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X-Ray Fluorescence Analysis of Ground Coffee

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Abstract Coffee is becoming one of the most popular beverages in Mexico. In the present work, X-ray Fluorescence (XRF) was used to determine the contents of several elements (with atomic numbers between 11 and 38) in 11 samples of commercial ground coffee, comparing with another one of soluble coffee and two of used ground coffee. Samples were dried at room temperature and pelletized. XRF analyses were carried out using a spectrometer based on an Rh X-ray tube, registering the characteristic x-rays with a Silicon Drift Detector. The system detection calibration and accuracy check was performed through the analysis of NIST certified reference materials 1547 (peach leaves), 1570a (spinach leaves), 1573a (tomato leaves), and 1571 (orchid leaves). As a general rule, the elemental concentrations measured are similar in all samples of coffee, in values not exceeding toxic levels. However, the differences among the elemental concentrations are shown.

Keywords: Ground coffee, Elemental analysis, XRF, Food analysis.

1. INTRODUCTION

Coffee is nowadays among the most popular beverages in Mexico. There was an estimated production in the country of 1×10^6 ton during the cycle 2014-2015, in 7.3×10^5 hectares of land. Moreover, coffee consumption grew at a rate of around 5% per year until 2015, reaching a total of 1.1×10^6 ton [1].

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Of this, 78% corresponds to instant coffee and the remaining 22% to ground coffee.

Coffee is grown as two species: *Cofea arabica* and *Cofea canephora*. They are commonly known as *arabica* and *robusta*. Its active substance is the alkaloid caffeine. Effects of coffee on human health are still under strong debate. Some authors suggest that drinking two to four cups of coffee per day benefit health, reducing the risk of colon cancer, gallstones, liver cirrhosis and Parkinson's disease [2, 3].

Processing starts from green coffee beans subjected to a thermal procedure, ending as roasted coffee beans. To produce instant coffee, the soluble and volatile components of the roasted beans are extracted. They provide the coffee aroma and flavor; it is possible to do it by means of water. Pressurized liquid water heated to around 175 °C is employed for this process. The coffee concentration in the resulting liquid is then augmented by either evaporation or freeze concentration.

Due to the economical relevance of coffee, extensive research has been published, in particular regarding its elemental composition, using many analytical techniques. For instance, Atomic Absorption Spectroscopy (AAS) was used by Grembecka et al. [3] to determine concentrations of 14 elements, and used them to differentiate the types of coffee (ground, instant) using multivariate statistics. Valentin and Watling [4] employed Inductively Coupled Plasma spectroscopies (ICP) to determine the provenance of coffee samples from 15 countries, based on the contents of 59 elements. Antoine et al. [5], with measurements through Neutron Activation Analysis (NAA) and other methods, determined the origin of ground coffee consumed in Jamaica. Debastiani et al. [6] analyzed Brazilian coffee samples with Particle Induced X-ray Emission (PIXE). Finally, Martín et al. [7] were able to establish differences between *arabica* and *robusta* samples based on elemental concentrations measured with ICP.

Furthermore, several studies have been conducted recently to determine the elemental concentrations in several types of food with high consumption in Mexico, employing x-ray spectrometric methods, such as X-ray Fluorescence (XRF) or PIXE. This way, elemental contents in tomato paste samples from five countries were determined using PIXE and ion backscattering [8]. Also, concentrations in many varieties of dried chili peppers were measured with XRF, finding unusually elevated values for Br [9]. Additionally, the concentrations of 10 elements were determined in commercial breakfast cereals of several types using XRF and PIXE [10].

With all this in mind, it was considered important to start a more thorough characterization of coffee consumed in Mexico, both ground and instant, either

to determine its nutritional properties, purity, or origin. As a first step, this work is aimed to demonstrate the viability of using XRF to quantify elemental concentrations in ground coffee samples, both fresh and used, as well as instant coffee. The data should provide information about possible differences in several elements, which might be fixed as indicators of coffee properties or provenance.

2. MATERIALS AND METHODS

Three types of coffee samples were obtained: ground coffee (11 samples), used ground coffee (two samples), and instant coffee (one sample). All of them were dried at room temperature, ground in an agate mortar and deposited inside polyethylene vials covered with 3.5 μm thick Mylar® films. A description of the samples is presented in Table 1. In general, it was not possible to determine if the samples were *arabica* or *robusta*.

XRF analysis was carried out using a spectrometer based on an Rh anode x-ray tube [11], with x-ray spectra detection through an Amptek® X-123SDD complete spectrometer (Bedford, MA, USA). The tube operated at a 35 kV voltage and a 500 μA current. Under these working conditions, primary photon scattering in the samples was strongly reduced. Collection time for each spectrum was 600 s. The spectra were collected with the attached Amptek® multichannel buffer and a personal computer. Pressure at the irradiation chamber was of the order of 5×10^{-6} torr.

Table 1: Description of coffee samples.

Sample	Type
Jekemir	Ground
Member´s Mark	Ground
Los Portales	Ground
Member´s Mark (*arabiga*)	Ground
Chiapaneco	Ground
La Onza (Coatepec)	Ground
Capeltic (Chiapas)	Ground
Blasón Gourmet	Ground
Casero 1 (*arabiga*)	Ground
Casero 2 (*arabiga*)	Ground
Cafesín	Ground and used
Diemme	Ground and used
Dolce Gosto (Lungo)	Ground (capsule)
Nescafé Dolca	Instant

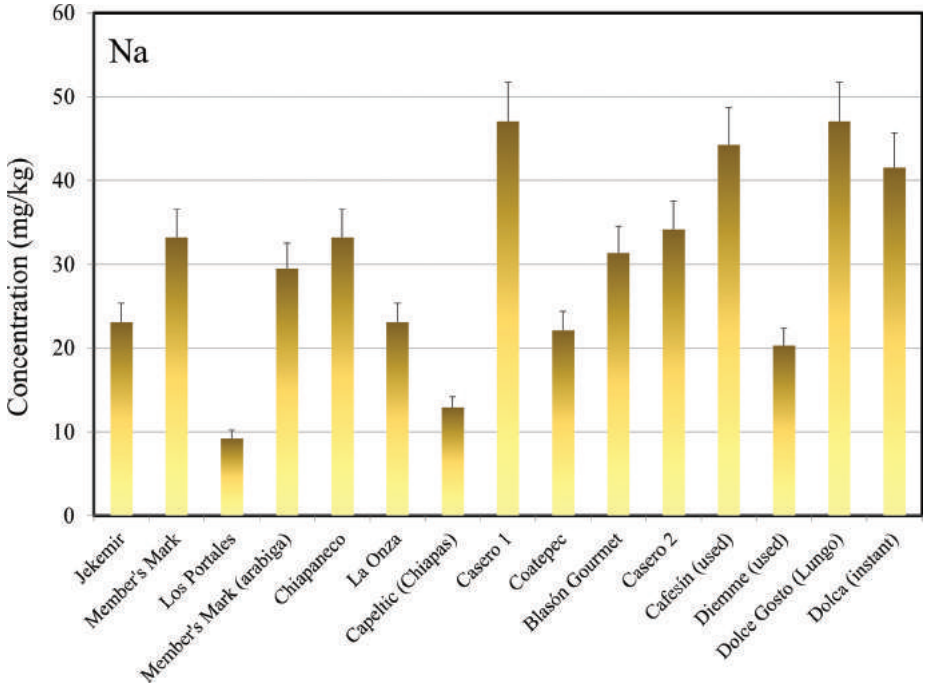
The system detection calibration was performed through the analysis of National Institute of Standards and Technology (NIST) certified reference materials 1547 (peach leaves), 1570a (spinach leaves), and 1573a (tomato leaves). Accuracy determination was then done by analyzing a sample of NIST reference material 1571 (orchard leaves). Spectra were deconvoluted with the open-access QXAS computer code [12].

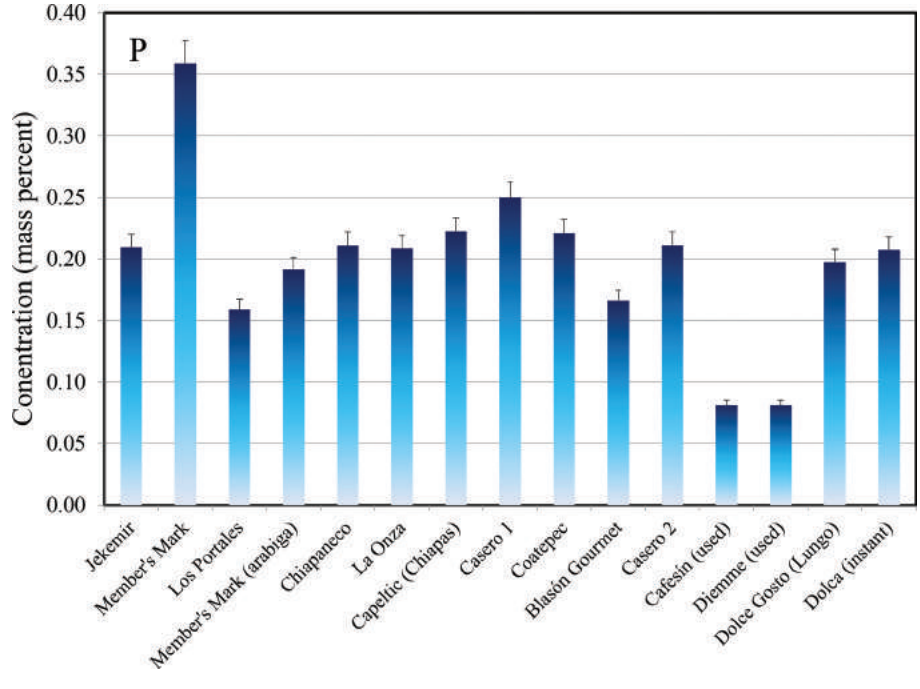
3. RESULTS AND DISCUSSION

The first result is the accuracy determination after analysis of the orchard leaves standard (NIST 1571). The elements P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Rb, and Sr were detected, quantified, and compared to the values given in the certificate. All of the measured elemental concentrations, except S and Cl, agree with the certified values within 20% or are even equal. In the case of S and Cl the disagreement (60% and –24%, respectively) is explained because their concentrations are not certified in the reference material. The overall consequence is that XRF may be considered as reliable in this study.

Regarding the coffee samples, a total of 14 elements were found: Na, Mg, P, S, K, Ca, Cr, Mn, Fe, Cu, Zn, Br, Rb, and Sr. Table 2 displays the average elemental concentrations in ground coffee, as well as the data for used ground coffee and instant coffee, all for dry mass. Experimental uncertainties range from 15% for trace elements (like Na, Mn, Cu, Zn, Sr), down to 4% for the major elements (K, Ca).

The concentrations of nine elements (Na, Mg, S, Mn, Fe, Cu, Zn, Rb, Sr) were similar among all the samples, including the used and instant coffee. An exception is Fe for the *Los Portales* sample, with a 560 mg kg^{-1} value, which is extremely high and may be attributed to the grinding machine used to process the roasted coffee. Nevertheless, the remaining elements showed strong differences among new ground coffee, used coffee, and instant coffee. Figure 1 presents the major nutrients Na, P, K, and Ca data for all samples, while Figure 2 displays concentrations of Cr and Br. In the case of Na, it is readily seen that no pattern can be identified for the three kinds of samples, as stated above. However, P, K, and Ca are strongly reduced in the used samples, most probably by a scavenging process by hot water during the brewing process. Additionally, Cr is increased in the *Cafesín* sample, possibly because a contamination from the coffee maker. Finally, the instant coffee sample *Dolca* has very high contents of Br. This is not easily explained, unless the manufacturer employs some Br-based compound as pesticide.


Na
Concentration (mg/kg)
60
50
40
30
20
10
0
Jekemir
Member's Mark
Los Portales
Member's Mark (arabiga)
Chiapaneco
La Onza
Capeltic (Chiapas)
Casero 1
Coatepec
Blasón Gourmet
Casero 2
Cafesin (used)
Diemme (used)
Dolce Gosto (Lungo)
Dolca (instant)


P
Conentration (mass percent)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Jekemir
Member's Mark
Los Portales
Member's Mark (arabiga)
Chiapaneco
La Onza
Capeltic (Chiapas)
Casero 1
Coatepec
Blasón Gourmet
Casero 2
Cafesin (used)
Diemme (used)
Dolce Gosto (Lungo)
Dolca (instant)

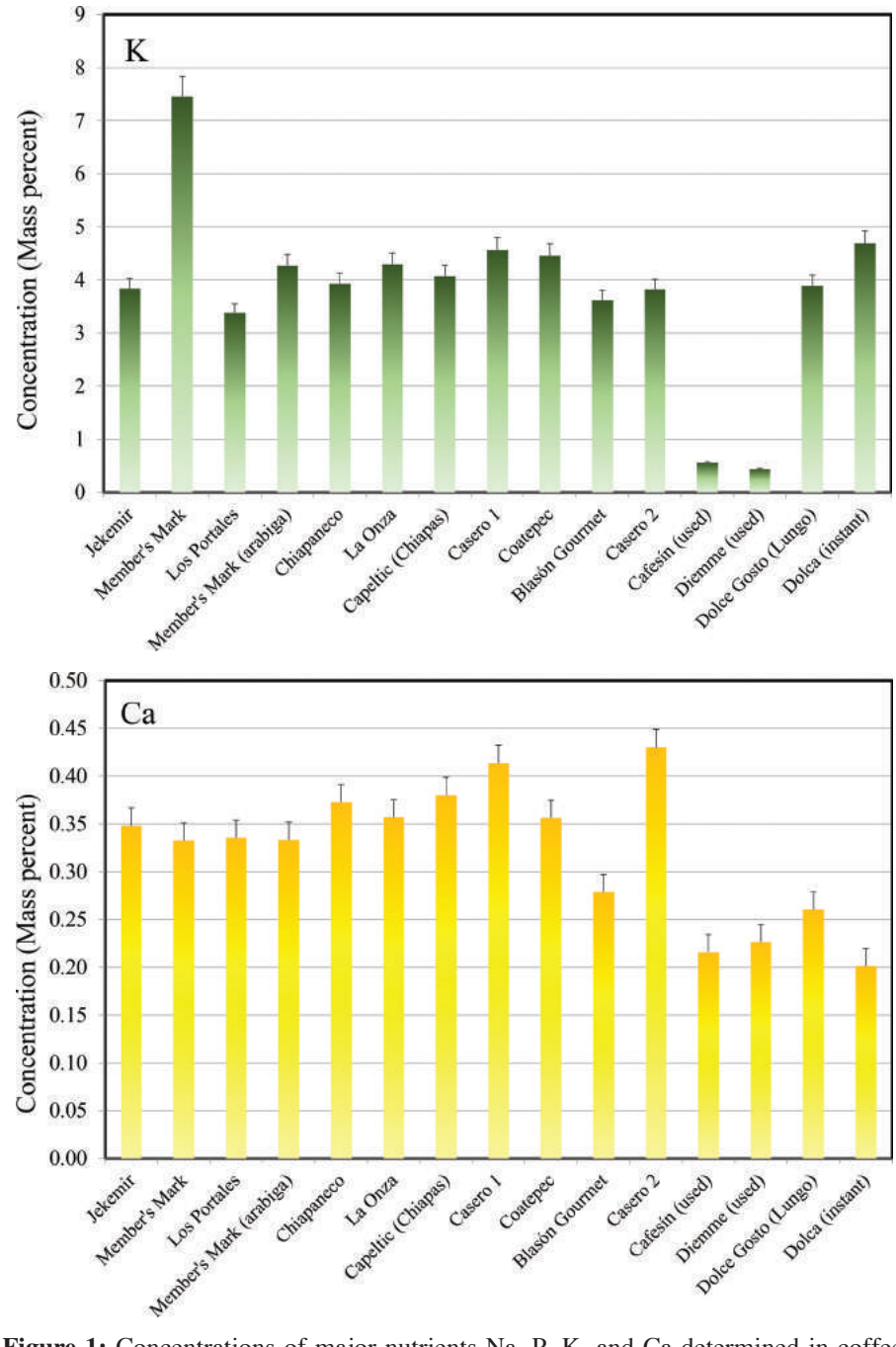


Figure 1: Concentrations of major nutrients Na, P, K, and Ca determined in coffee samples.

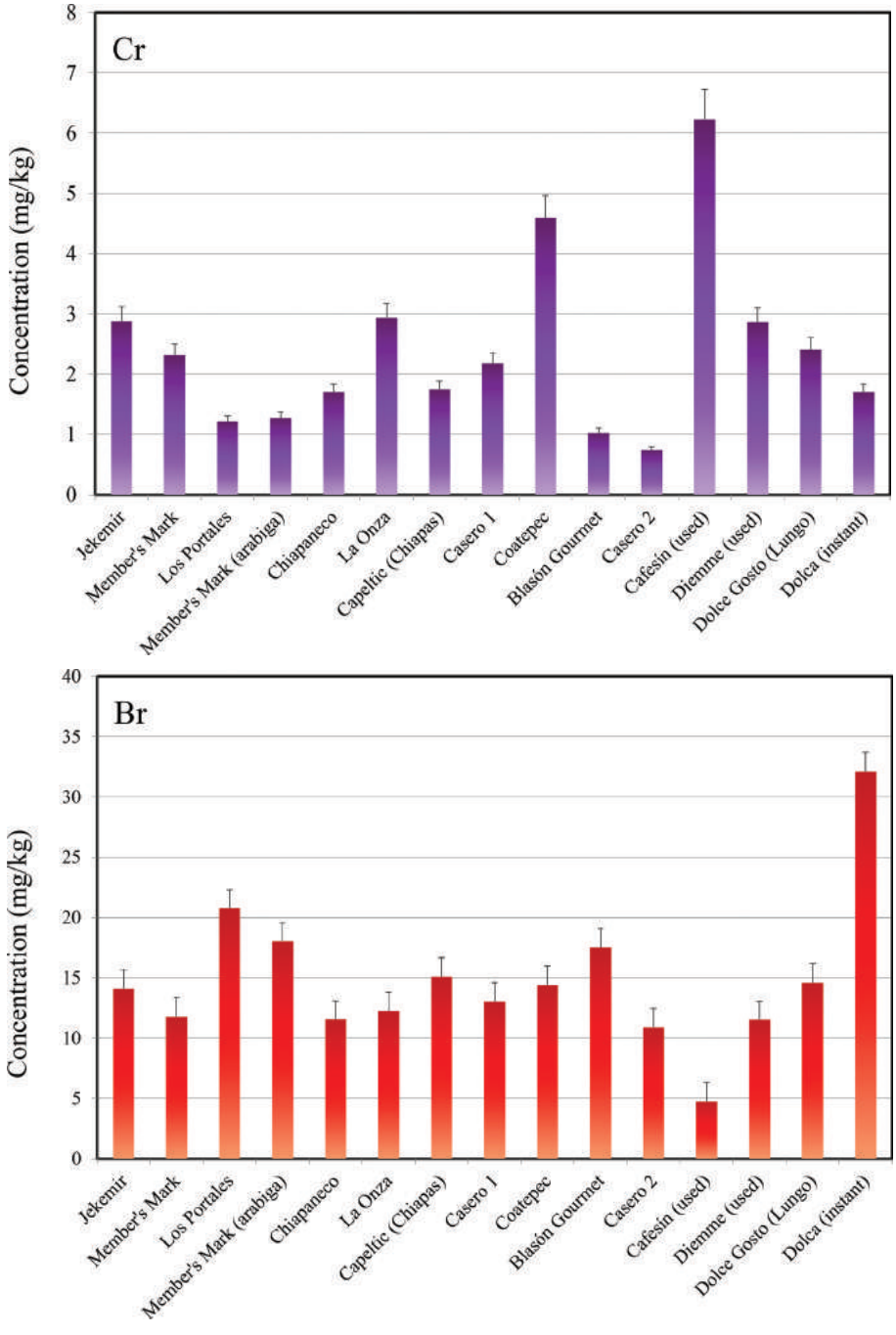


Figure 2: Concentrations of elements Cr and Br determined in coffee samples.

Table 2: Elemental concentrations determined in coffee samples: mean, minimum, and maximum for ground, coffee; used (*Cafesín* and *Diemme*), and instant coffee *Dolca*.

Element	Units	Mean ground coffee	Minimum ground coffee	Maximum ground coffee	Used *Cafesín*	Used *Diemme*	*Dolca*
Na	mg kg^{-1}	29	9.2	47	44	20	42
Mg	%	0.20	0	0.38	0	0.11	0.24
P	%	0.22	0.17	0.36	0.81	0.81	0.21
S	%	0.18	0.15	0.21	0.067	0.079	0.096
K	%	4.3	3.4	7.5	0.55	0.46	4.7
Ca	%	0.35	0.26	0.43	0.22	0.23	0.20
Cr	mg kg^{-1}	2.1	0.74	4.6	6.2	2.9	1.7
Mn	mg kg^{-1}	47	18	82	13	26	14
Fe	mg kg^{-1}	143	85	560	75	69	72
Cu	mg kg^{-1}	5.8	2.1	7.6	6.7	9.9	1.2
Zn	mg kg^{-1}	9.7	2.1	20	11	20	5.2
Br	mg kg^{-1}	15	11	21	4.7	12	32
Rb	mg kg^{-1}	18	10	25	2.5	9.9	18
Sr	mg kg^{-1}	35	17	49	8.3	18	9.2

A further test in the analytical results can be carried out through a comparison with other published works where results of elemental analyses of ground coffee samples were presented. Table 3 displays such data for selected elements, compared to the average of ground coffee from this work. It is possible to see that concentrations in the latter values are of the same order as those of the previous papers, although higher for K, Ca, and Fe. More research must be followed to find out the explanation of the higher averages.

Table 3: Comparison of elemental concentrations in ground coffee published in several studies.

Source	P %	K %	Ca %	Mn mg kg^{-1}	Fe mg kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}
Martín et al. [7]	0.12	1.27	0.088	28	40	11.9	5.1
Antoine et al. [5]	0.14	1.88	0.13	23	39	12.6	6.3

Ranic et al. [13]	–	1.81	0.11	33	39	18	6.0
Grembecka et al. [3]	0.23	1.37	0.084	22	42	16.1	5.3
Debastiani et al. [6]	0.27	2.13	0.14	33	65	19.4	8.4
Anderson [14]	0.20	1.90	0.12	25	13	14.0	8.0
This work	0.22	4.30	0.35	47	143	5.8	9.7

As discussed in all the works cited in Table 3, the concentrations measured for every element are not expected to reach toxic levels. Regrettably, no official standards exist for elemental concentrations in ground coffee, not even in the *Codex Alimentarius*, the official standard for many foods developed by the Food and Agriculture Organization. Thus, it is not possible to state if the measured concentrations fulfill any official limit in ground coffee.

CONCLUSIONS

From the results presented above, it is possible to assure that the analyses with XRF are accurate. Moreover, there are significant differences in the concentrations of several elements (like P, K, Ca) among roasted ground coffee, used ground coffee, and instant coffee specimens, probably because water drags these elements during the brewing. Instant coffee has very high Br concentration and used coffee may present Cr contamination during brewing. Elemental contents are similar to those determined in previous studies of roasted ground coffee, although the average looks higher for a few cases. It is not possible to see a definite disagreement in elemental concentrations to identify origin of the samples.

For future work, an extensive collection of samples must be carried out, including more instant coffee samples. The origin of coffee samples must be clearly established, possibly with the application of multivariate statistical analysis (like Principal Component Analysis) to a wider sample set. Finally, samples obtained directly from producers might be collected.

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