



A novel, rapid and simple acid extraction for multielemental determination in chocolate bars



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ABSTRACT

A novel and simple method based on acid extraction was developed for the determination of Ca, Na, K, P, Mg, Cu, Mn and Zn in chocolate bars by inductively coupled plasma techniques, ICP OES and ICP-MS. The parameters time, temperature and nitric acid concentration were studied in multivariate form using a certified chocolate material. In the optimized conditions 20 mL of 1.4 mol L⁻¹ HNO₃, a temperature of 100 °C and 6 min of extraction were selected. Certified chocolate reference material was analyzed and the results were in agreement with certified concentrations (recoveries between 98% and 107%). In addition, the results obtained by analyzing six different chocolate samples with different cocoa contents (ranging between 28% and 85%) by the proposed method were compared with those obtained by microwave-assisted acid digestion. Recoveries were in the range of 90–110%. The proposed acid extraction was successfully applied to sixteen chocolate samples and the results indicated that concentrations of K, Mg, P, Cu, Mn and Zn increase with the cocoa content and an opposite effect was observed for Na and Ca. The proposed method is a good alternative to conventional acid digestion procedure and can be applied to routine analysis of major and minor constituents in chocolate bars.

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1. Introduction

Chocolate is a food product largely consumed due to its flavor, texture and eating pleasure. Its main components come from fermented, crushed, and roasted cocoa beans, the seeds of the tropical *Theobroma Cacao L* tree [1].

Primarily, chocolates can be classified as white, milk and dark, depending mainly on the amounts of cocoa mass, cocoa butter and milk added in manufacturing process. Within these types, dark chocolate has the largest amount of cocoa mass and the smallest amount of added fats. On the other hand, milk and white chocolates contain higher amounts of milk and cocoa butter than dark chocolates; their components are similar to each other but white chocolate has no cocoa mass in its composition [2,3].

Although there are relatively high levels of sugar and fat, several publications have suggested that consumption of chocolates and other cocoa derivatives may have positive health implications, contributing to reduction of cancer risk, cardiovascular disease, hypertension, arterial disease and diabetes, and some of these benefits are attributed to the antioxidant activity of the high levels of flavonoids and polyphenols [1,4–9]. In addition, cocoa beans contain several minerals and many of them can remain in their processed derivative products. In this way, chocolates can be an important source of some essential elements such as Fe, K, Mg, Ca, Zn and Mn [10–12]. However, some studies

showed that potentially toxic elements can also be found, mainly in dark chocolates [13–17].

Taking into account that children are large consumers of chocolate, the development of efficient analytical methods for controlling major and minor inorganic constituents is an important task and, at the same time, an analytical challenge due to the complexity of the matrix (large amounts of organic matter, including macromolecules and a lipid content ranging between 28% and 31%) [1,2].

The literature reports procedures for chocolate sample treatment involving principally dry ashing, wet and microwave-assisted acid digestion prior the use of atomic absorption spectrometry or inductively coupled plasma based techniques [13–18]. However, these procedures require the use of large amounts of pure reagents, generate hazardous residues, are time-consuming in the overall analytical procedure and can be expensive (microwave digestion systems) [19]. Currently, there is no alternative procedure to conventional acid digestion available for simultaneous determination of inorganic constituents in chocolate bars; however, some methods based on atomic absorption spectrometry after emulsification or slurry sampling have been reported.

Leggieri et al. proposed emulsification-based methods for the determination of Na, K, Ca, Mn, Zn and Fe by flame atomic absorption spectrometry (FAAS) [12], and to determine Cu, Mn and Al by graphite furnace atomic absorption spectrometry (GFAAS) [20]. In addition, Karadjova et al. proposed a slurry sampling method for determination of Cd, Co, Cr, Cu, Fe, Ni and Pb by GFAAS [21]. Even though these alternative methods provide a rapid procedure for sample treatment, since the digestion of the sample matrix is not necessary, drawbacks can arise

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from lower stability, instrument calibration, inhomogeneity, clogging of the nebulizer, use of organic reagents and the high amounts of organic matter.

On the other hand, a preconcentration procedure using cloud point extraction for the determination of Cu and Zn in powdered chocolate by FAAS was proposed by Ferreira et al. [22]. However, the cloud point extraction requires the analyte in solution and chocolate samples would have to be digested before separation.

Based on these difficulties and considering that inductively coupled plasma techniques (ICP OES and ICP-MS) have become the choice for rapid multielemental determinations, a novel and simple analytical method based on rapid acid extraction was developed and optimized using a multivariate procedure. This was then applied for the determination of Ca, Na, K, P and Mg by ICP OES and Cu, Zn and Mn by ICP-MS in chocolate bars.

2. Materials and methods

2.1. Instrumentation

The measurements of the major elements (Na, K, Mg, Ca and P) were carried out using an inductively coupled plasma optical emission spectrometer (ICP OES) model Optima 8300 DV (Perkin Elmer, Norwalk, CT), equipped with a peristaltic pump, a concentric nebulizer and a quartz demountable plasma torch. The equipment was operated in radial configuration for Na and K, and in axial configuration for P, Mg, and Ca. The operational parameters used for the analytical measurements were: radio frequency power of 1300 W, sample flow rate of 1 mL min⁻¹, plasma argon flow rate of 15 L min⁻¹, nebulization flow rate of 0.6 L min⁻¹ and auxiliary argon flow rate of 1.5 L min⁻¹. The selected wavelengths (nm) used for each element were: 285.213 (Mg), 178.221 (P), 589.590 (Na), 317.933 (Ca) and 766.474 (K).

The minor element determinations (Cu, Zn and Mn) were carried out using an inductively coupled plasma quadrupole mass spectrometer (ICP-MS) instrument, model 7700x (Agilent, Hachioji, Japan), equipped with octopole reaction system (ORS³). The analyses were made using no gas (without He gas) and high energy helium – HEHe (He gas flow rate 10 mL min⁻¹) conditions and the better recovery values were obtained in the presence of He gas. The helium gas flow rate (10 mL min⁻¹) introduced through ORS³ was used to overcome possible spectral interferences (³⁹K¹⁶O⁺ for ⁵⁵Mn⁺, ⁴⁰Ar²⁵Mg⁺ for ⁶⁵Cu⁺ and ⁴⁰Ar²⁶Mg⁺ for ⁶⁶Zn⁺), considering the content of chocolate matrix. The sample introduction system was composed of a concentric Seaspray nebulizer (nebulization flow rate aspiration 0.4 mL min⁻¹) coupled to a Scott-type spray chamber and an interface consisting of Ni sampler and skimmer cones. Radio frequency applied power was 1550 W, while central plasma, auxiliary and nebulizer gas flow rates were 15, 1.1 and 0.9 L min⁻¹, respectively. Measurements were performed using 0.5 ms as dwell time and three points per peak and the sampling depth used was 8 mm. The ⁷²Ge⁺ isotope (12.5 µg L⁻¹) was

used as internal standard to compensate for matrix effects, and the isotopes monitored were ⁵⁵Mn⁺, ⁶⁵Cu⁺, and ⁶⁶Zn⁺. Liquid argon and He gases (99.996% pure, White Martins, São Paulo, Brazil) were used for all plasma measurements.

2.2. Reagents, standards and certified materials

Analytical-grade reagents and deionized water (Milli-Q system, 18.2 MΩ cm, Millipore, Bedford, MA) were used to prepare all solutions and standards. The glass and quartz materials were soaked in 10% v v⁻¹ HNO₃ solution for 24 h, washed with deionized water and dried before use. The analyte solutions used for external calibration were prepared from 1000 mg L⁻¹ and 4000 mg L⁻¹ standard solutions (Merck, Darmstadt, Germany). Appropriate dilutions were made from the standard solutions and these solutions were stored in polyethylene flasks under refrigeration.

A certified reference material of baking chocolate (NIST 2384) from the National Institute of Standards and Technology – NIST (Gaithersburg, MD) was used to verify the accuracy of the proposed method.

Sixteen chocolate samples from different brands and types (labeled by the manufacturers as white, milk and dark chocolate), and six chocolate samples from the same brand with different cocoa contents (ranging between 28% and 85%) were analyzed in this study. They were purchased in the local markets in Campinas, State of São Paulo, Brazil in the January–March 2014 period.

2.3. Study of acid extraction

A 2³ factorial design with a central point was used with the aim to study the following variables: temperature (60, 80 and 100 °C), time (3, 6 and 9 min) and nitric acid concentration (0.3, 0.85 and 1.4 mol L⁻¹). The response for this experimental design (overall response, OR) was obtained by evaluating the recovery percentages for the elements from certified reference material of baking chocolate. The OR is given by the following expression:

$$OR = [R(X1)/LR(X1) + R(X2)/LR(X2) + \dots + R(Xn)/LR(Xn)] \quad (1)$$

where $R(Xn)$ is the recovery of an element in a particular experiment and $LR(Xn)$ is the largest recovery in the set of experiments for that element [23,24]. All experiments were carried out in a random sequence, and the statistically significant effects were studied using the Minitab 17.1 (Minitab Inc., State College, PA) software.

In the optimized conditions, certified reference material and chocolate bars were scratched (using a ceramic knife) and scraps were accurately weighed (300 mg) into a 50 mL beaker. After that 20 mL of 1.4 mol L⁻¹ HNO₃ (approximately 100 °C) was added. Magnetic stirring (300 rpm) was maintained for 6 min at 100 °C. Then, the sample was cooled down to room temperature in a water bath before transferring

Table 1
Overall response (OR) for different extraction conditions of 2³ experimental design.

Experiment	T	t	A	Recovery (%)								
	(°C)	(min)	(mol L ⁻¹)	Ca	Na	K	P	Mg	Cu	Mn	Zn	OR
1	60	3	0.3	89	21	91	75	90	91	80	98	6.03
2	100	3	0.3	103	23	97	81	101	93	83	103	6.49
3	60	9	0.3	90	28	93	77	93	92	82	99	6.21
4	100	9	0.3	106	45	104	92	107	102	94	104	7.17
5	60	3	1.4	92	63	94	80	99	92	91	100	6.77
6	100	3	1.4	109	96	108	94	108	94	103	104	7.77
7	60	9	1.4	94	72	92	78	98	89	87	99	6.74
8	100	9	1.4	106	103	102	101	106	99	99	102	7.80
9	80	6	0.85	100	45	96	80	105	89	85	102	6.68
10	80	6	0.85	104	41	99	81	106	97	88	103	6.83
11	80	6	0.85	98	39	94	79	103	95	90	105	6.69

T, temperature; t, time and A, nitric acid concentration.

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