

Development of Analytical Method for Determination of Inorganic Constituents in Powder Refreshment Using Dilute Mineral Acids and Detection by ICP OES

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An analytical method for multi-elementary determination in powder refreshment, based on sample digestion using dilute mineral acids and detection by inductively plasma coupled optical emission spectrometry (ICP OES) is proposed. Chemometric tools, such as fractional factorial design and principal component analysis (PCA) and hierarchical cluster analysis (HCA) were applied to optimize the sample preparation conditions in closed block digester, and Doehlert design for spectrometer operation. Addition and recovery tests and analyses of certified reference material were performed to evaluate the precision and accuracy, and the results confirm the reliability of the proposed method. Limits of quantification (LOQ) between 0.02 and 36 $\mu\text{g g}^{-1}$ were obtained. The analytical method was applied for determination of 24 inorganic constituents in 20 powder refreshment samples. Calcium, K, Mg, Na, P, S and Ti presented the highest concentrations. The analytical method was adequate for the determinations of inorganic constituents in powder refreshment samples by ICP OES.

Keywords: chemometric tools, elemental composition, powder refreshment, sample preparation, ICP OES

Introduction

Processed liquid fruit juices are usually prepared from fruits *in natura* and are widely consumed as an alternative source of nutrients such as vitamins, proteins, macro and microelements and other phytochemicals in human nutrition.^{1,2}

Alternatively, powdered drink mixes, also known as powder refreshments, are increasingly and widely

consumed, due to their low price and easy preparation. Compared to liquid processed fruit juices, additional advantages attributed to these processed-food products are reduced volume, weight and package, longer shelf life, easy storage and transportation. Additionally, they are widely used as ingredients in many other recipes such as sweets, ice creams, cakes, being quite popular. However, their production goes through several manufacturing processes, which can lead to product contamination.³⁻¹⁰ Considering the widespread use of these products and how their composition can affect human

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health, the control of their composition becomes of great importance.

Powder refreshment is defined by Brazilian Ministry of Agriculture, Livestock and Supply (Ministério da Agricultura, Pecuária e Abastecimento, MAPA), through Ordinance No. 544, November 16, 1998,¹¹ as “the product based on fruit juice or plant extracts and sugars, it also may contain hypocaloric and non-caloric sweeteners, for immediate preparation and consumption by addition of drinking water”. However, similarly to all other processed foods, powder refreshment production requires regulation, since potentially toxic substances can be incorporated. The following chemical elements and respective maximum concentrations (in mg kg⁻¹) are considered as contaminants in refreshment and soda: arsenic (0.20), cadmium (0.20), copper (5.00), chromium (0.10), lead (0.20), mercury (0.01), nickel (0.10), selenium (0.30), tin (250.00), and zinc (5.00), according to Brazilian Health Surveillance Agency (Agência Nacional de Vigilância Sanitária, ANVISA).¹² Dyes are the main additives of the colorants contained in these products, and are added aiming color intensification, correction of natural variations of the color, and to compensate for discoloration due to exposure to light, air, temperature, humidity and storage.¹⁰ Chemical preservatives are also part of the powder refreshment formulation and are used in form of salt to avoid degradation and to increase the shelf life of the product before consumption.¹³

Alongside many available analytical methods, atomic spectrometry techniques are well reported in the literature as suitable for elemental determination in foods, including fruit juice samples, due to their sensitivity, selectivity and specificity and quite often selected as an appropriate method. Among atomic spectrometry techniques, flame atomic absorption spectrometry (FAAS),¹⁴ graphite furnace atomic absorption spectrometry (GF AAS),¹⁵ hydride generation atomic absorption spectrometry (HG-AAS),¹⁵ energy dispersive X-ray fluorescence spectrometry (EDXRF),¹⁶ inductively coupled plasma optical emission spectrometry (ICP OES)^{1,17-19} and inductively coupled plasma mass spectrometry (ICP-MS) are included.²⁰⁻²²

Compared to the techniques above described, inductively coupled plasma (ICP) based methods stand out due to some features that promote greater analytical frequency, with adequate sensitivities, multi-elementary determination capabilities, profitable for characterization and evaluation of probable food trends.²²⁻²⁵

Inductively coupled plasma optical emission spectrometry (ICP OES) is widely used since it presents the advantage of performing simultaneous multi-elemental determinations for all types of samples, including foods.^{1,18,19,24}

Usually, ICP OES presents limited conditions of sensibility compared to ICP-MS, but even so, adequate values are obtained for analysis of foodstuffs. In addition, conventionally this technique requires the sample to be converted to a solution, requiring decomposition or extraction steps prior the introduction into the instrument. Thus, in order to attain an adequate digestion procedure and to accomplish the determination of the elements, an optimization of the composition of the reagents and the experimental conditions for analysis of the sample may be necessary.^{1,4,18,25,26}

The acid digestion is an important procedure for sample treatment aiming inorganic constituent determinations, and it is considered the most efficient procedure for treatment of foods for multi-elementary determination. Acid digestion is carried out mainly in microwave ovens and in block digester systems, wherein some variables, such as, the ratio between the amounts of reagents and the sample, temperature and time of digestion can affect the efficiency of the decomposition process.^{4,24-26} The use of acid digestion for sample preparation of powder refreshment using closed block digester is still rare or non-existent.

Digestion of powder refreshment samples may require the use of acid medium due to complexity of the matrix. These samples have high content of organic matter, mainly due to sugar. Conventionally, sample preparation through digestion is time consuming and tedious, therefore simple alternative procedures, such as sample dilution followed by direct analysis, are proposed. However, the direct analysis with no pretreatment of the sample may present problems of matrix effect in the analytical process.^{1,5,22-26} It is noteworthy that no procedure for preparation of powder refreshment sample using wet decomposition has been reported.

Considering the increasing demand for food and the importance of safe composition for human health, the main objective of this work was the development of a method entailing the optimization of a wet sample preparation procedure using diluted acids for multi-elementary determination in powder refreshment by ICP OES. Furthermore, chemometric tools were applied to the optimization of sample preparation procedure, using acid digestion in closed block digester, as well as the operational conditions of the inductively coupled plasma optical emission spectrometer.^{22,25,27-29}

Experimental

Reagents and solutions

All reagents used were of analytical grade. The solutions were prepared with deionized water to a resistivity

of 18.2 M Ω cm, purified in a Milli-Q system (Millipore, Bedford, MA, USA). Nitric acid 65% m m⁻¹ (Merck, Darmstadt, Germany), peroxide hydrogen 30% m m⁻¹ (Merck, Darmstadt, Germany) and hydrofluoric acid 48% m m⁻¹ (Merck, Darmstadt, Germany) were used for sample digestion procedure.

In all samples, 4% m v⁻¹ boric acid solution was added to the solutions after digestion, including analytical blank solutions, to complex the fluoride ions and avoid damage to the spectrometer, since HF can attack its quartz components.¹⁸

Sodium hydroxide solution, 0.1000 mol L⁻¹, was standardized with potassium hydrogen phthalate P.A. (JT Baker, São Paulo, Brazil) employing a 0.1% m v⁻¹ phenolphthalein solution, as chemical indicator, and used to evaluate the acidity of the samples after digestion.

All glassware and materials used in the present study were kept in 10% v v⁻¹ HNO₃ solution for at least 24 h, and after that they were rinsed with deionized water and dried at room temperature.

Instrumental

A forced-air oven (model MA 035, Marconi, São Paulo, Brazil) was used in the drying of the powder refreshment samples. Analytical balance (model Toledo AB 204-05, Mettler-Toledo, Polaris Parkway, Columbus, USA) was used to measure the sample masses. Sample digestion was carried out in a temperature-controlled block digester equipped with polytetrafluoroethylene (PTFE) flasks and lids (model TE007-A, TECNAL, São Paulo, SP, Brazil).

Elemental determination was performed using an inductively coupled plasma optical emission spectrometer with axial configuration (model ES-720, Agilent, Mulgrave, Australia). Signal intensity measurements of the analytes in all solutions and samples were carried out at wavelengths (nm) as following: Al I (308.215), As I (193.696), Ba II (614.171), Be I (234.861), Bi I (223.061), Ca II (317.933), Cd I (228.802), Co II (238.892), Cr II (267.716), Cu II (213.598), Fe II (239.563), K I (766.491), Mg II (279.553), Mn II (259.372), Na I (330.237), Ni II (231.604), P I (213.618), Pb II (220.353), Sn I (283.998), Sr II (216.596), Ti II (334.941), V II (292.401) and Zn II (213.857), where (I) is atomic line and (II) is ionic line.

The spectrometer was equipped with a solid state detector, cooled to -35 °C by a Peltier system, covering a wavelength range from 167 up to 780 nm. Argon gas with a minimum purity of 99.9999% (White Martins, São Paulo, Brazil) was used for plasma generation and nebulizer gas flow rate. The applied conditions were the

Sturman-Masters nebulizer chamber, V-Groove nebulizer, a 2.4 mm injector tube diameter, 1.0 s signal integration time, sample introduction rate of 0.8 mL min⁻¹, auxiliary gas flow of 1.5 L min⁻¹, plasma gas flow of 15.0 L min⁻¹, radiofrequency power of 1.2 kW, and nebulizer gas flow rate of 0.8 L min⁻¹.

For calibration curves a 10 mg L⁻¹ multi-element standard solution, containing Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, Sr, Ti, V and Zn, was prepared by proper dilution of a 100 mg L⁻¹ standard solution (Specsol[®], São Paulo, Brazil). For macroelements, 1000 mg L⁻¹ monoelemental standard solutions, containing Ca, K, Mg, Na, P and S (Specsol[®], São Paulo, Brazil), were used. External calibration curves were prepared in concentrations between 0.1 up to 10.0 mg L⁻¹ for Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, Sr, Ti, V, Zn and between 5.0 up to 200 mg L⁻¹ for Ca, K, Mg, Na, P and S.

Sampling of powder refreshment samples

Twenty powder refreshment samples, in sachet packages and randomly selected on the shelves, were purchased from supermarkets in Aracaju City, Sergipe, Brazil. The samples were dried at a temperature of 40 °C in an oven for 24 h. After drying, they were macerated, using mortar and pestle, to a particle size smaller than 150 μ m.

Chemometric tools applied for optimization of analytical method

The optimization of the digestion procedure of powder refreshment samples was performed using a 2⁵⁻¹ fractional factorial design. The concept of the multiple response function was applied to evaluate the experimental design.²⁵ The following independent factors were selected: concentration of HNO₃ (1.0-3.0 mol L⁻¹), concentration of H₂O₂ (1.0-4.0% m m⁻¹), concentration of HF (0.0-2.74 mol L⁻¹), heating temperature of the digester block (150-190 °C) and digestion time (60-120 min). Triplicate of the central point was used to estimate the experimental error. The experiments were performed randomly. The inorganic constituent concentrations, obtained in one commercial sample, grape flavor powder refreshment, were employed as the response of the fractional factorial design.

A Doehlert design was proposed to optimize the operating conditions of the spectrometer using the radiofrequency power (RFP: 1000-1400 W) and the nebulization gas flow rate (NGF: 0.6-1.0 L min⁻¹) as variables of the matrix. The ratios of the emission intensities between the ionic magnesium lines and the

atomic magnesium (Mg II 280.265 nm / Mg I 285.213 nm) were used as response.³⁰ To estimate the experimental error, replicates of the central point were performed. One commercial sample of refreshment, digested using the optimized procedure, was employed in this study.

To evaluate the contributions of the chemical elements determined in the experiments, multivariate data analyses, such as principal component analysis (PCA) and hierarchical cluster analysis (HCA), were applied to the concentrations obtained from fractional factorial design. The experimental data were processed using the statistical software, Statistica version 10.0.³¹

Residual acid concentration

After digestion in a closed digestion block, residual acid concentration was determined by titration of a 0.5 mL aliquot of the digested samples, diluted to 20.0 mL with deionized water and addition of two drops of phenolphthalein as indicator. The samples were then titrated with a 0.1000 mol L⁻¹ NaOH standardized solution. All analyses were made in triplicate.

Procedure for digestion of powder refreshment samples

Approximately 0.2000 ± 0.0001 g of each sample was measured and transferred to PTFE flasks. Then, volumes of 0.70 mL of HNO₃ 65% m m⁻¹, 1.35 mL of H₂O₂ 30% m m⁻¹ and 1.00 mL of HF 48% m m⁻¹ were added. The PTFE flasks were kept open and standing still for 30 min, and after that, 6.95 mL of deionized water were added, the flasks were closed and submitted to heating in a block digester at a temperature of 150 °C, during 120 min. Analyses of the samples were performed in triplicate.

The samples, after digestion procedure, were cooled to room temperature to avoid losses of the analytes, then quantitatively transferred to 50.0 mL Falcon flasks, and 3.00 mL of H₃BO₃ 4% m v⁻¹ were added to eliminate the excess of HF, which can cause damage to the ICP OES components. The flasks were filled up to a final volume of 15.0 mL with deionized water and stored at 4 °C for subsequent determination of the inorganic constituents by ICP OES. Analytical blank solutions of the reagents were prepared for quality control.

Accuracy of the proposed analytical method was evaluated through analysis of the certified reference material (CRM), apple leaves (NIST 1515), peach leaves (NIST 1547), tomato leaves (CRM-Agro C1003a) and tea (NCS DC 73351). Addition and recovery tests were performed in two samples (A / grape and F / strawberry) at three concentration levels, by addition of 0.3, 0.5 and

1.0 mg L⁻¹ of Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Sr, V and Zn; 2.00, 5.00, and 10.0 mg L⁻¹ of Fe and Ti, and 5.0, 10.0 and 30.0 mg L⁻¹ of Ca, K, Mg, Na, P and S. Precision was evaluated by relative standard deviation (RSD) of the results obtained in triplicate (n = 3).

Results and Discussion

Optimization of the preparation procedure for powder refreshment samples

The optimization of the treatment procedure for powder refreshment samples was performed using one commercial sample, grape flavor. A 2⁵⁻¹ fractional factorial design with triplicate of the central point was used to evaluate the composition of the reagents and the experimental conditions for sample digestion in the closed digestion block. The following factors were chosen: concentrations of HNO₃, H₂O₂, HF, temperature and time of digestion.

Titanium element is present in great amount in powder refreshment samples as titanium dioxide (TiO₂), used as whitening agent in these and other types of food.^{29,32} Therefore, hydrofluoric acid is required to achieve the total digestion of the sample and, consequently, the determination of total concentration of titanium. Factorial design was applied to evaluate the influence of the factors on the digestion procedure, employed to the powder refreshment samples, through the obtained concentrations of Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr, Ti and Zn in grape flavor commercial sample by ICP OES. The concept of multiple response (MR) was the dependent variable for the simultaneous analysis of the data obtained by the proposed design. The real and coded values for the variables, as well as MR and determination of the elements are shown in Table 1.

Equation 1 presents the expression to obtain the MR.^{21,27}

$$MR = \frac{R_{x1}}{R_{Max1}} + \frac{R_{x2}}{R_{Max2}} + \frac{R_{x3}}{R_{Max3}} + \dots + \frac{R_{xn}}{R_{Maxn}} \quad (1)$$

where, R_{xn} is the analytic response of the element concentration in each experiment, and R_{Maxn} is the maximum response of the maximum element concentration in each experiment.

Fractional factorial design evaluation takes into account the probable confounding factors and their interactions. The confounding factors between the contrasts were assessed based on resolution V predictions. The interpretation of the 2⁵⁻¹ fractional factorial design results can be achieved by the data shown in Table S1 (in Supplementary Information (SI) section), which presents the confounding and its effects for

Table 1. Matrix of 2^{5-1} fractional factorial design: coded values, real values, inorganic constituent concentrations and multiple response (MR)

Experiment	Coded (real value)					Concentration value											MR
	[HNO ₃] / (mol L ⁻¹)	[H ₂ O ₂] / (% m m ⁻¹)	HF / (mol L ⁻¹)	Temperature / °C	time / min	Na / %	Al / (µg g ⁻¹)	Ba / (µg g ⁻¹)	K / (µg g ⁻¹)	Ca / (µg g ⁻¹)	Zn / (µg g ⁻¹)	Ti / (µg g ⁻¹)	Sr / (µg g ⁻¹)	Mn / (µg g ⁻¹)	Mg / (µg g ⁻¹)	Fe / (µg g ⁻¹)	
1	-1 (1.0)	-1 (1.0)	-1 (0.0)	-1 (150)	+1 (120)	19.6	6.03	14.7	307	3366	0.413	0.00	6.02	0.536	202	302	7.23
2	+1 (3.0)	-1 (1.0)	-1 (0.0)	-1 (150)	-1 (60)	20.9	7.77	15.7	309	3375	0.221	0.00	5.87	0.500	204	309	7.21
3	-1 (1.0)	+1 (4.0)	-1 (0.0)	-1 (150)	-1 (60)	20.1	8.57	15.8	354	3553	0.147	0.00	6.38	0.414	207	262	7.17
4	+1 (3.0)	+1 (4.0)	-1 (0.0)	-1 (150)	+1 (120)	19.1	8.94	15.1	307	3450	0.294	0.00	6.14	0.497	204	303	7.23
5	-1 (1.0)	-1 (1.0)	+1 (2.74)	-1 (150)	-1 (60)	18.1	29.82	14.7	320	3667	0.791	57.8	6.57	0.521	218	304	9.46
6	+1 (3.0)	-1 (1.0)	+1 (2.74)	-1 (150)	+1 (120)	18.9	26.52	15.1	314	3630	0.583	59.9	6.60	0.902	219	356	9.82
7	-1 (1.0)	+1 (4.0)	+1 (2.74)	-1 (150)	+1 (120)	18.8	29.97	15.5	338	3878	0.781	62.2	6.93	0.518	223	285	9.73
8	+1 (3.0)	+1 (4.0)	+1 (2.74)	-1 (150)	-1 (60)	21.1	28.46	15.8	323	3759	0.846	57.9	6.62	0.580	217	331	9.85
9	-1 (1.0)	-1 (1.0)	-1 (0.0)	+1 (190)	-1 (60)	21.4	20.67	17.4	357	3911	0.458	0.00	6.77	0.596	224	313	8.57
10	+1 (3.0)	-1 (1.0)	-1 (0.0)	+1 (190)	+1 (120)	20.8	13.52	15.8	324	3595	0.877	0.00	6.44	0.492	207	305	8.15
11	-1 (1.0)	+1 (4.0)	-1 (0.0)	+1 (190)	+1 (120)	22.1	9.58	16.5	327	3503	0.472	0.00	6.36	0.587	205	265	7.72
12	+1 (3.0)	+1 (4.0)	-1 (0.0)	+1 (190)	-1 (60)	18.3	11.42	16.5	277	3445	0.557	0.00	6.01	0.456	196	260	7.29
13	-1 (1.0)	-1 (1.0)	+1 (2.74)	+1 (190)	+1 (120)	21.8	11.47	15.9	305	3580	0.559	57.7	4.50	0.376	188	221	8.00
14	+1 (3.0)	-1 (1.0)	+1 (2.74)	+1 (190)	-1 (60)	20.3	22.09	15.1	301	3427	0.570	49.2	6.20	0.534	201	315	8.80
15	-1 (1.0)	+1 (4.0)	+1 (2.74)	+1 (190)	-1 (60)	19.5	22.94	14.8	305	3317	0.477	47.2	5.88	0.411	198	278	8.34
16	+1 (3.0)	+1 (4.0)	+1 (2.74)	+1 (190)	+1 (120)	19.1	24.59	14.3	287	3266	0.950	50.2	5.80	0.468	196	299	8.86
17	0 (2.0)	0 (2.5)	0 (1.37)	0 (170)	0 (90)	18.7	28.04	14.0	283	3357	0.821	58.5	5.70	0.365	202	250	8.73
18	0 (2.0)	0 (2.5)	0 (1.37)	0 (170)	0 (90)	18.3	20.85	14.1	297	3126	0.796	54.8	5.48	0.406	192	255	8.35
19	0 (2.0)	0 (2.5)	0 (1.37)	0 (170)	0 (90)	18.3	19.91	13.9	282	3135	0.789	48.3	5.48	0.383	198	268	8.20

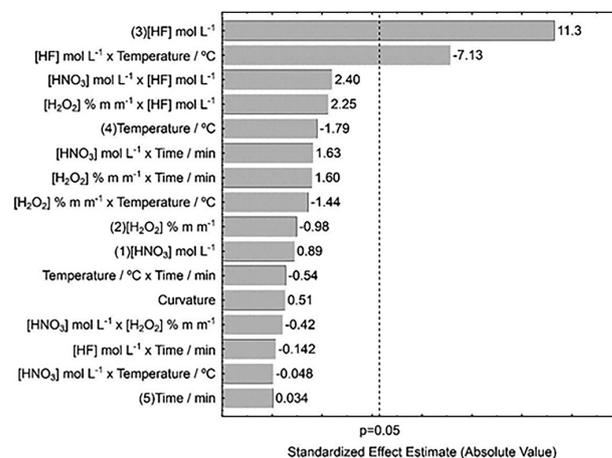
the contrasts. The concentration of hydrofluoric acid (HF, in mol L⁻¹) and interaction (HF, in mol L⁻¹ × temperature, in °C) were the factors with the highest values of effects for contrasts and are significant for the digestion procedure of the powder refreshment samples.

The fourth-order interaction (1 × 2 × 4 × 5) could cause a confounding with the first order main effect (HF, in mol L⁻¹), in obtaining the same contrasts, however, the effects of the first order contrasts of the main factors are usually greater than the effects of higher order contrasts.³³ Therefore, the effects of the interactions (1 × 2 × 4 × 5) were not so significant in the digestion procedure evaluated in this study.

The interaction contrast of second order (HF, in mol L⁻¹ × temperature, in °C) presented the same contrast value of the third order interaction ([HNO₃] mol L⁻¹ × [H₂O₂] % m m⁻¹ × time, in min), with a confounding for the estimated effect, but, as in the previous situation, the higher order interactions present low-value effects. So, the second order interaction (HF, in mol L⁻¹ × temperature, in °C) presents a more significant effect. Although there were confoundings, the effects were evaluated considering a resolution V, consequently there was no significant difference for the digestion procedures of the powder refreshment samples.

Figure 1 shows the Pareto chart used to evaluate the contrasts obtained by the factors related to MR function. The bars correspond to the values of the standardized

effects of all variables and their possible interactions, and the dashed line represents the value of $p = 0.05$, statistically significant at 95% confidence level.³³

**Figure 1.** Pareto chart for 2^{5-1} fractional factorial design.

The factor with significant effect and positive value, within the experimental domain studied, as shown in the Pareto chart, was (HF, in mol L⁻¹), while the second order interaction (HF, in mol L⁻¹ × temperature, in °C) presented a significant effect but with a negative value. Through the obtained results (Table 1), it can be observed that, when the maximum concentration of HF and the lower temperature are used, the dissolution of the elements is favored, as shown by experiments 5, 6, 7 and 8. For these experiments

MR values were higher, mainly due to the contribution of the concentration values of Al, Ca, Mg and Ti. The evaluation of the curvature presented a non-significant contrast value for MR, namely, the mathematical model reveals a linearity between the response, especially for the factor concentration of HF and the interaction between HF concentration and digestion temperature.

The use of HF concentration at maximum level in these experiments, resulted in an increase of the MR response. The addition of HF to the digestion medium containing the other reagents favored the dissolution of Al, Ca, Mg and Ti oxides, as soluble complexes.³³ On the other hand, the use of only HNO₃ and H₂O₂ did not promote the complete dissolution of Ti, as shown in the results obtained for the experiments 1-4 and 9-12.

Analyses of variance (ANOVA) are presented in Table S2, in SI section, and show the values found for evaluation of the mathematical model through the lack of fit (p -value ≥ 0.05), related to data obtained from the 2⁵⁻¹ fractional factorial design, with multiple response function for sample preparation, before multi-elementary determination by ICP OES. The values show that, regarding the digestion procedure, the effects of the contrasts were significant for HF concentration and the interactions between HF concentration and temperature. The p -value for lack of fit was 0.66, higher than 0.05; meaning that there is no lack of fit for the model at a 95% confidence level.³⁴

The quality of fit of the mathematical model can be confirmed through the plot of the predicted values *versus* observed values as shown in Figure S1, in Supplementary Information. The obtained graph shows good agreement between predicted and experimental values, presenting a correlation coefficient (r) ≥ 0.99 , a clear evidence of the good fit of the model.

Residual acid concentration of the solutions was evaluated after digestion of powder refreshment samples, in the closed heating block. This assessment was carried out by acid-base titration of an aliquot of the samples with a 0.1000 mol L⁻¹ NaOH standardized solution.

The residual acid concentration was approximately 1.52 mol L⁻¹ for the established condition of sample preparation (experiment 7), after dilution to 15 mL with deionized water, which is suitable for analysis by ICP OES using nebulizer introduction system.³⁰ However, a residual acid concentration of 2.28 mol L⁻¹ was obtained in the reaction flask of experiment 7. The residual acid concentration (HNO₃ + HF) percentages were between 47.6 and 91.5% for the proposed design, as seen in Table S3 (Supplementary Information). The average concentration of center point was $48.7 \pm 1.1\%$, with RSD of 2.3%

($n = 3$), showing good precision. A simple and inexpensive closed digestion block, such as the device used in this study, presented an efficiency for the process similar to those accomplished by microwave-assisted digestion systems.³⁵ According to literature,³⁶ HNO₃ is expected to be regenerated in the presence of H₂O₂ during digestion in a closed system. Most likely in the closed digestion block, the consumption of HF concentration may be related to decomposition reactions of metal oxides.

Considering that the variation among MR values for experiments 5, 6, 7 and 8 was minimal, the residual acid concentration of the digested solutions was evaluated and experiment 7 presented the lowest acid concentration at the end of the sample digestion procedure. Also, the determination of Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr, Ti and Zn in powder refreshment provided concentrations of the same magnitude of the other experiments. Therefore, experiment 7, which uses the lower concentration (1.0 mol L⁻¹) of HNO₃ in the studied domain, was adopted as the sample preparation method.

Multivariate data analysis

Response surface methodology (RSM) is usually applied to optimize procedures, but multivariate data analysis can be used to identify similar response surfaces and simplify the optimization procedure.³⁷ In our work, multivariate data analysis was used aiming to establish the influences of the variables on the 19 experiments carried out. The data matrix 19 \times 11 obtained for the PCA and HCA was created using the concentration of the 11 elements, obtained through the 2⁵⁻¹ fractional factorial design (columns) and the 19 performed experiments (lines). The data were preprocessed by autoscaling for data matrix construction.

Principal component analysis

The first principal component PC1 was accountable to explain 41.98% of the variance, followed by PC2 that explained 28.78% of the total variance. The two first principal components altogether were accountable for 70.76% of the total accumulated variance and, consequently, comprising the highest loading values for the 11 chemical elements and eigenvalues greater than one. For Ba, Ca, Fe, K, Mg, Mn and Sr concentrations by PC1, negative loadings were achieved. Through PC2, negative loadings were obtained for Al, Ti and Zn, while Ba and Na presented positive loading values. The spatial distribution of the variables is shown in the loading graphic of PC1 *versus* PC2 in Figure S2, in the Supplementary Information.

Figure 2 shows the graph of scores with three distinct groups related to the concentrations of the 11 elements, evaluated through the 19 experiments performed according to the experimental design. The first group was formed by experiments 1, 2, 3, 4, 9, 10, 11, 12 and 13 and are located on the axis of positive scores values of PC2, showing that the highest concentrations of Ba, K and Na were the main influence in the separation of this group.

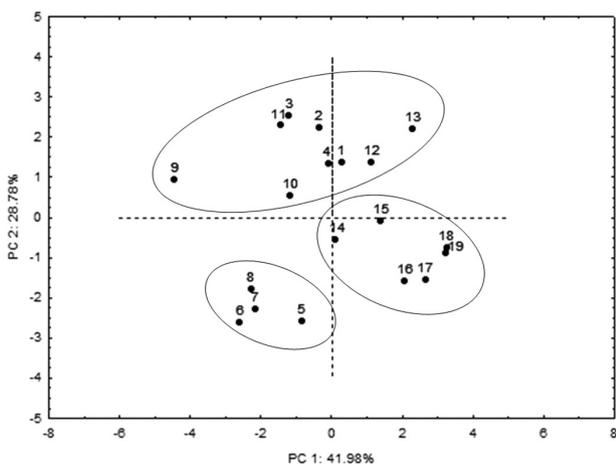


Figure 2. Scores graphic for PC 1 versus PC 2 related to the 19 experiments used in the 2^{5-1} fractional factorial design.

The second group was formed by the experiments 5, 6, 7 and 8, located in the axes of negative scores values of PC1 and PC2, characterizing the experiments with higher concentrations, determined by the elements Al, Ca, Fe, Mg, Mn, Zn and Ti. The use of higher HF concentration, 2.74 mol L^{-1} , resulted in an increase of the concentrations of the elements.

The third group, formed by experiments 14, 15, 16, 17, 18 and 19, is located at the axis of positive scores values of PC1 and negative scores in PC2, whose characteristics are the higher concentrations of Al, Zn and Ti. In these experiments, carried out using HF, there was an improvement in the dissolution of these elements within the digestion media. The localization of experiment 13 in this group 1, even though using the maximum level of HF, is related to the obtained concentrations of Ba and Na, and consequently dissimilar to the other experiments using HF. The experiment 9 distanced itself from group 1 even though HF was not used, probably due to the contribution of the loadings of the elements Ba, Ca, K, Na and Sr with higher concentrations in this experiment.

Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) was applied aiming to achieve a better characterization of the group formation

and to confirm the results obtained by PCA analysis. The 19 experiments were grouped hierarchically using autoscaling of the element concentrations. Ward's method was applied and the similarities between the experiments were calculated from Euclidean distances. The dendrogram presented in Figure S3, in SI section, also shows the formation of three distinct groups clustered according to their similarities, confirming the results obtained by PCA analysis.

After application of the chemometric tools for analyses of the data, through fractional factorial design and multivariate data analysis, digestion procedure based on experiment 7 was established as the optimal condition. Both techniques were effective strategies to be employed in optimizing the sample preparation conditions. Thus, in the subsequent experiments the following conditions were used, for 0.20 g of powder refreshment sample: 0.70 mL (1.0 mol L^{-1}) of HNO_3 , 1.35 mL ($4.0\% \text{ m m}^{-1}$) of H_2O_2 , 1.0 mL of HF $48\% \text{ m m}^{-1}$ (2.34 mol L^{-1}), addition of 6.95 mL of deionized water, to a 10 mL reaction final volume, $150 \text{ }^\circ\text{C}$ digestion temperature, and 120 min digestion time.

Optimization of spectrometer operation conditions

To ensure the efficiency of inductively coupled plasma optical emission spectrometer analyses, a Doehlert design was applied to obtain operational conditions for higher plasma robustness, through measurements of Mg intensities in one powder refreshment digested sample.^{23,25,38} The optimization was performed for the following variables: nebulization gas flow rate (NGF) and radiofrequency power (RFP). The experiments were carried out randomly with quadruplicate of the center point to estimate the experimental error. The intensity ratios of magnesium spectral lines, Mg II 280.270 nm and Mg I 285.213 nm were used as response to evaluate and optimize the operational conditions for the determination of the elements in the digested powder refreshment.^{30,39} For plasma robustness condition, the Mg II/Mg I ratio can be equal or higher than 8.⁴⁰ Table S4, in SI section, presents the coded values, real values and Mg II/Mg I ratio obtained using one of the powder refreshment digested sample.

The best condition, the highest Mg II/Mg I ratio, was achieved for experiment 2, as shown in Table S4, in SI section. In these conditions the radiofrequency power applied was 1400 W, the maximum RF reached by the instrument. Experiments 7, 8 and 10, center point, also presented conditions of instrumental robustness and were chosen as compromise conditions for analysis by ICP OES.

From the proposed Doehlert design, a response surface graph was generated as presented in the Figure S4, in SI section. Applying the criterion of inspection to the generated graphical contour of the Doehlert design (Figure S5, in SI section), it was found that, employing a 0.9 L min^{-1} nebulizer gas flow rate and a radiofrequency power of 1400 W (experiment 2), a better response in a maximum region is achieved. As can be observed in the plot, high values of radiofrequency power along with high values of nebulization gas flow rate, up to 1.0 L min^{-1} , promote an increase in the plasma robustness. However, an application of 0.8 L min^{-1} of nebulization gas flow rate and a radiofrequency power of 1200 W also presented a response in an optimal region, besides the additional advantage of being an experimental condition that prevents the system to operate under extreme conditions.

Therefore, the determination of the elemental composition in powder refreshment samples was carried out according to the operational conditions, established for the spectrometer: nebulization gas flow rate of 0.8 L min^{-1} and radiofrequency potency of 1200 W.³⁸⁻⁴⁰

The quality of fit for the mathematical model was evaluated through the analysis of variance (ANOVA) as shown in Table S5, in SI section. The lack of fit was assessed using *p*-value, and the obtained value, 0.424, higher than 0.05, ensures that the model does not present a lack of fit, using the ratio Mg II/Mg I as response, at a confidence level of 95%.

Linear regression analysis was applied to evaluate the adjustment between the predicted values *versus* observed values for the Mg II/Mg I ratio as presented in Figure S6, in SI section. The results confirm a good model fit between the predicted values *versus* observed values, considering a correlation coefficient (*r*) of 0.99.³³ In this work, the model used is adequate to the proposed method, which establishes as compromise conditions nebulization gas flow rate of 0.8 L min^{-1} and radiofrequency power of 1200 W, for the determination of chemical composition of powder refreshment by ICP OES.³⁸⁻⁴⁰

Figures of merit

Limits of detection (LOD) and quantification (LOQ) for the proposed method were established using the obtained equivalent background concentration (BEC) and the signal-to-background ratios (SBR), based on the definition of the International Union of Pure and Applied Chemistry (IUPAC),⁴¹ through the following equation:

$$\text{BEC} = C_{\text{Standard}} / \text{SBR}; \text{SBR} = (I_{\text{Standard}} - I_{\text{Blank}}) / I_{\text{Blank}} \quad (2)$$

where, C_{standard} is the standard concentration; I_{Standard} and I_{Blank} are the intensities of standard solution and blank solution, respectively.

Limit of detection (LOD) is defined as the low concentration that can be measured by the analytical method and different from the signal-to-background in a ratio of to 1:3. In this work, LOD was calculated using the equation: $\text{LOD} = (3 \times \text{BEC} \times \text{RSD}/100)$, in which the relative standard deviation (RSD) was obtained through ten signal measurements of the blank solution. Limit of quantification (LOQ) is defined as the lowest concentration that can be measured through the analytical method with good precision and accuracy. It was calculated using the signal-to-background ratio equal to 1:10 through the equation as $\text{LOQ} = (10 \times \text{BEC} \times \text{RSD}/100)$. The values obtained for LOD ranged between 0.010 and $11 \mu\text{g g}^{-1}$, and LOQ values were from 0.020 to $36 \mu\text{g g}^{-1}$, as presented in Table 2.

Precision refers to the proximity of the results obtained in a series of repeated measurements for the same sample. This is considered on three levels. Accuracy is the proximity of the results obtained by the analytical method under study to the true value.⁴² In this work, accuracy of the analytical method was evaluated through addition and recovery tests at three levels of concentrations for each element. The tests were performed in two samples (A / grape and F / strawberry), and the addition of the elements was carried out before the addition of reagents and the digestion process. Determinations were performed for the following concentrations: 0.30; 0.50 and 1.00 mg L^{-1} of microelements, and 2.00; 5.00; and 10.0 mg L^{-1} of Fe and Ti. For macroelements, the added concentrations were: 5.00, 10.0 and 30.0 mg L^{-1} of Ca, Mg and P, and 10.0, 30.0, and 50.0 mg L^{-1} of K, Na and S, prior the treatment of the sample with HNO_3 , H_2O_2 and HF.

Table 2 shows a summary of the recoveries shown in Table S6, in SI section, obtained from the addition and recovery test using the proposed method, where all detailed recovery values can be found. Recovery percentages were between 80.0 ± 0.9 and $119 \pm 3\%$, ensuring good accuracy of the proposed method. Among microelements, the percentage of recovery varied between $80.0 \pm 0.9\%$ (Al) and $119 \pm 3\%$ (Ti). For macroelements the percentage varied between $81 \pm 3\%$ (Ca) and $115 \pm 4\%$ (S).

Precision, expressed as relative standard deviation (RSD), was evaluated by the repeatability of a set of measurements and the found values were better than 9.9% ($n = 3$), as shown in Table S6, in SI section, considered acceptable for multi-elementary determination by ICP OES. Especially for Ti, which is found in great amounts in these types of samples and it is hard to dissolve, good recoveries

Table 2. Values for limits of detection (LOD) and quantification (LOQ) and the recoveries for addition and recovery test obtained by the proposed analytical method by ICP OES

Element	LOD / ($\mu\text{g g}^{-1}$)	LOQ / ($\mu\text{g g}^{-1}$)	Recovery / %	Element	LOD / ($\mu\text{g g}^{-1}$)	LOQ / ($\mu\text{g g}^{-1}$)	Recovery / %
Al	3.7	12	(80.0 \pm 0.9)-(112 \pm 2)	Mg	0.40	1.2	(100 \pm 3)-(105 \pm 1)
As	0.90	3.0	(105 \pm 1)-(118 \pm 4)	Mn	0.030	0.10	(92 \pm 2)-(103 \pm 2)
Ba	0.010	0.020	(92 \pm 2)-(102 \pm 3)	Na	1.1	3.8	(85 \pm 5)-(109 \pm 4)
Be	0.010	0.020	(100 \pm 2)-(108 \pm 1)	Ni	0.10	0.30	(96 \pm 2)-(105.4 \pm 0.6)
Bi	0.50	1.7	(92 \pm 4)-(100 \pm 4)	P	0.80	2.7	(92 \pm 6)-(114 \pm 2)
Ca	1.6	5.2	(81 \pm 3)-(108 \pm 3)	Pb	0.70	2.2	(93.9 \pm 0.8)-(104.6 \pm 0.3)
Cd	0.10	0.20	(106 \pm 2)-(116 \pm 1)	S	2.8	9.4	(98 \pm 3)-(115 \pm 4)
Co	0.050	0.20	(89 \pm 2)-(95 \pm 1)	Sn	0.70	2.4	(94 \pm 2)-(101 \pm 1)
Cr	0.10	0.20	(98 \pm 2)-(108 \pm 2)	Sr	0.10	0.40	(100 \pm 2)-(111.2 \pm 0.4)
Cu	0.20	0.60	(97 \pm 1)-(106 \pm 1)	Ti	0.10	0.30	(106 \pm 11)-(119 \pm 3)
Fe	0.46	1.5	(95 \pm 8)-(109 \pm 5)	V	0.030	0.10	(96 \pm 2)-(104.4 \pm 0.8)
K	11	36	(85 \pm 1)-(105 \pm 4)	Zn	0.20	0.80	(102 \pm 2)-(113 \pm 1)

Results expressed as mean \pm standard deviation (n = 3). ICP OES: inductively coupled plasma optical emission spectroscopy.

were achieved. The addition of HF to the digestion media containing HNO₃ and H₂O₂ was effective in promoting the solubilization of the Ti oxides and making it possible the determination in powder refreshment samples with good accuracy.³³

Accuracy was also evaluated by determination of the elements in certified reference materials (CRM) of apple leaves (NIST 1515), peach leaves (NIST 1547), tomato leaves (CRM-Agro C1003a) and tea (NCS DC 73351). The results, presented in Table 3, show good agreement between the obtained values and the certified values, ranging from 80.5 \pm 0.2 to 117 \pm 24%. The only exception was for Al concentration in CRM of tea (NCS DC 73351) with an agreement of 73.3 \pm 0.3%. This sample presents just an informed value for Al concentration, and as notified by the certified document, its homogeneity and stability were questioned during the manufacture of the material.

Since these CRM samples matrix are more complex than the powder refreshment samples, with higher content of organic and inorganic materials, and even so, the obtained results were concordant, it is possible to conclude that the digestion procedure, employing diluted acids in a closed digestion block, presents good efficiency for multi-elemental analysis by ICP OES, with good precision and accuracy.

In this work, the obtained LOQ values were lower than the limits established by Brazilian Health Surveillance Agency (Agência Nacional de Vigilância Sanitária, ANVISA), through Decree No. 55.871, March 26, 1965,¹² for Cd (0.20 mg kg⁻¹), Cu (5.00 mg kg⁻¹), Sn (250.00 mg kg⁻¹) and Zn (5.00 mg kg⁻¹), therefore suitable for their determination in refreshment and soda samples.

Analytical application in powder refreshment samples

The developed analytical method for multi-elementary determination was applied to twenty powder refreshment samples. The obtained concentration values are presented in Table 4. Concentrations obtained for Al, As, Ba, Be, Bi, Cd, Co, Cr, Ni, Pb, Sn and Zn were below LOQ. For the other elements, the concentrations were between <0.1 $\mu\text{g g}^{-1}$ (V) and 1.42 \pm 0.02% (K). For Ca, K, Na, P and S higher concentration values were found, probably because these are essential elements and are present in samples as additives and preservatives in various types of foods, including fruit juice.^{22,25,36} For sodium, the R / orange sample was the only one presenting concentration below the LOQ, the other samples presented high concentrations of Na. The D / grape sample presented higher concentrations of Ca, Cu, K, P, Sr and S.

Concentrations found for Fe ranged between < 1.5 and 456 \pm 14 $\mu\text{g g}^{-1}$. These high contents of Fe are due to the addition, during the manufacturing process, as nutritional supplement, according to the nutritional information found on the powder refreshment package labels. The content of Fe (2.1 mg) *per* portion (6.0 g), informed on the label, was in agreement with the concentrations found for brands A / grape and B / strawberry. For brands E / tangerine, F / strawberry and G / mango, the concentrations of Fe were 2.6, 2.5 and 2.7 mg *per* portion (6.0 g), respectively, values higher than those informed on the label. The samples S / passion fruit and T / orange presented concentrations of Fe below those reported on the package. The other brands presented concentrations of Fe below the LOQ value, however, they were in agreement with the label of nutritional information, since they were non-enriched powder refreshment samples.

Table 3. Results obtained for analysis of CRM using the proposed analytical method and detection by ICP OES

CRM	Element	Certified value / ($\mu\text{g g}^{-1}$)	Found value / ($\mu\text{g g}^{-1}$)	Agreement / %	Element	Certified value / ($\mu\text{g g}^{-1}$)	Found value / ($\mu\text{g g}^{-1}$)	Agreement / %
NIST 1515	Al	284.5 ± 5.8	239 ± 25	84.0 ± 8.8	Mn	54.1 ± 1.1	44.4 ± 1.3	82.1 ± 2.4
	Ba	48.8 ± 2.3	46.9 ± 2.9	96.1 ± 5.9	Ni	0.936 ± 0.094	0.95 ± 0.02	101.5 ± 2.1
	Ca	15250 ± 100	14682 ± 300	96.3 ± 2.0	P	1593 ± 68	1423 ± 38.4	89.3 ± 2.4
	Fe	82.7 ± 2.6	95 ± 1.5	115 ± 1.8	S	(1800)	1883 ± 145	104.6 ± 8.0
	K	16080 ± 210	16676 ± 451	103.7 ± 2.8	Zn	12.45 ± 0.43	12.2 ± 0.7	98.0 ± 5.6
	Mg	2710 ± 120	2437 ± 53	89.9 ± 2.0				
NIST 1547	Al	248.9 ± 6.5	292 ± 60	117 ± 24	K	24330 ± 380	20120 ± 67	82.7 ± 0.3
	Ba	123.7 ± 5.5	107 ± 11	86.5 ± 8.9	Mg	4320 ± 150	4016 ± 287	93.0 ± 6.6
	Ca	15590 ± 160	13354 ± 38	85.6 ± 0.2	Mn	97.8 ± 1.8	84.8 ± 5.5	86.7 ± 5.6
	Cd	0.0261 ± 0.0022	< 0.2	n.d.	Ni	0.689 ± 0.095	0.64 ± 0.03	92.8 ± 4.3
	Cr	(1.00)	1.1 ± 0.01	110 ± 1.0	P	1371 ± 82	1304 ± 37	95.1 ± 2.7
	Cu	3.75 ± 0.37	3.18 ± 0.05	84.8 ± 1.3	S	(2000)	1830 ± 153	91.5 ± 7.6
	Fe	219.8 ± 6.8	204 ± 7.3	92.8 ± 3.3	Zn	17.97 ± 0.53	16.5 ± 0.7	91.8 ± 3.9
CRM-Agro C100-3a	As	19.0 ± 2.8	15.3 ± 0.04	80.5 ± 0.2	Mn	470 ± 69	408 ± 8.4	86.8 ± 1.8
	Cd	26.6 ± 2.1	28.2 ± 0.86	106.0 ± 3.2	Na	2710 ± 840	3071 ± 226	113 ± 8.3
	Cr	6.7 ± 1.5	6.25 ± 0.1	93.3 ± 1.5	Ni	3.16 ± 0.87	3.16 ± 0.18	100 ± 5.7
	Cu	1130 ± 140	1003 ± 32	88.8 ± 2.8	P	4370 ± 740	4779 ± 134	109.4 ± 3.0
	Fe	1120 ± 190	1041 ± 16	92.9 ± 1.4	Zn	37.5 ± 5.0	36.2 ± 1.5	96.5 ± 4.0
	Mg	4110 ± 360	3769 ± 120	91.7 ± 2.9				
NCS DC 73351	Al	(0.3%)	(0.220 ± 0.001)	73.3 ± 0.3	K	(1.66 ± 0.12)	(1.62 ± 0.02)	97.6 ± 1.2
	Ba	58 ± 6	54.6 ± 1.3	94.1 ± 2.2	Mg	(0.17 ± 0.02)	(0.16 ± 0.002)	94.1 ± 1.2
	Ca	0.43 ± 0.04%	0.400 ± 0.005%	93.0 ± 1.2	Mn	1240 ± 70	1096 ± 26	88.4 ± 2.1
	Cd	0.057 ± 0.010	< 0.2	n.d.	Ni	4.6 ± 0.5	4.10 ± 0.1	89.1 ± 2.2
	Cr	0.80 ± 0.03	0.78 ± 0.02	97.5 ± 2.5	P	2840 ± 90	2760 ± 77	97.2 ± 2.7
	Cu	17.3 ± 1.8	14.0 ± 0.1	81.0 ± 0.6	S	(0.245 ± 0.022)	(0.254 ± 0.002)	103.7 ± 0.8
	Fe	264 ± 15	238 ± 5.4	90.2 ± 2.0	Zn	26.3 ± 2.0	26.6 ± 0.6	101.1 ± 2.3

Results expressed as mean ± confidence interval at 95% (n = 3). Values between parentheses: informed value; NIST 1515: apple leaves; NIST 1547: peach leaves; CRM-Agro C1003a: tomato leaves; NCS DC 73351: tea; n.d.: not determined.

Table 4. Results of the concentrations of Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sr, Ti and V in powder refreshment samples by ICP OES

Sample	Ca / %	Cu / ($\mu\text{g g}^{-1}$)	Fe / ($\mu\text{g g}^{-1}$)	K / %	Mg / ($\mu\text{g g}^{-1}$)	Mn / ($\mu\text{g g}^{-1}$)	Na / %	P / %	S / %	Sr / ($\mu\text{g g}^{-1}$)	Ti / %	V / ($\mu\text{g g}^{-1}$)
A / grape	0.370 ± 0.003	0.63 ± 0.060	350 ± 6	0.053 ± 0.001	32.7 ± 1.8	2.76 ± 0.01	0.45 ± 0.02	0.170 ± 0.001	0.310 ± 0.002	1.87 ± 0.10	< 0.3 $\mu\text{g g}^{-1}$	< 0.1
B / strawberry	0.410 ± 0.011	0.65 ± 0.060	361 ± 19	0.042 ± 0.003	86.3 ± 1.0	1.50 ± 0.02	0.94 ± 0.05	0.230 ± 0.007	0.110 ± 0.004	7.80 ± 0.20	0.041 ± 0.001	0.33 ± 0.03
C / passion fruit	0.0980 ± 0.002	< 0.6	< 1.5	0.015 ± 0.001	170.0 ± 1.0	0.39 ± 0.01	0.39 ± 0.01	0.054 ± 0.001	0.050 ± 0.001	3.21 ± 0.10	0.400 ± 0.008	3.61 ± 0.02
D / grape	0.880 ± 0.007	2.86 ± 0.18	< 1.5	1.42 ± 0.02	91.9 ± 1.2	1.28 ± 0.02	0.27 ± 0.01	0.700 ± 0.007	0.410 ± 0.003	5.88 ± 0.40	0.033 ± 0.0003	0.240 ± 0.004
E / tangerine	0.730 ± 0.004	1.52 ± 0.09	440 ± 21	0.068 ± 0.001	445.0 ± 3.4	1.92 ± 0.04	0.49 ± 0.01	0.380 ± 0.001	0.100 ± 0.001	14.0 ± 0.10	0.064 ± 0.0003	0.500 ± 0.004
F / strawberry	0.720 ± 0.003	1.88 ± 0.21	428 ± 21	0.049 ± 0.001	176.0 ± 1.2	1.68 ± 0.06	0.89 ± 0.03	0.420 ± 0.004	0.110 ± 0.001	23.4 ± 0.40	0.091 ± 0.0021	0.77 ± 0.05
G / mango	0.570 ± 0.010	< 0.6	456 ± 14	0.037 ± 0.002	36.8 ± 1.4	4.73 ± 0.44	0.64 ± 0.04	< 2.7 $\mu\text{g g}^{-1}$	< 9.4 $\mu\text{g g}^{-1}$	< 0.4	0.210 ± 0.009	< 0.1
H / tangerine	0.0350 ± 0.001	< 0.6	< 1.5	0.021 ± 0.002	13.4 ± 0.9	< 0.1	0.49 ± 0.02	< 2.7 $\mu\text{g g}^{-1}$	< 9.4 $\mu\text{g g}^{-1}$	< 0.4	0.051 ± 0.001	< 0.1
I / pineapple	0.0750 ± 0.008	< 0.6	< 1.5	0.034 ± 0.003	14.2 ± 0.8	0.40 ± 0.04	0.81 ± 0.01	< 2.7 $\mu\text{g g}^{-1}$	< 9.4 $\mu\text{g g}^{-1}$	< 0.4	0.083 ± 0.003	< 0.1
J / pineapple	0.630 ± 0.024	< 0.6	< 1.5	0.033 ± 0.002	126.0 ± 6.9	0.61 ± 0.04	0.44 ± 0.02	< 2.7 $\mu\text{g g}^{-1}$	< 9.4 $\mu\text{g g}^{-1}$	< 0.4	0.200 ± 0.015	< 0.1
K / orange	0.480 ± 0.001	< 0.6	< 1.5	< 36 $\mu\text{g g}^{-1}$	140.0 ± 8.0	< 0.1	0.47 ± 0.01	0.210 ± 0.0004	0.180 ± 0.001	< 0.4	0.130 ± 0.007	< 0.1
L / orange with lemon	0.220 ± 0.001	< 0.6	< 1.5	0.042 ± 0.001	71.2 ± 1.1	< 0.1	0.10 ± 0.01	0.090 ± 0.001	0.072 ± 0.001	< 0.4	< 0.3 $\mu\text{g g}^{-1}$	< 0.1
M / pineapple	0.300 ± 0.002	< 0.6	< 1.5	< 36 $\mu\text{g g}^{-1}$	68.6 ± 5.0	< 0.1	0.22 ± 0.01	0.140 ± 0.0002	0.110 ± 0.004	< 0.4	0.042 ± 0.001	< 0.1
N / mango	0.350 ± 0.005	< 0.6	< 1.5	< 36 $\mu\text{g g}^{-1}$	33.2 ± 1.7	< 0.1	0.45 ± 0.02	0.140 ± 0.001	0.150 ± 0.009	< 0.4	0.150 ± 0.003	< 0.1
O / lemon	0.320 ± 0.024	< 0.6	< 1.5	< 36 $\mu\text{g g}^{-1}$	122.0 ± 4.9	< 0.1	0.16 ± 0.02	0.180 ± 0.011	0.130 ± 0.007	< 0.4	< 0.3 $\mu\text{g g}^{-1}$	< 0.1
P / strawberry	0.240 ± 0.004	< 0.6	< 1.5	< 36 $\mu\text{g g}^{-1}$	58.8 ± 1.6	< 0.1	0.20 ± 0.01	0.120 ± 0.005	0.070 ± 0.006	< 0.4	0.015 ± 0.001	< 0.1
Q / tangerine	0.250 ± 0.004	< 0.6	< 1.5	0.030 ± 0.003	46.5 ± 0.9	< 0.1	0.10 ± 0.01	0.140 ± 0.008	0.083 ± 0.0004	< 0.4	0.032 ± 0.002	< 0.1
R / orange	0.250 ± 0.007	< 0.6	< 1.5	0.350 ± 0.002	104.0 ± 1.0	< 0.1	< 3.8 $\mu\text{g g}^{-1}$	0.140 ± 0.002	0.120 ± 0.001	< 0.4	0.045 ± 0.002	< 0.1
S / passion fruit	0.150 ± 0.007	< 0.6	138 ± 2	< 36 $\mu\text{g g}^{-1}$	16.0 ± 1.6	< 0.1	0.15 ± 0.01	0.061 ± 0.003	0.100 ± 0.002	< 0.4	0.030 ± 0.003	< 0.1
T / orange	0.190 ± 0.008	< 0.6	208 ± 12	< 36 $\mu\text{g g}^{-1}$	53.2 ± 2.9	< 0.1	0.12 ± 0.01	0.083 ± 0.004	0.110 ± 0.004	< 0.4	0.050 ± 0.002	< 0.1
Minimum	0.0350	< 0.6	< 1.5	< 36	13.4	< 0.1	< 3.8	< 2.7	< 9.4	< 0.4	< 0.3	< 0.1
Maximum	0.880	2.86	456	1.42	445	4.73	0.94	0.700	0.410	23.4	0.400	3.61
Number of samples	20	05	07	13	20	10	19	16	16	06	17	05
Average	0.363	1.51	340	0.169	95.3	1.70	0.41	0.204	0.138	9.36	0.098	1.09
Standard deviation	0.231	0.83	113	0.371	93.7	1.30	0.26	0.162	0.091	7.38	0.095	1.27
^a ANVISA / ($\mu\text{g g}^{-1}$)	n.d.	5.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

^aRecommended values by ANVISA, Resolution No. 55,871, 1965, March 26.¹² Results expressed as average ± standard deviation (SD, n = 3). n.d.: not determined.

For Cu, it was found concentrations in the following samples: A / grape, B / strawberry, D / grape, E / tangerine and F / strawberry; probably due to the manufacturing process. The other samples presented concentrations below the LOQ. High concentrations were obtained for Ti, ranging between $< 0.3 \mu\text{g g}^{-1}$ and $0.400 \pm 0.008\%$, with an average of 0.098% and standard deviation (SD) of 0.095% ($n = 17$) in the samples. The sample C / passion fruit presented higher concentration of Ti. Only for A / grape, L / orange with lemon and O / lemon samples the concentrations were below LOQ. Titanium dioxide (TiO_2) is added to several food samples as a whitening agent,³² so it is not surprising the contents found in the powder refreshment analyzed in this work.

The results of the average concentrations for the chemical elements in powder refreshment samples, in ascending order, are as following: Na (0.41%) > Ca (0.363%) > P (0.204%) > K (0.169%) > S (0.138%) > Ti (0.098%) > Fe ($340 \mu\text{g g}^{-1}$) > Mg ($95.3 \mu\text{g g}^{-1}$) > Sr ($9.36 \mu\text{g g}^{-1}$) > Mn ($1.70 \mu\text{g g}^{-1}$) > Cu ($1.51 \mu\text{g g}^{-1}$) > V ($1.09 \mu\text{g g}^{-1}$). According to limits established by ANVISA (Decree No. 55.871, March 26, 1965)¹² for As (0.20 mg kg^{-1}), Cd (0.20 mg kg^{-1}), Cu (5.00 mg kg^{-1}), Sn ($250.00 \text{ mg kg}^{-1}$) and Zn (5.00 mg kg^{-1}), all analyzed samples were suitable for consumption, as the values for these chemical elements were below the LOQ of the analytical method (Cd: 0.20 mg kg^{-1} ; Cu: 0.60 mg kg^{-1} ; Sn: 2.4 mg kg^{-1} ; Zn: 0.80 mg kg^{-1}), except for As whose quantifying concentration of the analytical method was higher than 3.0 mg kg^{-1} .

Conclusions

In this work, an analytical method for Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sn, Sr, Ti, V and Zn determination was developed and described. Good efficiency, precision and accuracy were achieved for the multi-elementary determinations in twenty powder refreshment samples by ICP OES.

Chemometric tool, a 2^{5-1} fractional factorial design, was applied to optimize the conditions of the sample treatment procedure and the use of HF, in addition to HNO_3 and H_2O_2 , was required to promote the complete dissolution of Al, Ca, Mg and Ti oxides, allowing the determination of the total content of these elements, especially Ti, present in high concentration since it is used as whitening agent. Operational parameters of the ICP OES instrument, nebulization gas flow rate (NGF) and radiofrequency power (RFP), were also optimized through Doehlert design.

Concentrations of Al, As, Ba, Be, Bi, Cd, Co, Cr, Ni, Pb, Sn and Zn in refreshment samples were below

LOQ of the analytical method. High concentrations of Ca, K, Na, P and S were found since these are essential elements and are added as additives and preservatives. Because of the nutritional value, Fe concentration is added to foods and it was found in high concentrations in five powder refreshment samples. In this work, the order of concentration values found for chemical elements in powder refreshment samples were as following: Na > Ca > P > K > S > Ti > Fe > Mg > Sr > Mn > Cu > V.

In all analyzed samples, the content of the chemical elements was in compliance with Brazilian legislation (ANVISA, Decree No. 55.871, March 26, 1965), which establishes maximum permissible levels for Cd, Cu, Sn and Zn in powder refreshment samples.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

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Author Contributions

Samir H. Santos was responsible for the conceptualization, formal analysis, investigation, methodology, validation, and writing original draft; Silvanio S. L. Costa for the conceptualization, formal analysis, methodology and validation; Sidnei O. Souza for the methodology, validation and software; Karina S. Garcia for methodology and supervision; Sarah A. R. Soares for the methodology, supervision, and writing original draft; Carlos A. B. Garcia for the methodology and supervision; Tarcísio S. Almeida for the supervision, writing review and editing; Rennan G. O. Araujo for the writing review and editing, supervision and project administration.

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