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A Simple and Reliable Method to Determine 16 Trace Elements by ICP OES in Ready to Drink Beverages

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Abstract

In this work, multivariate experiments were carried out to optimize a simple and reliable method for determination of 16 trace elements (Al, As, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sb, Se, Sr, Sn, and Zn) in ready to drink beverages by ICP OES. The multivariate methodology to optimize ICP OES parameters consisted in a 2^{4-1} and a 2^3 central composite design, where the variables studied were radio frequency power, nebulization flow rate, auxiliary argon flow rate, and argon plasma flow rate and the responses were signal to background ratio (SBR) and the plasma robustness. The compromised conditions were RF power, 1.35 kW; nebulization flow rate, 0.50 L min^{-1}; auxiliary argon flow rate, 0.55 L min^{-1}; and argon plasma flow rate, 12.0 L min^{-1}. Under these conditions, the microwave digestion using diluted oxidant mixture provided recoveries between 79 and 110% for quantifiable trace elements in two reference materials (corn brand and tea leaves) and 81 and 118% in spiked experiments. The method was successfully applied to 10 samples of ready to drink beverages (fruit juice, soy-based beverages, and tea), and the levels found were below the maximum allowed for inorganic contaminants by Brazilian, European, and MERCOSUL regulations.

Keywords Trace elements · Soy · Tea · Fruit juice · ICP OES

Introduction

Non-alcoholic beverages are considered a remarkable source of nutrients such as minerals, vitamins, and amino acids. Its consumption increased in the last years due to the concerning about the diet influence in health and products with more nutritional contents (Behrens and Da Silva 2004).

One of the oldest beverages is tea, originally prepared by infusions of *Camellia sinensis* leaves after drying or fermentation process (Silva et al. 2010). Nowadays, many varieties are found in markets, such as the herbal teas and the ice teas (or tea soft drinks) with added flavors (such as lemon, peach, and berries). Its consumption is usually associated with prevention of heart diseases, skin cancer, and reduction of cholesterol levels (Jin et al. 2005). Soy-based food is also associated with health benefits such as prevention of heart diseases, osteoporosis, and reduction of menopause symptoms (Behrens and Da Silva 2004). In Brazil, soy-based beverages must contain soy sources with minimum of 70% of the casein amino acid content, considering the extract, the concentrate protein, the isolated protein, and the texturized protein as soy sources (Brazil 2000). Fruit juices are common in infant feed, especially in soft drink replacement. They are commercialized in three main forms: the whole (or natural), the nectar, and the fruit pulp (usually diluted with water or milk). However, the main differences in composition are related to the presence of sugar or additives.

These beverages have a wide consumption by people of all ages, with children more susceptible to the effects of non-essential trace elements that may be present in foods (FAO/WHO 2017). Some non-essential trace elements are considered inorganic contaminants and maximum levels allowed were established worldwide: Brazilian (2013) and MERCOSUL (2011) regulations set As (0.10 mg kg^{-1}), Cd, and Pb (0.05 mg kg^{-1}) for fruit juices; Cd (0.02 mg kg^{-1}), As, and Pb (0.05 mg kg^{-1}) for non-alcoholic drinks and Sn (150 mg kg^{-1}) in canned beverages; Brazilian regulation (1965) sets Sb (1.00 mg kg^{-1}) and Ni (3.00 mg kg^{-1}) in fruit juices and Cr (0.10 mg kg^{-1}) in any type of food; and the

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European regulation (2006) sets Sn (100 mg kg^{-1}) for canned beverages and Pb (0.050 mg kg^{-1}) in fruit juices.

Due to all exposed, desirable method for trace elements analysis must be reliable, simple, fast, and with a low consumption of chemicals—in agreement with the "green chemistry" concept (Gałuszka et al. 2013). Some research groups have dedicated their efforts to the development of simple methods applicable to beverages.

Sousa et al. (2005) and Milani et al. (2015) successfully proposed the direct analysis for minerals in coconut water by ICP OES and trace elements in tea infusions by ICP-MS, respectively. Cindrić et al. (2011) proposed the use of dilution in nitric acid as a reliable method for mineral and trace elements in apple juice by ICP OES, and Szymczycha-Madeja and Welna (2013) performed a study comparing different methods for trace element determination in fruit juice from Poland and verified that the dilution in nitric acid and centrifugation provide the best recovery values. One year later, the same researchers reported an assessment of different fast methods for trace elements in slim coffee by ICP OES (Szymczycha-Madeja et al. 2014).

Regarding methods with acid extraction or digestion, Morgano et al. (1999) proposed the acid extraction as a reliable method for mineral determination in several fruit nectars from Brazil and Boa Morte et al. (2008) studied minerals and trace elements in soy protein formulations using a classic acid digestion in a hot plate by ICP OES. Llorent-Martínez et al. (2012) applied the microwave-assisted digestion for elements in yogurts and soy-based products by ICP-MS, and Jalbani et al. (2010) also applied this sample preparation method to perform a Cu, Fe, and Zn study in different juices from Pakistan.

However, to the best of our knowledge, just a few studies were reported employing multivariate approaches or multiples response for trace elements in food, commonly applied to a single food matrix. Peixoto et al. (2012) evaluated a method for metallic elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, V, and Zn) in chocolate drink powder by ICP OES using the plasma robustness and signal to background ration (SBR) for optimization. Froes et al. (2009) evaluated a method for 13 microelements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, and Zn) in fruit juice by ICP OES combining the evaluation of plasma conditions (nebulization gas flow rate, RF power, and sample flow rate) by a 2^3 factorial design with multivariate analysis (hierarchical cluster and principal component analyses). In this study, the researches focus their efforts in a method for trace elements determination in fruit juice samples (grape, orange, strawberry, pineapple, and passion fruit) combining sample dilution and ICP OES conditions, such as shear gas interface and optimized plasma conditions.

The multivariate methodology is a valuable tool in method optimization providing a reliable, fast, and economical response. This algorithm allows evaluating more variables simultaneously, their interactions, and the significance of their effects in a mathematic model (Ferreira 2015).

In this context, this study focused to develop a simultaneous, simple, and reliable method for 16 trace elements (Al, As, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sb, Se, Sr, Sn, and Zn) analyses applicable to different ready to drink beverages, such as fruit juice, soy-based drink, and tea. For this, a multivariate approach was used for optimization of ICP OES parameters and the proposed method was validated and applied to commercial samples from Brazil.

Materials and Methods

Reagents, Solutions, and Samples

Materials were decontaminated using 20% (*v*/*v*) HNO_3 bath for at least 12 h prior analysis and thus rinsed with purified water. Water was purified (18.2 MΩ cm) by the osmosis reverse system (Gehaka, São Paulo, Brazil) and nitric acid by sub-boiling distilled acid (Berghof, Eningen, Germany). Hydrochloric acid 37% (*v*/*v*) and hydrogen peroxide 30% (*v*/*v*) (Merck, Darmstadt, Germany) were also employed in assay. Analytical curves were prepared by dilutions of 1000 mg L^{-1} Se, Sb (Fluka, Sigma–Aldrich, Steinheim, Germany), and multielementary standards (Merck, Darmstadt, Germany) in 5% (*v*/*v*) HNO_3: 2.5–5000 μg L^{-1} for Al, Fe, and Mn; 1.0–1000 μg L^{-1} for Cu, Sn, and Zn; 1.0–500 μg L^{-1} for As, Cd, Co, Cr, Li, Ni, Pb, Sb, Se, and Sr.

The optimized procedure was applied in 10 ready to drink beverages purchased in markets in Campinas city, Brazil. Samples considered the flavors and brands available: tea drinks (mate, black, green, and white tea); soy-based beverages (apple, grape, and orange), and whole fruit juice (apple, grape, and orange).

Apparatus

Sample preparation was evaluated by acid extraction using an orbital shaker (Marconi, São Paulo, Brazil) and acid digestion using a closed microwave digestion system (Start D, Milestone, Sorisole, Italy) equipped with 24 PTFE vessels.

Trace elements were determined using an ICP OES (5100 VDV, Agilent Technologies, Tokyo, Japan). The optimized conditions are summarized in Table 1, and emission wavelengths were selected considering the absence of spectral interferences.

To define the ICP OES parameters that allowed a method with high sensitivity, two designs of experiments were performed:

Table 1 ICP OES and microwave system conditions for trace elements determination in ready to drink beverages

ICP OES				
RF power (kW)	1.35			
Plasma view	Axial			
Ar flow rate (L min^{-1})	12.0			
Ar auxiliary flow rate (L min^{-1})	0.50			
Nebulizer type and flow rate (L min^{-1})	*SeaSpray*; 0.55			
Spray chamber	Quartz, double-pass			
Replicates (*n*)	3			
Wavelengths (nm)	Al (396.152); As (193.696); Cd (214.439); Co (228.615); Cr (267.716); Cu (324.754); Fe (259.940); Li (670.783); Mn (257.610); Ni (221.648); Pb (220.353); Sb (206.834); Se (196.026); Sn (189.925); Sr (421.552); Zn (213.857)			
Closed microwave digestion system				
Step	1	2	3	4
Temperature (°C)	120	120	140	140
Power (W)	1000	1000	1000	1000
Time (min)	15	03	10	15

- a fractional two-level factorial design (2^{4-1}) to verify the effect of the main parameters (RF power, nebulizer flow rate, Ar auxiliary flow rate, and Ar flow rate) in the sensitivity, evaluated by signal to background ratio (SBR) of Mn 257.610 nm (Peixoto et al. 2012), and the plasma robustness, evaluated by the ratio between the signal of emission lines of Mg II (280.270 nm) and Mg I (285.213 nm) (Mermet 1991).
- a 2^3 central composite design of experiments between the significant variables, at 95% of the confidence level, that may influence the sensitivity and plasma robustness.

The levels and the responses observed are described in details in Tables 2 and 3 ("Results and Discussion" section).

Method Evaluation and Data Quality Control

Two sample preparation methods were evaluated: method A (acid extraction) and method B (closed microwave acid digestion) using two certified reference materials (CRM): corn bran (RM 8433, NIST, Maryland, USA) and tea leaves (INCT-TL-1, Instytut Chemii i Techniki Jądrowej, Warszawa, Poland).

- Method A (adapted from Morgano et al. (1999)): 250 mg of CRM and 5 mL of HCl were transferred to graduate plastic tubes. The tubes were kept under orbital shaker for 3 h and purified water was added to 20 mL final volume. The resulting solutions were filtrated through a 45-µm

Table 2 2^{4-1} Design of experiments applied for ICP OES conditions optimization. Codified variables are presented between parentheses

Exp.	Parameters				Responses			
	RF power (kW)	Nebulizer flow rate (L min^{-1})	Ar auxiliary flow rate (L min^{-1})	Ar flow rate (L min^{-1})	SBR		Mg(II)/Mg(I)	
1	1.20 (− 1)	0.60 (− 1)	0.80 (− 1)	12.0 (− 1)	1104.04	1104.45	5.37	5.36
2	1.30 (+ 1)	0.60 (− 1)	0.80 (− 1)	15.0 (+ 1)	1163.45	1173.10	5.64	5.66
3	1.20 (− 1)	0.80 (+ 1)	0.80 (− 1)	15.0 (+ 1)	820.67	818.32	3.59	3.61
4	1.30 (+ 1)	0.80 (+ 1)	0.80 (− 1)	12.0 (− 1)	792.91	794.80	4.01	4.01
5	1.20 (− 1)	0.60 (− 1)	1.00 (+ 1)	15.0 (+ 1)	1187.41	1187.18	5.32	5.32
6	1.30 (+ 1)	0.60 (− 1)	1.00 (+ 1)	12.0 (− 1)	1047.59	1043.22	5.58	5.55
7	1.20 (− 1)	0.80 (+ 1)	1.00 (+ 1)	12.0 (− 1)	676.18	680.11	3.36	3.39
8	1.30 (+ 1)	0.80 (+ 1)	1.00 (+ 1)	15.0 (+ 1)	846.03	843.92	3.81	3.82

Table 3 23 central composite design of experiments applied for ICP OES conditions optimization. Codified variables are presented between parentheses

Exp.	Parameters			Responses	
	RF power (kW)	Nebulizer flow rate (L min^{-1})	Ar auxiliary flow rate (L min^{-1})	SBR (Mn)	Mg(II) /Mg(I)
9	1.30 (− 1)	0.40 (− 1)	0.40 (− 1)	194.85	3.53
10	1.40 (+ 1)	0.40 (− 1)	0.40 (− 1)	201.12	3.68
11	1.30 (− 1)	0.40 (− 1)	0.60 (+ 1)	185.25	3.89
12	1.40 (+ 1)	0.40 (− 1)	0.60 (+ 1)	196.74	3.99
13	1.30 (− 1)	0.60 (+ 1)	0.40 (− 1)	541.07	5.78
14	1.40 (+ 1)	0.60 (+ 1)	0.40 (− 1)	505.86	6.01
15	1.30 (− 1)	0.60 (+ 1)	0.60 (+ 1)	510.56	5.65
16	1.40 (+ 1)	0.60 (+ 1)	0.60 (+ 1)	478.99	5.95
17	1.35 (0)	0.33 (− √3)	0.50 (0)	37.47	2.20
18	1.35 (0)	0.67(+ √3)	0.50 (0)	907.54	5.50
19	1.35 (0)	0.50 (0)	0.33(− √3)	659.81	5.50
20	1.35 (0)	0.50 (0)	0.67(+ √3)	577.47	5.68
21	1.27(− √3)	0.50 (0)	0.50 (0)	574.72	5.41
22	1.43(+ √3)	0.50 (0)	0.50 (0)	564.20	5.69
23	1.35 (0)	0.50 (0)	0.50 (0)	629.32	5.56
24	1.35 (0)	0.50 (0)	0.50 (0)	580.94	5.56
25	1.35 (0)	0.50 (0)	0.50 (0)	580.82	5.57

cellulose acetate membrane (Merck-Millipore, Darmstadt, Germany).

- Method B (adapted from Milani et al. (2016)): 250 mg of MRC were weighed in a PTFE vessel and 10 mL of diluted oxidant solution (consisted of 5 mL purified water + 4 mL purified nitric + 1 mL hydrogen peroxide) were added. Sample decomposition was performed using conditions described in Table 1. The solutions were transferred to graduated plastic tubes using purified water to 20 mL final volume. For beverages, 2 mL of the sample were used.

All analyses were performed in triplicate, and blank experiments were prepared in each batch following the same procedure used for samples. The analytical method was validated based in INMETRO (2016) recommendations, and the figures of merit evaluated were:

- Linearity: evaluated by correlation coefficients (r values);
- Specificity (or matrix effect): evaluated preparing curves by standards addition and external calibration and comparing the values of angular coefficients;
- Limits of detection and quantification: calculated as LOD = 0 + $t_{(n-1,\,1-\alpha)}$.s and LOQ =10.s, being "s" = standard deviation of seven blank experiments and *t* for 99% confidence level;
- Accuracy: calculated using the recovery (ratio, in percentage, between observed and expected value) of certified reference materials and spiked experiments;
- Precision: verified by the coefficient of variation (CV) of seven independent replicates.

Statistical analyses were performed using the Statistica software (StatSoft, Tulsa, OK, USA) considering 95% confidence level.

Results and Discussion

ICP OES Parameter Optimization

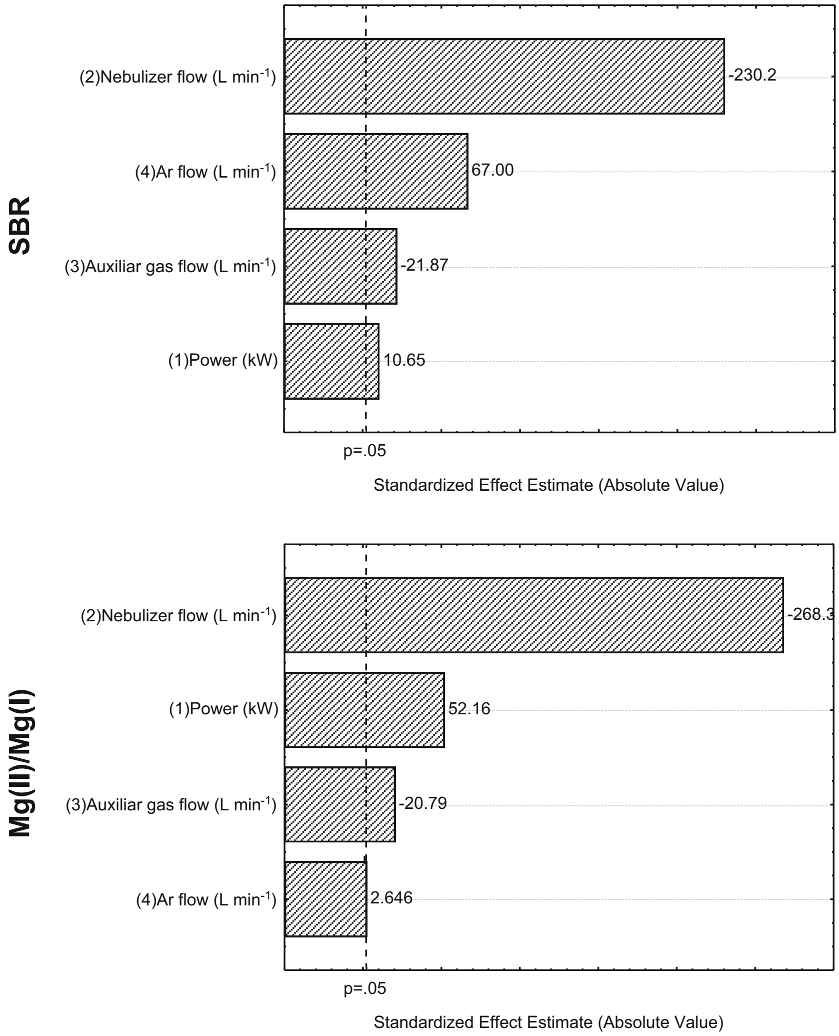
The ICP OES optimization was performed evaluating four of the most important parameters that may influence plasma robustness and sensitivity: RF power, nebulizer flow rate, auxiliary Ar flow rate, and Ar plasma flow rate. Firstly, a fractional two-level factorial design ($2^{4\text{-}1}$) was carried out in order to verify the influence of these variables on the ICP OES responses. For these experiments, a pool containing samples of beverages (fruit juice, soy-based beverage, and tea drink) containing Mg and Mn levels was used and the results are shown in Table 2 and Fig. 1.

The results presented in Table 2 reveal that the classical concept of plasma robustness was not achieved in the experiments, once values above eight were not observed (Mermet 1991). Dennaud et al. (2001) proposed in their study a correction factor related to each ICP OES instrument, considering the existence of a slope near the two wavelengths of Mg. However, analyzing the two responses in parallel verifies that the lowest values of SBR and Mg(II)/Mg(I) ratio were observed in the experiment 7 which employed the lowest value of RF power (1.20 kW) and the high nebulizer and Ar auxiliary flow rates (0.80 and 1.00 L min^{-1}, respectively). From thePareto chart (Fig. 1), negative values were observed for nebulizer and Ar auxiliary flow rates in both responses (SBR and plasma robustness) and positive values for RF power (10.65 and 52.16, respectively). It is also possible to notice that the variables RF power, nebulizer, and Ar auxiliary flow rates present significant effects at the 95% confidence level in the two responses monitored.

A 2^3 central composite design of experiments between the significant variables, at 95% of the confidence level, was performed, and the results are presented in Table 3 and Fig. 2. For argon plasma flow rate, the lowest value (12.0 L min^{-1}) was selected for analysis.

From the results shown in Table 3, it was verified that the highest value of SBR was provided by experiment 18 (907.54) and for Mg(II)/Mg(I) by experiments 14 and 16 (6.01 and

Fig. 1 Pareto chart for plasma robustness, ratio Mg(II)/Mg(I), and sensibility, SBR, observed in 2^{4-1} design of experiment



5.95, respectively). In these experiments, it is remarkable the influence of RF power and nebulizer flow rate: positive values provided the highest values in both responses evaluated.

In Fig. 2 is shown the surfaces obtained in this quadratic model. Considering all exposed and the compromised condition of plasma robustness and sensitivity, the optimized conditions were set: RF power = 1.35 kW, nebulizer flow rate = 0.50 L min^{-1}, and Ar auxiliary flow rate = 0.55 L min^{-1}. It is important to remark that the results obtained in this study indicated that the interpretation of these two responses in parallel is indispensable for a better optimization of ICP OES and univariate methodologies may not lead to the best conditions of analysis.

Sample Preparation Method: Evaluation of Different Approaches and Figures of Merit

Two sample preparation methods were evaluated for trace elements determination using the optimized ICP OES conditions: the acid extraction and the microwave-assisted digestion using diluted oxidant mixture. Both of them consist of fast methods of analysis using low amounts of chemicals. Two certified reference materials with similar composition to the samples were analyzed once no reference material for beverages was available. The results are reported in Table 4.

The acid extraction method (method A) employed HCl at room temperature, and it was previously reported by Morgano et al. (1999) for mineral determination in fruit nectars commercialized in Brazil. Although this method presented satisfactory recovery for Cu, Mn, Sr, and Zn in both reference materials, for others trace elements, the microwave-assisted digestion (method B) represents a better choice, being found recovery values between 79 and 110% accordingly to the AOAC (2013) recommendations: 80–110% (1 mg kg^{-1}) and 60–115% (10 μg kg^{-1}).

The proposed method was validated according to the INMETRO (2016) recommendations. The figures of merit linearity, specificity, limits of detection and quantification, accuracy, and precision were evaluated and the obtained results are presented in Tables 5 and 6.

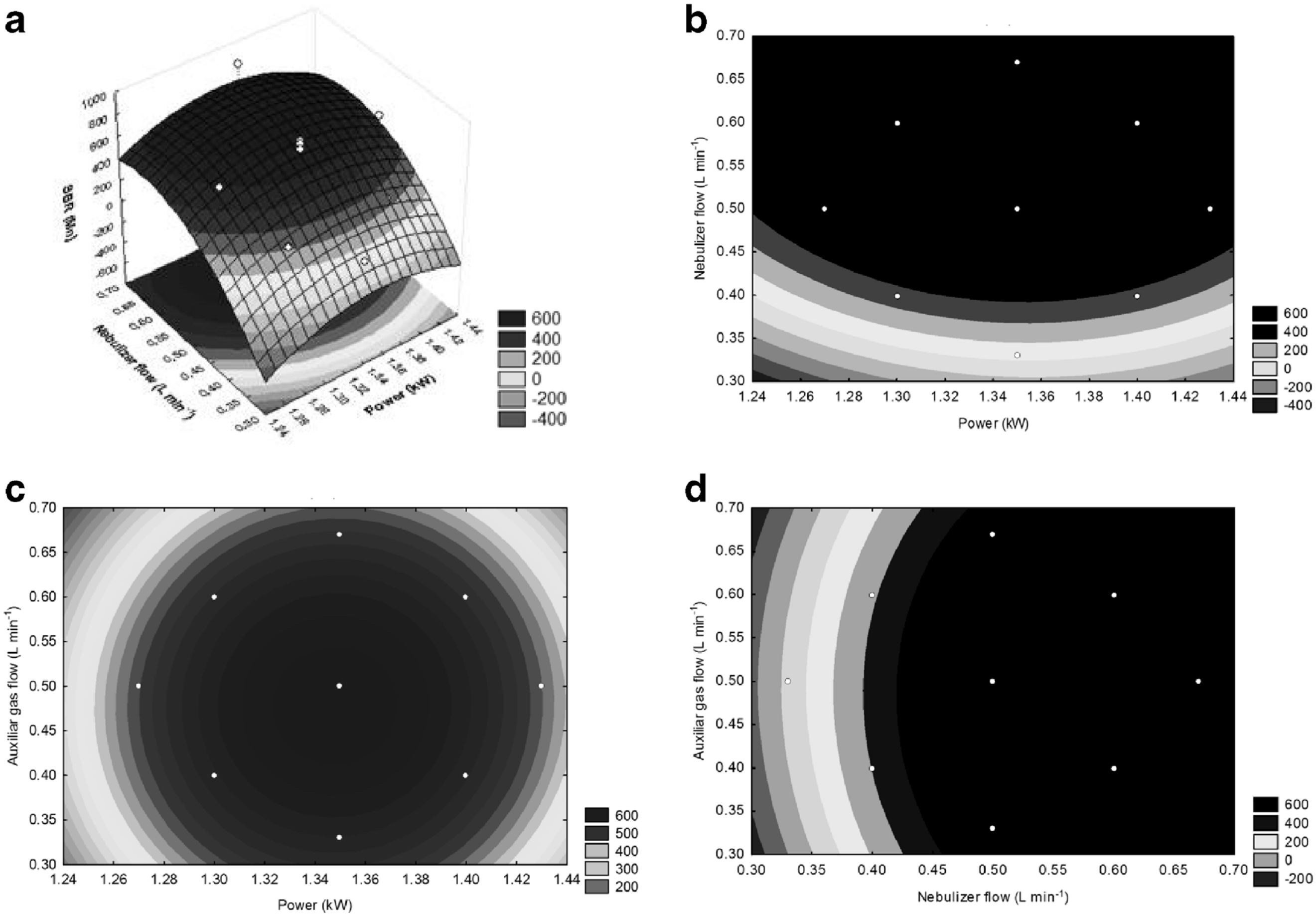


Fig. 2 Surfaces observed for SBR response in 2^3 central composite design of experiments applied for ICP OES parameters optimization. **a** Nebulizer flow rate × RF power × Ar auxiliary flow rate (set at 0.55 L min^{-1}). **b** Nebulizer flow rate × RF power. **c** Ar auxiliary flow rate × RF power. **d** Ar auxiliary flow rate x nebulizer flow rate

The specificity or matrix effect was evaluated by preparing curves by standards addition (beverage samples after microwave digestion) and external calibration (in 5% *v*/*v* HNO_3) and comparing the values of angular and correlation coefficients. From results that are detailed in Table 5, it is possible to affirm that the matrix presents no effect in trace element determination, since the variation between angular coefficients was lower than 14%. In addition, values of *r* (Pearson coefficient) were close to 1.0000 for all analytical curves and the external calibration method was chosen due to its simple preparation (successive dilutions of aqueous standards in nitric solution). The absence of interference in emission lines selected was also observed.

The limits of detection (LOD) and quantification (LOQ) were calculated as LOD = 0 + $t_{(n-1,\ 1-\alpha)}$.s and LOQ = 10.s, being “s” = standard deviation of seven blank experiments and $t = 3143$ (99% confidence level) and considered the sample volume (2 mL) and the final volume (20 mL). The limits of detection and quantification were below to 12.0 and 38.2 μg L^{-1}, respectively, for all trace elements. These values are adequate for beverages analysis considering the values established by Brazilian (Brazil (1965) and Brazil (2013)), MERCOSUL (2011), and European (2006) regulations.

The linearity was achieved in the analytical curves ranges and may be observed by *r* values above 0.9999 (Table 5). Precision was evaluated by the CV of seven replicates of tea, soy-based beverage, and fruit juice samples. Overall, high CV values were observed for trace elements in fruit juice. For instance, whole fruit juices were used in this study and these samples may contain pulp, skins, stems, and seeds. In general, CV values were below 10% and the values are in accordance with the established by INMETRO (2016) and AOAC (2013), being acceptable values under 11% (for 1 mg kg^{-1} level). Detailed values for each matrix and trace elements are described in Table 6.

For accuracy, in addition to the experiments performed in certified reference materials (Table 4), spiked experiments were performed in three levels (level 1 = 5 μg L^{-1}; level 2 = 50 μg L^{-1}; level 3 = 500 μg L^{-1}; except for Al,

Table 4 Trace elements results for method A (acid extraction, $n = 3$) and method B (microwave-assisted digestion, $n = 3$) in certified reference materials

Trace elements	Tea Leaves (INCT-TL-1)						Corn Bran (NIST RM 8433)					
	Certified value		Method A		Method B		Certified value		Method A		Method B	
			Value	REC	Value	REC			Value	REC	Value	REC
Al	2290 ± 280	mg kg^{-1}	1839 ± 31	80%	2050 ± 42	90%	1.01 ± 0.55	mg kg^{-1}	< 0.90	–	1.11 ± 0.28	110
As	106 ± 21	µg kg^{-1}	< 190	–	< 190	–	2 ± 2	µg kg^{-1}	< 190	–	< 190	–
Cd	30.2 ± 4.0	µg kg^{-1}	< 41	–	< 41	–	12 ± 5	µg kg^{-1}	< 41	–	< 41	–
Co	387 ± 42	µg kg^{-1}	210 ± 13	54%	312 ± 36	81%	6 ± 6	µg kg^{-1}	< 90	–	< 90	–
Cr	1.91 ± 0.22	mg kg^{-1}	1.31 ± 0.07	68%	1.63 ± 0.03	85%	101 ± 87	µg kg^{-1}	59 ± 18	58	82 ± 15	81
Cu	20.4 ± 1.5	mg kg^{-1}	19.2 ± 2.0	94%	17.9 ± 0.3	88%	2.47 ± 0.40	mg kg^{-1}	2.31 ± 0.01	94	2.16 ± 0.04	88
Fe	432*	mg kg^{-1}	212 ± 15	49%	371 ± 5	86%	14.8 ± 1.8	mg kg^{-1}	11.9 ± 0.2	80	13.0 ± 0.8	88
Mn	1570 ± 110	mg kg^{-1}	1296 ± 26	82%	1574 ± 23	100%	2.55 ± 0.29	mg kg^{-1}	2.20 ± 0.02	86	2.30 ± 0.03	90
Ni	6.12 ± 0.52	mg kg^{-1}	4.53 ± 0.34	74%	6.12 ± 1.47	100%	158 ± 54	µg kg^{-1}	86 ± 23	54	160 ± 5	101
Pb	1.78 ± 0.24	mg kg^{-1}	0.87 ± 0.98	49%	1.55 ± 0.28	87%	140 ± 34	µg kg^{-1}	< 165	–	146 ± 24	104
Sb	50*	µg kg^{-1}	< 286	–	< 286	–	4*	µg kg^{-1}	< 286	–	< 286	–
Se	76*	µg kg^{-1}	< 374	–	< 374	–	45 ± 8	µg kg^{-1}	< 374	–	< 374	–
Sr	20.8 ± 1.7	mg kg^{-1}	18.0 ± 0.3	87%	17.07 ± 0.03	82%	4.62 ± 0.56	mg kg^{-1}	4.14 ± 0.05	89	4.08 ± 0.07	88
Zn	34.7 ± 2.7	mg kg^{-1}	29.8 ± 0.9	86%	36.1 ± 2.2	104%	18.6 ± 2.2	mg kg^{-1}	15.7 ± 0.2	84	14.7 ± 0.1	79

REC recovery (ratio, in percentage, between certified and obtained value)

*Value not certified

Fe, and Mn being level 1 = 50 µg L^{-1}; level 2 = 500 µg L^{-1}; level 3 = 5000 µg L^{-1}) using samples of ready to drink beverages. Overall, the recovery ranged between 81 and 118% for all trace elements and they were adequate considering the AOAC (2013) and INMETRO (2016) recommendations.

Table 5 Results of matrix effect evaluation for trace elements in ready to drink beverages ($n = 3$)

Trace elements	5% (*v*/*v*) HNO_3		Standards addition					
			Fruit juice		Soy-based beverages		Tea drinks	
	α	r	α	r	α	r	α	r
Al	79.6	1.0000	72.3	1.0000	71.0	1.0000	70.7	1.0000
As	2.4	1.0000	2.2	1.0000	2.2	0.9999	2.2	1.0000
Cd	74.1	1.0000	67.2	1.0000	67.3	1.0000	67.6	1.0000
Co	47.0	1.0000	43.7	1.0000	43.9	1.0000	44.9	1.0000
Cr	130.5	1.0000	124.5	1.0000	124.8	1.0000	127.2	1.0000
Cu	98.8	0.9999	97.3	0.9999	96.7	0.9999	98.3	0.9999
Fe	37.4	1.0000	36.8	1.0000	35.8	1.0000	34.1	0.9998
Li	6575	1.0000	6492	1.0000	6441	1.0000	6496	1.0000
Mn	577.6	0.9999	559.1	1.0000	543.8	1.0000	554.9	1.0000
Ni	4.3	0.9999	4.0	1.0000	4.0	1.0000	4.0	0.9997
Pb	11.9	1.0000	10.3	1.0000	10.3	1.0000	10.5	1.0000
Sb	4.6	1.0000	4.1	1.0000	4.1	1.0000	4.1	1.0000
Se	2.9	1.0000	2.5	1.0000	2.5	1.0000	2.5	1.0000
Sn	3.0	1.0000	2.7	0.9999	2.7	0.9999	2.8	0.9999
Sr	3762	1.0000	3455	1.0000	3514	1.0000	3590	0.9998
Zn	89.6	1.0000	78.4	0.9999	77.1	0.9997	77.1	0.9998

α = angular coefficient; r = Pearson coefficient

Table 6 Results for figures of merit evaluation by microwave closed digestion: limits of detection and quantification, precision (coefficient of variation (CV)), and accuracy (spiked tests in three levels of concentration)

Element	LOD (μg L^{-1})	LOQ (μg L^{-1})	Precision (CV, %)			Recovery (%)								
			Fruit juice	Soy-based beverage	Tea	Fruit juice			Soy-based beverages			Tea drinks		
						Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
Al	4.0	12.8	25	1.5	7.0	85 ± 11	89 ± 2	87 ± 1	94 ± 1	82 ± 5	86 ± 1	113 ± 8	96 ± 5	91 ± 2
As	12.0	38.2	4.8	4.5	6.8	87 ± 3	90 ± 4	94 ± 2	93 ± 1	88 ± 4	88 ± 4	104 ± 16	96 ± 6	97 ± 2
Cd	1.2	3.8	2.7	1.5	2.1	95 ± 2	97 ± 3	95 ± 2	94 ± 3	92 ± 1	86 ± 4	96 ± 4	94 ± 2	95 ± 3
Co	2.8	9.0	2.7	1.2	2.2	93 ± 2	95 ± 3	95 ± 1	87 ± 4	85 ± 1	82 ± 4	85 ± 3	90 ± 2	92 ± 3
Cr	3.4	10.9	2.8	2.1	2.2	98 ± 1	98 ± 3	98 ± 1	99 ± 3	95 ± 2	89 ± 5	98 ± 5	94 ± 2	96 ± 3
Cu	2.5	7.9	4.3	1.5	2.2	101 ± 2	104 ± 4	104 ± 1	101 ± 5	98 ± 1	94 ± 5	98 ± 6	97 ± 2	101 ± 3
Fe	4.0	12.7	10	6.4	2.6	99 ± 9	98 ± 1	90 ± 2	95 ± 6	86 ± 6	85 ± 4	95 ± 2	96 ± 3	92 ± 2
Li	2.0	6.2	3.0	0.7	2.0	101.6 ± 0.2	99 ± 3	95 ± 1	103 ± 2	101 ± 1	93 ± 4	110 ± 5	100 ± 2	96 ± 3
Mn	0.4	1.4	4.3	3.2	8.3	105 ± 5	103 ± 2	95 ± 1	96 ± 3	89 ± 5	87 ± 4	118 ± 8	105 ± 6	96 ± 2
Ni	8.1	25.7	2.0	6.2	3.7	85 ± 17	96 ± 2	98 ± 1	96 ± 14	95 ± 6	95 ± 5	96 ± 20	97 ± 4	99 ± 3
Pb	3.4	10.9	3.3	3.1	2.4	89 ± 13	91 ± 3	90 ± 1	97 ± 8	88 ± 3	81 ± 3	81 ± 0	89 ± 2	91 ± 3
Sb	3.2	10.3	1.9	3.9	2.9	92 ± 6	92 ± 2	93 ± 1	89 ± 9	88 ± 3	85 ± 4	92 ± 3	90 ± 3	93 ± 3
Se	8.4	26.7	6.3	6.4	3.1	108 ± 17	103 ± 7	97 ± 3	88 ± 14	94 ± 6	85 ± 5	94 ± 9	92 ± 3	89 ± 3
Sn	5.7	18.0	2.4	5.7	2.3	82 ± 14	101 ± 2	98 ± 1	106 ± 2	96 ± 6	92 ± 5	95 ± 1	99 ± 2	100 ± 3
Sr	0.3	1.1	3.6	2.4	2.3	91 ± 3	94 ± 3	94 ± 1	100 ± 24	92 ± 2	84 ± 5	96 ± 5	91 ± 2	92 ± 2
Zn	1.2	3.7	9.2	6.2	2.5	92 ± 8	91 ± 1	86 ± 1	93 ± 6	81 ± 4	82 ± 1	95 ± 2	90 ± 3	87 ± 2

Recovery levels: Al, Fe, Mn, level 1 = 50 μg L^{-1}; level 2 = 500 μg L^{-1}; level 3 = 5000 μg L^{-1}; others, level 1 = 5 μg L^{-1}; level 2 = 50 μg L^{-1}; level 3 = 500 μg L^{-1}

Analytical Application in Ready to Drink Samples Purchased in Brazil

The proposed method was applied for trace elements determination in ready to drink beverages commercialized in Campinas city, southeastern Brazil. The analysis was performed in triplicate, and blank experiments were performed in each batch. The results are shown in Table 7.

Some trace elements were presented in levels < LOQ method, such as As, Cd, Co, Cr, Li, Pb, Sb, and Sn in all samples in this study. Black, green, and white tea samples presented similar levels considering a previous work (Milani et al. 2016) for Al, Fe, Mn, Se. and Zn in which the trace element behavior in several tea infusions was studied.

For soy-based beverages, few studies are reported in literature. The Al, Cu, and Fe levels found in this work were lower than those found by Boa Morte et al. (2008), which determined minerals in soy protein formulations from Brazil using the acid digestion in hot plate. Barbosa et al. (2015) performed a study with soy-based food, including soy extract, whole soy flour, textured soy protein, and soybean (transgenic and non-transgenic). The authors developed a method for trace elements by microwave digestion and ICP OES and ICP-MS. The levels reported for Cu, Fe, Mn, Ni, Se, Sr, and Zn were lower than those found in this study, supporting the use of different soy source, such as isolate soy protein or soybeans.

For fruit juices, quantifiable levels of Al, Cu, Fe, Mn, Se, Sr, and Zn were observed in all samples. Szymczycha-Madeja and Welna (2013) evaluated several trace elements in seven fruit juices from Poland and found higher levels for these elements. Cindrić et al. (2011) studied minor and major elements in fresh prepared apple juices, and they found trace element levels lower than those found in this study.

Regarding the maximum levels allowed for inorganic contaminants in beverages, the results demonstrated that no levels were found above the thresholds established by Brazilian (2013) and MERCOSUL (2011) regulations for As (0.10 mg kg^{-1}), Cd, and Pb (0.05 mg kg^{-1}) in fruit juices; As, Pb (0.05 mg kg^{-1}), and Cd (0.02 mg kg^{-1}) for non-alcoholic drinks; Sn (150 mg kg^{-1}) for canned beverages; Brazilian regulation (1965) for Sb (1.00 mg kg^{-1}) and Ni (3.00 mg kg^{-1}) for fruit juices, Cr (0.10 mg kg^{-1}) in foods; European regulation (Commission Regulation 2008) for Sn (100 mg kg^{-1}) in canned beverages and Pb (0.050 mg kg^{-1}) in fruit juices.

Table 7 Trace elements levels in ready to drink beverages commercialized in Brazil

Type	Flavor	Elements (μg L^{-1})							
		Al	As	Cd	Co	Cr	Cu	Fe	Li
Juice	Apple	48.9 ± 2.3	< 38.2	< 3.8	< 9.0	< 10.9	230 ± 3	363 ± 6	< 6.2
	Grape	122 ± 9	< 38.2	< 3.8	< 9.0	< 10.9	568 ± 12	852 ± 7	< 6.2
	Orange	19.7 ± 3.0	< 38.2	< 3.8	< 9.0	< 10.9	188 ± 4	545 ± 8	< 6.2
Soy-based beverage	Apple flavor	149 ± 1	< 38.2	< 3.8	< 9.0	< 10.9	146 ± 4	968 ± 19	< 6.2
	Grape flavor	356 ± 4	< 38.2	< 3.8	< 9.0	< 10.9	258 ± 4	1254 ± 15	< 6.2
	Orange flavor	311 ± 4	< 38.2	< 3.8	< 9.0	< 10.9	202 ± 6	1110 ± 21	< 6.2
Tea	Black	2437 ± 50	< 38.2	< 3.8	< 9.0	< 10.9	< 7.9	193 ± 9	< 6.2
	Green	3504 ± 34	< 38.2	< 3.8	< 9.0	< 10.9	< 7.9	48.0 ± 9.1	< 6.2
	Mate	398 ± 13	< 38.2	< 3.8	< 9.0	< 10.9	< 7.9	162 ± 23	< 6.2
	White	1279 ± 29	< 38.2	< 3.8	< 9.0	< 10.9	< 7.9	14.0 ± 2.1	< 6.2
Type	Flavor	Elements (μg L^{-1})							
		Mn	Ni	Pb	Sb	Se	Sn	Sr	Zn
Juice	Apple	512 ± 9	< 25.7	< 10.9	< 10.3	109 ± 4	< 18.0	82.0 ± 1.2	249 ± 3
	Grape	1998 ± 22	33.7 ± 1.3	13.4 ± 1.2	37.5 ± 5.3	123 ± 18	< 18.0	559 ± 8	817 ± 22
	Orange	240 ± 3	< 25.7	12.9 ± 0.8	16.5 ± 1.1	103 ± 9	< 18.0	196 ± 6	232 ± 8
Soy-based beverage	Apple flavor	349 ± 3	28.3 ± 3.2	< 10.9	< 10.3	49.9 ± 23.9	< 18.0	631 ± 15	5107 ± 95
	Grape flavor	386 ± 2	25.8 ± 2.9	< 10.9	< 10.3	37.3 ± 1.5	< 18.0	669 ± 6	5016 ± 32
	Orange flavor	338 ± 3	44.2 ± 3.5	< 10.9	< 10.3	50.0 ± 2.3	< 18.0	437 ± 5	5208 ± 135
Tea	Black	1337 ± 12	< 25.7	< 10.9	< 10.3	35.1 ± 3.8	< 18.0	121 ± 1	46.4 ± 10.3
	Green	3883 ± 41	< 25.7	< 10.9	< 10.3	31.0 ± 2.9	< 18.0	39.1 ± 0.2	59.1 ± 2.5
	Mate	5109 ± 116	< 25.7	< 10.9	< 10.3	55.4 ± 0.6	< 18.0	186 ± 4	163 ± 18
	White	731 ± 10	< 25.7	< 10.9	< 10.3	< 26.7	< 18.0	39.2 ± 0.9	34.2 ± 4.2

Conclusions

The microwave-assisted digestion procedure using dilute oxidant mixture and the multivariate ICP OES optimization was proved to be applicable for trace elements in several beverages ready to drink (tea, soy-based beverages, and fruit juices). The optimization of ICP OES parameters was performed using two designs of experiments, the first to select significant variables (at 95% of the confidence level) and the last a 2^3 central composite design. Although classical plasma robustness was not achieved, the proposed method presented high sensitivity, with detection limits below 12.0 μg L^{-1} and accuracy between 81 and 118% for all trace elements using spiked experiments. Samples purchased in Brazil did not presented levels above the threshold established by Brazilian, MERCOSUL, and European regulations for inorganic contaminants.

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Compliance with Ethical Standards

Conflict of Interest Raquel F. Milani declares that she has no conflict of interest. Marcelo A. Morgano declares that he has no conflict of interest. Solange Cadore declares that she has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

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