Exploratory analysis and inductively coupled plasma optical emission spectrometry (ICP OES) applied in the determination of metals in soft drinks

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ABSTRACT

A 2^3 factorial design and a CCD (Central Composite Design) were employed to optimize the operational conditions for determining Al, Ba, Ca, Cd, Cr, Cu, K, Mg, Na, Ni, Pb, Sn and Zn in soft drink samples by inductively coupled plasma optical emission spectrometry (ICP OES). Satisfactory parameters of merit were obtained (Plasma stability, linearity, SBR, BEC, LOD and LOQ). The accuracy was evaluated by means of a recovery study. Thirty five soft drink samples were analyzed. The results obtained were used in an exploratory analysis, in which principal component analysis and cluster analysis were applied in order to differentiate the several soft drink classes. Adequate LOQ values were obtained for all elements (0.34 µg L^{-1} for Ca to 88.7 µg L^{-1} for Mg) and the recovery study results ranged between 80 and 100%. Cluster analysis revealed four sample classes characterized by flavor and other characteristics, such as being light, diet, low calorie or regular beverages. A model with 4 PCs was obtained by means of a principal component analysis, which explained 99.8% of the total variance.

1. Introduction

Although soft drinks do not contain much nutritional value, they are widely consumed all over the world due to the diversity of flavors and also because of their diet, light and low calorie versions [1]. News soft drink brands are becoming available in the market, which represents a potential risk, since several products inappropriate for consumption may be inserted into the popular diet. There is a large variety of potential contaminants in soft drinks (Al, As, Cd, Cr, Cu, Hg, Pb, Se and others). Therefore, the mineral composition of such beverages should be investigated.

Some analytical techniques have been used to determine the mineral composition of soft drinks. Castro et al. [2] used a factorial design in the optimization of the preconcentration procedure to determine copper by flame atomic absorption spectrometry (FAAS). They obtained a detection limit of 3.9 µg L^{-1} and a relative standard deviation of 1.8%. Graphite furnace atomic absorption spectrometry (GF AAS) was employed by Seruga et al. [3] to determine Al in soft drink samples that had been stored for 12 months. They verified that the aluminum concentration had increased during the storage time. The same method was used by Garcia et al to determine chromium in soft-drink samples pretreated with HNO_3 and V_2O_5 [4]. Chromium concentration levels in the samples ranged between 3.60 and 60.5 µg L^{-1}. López et al. [5] applied GF AAS to

determine Al in soft drinks. Concentration levels in the samples analyzed ranged from 44.6 to 1053.3 µg L^{-1}. Amorin et al. [6] also used GF AAS in a comparative study between conventional and multivariate methods for aluminum determination in soft drinks. The limits of detection obtained for the conventional and multivariate methods were 17.9 µg L^{-1} and 11.3 µg L^{-1}, respectively, and the recovery results were close to 100%.

Inductively coupled plasma optical emission spectrometry (ICP OES) has proved to be a rapid and accurate technique for mineral composition analysis [7]. The great amount of data obtained by this technique can be evaluated by exploratory analysis methods, such as hierarchical cluster analysis (HCA) and principal component analysis (PCA). This allows sample distinction, as well as identification of the factor of distinction [8,9]. Ferreira et al. [7] used ICP OES to determine Ca, Cu, K, Mg, Na, P and S in grape juice and soft drinks. The experimental results were evaluated by exploratory analysis methods (HCA and PCA), which allowed the discrimination between grape and soft drink samples. Theses same methods (HCA and PCA) were used by Zucchi et al. [10] to evaluate data obtained in the analysis of soft drinks and bottles by synchrotron radiation total reflection X-ray fluorescence spectrometry (SRTXRF). They verified similarity between the samples according to the flavor, regardless of the brand. This work proposes to determine the mineral composition of soft drinks with different characteristics (brand, flavor and the fact of being light, diet, low calorie or regular) and evaluate the data obtained employing exploratory analysis for a better interpretation of the results.

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2. Experimental

2.1. Apparatus

Measurements were performed using an inductively coupled plasma optical emission spectrometer model Optima™ 2000 DV ICP-OES (Dual View, PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) with axial (AX-ICP-OES) and radial configurations (RD-ICP-OES). The radio frequency source (40 MHz) provided a power of 0.75–1.5 kW. A 79 lines nm-1 echelle grating was used, as well as a solid-state detector, a cross-flow nebulizer coupled with a double-pass Scott-type spray chamber and an interface shear gas. The sample introduction system was automated using a 90 Plus autosampler (PerkinElmer). The remaining operational conditions are shown in Table 1, along with the elements studied and the respective wavelengths used.

2.2. Reagents, solutions and samples

Reference solutions, 1000 mg L^{-1}, of Al, Ba, Ca, Cd, Cr, Cu, K, Mg, Na, Ni, Pb, Sn and Zn with a high degree of analytical purity (ICP Standard, Merck Certipur®) were used in this study. A multi-element solution containing 100 mg L^{-1} of the above-mentioned elements in 2% (v/v) HNO$_3$ (VETEC 70% analytical reagent) was previously prepared and used to obtain the calibration curves (aqueous calibration curve and matrix matching calibration curve with 0.05, 0.5, 2.0 and 5.0 mg L^{-1} of elements). Water deionized through a MILLI-Q system (Millipore, Bedford, MA) was used to prepare all solutions.

The thirty five soft drink samples were purchased from stores located in the state of Minas Gerais, Brazil. The soft drink samples were degasified in an ultrasonic bath (Branson 3210, Danbury, USA) for 40 min and diluted 1:1 with HNO$_3$ 2% (v/v). A 1:14 dilution of some samples was necessary for Na and K analysis. Table 2 contains the description of the soft drink samples.

2.3. Multivariate optimization

The simultaneous effect over plasma robustness caused by variables nebulization gas flow rate, sample flow rate and applied power was evaluated by means of a 2^3 factorial design. After identifying the variables that were significant for the experiment (2^3 factorial design) a central composite design (CCD) was used to determine the critical levels of these variables [11]. The Mg II/Mg I ratio was the robustness criterion [12–13] and it was used as response for both optimization designs. The intensity lines of ionic Mg (II) and atomic Mg (I) were measured in soft drink diluted 1:1 in HNO$_3$ 2% (v/v) spiked with 2.0 mg L^{-1} of Mg. Table 3 presents the factors and levels used in the 2^3 factorial design, as well as the CCD developed using the software Statistica [14].

Table 1
Operational conditions of the ICP OES.

Parameter	
Applied power (kW)	1.1–1.4
Nebulization gas flow rate (L min^{-1})	0.4–1.1
Auxiliary gas flow rate (L min^{-1})	0.2
Plasma gás flow rate (L min^{-1})	15
Sample gas flow rate (mL min^{-1})	1.0–1.5
Injector tube diameter (mm)	2.0
View	Axial
Interface	Shear gas
Element (λ/nm)	Al 396.152; Ba 455.403;
	Ca 317.933; Cu 324.754;
	Fe 239.562; K 766.490;
	Mg 280.270; Mg 285.213;
	Mn 257.610; Na 589.592;
	Ni 221.647; Pb 220.353

Table 2
Descriptions of the soft drink samples.

	Name	Brand	Description		Name	Brand	Description
1	Le.A.l	A	Lemon light	19	Gu.P.1.n	P	Guaraná regular
2	Le.B.n	B	Lemon regular	20	Gu.P.2.n	P	Guaraná regular
3	Le.B.l	B	Lemon light	21	Mt.Q.1.n	Q	Mate regular
4	Le.C.n	C	Lemon regular	22	Mt.Q.2.n	Q	Mate regular
5	Le.D.n	D	Lemon regular	23	Mt.Q.d	Q	Mate diet
6	Or.E.lc	E	Orange low calorie	24	Cl.R.1.n	R	Cola regular
7	Or.E.l	E	Orange light	25	Cl.R.2.n	R	Cola regular
8	Or.E.n	E	Orange regular	26	Cl.S.n	S	Cola regular
9	Or.F.n	F	Orange regular	27	Cl.S.l	S	Cola light
10	Or.G.lc	G	Orange row calorie	28	Cl.T.1.n	T	Cola regular
11	Or.H.n	H	Orange regular	29	Cl.T.2.n	T	Cola regular
12	Or.I.n	I	Orange regular	30	Gr.U.n	U	Grape regular
13	Gu.J.lc	J	Guaraná low calorie	31	Gr.V.lc	V	Grape row calorie
14	Gu.K.lc	K	Guaraná low calorie	32	Gr.G.1.n	G	Grape regular
15	Gu.L.lc	L	Guaraná low calorie	33	Gr.G.2.n	G	Grape regular
16	Gu.M.l	M	Guaraná light	34	Gr.X.n	X	Grape regular
17	Gu.M.n	M	Guaraná regular	35	Ap.Z.n	Z	Apple regular
18	Gu.O.n	O	Guaraná regular		––		

2.4. Parameters of merit

2.4.1. Plasma stability

Plasma stability was evaluated by employing short and long term stability tests of the Mg II emission line at 280.265 nm with subsequent evaluation of relative standard deviation (R.S.D). A 1:1 soft drink solution in HNO$_3$ 2% (v/v) spiked with 2.0 mg L^{-1} of Mg was employed. For the short term stability test, 15 consecutive measurements of the Mg intensity line were made. As for the long term test, the emission line was monitored for a period of 2 h, in which measurements were accomplished every 15 min in a total of 8 measurements. These experiments were carried out employing previously established robust conditions.

2.4.2. Linearity and matrix effect

Linearity and a possible matrix effect were verified by means of an aqueous and a matrix matching calibration curve ($n = 3$ for both), constructed with Al, Ba, Cu, Mg, Fe, Na, K, Ca, Pb, Mn and Ni concentrations ranging from 0.05 to 5.0 mg L^{-1}. The slopes obtained for each of the curves were evaluated by statistical tests to verify the presence or not of significant matrix effect.

Table 3
Factors and levels used in the 2^3 factorial design and in the CCD.

Measurement	Nebulization gas flow rate (L min^{-1})		Applied power (kW)		Sample flow rate (mL min^{-1})	
	2^3 factorial	CCD	2^3 factorial	CCD	2^3 factorial	CCD
1	0.4	0.4	1100	1170	1.0	0.8
2	1.1	0.4	1100	1170	1.0	1.2
3	0.4	0.4	1100	1430	1.5	0.8
4	1.1	0.4	1100	1430	1.5	1.2
5	0.4	0.8	1500	1170	1.0	0.8
6	1.1	0.8	1500	1170	1.0	1.2
7	0.4	0.8	1500	1430	1.5	0.8
8	1.1	0.8	1500	1430	1.5	1.2
9	–	0.3	–	1300	–	1.0
10	–	0.9	–	1300	–	1.0
11	–	0.6	–	1081	–	1.0
12	–	0.6	–	1519	–	1.0
13	–	0.6	–	1300	–	0.7
14	–	0.6	–	1300	–	1.3
15*	–	0.6	–	1300	–	1.0
16*	–	0.6	–	1300	–	1.0
17*	–	0.6	–	1300	–	1.0
18*	–	0.6	–	1300	–	1.0
19*	–	0.6	–	1300	–	1.0

*Central point.