998). However, Aksuner et al. (2012), Mierzwa et al. (1998) and Soylak et al. (2007) reported a lower Zn value for different type of teas. Narin et al. (2004b) established that the concentration of Zn in black tea produced in Turkey was within the range of 110–146 $\mu g\ g^{-1}$. In the case of Cu, our results are close to values found in teas by Aksuner et al. (2012), Chen et al. (2009), Colak et al. (2005), Kara (2009) and Soylak et al. (2007) and are significantly lower than those reported by Malik et al. (2008) and Salahinejad and Aflaki (2010).

Additionally, teas and herbs can expose a health risk due to the presence of toxic or non-essential elements such Ba, Pb, Cd, and others like Cr, Ni and Sr, which are hazardous to humans depending on their oxidation states and concentrations (Başgel and Erdemoğlu 2006). For these elements, the following order can be described: Sr>Ba>Ni>Pb>Cr>Cd. The only exception is Slim Figure fat-burning tea, for which the following relation was noticed: Ba>Sr>Ni>Pb>Cr>Cd. Concentrations of Ba and Sr are very high (26.5–53.5 and 7.0–55.7 $\mu g\ g^{-1}$, respectively). In the case of Ni and Pb, their concentrations are also relatively high, i.e., within the

following ranges: 3.89–6.07 µg g^{-1} (Ni) and 3.63–6.16 µg g^{-1} (Pb). Only contents of Cr and Cd are lower and vary between 0.879 and 1.82 and between 0.222 and 0.262 µg g^{-1}, respectively. Concentrations of Sr were lower than those obtained by Kara (2009) and McKenzie et al. (2010) for black and green teas. Xie et al. (1998) reported the range of Ba and Sr concentrations in Chinese tea samples as 3.0–42 and 3.5–24 µg g^{-1}, respectively. Our results for Ni are lower than those observed by Colak et al. (2005) and Narin et al. (2004a), but are in a good accordance with those reported by Aksuner et al. (2012), Malik et al. (2008), Seenivasan et al. (2008) and Soylak et al. (2007). Concentrations of Pb are very similar to those determined by Chen et al. (2009) and Mierzwa et al. (1998), but slightly higher than these reported by Dash et al. (2008), Matsuura et al. (2001), Narin et al. (2004b) and Seenivasan et al. (2008). The level of Cr in slim teas is generally lower than that published in the relevant literature. The concentration range of Cr in tea commonly ranges from 1.7 to 16.9 µg g^{-1} (Dash et al. 2008; Narin et al. 2004a; Seenivasan et al. 2008). In case of Cd, our results were lower than those previously reported by Narin et al. (2004a) and Salahinejad and Aflaki (2010), but in a quite good agreement with those observed by Seenivasan et al. (2008).

Infusions of Slim Teas

Tea infusions were prepared according to recommendations of their manufacturers. In this case, one bag of each tea was placed in a glass beaker, 200 ml of boiling de-ionized water was added, covered and left for 10 min. Infusions were filtered through 0.45-µm syringe filters and analyzed by ICP OES using the calibration with simple working standard solutions. Percentages of the release of elements were calculated as ratios between concentrations of these elements determined in infusions and their total concentrations in the raw material.

As can be seen from Table 6, none of elements is extracted in 100 %. The highest percentages of the release (>80 %) are observed for Ni. Extraction efficiencies of Pb (67.3−80.2 %) and Mg (72.9−88.4 %) are also high. As compared to total concentrations is slim teas, released amounts of Cu, Sr and Zn are lower and quite differentiated, i.e., 20.4−66.2 %, 20.6−63.2 % and 26.5−63.0 % for Cu, Sr and Zn, respectively. In spite of the high total concentrations of Ca in teas, percentages of this element released into infusions are relatively low and vary from 21.5 % to 54.5 %. The lowest percentages of the release (< 15 %) are observed for Fe. Unfortunately, Cd was not detected in infusions of Slim Figure age 45+, 55+ and Slim Figure fat-burning. In the case of Slim Figure age 30+ and Figure 1, this element was extracted into infusions with the extraction efficiency of about 55 %.

The relationship between concentrations of studied elements in slim teas was determined by calculating the Pearson's correlation coefficients (r). Calculated values of r are listed in Table 7. It can be seen that there is a very high positive correlation ($r>0.9$) for concentrations of the following pairs of elements: Ba−Fe, Ba−Sr, Ca−Cr, Cr−Cu, Mn−Sr, and negative correlations only for two pairs: Mn−P and P−Zn. High correlations ($r=0.7$−0.9) were found for concentrations of Ba−Mn, Cr−Zn, Cu−Mn, Cu−Zn, Fe−Sr and Mn−Zn (all positive) as well as of Cr−Pb, Cu−P, Cu−Pb and P−Sr (all negative). For other pairs of elements, positive or negative correlations were moderate (r ±0.4 to ±0.7), low (r ±0.2 to ±0.4) or almost negligible (r 0 to ±0.2). All observed correlations may be attributed to similar chemical properties of selected elements, co-occurrence in the nature, common exposure sources as well as close associations of some elements in various physiological processes in plants.

Table 7 Pearson's correlation coefficients (r)

	Ba	Ca	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sr	Zn
Ba	1											
Ca	−0.254	1										
Cr	+0.123	**+0.927**	1									
Cu	+0.462	+0.437	**+0.942**	1								
Fe	**+0.931**	−0.146	+0.224	+0.288	1							
Mg	+0.137	+0.016	+0.004	+0.633	−0.216	1						
Mn	**+0.798**	+0.144	+0.496	**+0.807**	+0.608	+0.603	1					
Ni	+0.270	−0.621	−0.638	−0.023	+0.268	−0.209	−0.147	1				
P	−0.609	−0.366	−0.676	**−0.874**	−0.414	−0.684	**−0.961**	+0.326	1			
Pb	−0.437	−0.381	**−0.784**	**−0.871**	−0.391	−0.245	−0.566	−0.331	+0.573	1		
Sr	+0.956	−0.038	+0.338	+0.629	**+0.845**	+0.327	**+0.934**	+0.032	**−0.810**	−0.492	1	
Zn	+0.450	+0.540	**+0.764**	**+0.825**	+0.289	+0.645	**+0.880**	−0.520	**−0.972**	−0.499	+0.692	1

Very high and high correlations are indicated in bold

Conclusions

A simple and fast sample preparation procedure, based on a partial decomposition by means of the solubilisation in aqua regia (P3), was developed, and its suitability prior to the multi-element analysis of slim teas by ICP OES was assessed. This procedure allows reducing the amount of concentrated reagents, hence significantly diminishes the risk of the sample contamination. Moreover, it can be carried out at room temperature; therefore, losses of volatile analytes are completely eliminated. Finally, it enables us to considerably to reduce the analysis time. Analytical figures of merit, i.e., the accuracy and the precision, evaluated for the ICP OES method with the selected sample treatment are reasonably good; the method provides quantitative recoveries of studied elements and their adequate detectability. Certainly, it can be a very good alternative to time-consuming, laborious and inconvenient wet digestion procedures.

It was also found that the solubilisation in TMAH (procedure P4) can alternatively be used instead of both wet digestions (procedures P1 and P2) only to some selected elements, i.e., Cd, Cu and Ni. Unfortunately, the extraction in diluted HNO_3 (the procedure P5) was found to be unsuitable for a dependable determination of examined elements in slim teas.

Conflict of Interest Anna Szymczycha-Madeja declares that she has no conflict of interest. Maja Welna declares that she has no conflict of interest. Pawel Pohl declares that he has no conflict of interest. This article does not contain any studies with human or animal subjects.

References

Aksuner N, Henden E, Aker Z, Engin E, Satik S (2012) Determination of essential and non-essential elements in various tea leaves and tea infusions consumed in Turkey. Food Addit Contam Part B 5:126–132

Ashraf W, Mian AA (2008) Levels of selected heavy metals in black tea varieties consumed in Saudi Arabia. Bull Environ Contam Toxicol 81:101–104

Başgel S, Erdemoğlu SB (2006) Determination of mineral and trace elements in some medicinal herbs and their infusions consumed in Turkey. Sci Total Environ 359:82–89

Biego GH, Joyeux M, Hartemann P, Debry G (1998) Daily intake of essential minerals and metallic micropollutants from food in France. Sci Total Environ 217:27–36

Chen Y, Yu M, Xu J, Chen X, Shi J (2009) Differentiation of eight tea (*Camellia sinensis*) cultivars in China by elemental fingerprint of their leaves. J Sci Food Agric 89:2350–2355

Colak H, Soylak M, Turkoglu O (2005) Determination of trace metal content of various herbal and fruit teas produced and marketed in Turkey. Trace Elem Electrolytes 22:192–195

Dash K, Manjusha R, Thangavel S, Arunachalam J (2008) UV photolysis-assisted digestion of tea (*Camellia sinensis*) and thulsi (*Ocimum sanctum*) and their infusions: comparison of available trace elements. At Spectrosc 29:56–62

Ellison SLR, Barwick VI, Farrank TJD (2009) Practical statistics for the analytical scientists. RSC Publishing, Cambridge

Kara D (2009) Evaluation of trave metal concentrations in some herbs and herbal teas by principal component analysis. Food Chem 114: 347–354

Kingston HM, Jassie LB (1988) Introduction to microwave sample preparation – theory and practice. American Chemical Society, Washington

Kumar A, Nair AGC, Reddy AVR, Garg AN (2005) Availability of essential elements in Indian and US tea brand. Food Chem 89: 441–448

Li T, Yu LJ, Li MT, Li W (2006) A new approach of the standard addition method for the analysis of F, Al and K content in green tea. Microchim Acta 153:109–114

Malik J, Szakova J, Drabek O, Balik J, Kokoska L (2008) Determination of certain micro and macroelements in plant stimulants and their infusions. Food Chem 111:520–525

Matsuura H, Hokura A, Katsuki F, Itoh A, Haraguchi A (2001) Multielement determination and speciation of major-to-trace elements in black tea leaves by ICP-OES and ICP-MS with the aid of size exclusion chromatography. Anal Sci 17:391–398

McKenzie JS, Jurado JM, de Pablos F (2010) Characterisation of tea leaves according to their total mineral content by means of probabilistic neural networks. Food Chem 123:859–864

Mierzwa J, Sun YC, Chung YT, Yang MH (1998) Comparative determination of Ba, Cu, Fe, Pb and Zn in tea leaves by slurry sampling electrothermal atomic absorption and liquid sampling inductively coupled plasma atomic emission spectrometry. Talanta 47:1263–1270

Mokgalaka NS, McCrindle RI, Botha BM (2004) Multielement analysis of tea leaves by inductively coupled plasma optical emission spectrometry using slurry nebulization. J Anal At Spectrom 19:1375–1378

Narin I, Colak H, Turkoglu O, Soylak M, Dogan M (2004a) Heavy metals in black tea samples produced in Turkey. Bull Environ Contam Toxicol 72:844–849

Narin I, Tuzen M, Soylak M (2004b) Comparison of sample preparation procedures for the determination of trace heavy metals in house dust, tobacco, and tea samples by atomic absorption spectrometry. Ann Chim (Rome) 94:867–873

Nookabkaew S, Rangkadilok N, Satayavivad J (2006) Determination of trace elements in herbal tea products and their infusions consumed in Thailand. J Agric Food Chem 54:6939–6944

Özcan MM, Ünver A, Uçar T, Arslan D (2008) Mineral content of some herbs and herbal teas by infusion and decoction. Food Chem 106: 1120–1127

Salahinejad M, Aflaki F (2010) Toxic and essential mineral elements content in black tea leaves and their tea infusions consumed in Iran. Biol Trace Elem Res 134:109–117

Salvador MJ, Lopes GN, Filho VFN, Zucchi OLAD (2002) Quality control of commercial tea by x-ray fluorescence. X-Ray Spectrom 31:141–144

Seenivasan S, Manikandan N, Muraleedharan NN, Selvasundaram R (2008) Heavy metal content of black teas from south India. Food Control 19:746–749

Shen FM, Chen HW (2008) Element composition of tea leaves and tea infusions and its impact on health. Bull Environ Contam Toxicol 80: 300–304

Soylak M, Tuzen M, Souza AS, Korn MGA, Ferreira SLC (2007) Optimization of microwave assisted digestion procedure for the determination of zinc, copper and nickel in tea samples employing flame atomic absorption spectrometry. J Hazard Mater 149:264–268

Szymczycha-Madeja A, Welna M, Zyrnicki W (2013) Multi-element analysis, bioavailability and fractionation of herbal tea products. J Braz Chem Soc 24:777–787

Welna M, Szymczycha-Madeja A, Pohl P (2011) Quality of the trace element analysis: sample preparation steps. In: Akyar I (ed) Wide spectra of quality control, 1st edn. InTech, Croatia, pp 53–70

Welna M, Szymczycha-Madeja A, Pohl P (2013) A comparison of sample preparation strategies in the multi-elemental analysis of tea by spectrometric methods. Food Res Int 53:922–930

Xie M, von Bohlen A, Klockenkamper R, Jian X, Gunther K (1998) Multielement analysis of Chinese tea (Camellia sinensis) by total-reflection X-ray fluorescence. Z Lebensm Unters Forsch A 207:31–38