LIBS QUALITY CONTROL AND ORIGIN IDENTIFICATION OF HAND MADE MANUFACTURED CIGARS

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Abstract.

Tobacco is an agricultural product originating in America that is obtained by processing the leaves of various plants of the genus Nicotiana tabacum. It is the inedible product occupying most plantings in the world, according to a recent report from the UN Food and Agriculture Organization. Is consumed in various ways, but undoubtedly the most popular is smoking cigarettes. A particular segment of the tobacco industry is the manufacturing of hand-made cigars, which for some third-world countries is an important source of income. There are different qualities of cigars and a major problem is the adulteration that occurs for example when authentic high quality leaves are changed by others of less quality. A factor that influences the quality of the cigars is the smoke combustion process, that depends on several aspects, particularly the composition of the leaves.

We present a simple and quick technique for the quality control and origin identification of hand-made cigars, by using the Mg/Ca relationship measured with Laser Induced Breakdown Spectroscopy (LIBS) in the tobacco leafs and the wrapper of the cigars.

1. INTRODUCTION

Tobacco is a product of agriculture, originating in America and processed from the leaves of various plants of the genus Nicotiana tabacum. It is consumed in several ways, but undoubtedly combustion for smoking is the main. Tobacco is composed by an alkaloid named nicotine, which is found in the leaves in variable proportions (from less than 1% to 12%).

In worldwide agriculture, tobacco is the commercial plant inedible that occupies largest acreage [1]. Despite being a questioned product because its damage to human health, tobacco continues to be a crop of great economic importance. There are two classes of derivatives (called cigars) which are classified according to the market: firstly, the massive machine production of relative low cost cigars. Secondly, the hand-made cigars of high quality standards dedicated to unique and more exclusive markets. An emblematic case is the example of Cuban cigars, where the combination of climate, soil and unique culture of the crop, has given to this product his well-earned fame[2]. Then, the hand-made cigars industry is an important source of income as well as an essential part of tradition and national culture for different countries [3, 4].

Tobacco contains a number of chemical compounds affecting his quality. Of these, polyphenols and carbonyls play an important role in the flavor and aroma. In contrast, cellulose and mineral materials are decisive for combustion, while glucosides cause the bitter taste in the leaves and so in the final product. Of the elements present in the leaf, potassium is a major constituent of the ash that results in a continuous combustion without flame. Mg and Ca have a decisive influence on the incineration process[5]. Calcium, when is in excess, give as a result a compact ash that hinders the passage of air into the cigar, resulting in incomplete combustion. Instead, the presence of magnesium produces a porous and light colored ash, which improves combustion[6]. Acidic compounds of ash, chlorine, phosphorous, silicon and sulfur, in general, tend to retard the combustion. However, it is important to emphasize that the quality of combustion depends primarily on the preparation of the cigar, which is what ultimately ensures proper airflow and depends primarily on the manufacturer ability and experience.

Anyway, monitoring the composition of the leaves of tobacco is very important in all phases of the production process. In large cigarette industries this is solved because most of them count with adequate quality control laboratories that include several complex and costly instruments. The mineral composition is usually determined by Atomic Absorption, Atomic Emission or x-ray spectrometry[7-9]. Organic components could be determined by gas chromatography, high performance liquid chromatography or infrared spectrometry[10]. None of those instruments allow a quick, easy and in field elemental determination.

In the case of hand-made cigars manufacture where a relatively short scale production of specific kinds of cigars prevails, it is more difficult the access to high-cost analytical technique. Nevertheless, the hand-made cigar industry is particularly sensitive to the quality of the leaf plantations and the use of fertilizers and other chemicals that supply the industry.

For those reasons it would be desirable to control the raw material production before these are discharged into the production plant, which would be necessary to have analytical techniques that are simple, inexpensive and can preferably be used by operators with no high-level training.
Moreover, there are several production steps where it is important to monitor the leaves quality and origin. First, the leaves identification should occur in the plantation, in order to obtain a standard for comparison in the following production steps. Second, when leaves arrive to the factory, it would be important to ensure that the received leaves come from a particular plantation. It's important to take into account that factories are usually located in cities that are far from the plantations. Finally, to prevent adulteration or sales of cigars from illegal sources should be checked the origin of the leaves of the cigars sold in stores.
The inherent characteristics of Laser-induced Breakdown Spectroscopy (LIBS), makes it a good candidate to solve the problem described above. LIBS is an appealing technique compared with many other types of elemental analysis because setting up an apparatus to perform a measurement is in principle very simple. LIBS require no previous sample preparation; it has no limitations in sample dimensions and shapes. The analysis is micro-destructive and a low quantity of sample is needed, with minimal damage done to the sample. Chemical imaging of surfaces as spatial distribution profiles and depth profiling allows mapping and layer-by-layer analysis characterization of the composition of surface as well as substrate[11-15].
In this paper we developed a simple and quick technique based on Laser Induced Breakdown Spectroscopy (LIBS), that uses the Mg/Ca relationship in the tobacco leafs and the wrapper of the cigars for the quality control and origin identification of hand-made manufactured cigars

1. EXPERIMENTAL

Figure 1 show the experimental setup used. The ablation process was carried out by means of a 40 mJ, 10 ns pulses width, Nd:YAG laser working at 2 Hz repetition rate. The laser beam was focused on the sample using a 15 cm focal length lens. The energy of the laser pulse was controlled to have laser fluences (F) up to 15 J/cm^2. For analysis of the plasma emission a system composed by an optical fiber (0.5 mm opening), attached to a cross Czerny-Turner miniature spectrometer with a linear charge-coupled device (2048 pixels.) was used. This spectroscopic setup enables simultaneous detection of a large spectral region (from 250 to 1100 nm with a 0.3 nm spectral resolution) in a single laser shot.

In a typical cigar, five different parts can be distinguished (figure 2a). The head which is the region that goes in the smoker's mouth. The cigar band is a paper band that identifies the type and/or brand of the cigar. The wrapper is a spirally-rolled leaf of tobacco that covers the cigar. The foot is the end meant to be lit, and the dried bunches of leaves that are inside, shown in figure 2 b.

Ten different brands of cigars belonging from 5 different countries were analyzed as it is detailed in table 1. To ensure reproducibility of the results, for each brand at least 10 different cigars were analyzed corresponding to different years of production an acquired in different places. i.e: the Cuban cigars studied were acquired in Cuba, Argentina and Mexico stores. The same situation take place with the Nicaraguan cigars, obtained from stores located in Argentina, USA and Mexico. All the studied cigars were manufactured at different times. For each cigar we made measurements both, on the tobacco leafs and the wrapper. For this purpose the cigars were carefully disassembled and 3 cm sections of leafs were selected.

2. RESULTS AND DISCUSSION

The LIBS spectra were obtained by using single shots with fluences above the ablation thresholds (3,5±1.1 J/cm^2) of the tobacco leafs and the wrapper. Once it is known the ablation threshold, the better is to use a slightly greater than the threshold fluence and thus minimize the laser requirements allowing to use cheaper and compact equipment. In all cases a first shot was used to clean the surface.

Figure 3 shows a typical multi-line spectrum obtained for wrapper tobacco leafs of the cigars. As it is expected Mg, Ca, Na and K characteristic lines are clearly observed. The presence of those elements is related to several variables. Magnesium is part of the pyrrolidinic ring of the chlorophyll and the other elements are related to the metabolic processes of the vegetable cell. In the case of tobacco leafs, those elements could come also from the soil and fertilizing (if they were employed during the growing process of the plant). K and Na are closely related to the mechanism used by cells to obtain energy.

With the aim to measure the Mg/Ca relationship in the set of samples, representative characteristic lines of these elements were selected. The inset in figure 3 shows the spectral region between 382 and 398 nm in which lines of Mg I (382.9, 383.2, and 383.8 nm) and Ca II (393.4 nm) were identified. We chose these lines because they are very close in wavelength and consequently any change related with the absolute intensity of both lines will not be important.

It was previously demonstrated for other materials that the temporal evolution and the decay kinetics of the 383 nm lines of Mg and the 393.4 lines of Ca are the same [12]. By using a set up with a programmable time delay we confirm this result for the cigars samples. Figure 4 shows the temporal evolution of the 383 nm Mg lines compared with the 393.4 nm Ca II line. As it can be seen this behavior ensures that independently from the temporal delay used when the signal is acquired, the Mg/Ca relationship will be constant. To avoid bremsstrahlung and to have the better signal to ratio relationship in the spectrum, measurements were made with a delay of less than 1 µs.

Determination of Mg/Ca ratios in tobacco leafs and wrapper

For each cigar, LIBS spectra were obtained in ten different regions of the wrapper and the tobacco leafs respectively. In all cases the first laser pulse was used to clean the analyzed region. After that, no significant changes were observed between spectra from pulse to pulse. Then, ten spectra were averaged for better signal-to noise ratio.

The presence of Mg relative to Ca was determined from the averaged spectra of the tobacco leafs and wrapper by measuring the ratio of the line intensities $I_{Mg(383)/}I_{Ca(393)}$. Table 1 shows the mean values and dispersion of the Mg/Ca ratio in the wrapper and the tobacco leafs for the ten samples of cigars studied.

Figure 5 show Mg/Ca ratio intensity bar graphs, respectively, for wrapper (a) and tobacco leafs (b). Brand belonging to the same country are represented by a differently patterned bar. As it can be seen the three brands of Cuban cigars have the lowest Mg/Ca relationship both in the wrapper and the tobacco leaf, followed by one brand from Nicaragua and one brand from Brasil. For these brands the ratios behavior of wrapper and leaves are similar. The rest of the brands have higher values of the Mg/Ca. Figure 6 show the total Mg/Ca ratio intensity bar graphs defined as $(Mg/Ca)_{leafs}$ + $(Mg/Ca)_{wrapper}$ for the ten brands of cigars. The corresponding values and uncertainly can be found in the last column of table 1. From this result we proposed that the Total Mg/Ca ratio (the combination of Mg/Ca ratios of leafs and wrapper) can be used as characteristic reference values to identify the origin of the cigar as well as a quality control parameter in the production process of the cigars.

III. CONCLUSIONS

Based in LIBS it was developed a simple and fast technique for the quality control and identification of origin of hand-made manufactured cigars. By measuring the Mg/Ca relationship in the wrapper and the tobacco leafs, characteristic reference values of this parameter for each brand of cigar can be obtained. Also by using portable LIBS device, this method allows monitoring the origin of cigars leaves, comparing the Mg/Ca rates of cigar with the ratio of plantation leaves.

As it is well known, the Cuban and Nicaraguan cigars are recognized by smokers as the finest cigars of the world. This is in agreement with the result we obtained that shows that all the Cuban brands and one of the most recognized Nicaraguan brands have the lowest Mg/Ca relationship in comparison with other cigars. Although there is not an absolute indicator of handmade cigars quality, as this factor is highly subjective, the Mg / Ca could also be taken as a parameter for the recognition of the highest quality brands

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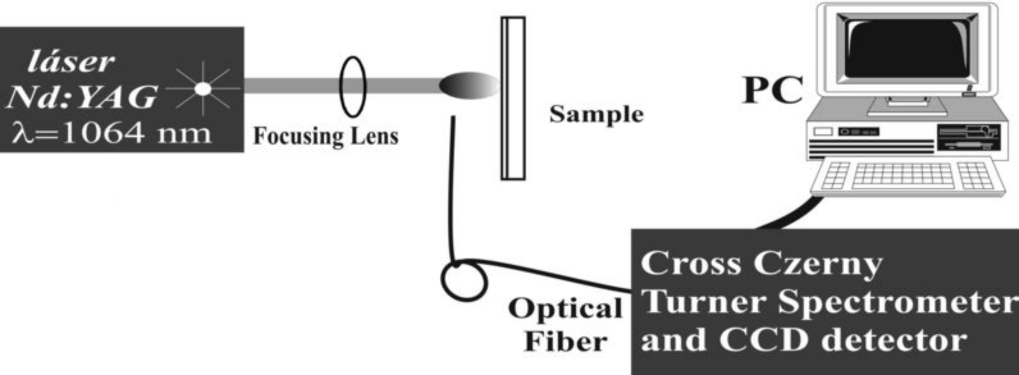
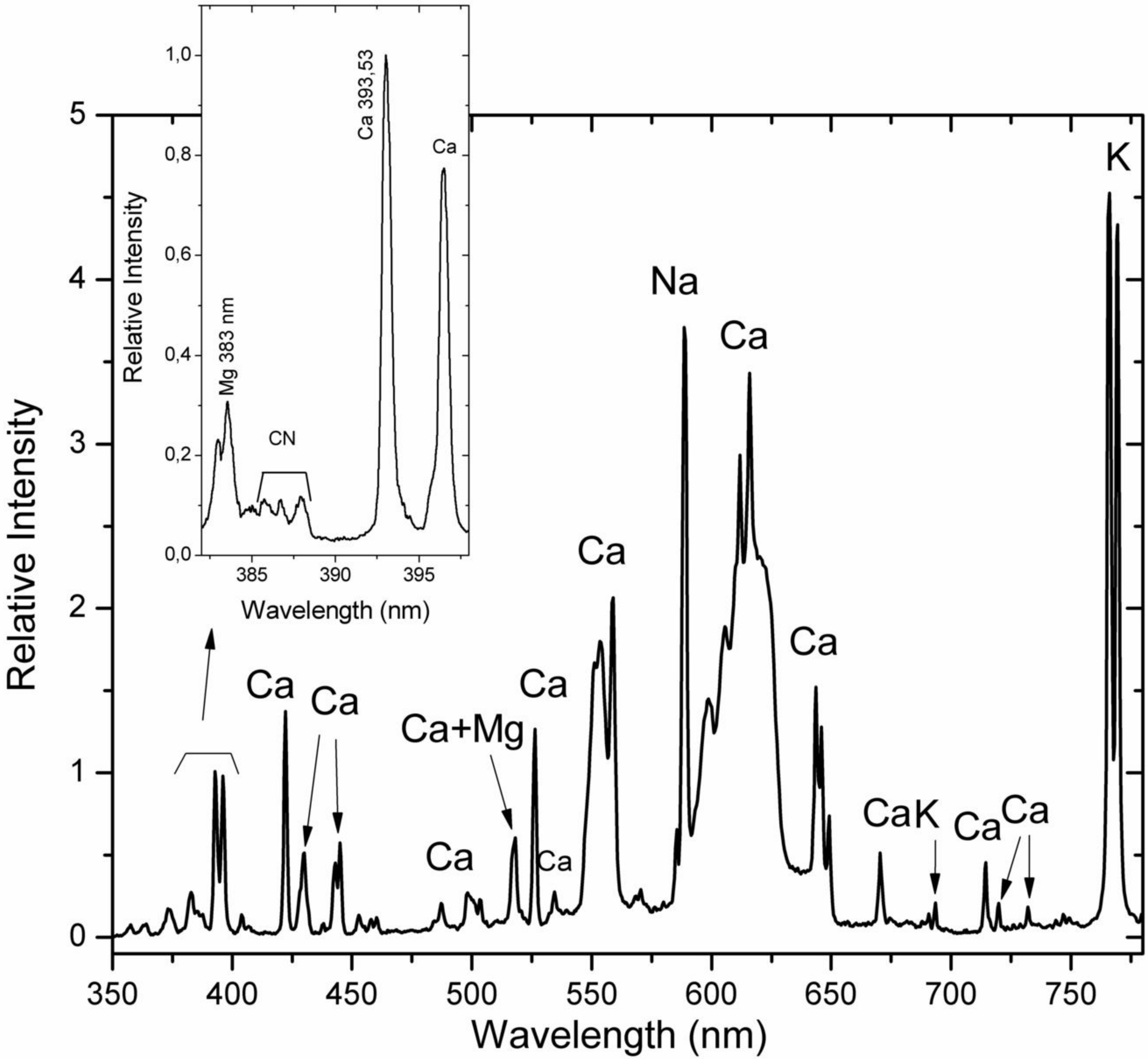
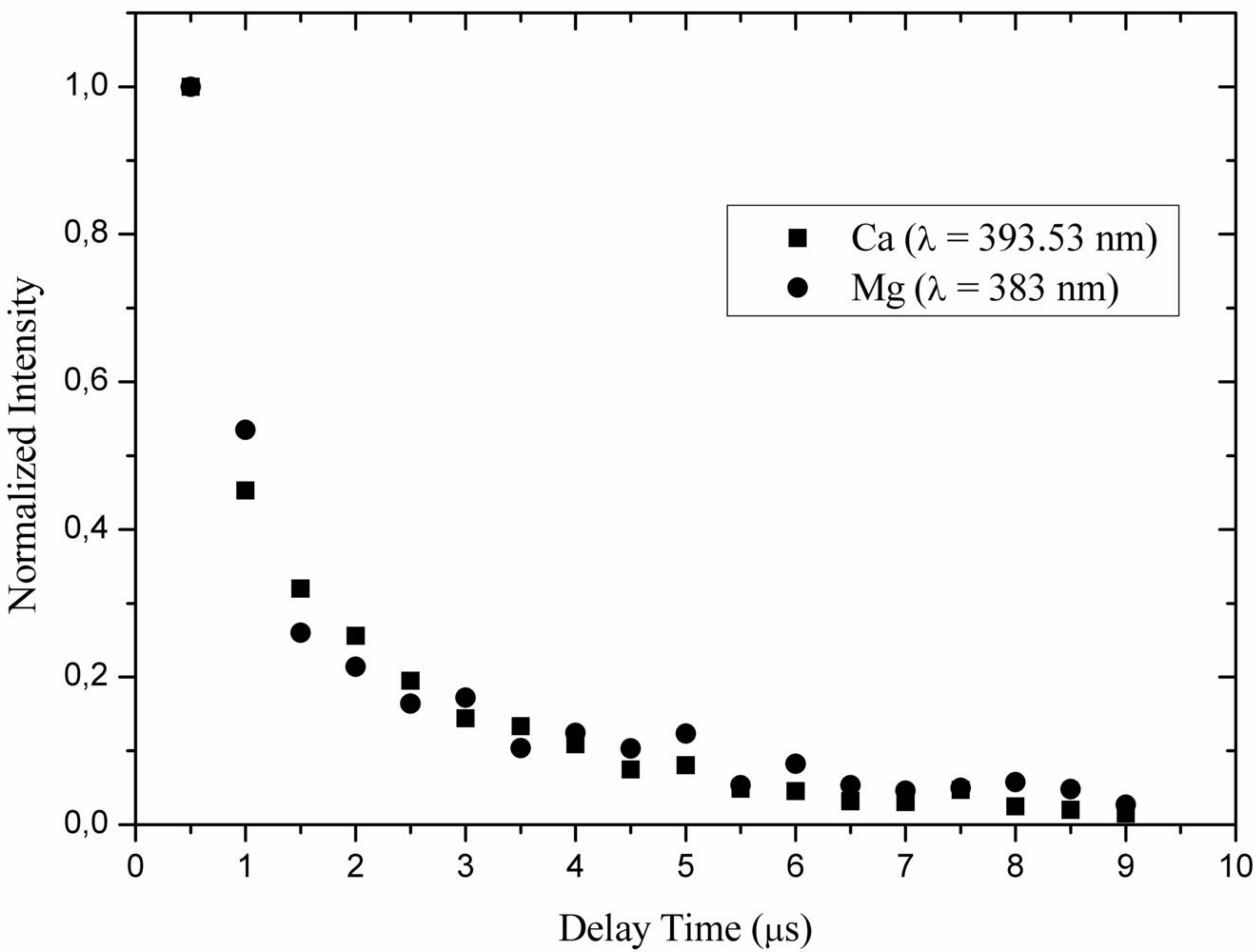

láser
Nd:YAG
λ=1064 nm
Focusing Lens
Sample
PC
Optical
Fiber
Cross Czerny
Turner Spectrometer
and CCD detector

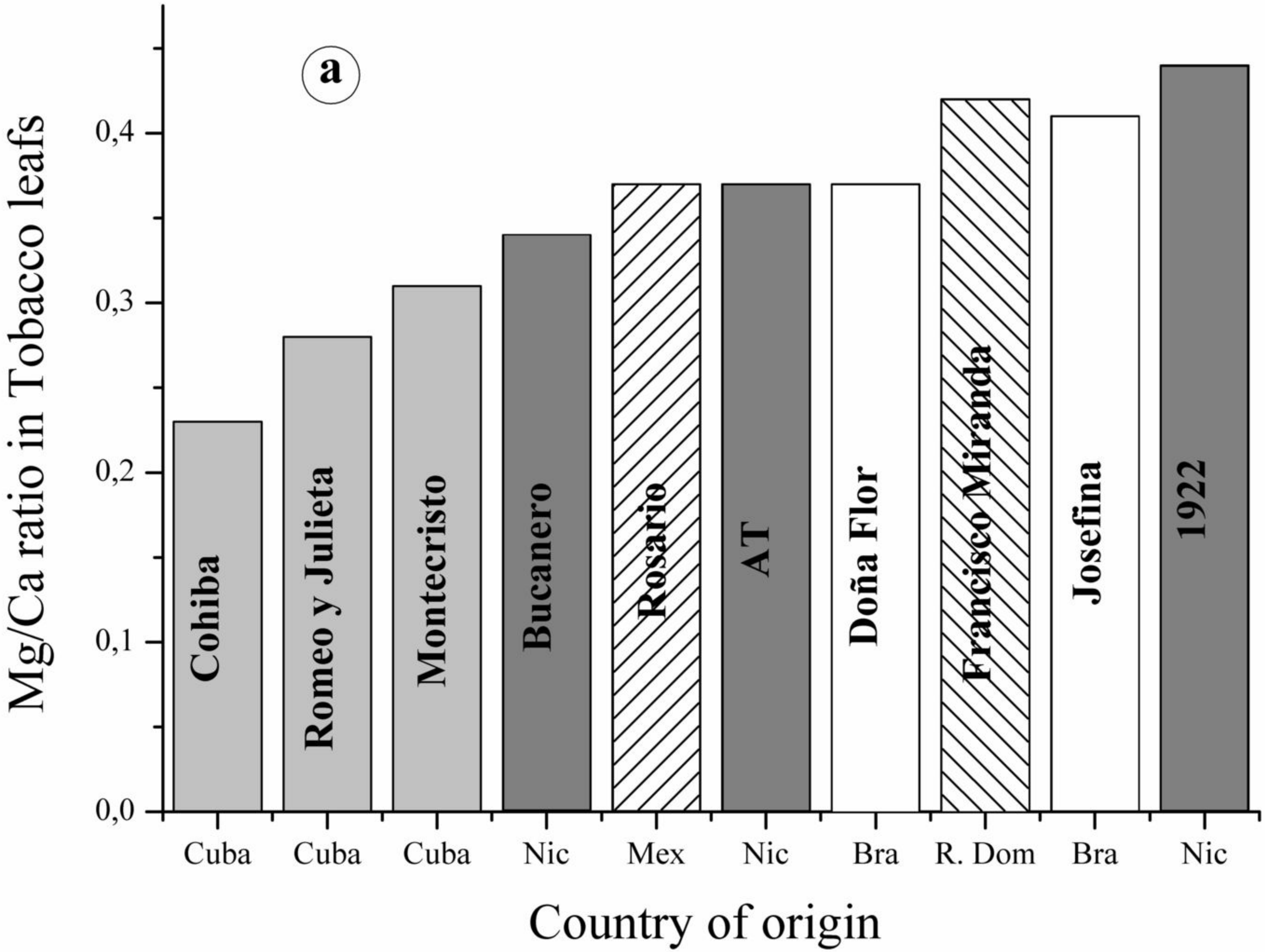

a
Head
Cigar
Band
Wrapper
Foot
ROMEO Y JULIETA
Desde 1875
HABANA · CUBA
b



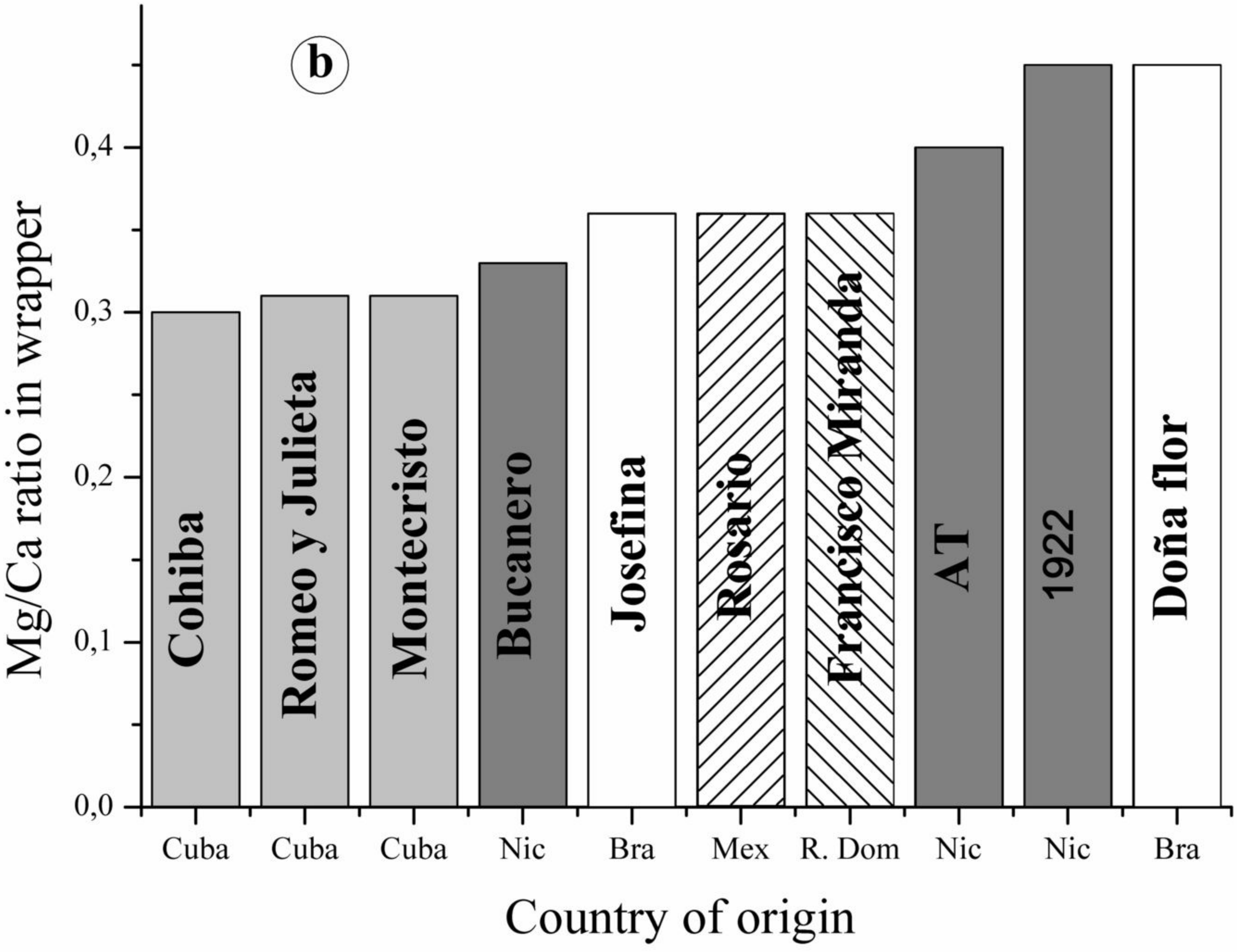
Relative Intensity
Wavelength (nm)
K
Na
Ca
Ca
Ca
Ca
Ca
Ca+Mg
Ca
Ca
Ca
CaK
Ca
Ca
Mg 383 nm
CN
Ca 393,53
Ca



Normalized Intensity
1,0
0,8
0,6
0,4
0,2
0,0
0
1
2
3
4
5
6
7
8
9
10
Delay Time (μs)
Ca (λ = 393.53 nm)
Mg (λ = 383 nm)



a
Mg/Ca ratio in Tobacco leafs
0,0
0,1
0,2
0,3
0,4
Cohiba
Romeo y Julieta
Montecristo
Bucanero
Rosario
AT
Doña Flor
Francisco Miranda
Josefina
1922
Cuba
Cuba
Cuba
Nic
Mex
Nic
Bra
R. Dom
Bra
Nic
Country of origin


b
Mg/Ca ratio in wrapper
0,0
0,1
0,2
0,3
0,4
Cohiba
Romeo y Julieta
Montecristo
Bucanero
Josefina
Rosario
Francisco Miranda
AT
1922
Doña flor
Cuba
Cuba
Cuba
Nic
Bra
Mex
R. Dom
Nic
Nic
Bra
Country of origin

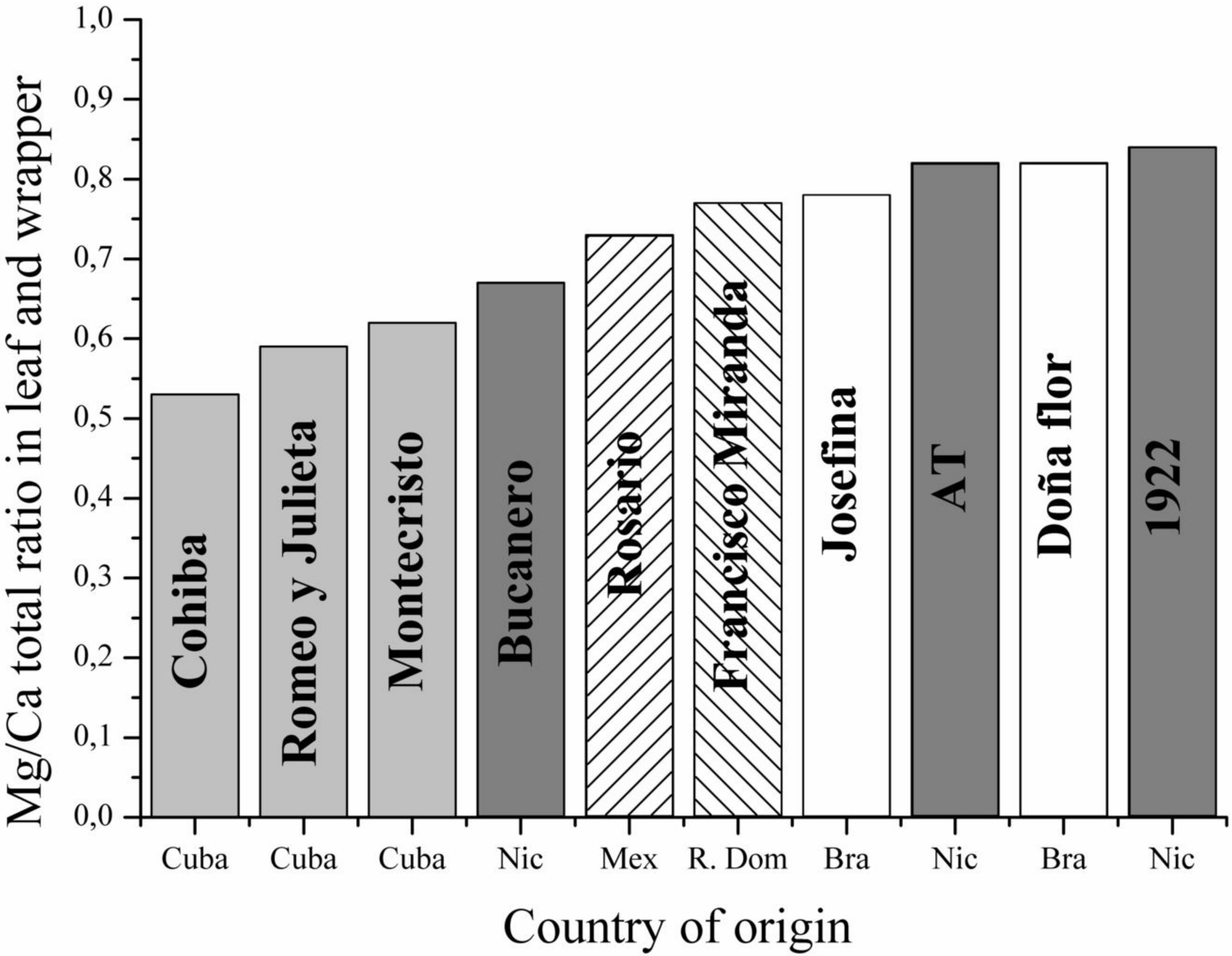

Mg/Ca total ratio in leaf and wrapper
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
Cohiba
Romeo y Julieta
Montecristo
Bucanero
Rosario
Francisco Miranda
Josefina
AT
Doña flor
1922
Cuba
Cuba
Cuba
Nic
Mex
R. Dom
Bra
Nic
Bra
Nic
Country of origin

Table 1: Table 1: Resume of Mg/Ca ratios results

Brand	**Country of origin**	**Mg/Ca ratio Wrapper**	**Mg/Ca ratio Tobacco leafs**	**Mg/Ca Leaf + Mg/Ca wrapper**
Cohiba	Cuba	0.30 +/- 0.02	0.23+/-0.02	0.53+/-0.04
Romeo y Julieta	Cuba	0.31 +/-0.02	0.28+/-0.02	0.59+/-0.04
Montecristo	Cuba	0.31 +/- 0.03	0.31+/-0.02	0.62+/-0.05
Bucanero	Nicaragua	0.33 +/- 0.03	0.34+/-0.03	0.67+/-0.06
Rosario	México	0.36 +/- 0.03	0.37+/-0.01	0.73+/-0.04
AT	Nicaragua	0.40 +/- 0.04	0.37+/-0.02	0.77+/-0.06
Francisco Miranda	Dominican Rep	0.36 +/-0.02	0.41+/-0.02	0.77+/-0.04
Josefina	Brasil	0.36 +/- 0.02	0.42+/-0.02	0.78+/-0.04
Doña Flor	Brasil	0.45 +/- 0.03	0.37+/-0.02	0.82+/-0.05
1922	Nicaragua	0.40 +/- 0.04	0.44+/-0.02	0.84+/-0.06