

Can Minerals Be Used as a Tool to Classify Cinnamon Samples? †

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Abstract: Cinnamon (*Cinnamomum zeylanicum*) is a spice largely consumed worldwide, but there is still restricted information about its fingerprint. This work aimed to investigate the mineral composition as a possible marker for the classification of cinnamon samples. To this aim, the mineral composition (P, S, Mg, Ca, K, Cu, Zn, B, Fe, Al, Mn, and Si contents) of 56 ground cinnamon samples from different regions of the State of São Paulo, Brazil was determined by inductively coupled plasma optical emission spectroscopy (ICP OES). Principal component analysis was exploited for sample classification, and the microelements presented the best correlation: PC1, PC2, and PC3 explained 93% of the observed variance at 95% confidence level. Si, Al, Fe, and Cu presented the most significant contribution to cluster analysis. Samples were classified into 6 groups, in which those presenting *C. zeylanicum* were well clustered, and the samples acquired in bulk as well as those whose labels declared traces of grains and/or spices presented the highest variability. Thus, it was pioneering demonstrated the possibility to identify *C. zeylanicum* in commercial cinnamon powders, using microelements as authenticity markers.

Keywords: food authenticity; microelements; macroelements; chemical targets; spices; foodstuff classification

1. Introduction

Cinnamon (*Cinnamomum zeylanicum*) is a spice originally from Asia, largely used worldwide for feeding and medicinal aims [1]. It presents a rich volatile composition, including bioactive compounds, such as cinnamic acid, cinnamate, and cinnamaldehyde [1,2]. Furthermore, benefits for human health, such as prevention of metabolic syndrome, insulin resistance, and reduction in lipids levels have been evidenced [3].

Spices are one of the most frequent and vulnerable foods to fraud worldwide [4]. The rising prices of cinnamon and the complexity of its production chain contribute to explain this vulnerability [4–6]. A typical fraud involves mislabeling with other lower-cost products with a similar composition, such as *Cinnamomum cassia*.

Food authenticity is important to protect the consumers, the food chains, and to mitigate food fraud [7]. Several strategies may be exploited to recognize standards for authentic foods, frequently involving instrumental techniques associated to chemometrics aiming at recognition of standards for

authentic and non-authentic food based on non-targeted (e.g., Infrared and Raman spectroscopy) or targeted (e.g., chromatography and DNA-based approaches) strategies [7,8].

Mineral composition has been used as a marker of food origin (*terroir*) and traceability of the geographic origin of foods, such as white tea [9], Spanish virgin olive oils [10], and yerba mate [11] were demonstrated. Moreover, the mineral composition determined by different spectroscopic techniques has been exploited to discriminate authentic and non-authentic food, such as ethnical foods [12], honey [13], and organic sugarcane juice [14].

In this context, the aim of this work was to evaluate the feasibility of mineral composition as a possible authenticity marker for classifying cinnamon samples commercialized in Brazil. To this aim, 12 elements (P, S, Mg, Ca, K, Cu, Zn, B, Fe, Al, Mn, and Si) were investigated as targets, also considering their importance for human nutrition. The analytical procedure was based on microwave-assisted acid digestion and elemental determination by inductively coupled plasma optical emission spectroscopy (ICP OES). Principal component analysis was exploited for sample classification.

2. Materials and Methods

2.1. Material

Samples of ground cinnamon ($n = 56$) were acquired in 15 different supermarkets of 4 different regions of the State of Sao Paulo, Brazil. From these 56 samples, 8 were acquired in bulk and 48 were from different brands and product batches. Samples were identified and stored under refrigeration until the digestion for mineral determination.

2.2. Methods

2.2.1. Sample Preparation

Samples were ground by using a cryogenic mill (Freezer Mill 6870, SPEX, USA) under the condition: 5 min of freezing followed by 5 cycles of 2 min of grinding (at 30 cps) intercalated with 1 min of freezing, in order to achieve a particle size lower than 100 μm . For microwave-assisted acid digestion (ETHOS 1600, Milestone, Italy), 500 mg of each ground sample was transferred to Teflon flasks and 6.0 mL of 2.0 mol L⁻¹ HNO₃ plus 2.0 mL of 30% *v/v* H₂O₂ were added. The heating program involved 6 steps (1.3 min/120 °C (ramp); 2. 2 min at 120 °C; 3. 3 min/160 °C (ramp); 4. 2 min at 160 °C; 5.5 min/220 °C (ramp) and 6. 20 min at 220 °C). After the digestion, the volume was adjusted to 25 mL with water.

2.2.2. Mineral Determination

The mineral content of the samples was determined by ICP OES (iCAP 7400, Thermo, Waltham, MA, USA), under optimized conditions: radio-frequency power: 1.2 kW; plasma gas flow rate: 12.0 L min⁻¹; nebulizer gas flow rate: 0.60 L min⁻¹; sample aspiration rate: 1.5 mL min⁻¹. The analyte concentrations were determined by external calibration. A certified reference material (CRM) with a similar composition to the samples (NIST SRM 1515—Apple leaves, Gaithersburg, USA) was used to evaluate the accuracy of the procedure. The limits of detection (LOD) and quantification (LOQ) were determined according to the Equations (1) and (2), respectively.

$$\text{LOD} = 3.3 * (\text{sdb}/\text{m}) \quad (1)$$

$$\text{LOQ} = 3 * \text{LOD} \quad (2)$$

In which sdb = standard deviation of 10 blank measurements; m = calibration curve slope for each element.

2.2.3. Sample Classification

Principal component analysis (PCA) by the software The Unscrambler X (version 10.4, CAMO Software, Norway, 2016) was exploited to evaluate the sample clustering. Data treatment was based on total composition of minerals in the samples and carried out at the 95% confidence level, also considering the identification of outliers.

3. Results and Discussion

3.1. General Information about Cinnamon Samples

Samples were first separated in 6 groups, considering the labelled information. Samples in group (A, $n = 9$) are declared to contain gluten; samples in group (B, $n = 17$) and (C, $n = 10$) declared being originated of *Cinnamomum zeylanicum*, but only samples in set (C) were specified to be originated in Sri Lanka; (D, $n = 8$) corresponded to samples bought in bulk; (E, $n = 8$) corresponded to “Chinese cinnamon” (*Cinnamomum cassia*); and (F, $n = 4$) corresponded to ground cinnamon that declared to contain traces of celery, mustard, and/or other spices. The prices of the samples varied from US\$ 0.02/g to US\$ 0.14/g.

3.2. Mineral Composition and Sample Classification

Both microwave-assisted acid digestion and ICP OES are well established for elemental determination in food samples [15]. In addition, coefficient of variations lower than 8% and the agreement of the determined mass fractions with the certified values are indicative of the good precision and accuracy for mineral determination in the samples. Ca, Mg, P, K, S, Fe, Al, and Si were determined in radial axial viewed configuration, while the microelements (Cu, Zn, B, and Mn) were determined by axial viewed configuration. The mass fractions are presented in Table 1.

Table 1. Mineral mass fractions (mg kg⁻¹) of cinnamon powder samples acquired in the Brazilian market. Mean values and uncertainties from triplicate measurements.

Element (Spectral Line)	Minimum Found	Maximum Found	NIST 1515 Found	NIST 1515 Certified Values	LOD	LOQ
P (213.618 nm)	5.19 ± 0.08	1223 ± 22	1583 ± 2	1610 ± 20	0.03	0.08
S (182.034 nm)	7.59 ± 0.06	1681 ± 16	1078 ± 6	N.A.	0.05	0.14
Mg (280.270 nm)	479 ± 2	1352 ± 17	2835 ± 8	2710 ± 80	0.06	0.18
Ca (422.673 nm)	5300 ± 30	13225 ± 49	13720 ± 93	15,260 ± 150	0.34	1.01
K (766.490 nm)	3877 ± 27	7183 ± 74	14,075 ± 175	16,100 ± 100	0.32	0.95
Cu (324.754 nm)	2.55 ± 0.03	10.5 ± 0.1	5.50 ± 0.07	5.6 ± 0.2	0.04	0.12
Zn (213.856 nm)	5.4 ± 0.1	24 ± 1	12 ± 1	12.5 ± 0.3	0.04	0.11
B (249.773 nm)	9.34 ± 0.04	17 ± 1	31.50 ± 0.06	27 ± 2	0.02	0.06
Fe (259.940 nm)	18.0 ± 0.5	1994 ± 49	61.6 ± 0.6	83 ± 5	0.01	0.04
Al (396.152 nm)	28.4 ± 0.4	2142 ± 13	295.87 ± 16.91	286 ± 9	0.10	0.30
Mn (257.610 nm)	137.9 ± 0.3	367 ± 2	56.11 ± 0.03	54 ± 3	0.0002	0.0006
Si (251.611 nm)	40.4 ± 0.9	2743 ± 52	551.24 ± 3.48	N.A.	0.60	1.80

N.A. = Information not available.

The mineral mass fractions found in this procedure agreed to a preliminary study in which it was proposed to identify possible differences between *C. zeylanicum* and *C. cassia* based on chemical composition. In the previous study [16], the variability observed in the mass fractions were lower than in the present study, which can be explained by the higher samples analyzed in the present work. Samples commercialized in the Brazilian market showed higher amounts of minerals than some reported in the literature [2,17], which is expected by considering the different geographical origin of the samples.

Principal Component Analysis (PCA) was exploited to evaluate the clustering of the samples divided in the A, B, C, D, E, and F groups (as defined by topic 3.1), according to the mineral profile. After the analysis of perceptual maps, it was observed that microelements are highest correlated and

better explains the variability present in the sample set analyzed. So, the role of microelements in this classification was better investigated and a new classification model based on PCA was designed. The perceptual map showed that Fe, Cu, Al (as well as Si) presented the highest correlation and explained the variability of data, as previously indicated [16]. PC1, PC2 and PC3 are responsible for explaining 93% of the observed variance (Figure 1).

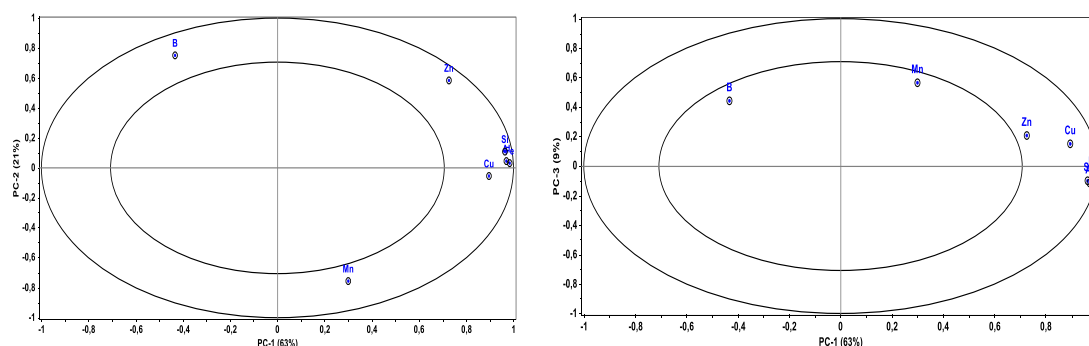


Figure 1. Perceptual maps obtained by PCA, in which PC1 explains 63% of the observed variance, PC2 21%, and PC3 9%, at the 95% confidence level.

The 6 groups of samples were coherently classified and the groups B and C (those in which *C. zeylanicum* was the ingredient) were strongly clustered. Samples acquired in bulk as well as those whose labels declared traces of grains and/or spices, i.e., groups A, D, F, presented the highest variability and were dispersed. The group in which *C. cassia* was the main ingredient (group E) presented a high clustering for 4 samples, although the other 4 samples were dispersed among other groups. Four samples were pointed out as outliers according to the model, one of them did not cluster to *C. zeylanicum* group, another is in the limit established, and 2 others did not present the same profile of all other samples analyzed. Figure 2 shows the clusters observed for the samples analyzed, demonstrating the possibility of using this approach for classification of cinnamon available in retail.

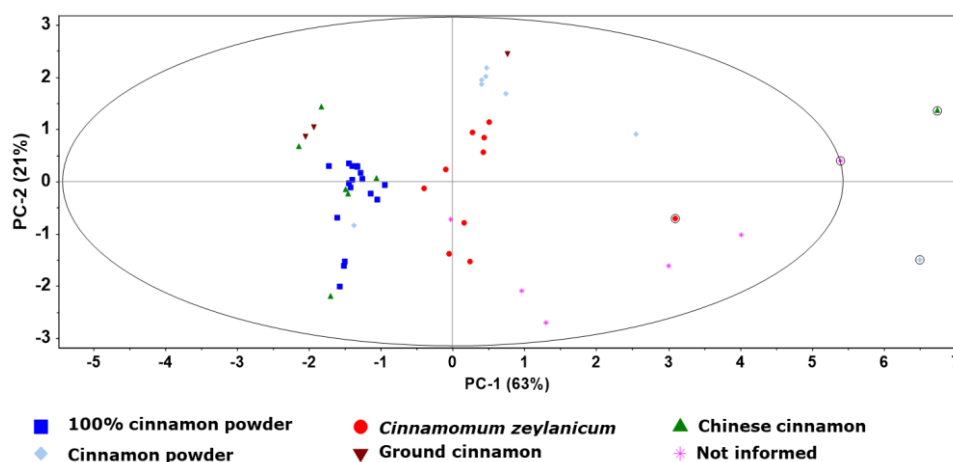


Figure 2. Sample distribution in the defined groups. Outliers were pointed out by circles.

4. Conclusions

The proposed strategy pioneering indicated the possibility to identify *C. zeylanicum* in commercial cinnamon powders, using microelements determined by ICP OES as authenticity markers. It also indicated the possibility to distinguish samples from *C. cassia* and others containing other grains, spices, and gluten, even though more studies are required to establish standard models for the classification of this product.

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