

## Elementary analysis in banana samples using X-Ray Fluorescence

Análise elementar em amostras de banana por Fluorescência de Raios-X

Análisis elemental en muestras de banano utilizando Fluorescencia de Rayos X

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### **Abstract**

This work aims to characterize the elemental concentrations of two banana types gold and silver. In both were analyze in the pulp and peel by X-Ray Fluorescence technique. The results showed that the elements in both types are more concentrated in the peel than in the pulp. In addition, it was also observed that the normalization of the peel and pulp concentrations for the elements K, Fe, Zn, Br, Rb, and Sr is higher in the silver banana compared to the gold banana. The results indicate that banana peels can be used to supplement nutritional deficiencies. The work also demonstrates the potential that X-Ray Fluorescence has in investigation of elemental composition of foods. As the technique has easy instrumentation and data interpretation, it can be implemented as a routine in the investigation of the elemental composition of foods. In addition, the technique has the advantage of carrying out in situ analyzes by portable instruments. These in situ investigations can even be applied to make quality control of bananas at the time of harvest.

**Keywords:** X-Ray Fluorescence; Banana; Elemental concentration.

### **Resumo**

Este trabalho tem como objetivo caracterizar as concentrações elementares de dois tipos de banana, ouro e prata. Ambos os tipos foram analisados, na polpa e na casca, pela técnica de Fluorescência de Raios-X. Os resultados mostraram que os elementos de ambos os tipos de banana estão mais concentrados na casca do que na polpa. Além

disso, também foi observado que a normalização das concentrações de casca e polpa para os elementos K, Fe, Zn, Br, Rb e Sr é maior na banana prata em relação à banana ouro. Os resultados indicam que as cascas de banana podem ser utilizadas para suprir deficiências nutricionais. O trabalho também demonstra o potencial que a Fluorescência de Raios-X tem na investigação da composição elementar de alimentos. Por possuir fácil instrumentação e interpretação dos dados, a técnica pode ser implementada rotineiramente na investigação da composição elementar dos alimentos. Além disso, a técnica tem a vantagem de realizar análises in situ por instrumentos portáteis. Essas investigações in situ podem até ser aplicadas para fazer o controle de qualidade da banana na época da colheita.

**Palavras-chave:** Fluorescência de Raios-X; Banana; Concentração elementar.

### Resumen

Este trabajo tiene como objetivo caracterizar las concentraciones elementales de dos tipos de banano, oro y plata. Ambos tipos fueron analizados, en la pulpa y en la piel, mediante la técnica de Fluorescencia de Rayos X. Los resultados mostraron que los elementos en ambos tipos de banano están más concentrados en la piel que en la pulpa. Además, también se observó que la normalización de las concentraciones de cáscara y pulpa para los elementos K, Fe, Zn, Br, Rb y Sr es mayor en el banano plateado que en el banano dorado. Los resultados indican que las cáscaras de plátano se pueden utilizar para suplir las deficiencias nutricionales. El trabajo también demuestra el potencial que tiene la fluorescencia de rayos X en la investigación de la composición elemental de los alimentos. Debido a su fácil instrumentación e interpretación de datos, la técnica se puede implementar de forma rutinaria en la investigación de la composición elemental de los alimentos. Además, la técnica tiene la ventaja de realizar análisis in situ utilizando instrumentos portátiles. Estas investigaciones in situ pueden incluso aplicarse para controlar la calidad de los bananos en el momento de la cosecha.

**Palabras clave:** Fluorescencia de Rayos X; Banano; Concentración elemental.

## 1. Introduction

Banana is one of the most versatile fruits when it comes to the culinary area. Due to its sweet flavor, that pleases palates, and nutritional value banana is one of the most consumed fruits in the world, making it an ingredient in food (Du et al., 2016; Yang, Tu, et al., 2019). These characteristics have sparked several studies about this fruit in several areas, such as culinary preparation (Akubor, 2003; Akubor et al., 2003; Almeida et al., 2017; Carneiro et al., 2020; L. O. Ribeiro et al., 2018; J. M. Santos, 2014), transportation and storage (Mugula et al., 1994; Nsumpi et al., 2020; Pathak et al., 2017; Yang, Zeng, et al., 2019), packaging (Fernando et al., 2020), and conservation (Chowdhury et al., 2020; Kritchenkov et al., 2020). According to the Food and Agriculture Organization of the United Nations - FAO, banana is produced in more than 130 countries, resulting in 18 million tons produced worldwide in 2014 (Cordoba et al., 2018). Brazil is the fourth largest banana producer in the world with approximately 7 million tons in 2017, representing 6% of the world production (de Sá et al., 2019). The banana is the most consumed fruit in Brazil in 2016 (G1, 2017) and the fifth in China in 2017 (Ji et al., 2020), with emphasis on the types silver banana (scientific name *musa paradisiac*) and banana gold (another variety of *musa paradisiac*). The basic characteristics of a healthy diet with the full use of food are the high nutritional value of the products, the low cost to purchase them, and the quick and easy preparation (SESC, 2003). With a view to making full use of the fruit in the areas of gastronomy and nutrition, research has been carried out related to enriching diets and contributing to minimizing food waste (Almeida et al., 2017; Ortiz et al., 2017; J. M. Santos, 2014).

Based on this idea, this work aims to characterize the concentrations of elements present in two banana types both in the pulp and in the peel using the X-Ray Fluorescence (XRF) spectroscopic technique to show that the banana peels have a high nutritional value. In 1996 Selema and Farago published a study on bananas comparing the skin and trunk mineral elements (Selema & Farago, 1996). Later in 2007, Emaga et al. compared the chemical composition of peels of different types of bananas (Happi Emaga et al., 2007). And in 2012 Ho, Aziah and Bhot investigated the mineral composition of banana pseudo-stem flour (Ho et al., 2012). However, to the best of our knowledge, no study has compared the elements present in the banana pulp, which is usually consumed, and in the peel, usually discarded as waste.

## 2. Methodology

### 2.1 Theoretical foundation

X-Ray Fluorescence (XRF) is a non-destructive technique that allows for a qualitative and quantitative analysis in which it establishes the proportion of each element present in the sample. The XRF is based on the characteristic X-Rays, that is, a source of ionizing radiation emits a beam of X-Rays towards the sample. When interacting with its atoms, it transfers energy to the electrons of these atoms to the point of removing them from its orbit, generating vacancies in the orbitals of each affected atom. To stabilize the atom again, electrons from more energetic orbitals jump into less energetic orbitals to fill the void. When carrying out this orbital transition, they emit this energy difference between one orbital and another, in the form of electromagnetic radiation, more specifically as a characteristic X-Ray. The energy distribution spectrum of the characteristic X-Rays is discrete, as they are dependent on the energy levels of the electrosphere (Ashida & Tsuji, 2014; dos Anjos et al., 2000; Grieken & Markowicz, 2001).

In order to carry out the analysis by X-Ray Fluorescence to characterize samples, it is necessary to carry out three steps: excitation of the elements that constitute the sample, dispersion of the characteristic X-Rays emitted by the sample, and detection of these X-Rays (Gama Filho, 2015; Grieken & Markowicz, 2001). Its main advantages are: non-destructible analysis, fast qualitative analysis, little interference between lines, simplicity in sample preparation, a wide range of elements that can be analyzed, easy operation and in situ analysis, in this case using portable equipment. These advantages give the technique a wide range of use (Ávila et al., 2021; A. V. C. Braga et al., 2020; A. V. de C. Braga et al., 2019; Valter S. Felix et al., 2018; Valter Souza Felix et al., 2021; Freitas, Ribeiro, Calza, Oliveira, Felix, et al., 2016; Freitas, Ribeiro, Calza, Oliveira, Silva, et al., 2016; Freitas et al., 2019; M. O. Pereira et al., 2021; Pimenta et al., 2020; I. M. N. Ribeiro et al., 2016; Rocha et al., 2021; Tavares et al., 2020). This technique is well consolidated in the elementary analysis in plants and vegetables (Marguí et al., 2009; Richardson et al., 1995; Spolnik et al., 1999).

The concentration ( $W_i$ ) of each element was obtained as a function of the average of the peak areas of each element divided by the counting time ( $I_i$ ), the sensitivity of each element ( $S_i$ ), the surface density of the sample ( $\rho D$ ) and the total mass absorption coefficient ( $X_i$ ) according to equation (1) (R. S. Santos, 2014).

$$W_i = \frac{I_i X_i}{S_i (1 - e^{-\rho D X_i})} \quad (1)$$

$X_i$  being determined as a function of the sample's mass absorption coefficient for energy  $E_0$  of the incident photons  $\mu(E_0)$ , the angle of incidence of radiation with energy  $E_0$  ( $\theta_{inc}$ ), the sample's mass absorption coefficient for energy  $E_i$  of the fluorescent radiation produced by the  $i$ -th element of the sample  $\mu(E_i)$  and the angle of incidence of radiation with energy  $E_0$  ( $\theta_r$ ) according to equation (2) (R. S. Santos, 2014).

$$W_i = \frac{\mu(E_0)}{\sin(\theta_{inc})} - \frac{\mu(E_i)}{\sin(\theta_r)} \quad (2)$$

### 2.2 Experimental procedure

The research was carried out according to the methodology described in this references (Koche, 2011; Lüdke & André, 1986; A. S. Pereira et al., 2018; Yin, 2014). Initially, some silver banana and gold banana samples were selected from an open market in Rio de Janeiro, Brazil. The pulp was separated from the peel, and the masses were measured separately. The

samples were placed in an oven at a temperature of approximately 60°C, to dehydrate (Celestino, 2010). Table 1 shows the evolution of the dehydration process of only one of the silver banana and gold banana samples:

**Table 1:** Drying of samples. mass in g; mass loss in %.

Time in an oven	Silver Banana				Gold Banana			
	Pulp		Peel		Pulp		Peel	
	mass	mass loss	mass	mass loss	mass	mass loss	mass	mass loss
0 h	115.44	----	51.84		81.04		35.87	
24 h	112.35	3	50.90	1	74.92	5	33.96	2
48 h	93.71	19	44.35	6	59.52	19	33.36	2
168 h	91.72	21	44.23	7	58.00	20	33.28	2

Source: Authors.

As soon as the sample masses remained constant, they were crushed in a blade mill (IKA, model A11 basic). Each crushed sample was sieved. With a precision scale (BEL Engineering Model: M254A) approximately 500mg of each sieved sample was separated. With a compactor and a hydraulic press (MARCON, Model: MPH-10), the samples were pressed for 10 minutes at a pressure of  $1.93 \times 10^8$  Pa. At the end of this process, silver and gold banana pulp and peel tablets were obtained. Each 2.54 cm diameter insert. Figure 1 shows the formed inserts. Tables 2 and 3 show the masses and densities of the tablets.

**Figure 1:** Tablet samples of silver banana peel (Cp), silver banana pulp (Bp), gold banana peel (Co), gold banana pulp (Bo).



Source: Authors.

**Table 2:** Mass and sample area.

Silver B. ( $\pm 0.0005$ g)		Gold B. ( $\pm 0.0005$ g)	
Pulp	Peel	Pulp	Peel
0.5017	0.5002	0.5004	0.5000
tablet area ( $\pm 0.005$ cm <sup>2</sup> )			5.0671

Source: Authors.

**Table 3:** Surface density of samples.

Silver B. ( $\pm 0.0005 \text{ g/cm}^2$ )		Gold B. ( $\pm 0.0005 \text{ g/cm}^2$ )	
Pulp	Peel	Pulp	Peel
0.0990	0.0987	0.0987	0.0986

Source: Authors.

To obtain the spectra (which will be presented in the results section) the following parameters were used: the X-Ray tube (AMPTEK, model Mini-X) was adjusted under the following conditions: voltage 35 kV, current 50  $\mu\text{A}$ , and counting time of 1000 seconds, and a Si-DRIFT detector (AMPTEK, model XR -100SDD) (Amptek, 2021). Three spectrum were obtained for each sample.

The spectra obtained from the AMPTEK DppMCA program provided the chemical elements of the samples. With the aid of the AXIL program, we obtained the sum of the area of all peaks for each spectrum. Afterwards, we calculated the average of the three measurements for each element's peak area divided by the counting time ( $t_i$ ). Figure 2 illustrates the irradiation setup. For absorption coefficients and sensitivity, the values used are shown in Tables 4 and 5.

**Figure 2:** Irradiation setup.



Source: Authors.

**Table 4:** Coefficients of absorption and energy of the incident photons.

$\mu(E_0)$	1.25547	$E_0 = 22.5 \text{ keV}$
$\mu(E_i)$	$3310 \times 10^{(-2.53)}$	

Source: (Spolnik et al., 1999).

**Table 5:** S<sub>i</sub> sensitivity of the system to the elements [10].

Atomic number Z	SENSITIVITY (cm <sup>2</sup> /g.s)
17	2736.8679
18	5163.0923
19	9255.9687
20	15801.3430
21	25741.3004
22	40099.1848
23	59856.7870
24	85796.2433
25	118332.5913
26	157371.4433
27	202226.0733
28	251618.3186
29	303770.4098
30	356575.0896
31	407814.8848
32	455392.5317
33	497535.0843
34	532942.9383
35	560868.5976
36	581124.4766
37	594030.9308
38	600323.0461
39	601037.0677
40	597395.5731
41	590706.1100
42	582282.6690

Source: (Spolnik et al., 1999).

### 3. Results and Discussion

From the obtained spectra, we verified the presence of the elements Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Rb, Sr in the gold and silver banana peels that according to Hassan et al., 2018, are part of most of the minerals that make up the banana peel (Hassan et al., 2018). Some of these elements have an essential function, such as prosthetic groups of some enzymes (Happi Emaga et al., 2007). In the pulp, the element Ca does not appear in any of the types, and the Cl does not appear in the silver banana. Table 6 shows the concentrations of the elements in part per million (ppm) in the banana peel and pulp and the concentration ratio between the peel and the pulp.

**Table 6:** Concentrations in ppm.

Element	Gold B. Pulp (± 0.5 ppm)	Gold B. Peel (± 0.5 ppm)	Silver B. Pulp (± 0.5 ppm)	Silver B. Peel (±0.5 ppm)	Gold B. Peel / Pulp	Silver B. Peel / Pulp
Cl	295.9	555.8	0	364.3	<b>1.9</b>	-
K	1403.0	3733.5	1234.8	4865.2	<b>2.7</b>	<b>3.9</b>
Ca	0	102.0	0	312.7	-	-
Mn	8.7	20.4	7.2	16.4	<b>2.4</b>	<b>2.3</b>
Fe	11.6	12.3	8.3	9.8	<b>1.1</b>	<b>1.2</b>
Cu	3.3	4.6	2.4	2.4	<b>1.4</b>	<b>1.0</b>
Zn	8.6	15.6	5.2	17.1	<b>1.8</b>	<b>3.3</b>
Br	2.0	5.7	1.6	8.9	<b>2.8</b>	<b>5.5</b>
Rb	26.6	48.2	5.3	13.6	<b>1.8</b>	<b>2.5</b>
Sr	2.7	16.6	3.2	22.7	<b>6.0</b>	<b>7.0</b>

Source: Authors.

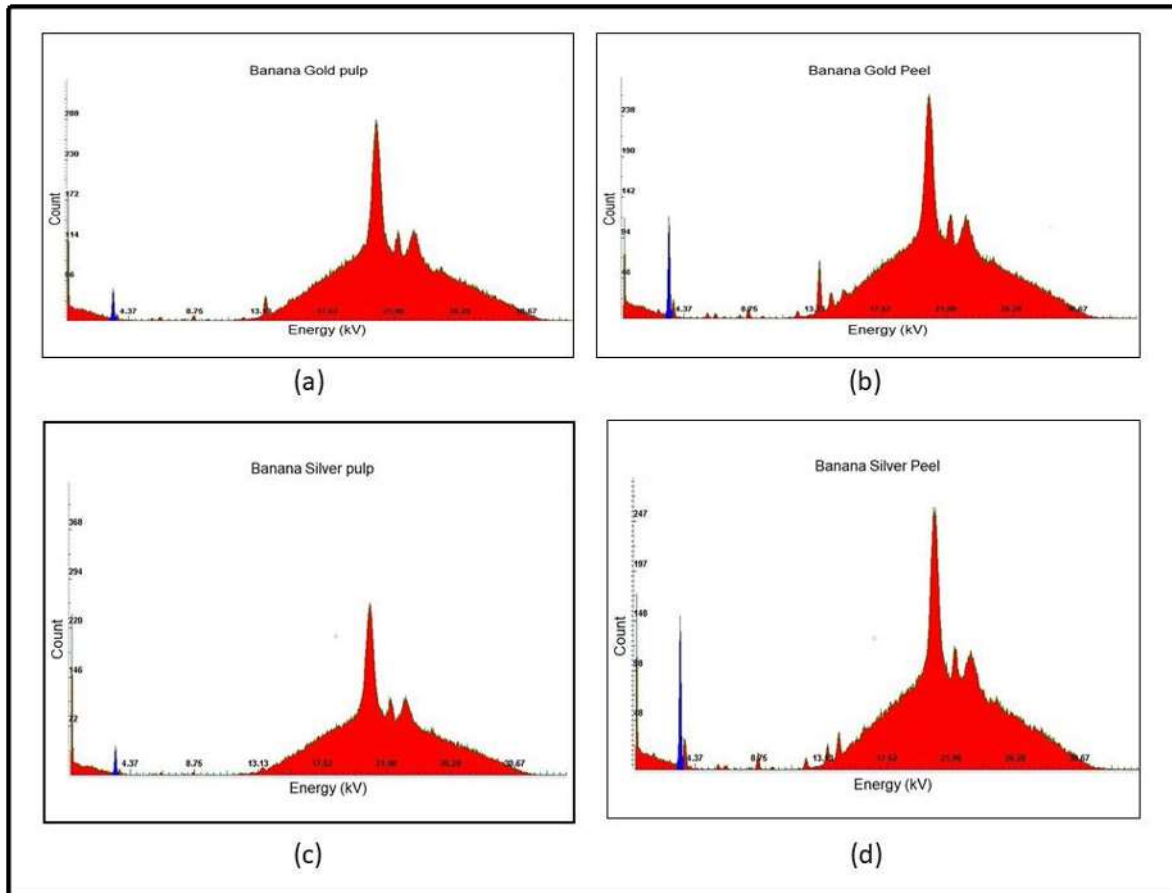
The vitamins, dietary fibers, minerals and many health-promoting bioactive phytochemicals from banana presents: antioxidant properties, reduce the risk of cardiovascular diseases and cancer, potential hepatoprotective effects, cholesterol reduction, precursors of vitamin A, antioxidant, antimicrobial, anti-inflammatory, antiallergic, among others (Sidhu & Zafar, 2018)

Potassium was the main element present in the pulp and peel. Other studies performed only on the peel also found potassium as the main element present (Happi Emaga et al., 2007). Manganese had an essential role in the photosynthesis process; 20 to 500 ppm is the usual range for this element (Selema & Farago, 1996; Valkovic, 1978). Small amounts of Rb have been detected. Rubidium can be a nutritional substitute for potassium (Valkovic, 1978). The Sr presence is not considered essential for plants (Selema & Farago, 1996). However, the quantities found are within the expected range; 1-200 ppm (Valkovic, 1978).

The consumption of vitamins and minerals has a fundamental role in human health and well-being (Ji et al., 2020). The consumption of minerals present in fruits is beneficial to the nervous system's functioning (Stefańska et al., 2014). Some elements, such as Fe (Sheikh et al., 2017) and K (Fullana et al., 2019), can alleviate depressive symptoms. A study conducted in mice revealed that banana consumption is associated with a decrease in symptoms of depression (Samad et al., 2017).

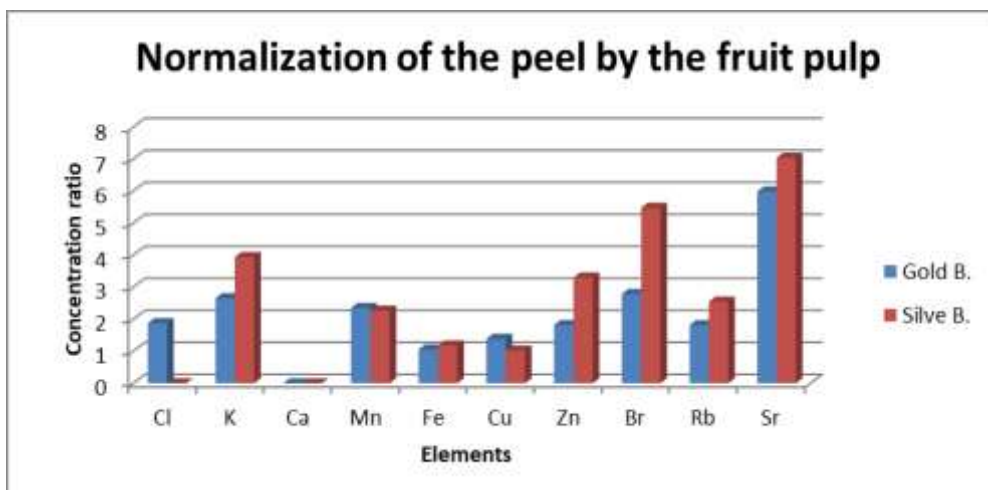
Figure 3 shows the spectra of the banana peel and pulp samples for and gold. Figure 4 shows the normalization of the concentrations between the pulp and the peel for the gold and silver bananas, making the ratio between the concentrations of the peel and the pulp.

**Figure 3:** Spectra for (a) gold banana pulp, (b) gold banana peel, (c) silver banana pulp, (d) silver banana peel.



Source: Authors.

**Figure 4:** Normalization of peel and pulp concentrations for silver and gold bananas.



Source: Authors.

#### 4. Conclusion

The results showed that not all the elements found in the peel were observed in the pulp, like Cl and Ca. We found that in both banana types, the concentration of all elements found is higher in the peel in both. Banana types as seen in Table 6.



As a reference for a source of potassium (Carneiro et al., 2020), it is worth mentioning that for silver bananas the concentration is about 4 times higher in the peel than in the pulp, and for gold bananas is about 2.5 times higher in the peel. The normalization of the concentrations illustrated in Figure 4 shows that for the elements K, Fe, Zn, Br, Rb, and Sr the relationship between the concentrations for the peel and for pulp is higher in the silver banana compared to the gold banana. That is, these elements are more concentrated in the peel than in the pulp in the silver banana compared to the gold banana.

Research on fruit and vegetable peels is a promising field in the food area. Investigating the nutritional value of the peels is a crucial step to spread the use in cooking of a part of the food that is usually neglected. It is recommended to investigate other foods and the nutritional value of the components found in this research.

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