The potential of accelerator-based techniques as an analytical tool for forensics: The case of coffee

P. Chytry[a,b], G.M.S. Souza[a], R. Debastiani[c,d], C.E.I. dos Santos[e], J.M.R. Antoine[f], A. Banas[g], K. Banas[g], L. Calcagnile[h,i], M. Chiari[j], I. Hajdas[k], M. Molnar[l], P. Pelicon[m], N. Pessoa Barradas[n], G. Quarta[h,i], F.S. Romolo[o], A. Simon[n], J.F. Dias[a,b,*]

[a] *LII – Ion Implantation Laboratory, Institute of Physics, Federal University of Rio Grande do Sul (UFRGS), Av Bento Gonçalves 9500, CP 15051, CEP 91501-970 Porto Alegre, RS, Brazil*
[b] *Graduate Program on Materials Science, Federal University of Rio Grande do Sul (UFRGS), Av Bento Gonçalves 9500, CEP 91501-970 Porto Alegre, RS, Brazil*
[c] *Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*
[d] *3DMM2O-Cluster of Excellence (EXC-2082/1-390761711), Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany*
[e] *Institute of Mathematics, Statistics and Physics, Federal University of Rio Grande, Campus Santo Antônio da Patrulha, CEP 95500-000 Santo Antônio da Patrulha, RS, Brazil*
[f] *International Centre for Environmental and Nuclear Sciences, University of the West Indies, 2 Anguilla Close, 7 Kingston, Jamaica*
[g] *SSLS – Singapore Synchrotron Light Source, National University of Singapore, 5 Research Link, Singapore 117603, Singapore*
[h] *CEDAD – Centre for Applied Physics, Dating and Diagnostics, Department of Mathematics and Physics Ennio de Giorgi, University of Salento, Piazza Tancredi 2, 73100 Lecce, Italy*
[i] *INFN – National Institute of Nuclear Physics, Lecce Section, Lecce, Italy*
[j] *INFN – National Institute of Nuclear Physics, Florence Section, Physics Department, Via Sansone 1, Sesto Fiorentino, 50019 Florence, Italy*
[k] *ETHZ – Eidgenössische Technische Hochschule Zürich, Laboratory for Ion Beam Physics, Otto-Stern-Weg 5, 8093 Zürich, Switzerland*
[l] *ICER – Isotope Climatology and Environmental Research, Institute of Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/c, 4026 Debrecen, Hungary*
[m] *Jozef Stefan Institute, Jamova cesta 39, P.O. Box 3000, 1000 Ljubljana, Slovenia*
[n] *International Atomic Energy Agency, Vienna International Centre, Vienna, Austria*
[o] *Universitá degli Studi di Bergamo, Department of Law, Via Moroni 255, 24127 Bergamo, Italy*

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ABSTRACT

We discuss how different accelerator-based techniques can be employed synergistically as a powerful analytical tool for forensic studies of foodstuff. Brazilian and Jamaican coffees were chosen as a showcase due to its popularity and potential risk of adulteration and/or falsification. Comprehensive characterization of major and trace elements, age since production and compound contents were achieved using different techniques, including PIXE (Particle-Induced X-ray Emission), FTIR (Fourier Transform Infrared), and AMS-^{14}C (Accelerator Mass Spectrometry – Radiocarbon Analysis). While PIXE provides information on the elements present in the samples, FTIR probes the types of compounds through their vibrational spectra. Finally, AMS-^{14}C is capable of dating organic samples regarding their harvesting time. Five different laboratories from research institutions around the world took part in the experiments. The integration of the results obtained with different techniques provided multifaceted perspectives on the coffee under study, thus allowing a direct assessment of the material for forensic purposes such as authentication, determination of provenance, and combat counterfeiting.

1. Introduction

According to the World Coffee Organization [1], the world coffee production reached about 9.9 billion kilograms in 2019–2020, with a market value of approximately 28 billion US dollars. The Brazilian production accounted for approximately 35% of this total, followed by Vietnam, Colombia and Indonesia [1]. Despite several other countries having far smaller production, some offer premium coffees

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[*] Corresponding author at: LII – Ion Implantation Laboratory, Institute of Physics, Federal University of Rio Grande do Sul (UFRGS), Av Bento Gonçalves 9500, CP 15051, CEP 91501-970 Porto Alegre, RS, Brazil.
E-mail address: jfdias@if.ufrgs.br (J.F. Dias).

like Kona coffee from Hawaii (USA) and Blue Mountain coffee from Jamaica. In all cases, coffee is prone to suffer from fraud due to several factors including market value and financial vulnerability of producers living in regions associated with economic and social problems [2]. For instance, adulterants such as corn and soybean, among others, have been found in Brazilian coffee [3]. Moreover, 10% of all reported cases of food fraud between 2007 and 2017 in Brazil were related to coffee and tea, while 50% of all frauds in this period were of the dilution type [2]. Counterfeiting premium coffees was also observed for Kona [4] and Blue Mountain [5] coffees, fostering the use of authentication methods, in order to preserve the reputation of these coffees [5,6]. Authentication of some coffees can have a strong impact on the economy of the producing region or country. Indeed, the individualization of coffee brands allows the distinction between high and low market value products, besides pinpointing their region of production, in efforts to protect those coffees with certified geographical origin. Authentication and provenancing is challenging for routine, stand-alone techniques, e.g. Inductively Couple Plasma-Mass spectrometry (ICP-MS) technique and its variants [7–9]. In this work, an alternative approach is presented based on a combination of nuclear methodologies capable of providing unique information in forensic science [10].

Nuclear analytical techniques are usually based on, but not restricted to, particle accelerators and research reactors. Moreover, they are not exclusively related to nuclear processes as the name suggests. For instance, Instrumental Neutron Activation Analysis (INAA) is a quantitative technique where neutrons, usually from a research reactor, interact with the nuclei of the target atoms. The nuclei that result from neutron capture reactions are excited and decay emitting gamma rays characteristic of the emitting isotopes. These gamma rays are then detected for spectroscopy purposes. The Particle-Induced X-ray Emission (PIXE) technique detects characteristic X-rays emitted upon relaxation (de-excitation) of excited target atoms induced by charged particles bombardment (usually protons). Both PIXE and INAA techniques are non-destructive, i.e. the material under analysis can be preserved for future scrutiny. Moreover, they are essentially element-sensitive (and isotope-specific in the case of INAA) techniques with limit of detection (LOD) on the order of parts per million (ppm). These features have proven these techniques valuable for a broad range of analyses in different fields, including medical sciences, biology, ecology, materials science, and physics, among others [11,12]. Although techniques like INAA and PIXE have been long explored as analytical tools for use in forensic studies [13,14], they are, to date, mostly used by academia to characterize materials with potential forensic appeal [15,16]. The analytical power of the PIXE technique was greatly improved with the advent of what is known as micro-PIXE that combines scanning capability with reduced beam spot size to the micrometer scale or even less [17,18]. Due to its sensitivity and spatial resolution, micro-PIXE offers advantages over widespread techniques like Scanning Electron Microscopy equipped with Energy-Dispersive Spectrometer (SEM-EDS). Indeed, micro-PIXE can be used for the quantitative characterization of sample features at the micrometer level [19–21].

An important complementary technique to those based on accelerators is the Infrared (IR) spectroscopy, which measures the interaction of infrared radiation with the material under study by detecting covalent bond vibrations and rotations of molecules present in the sample upon resonant absorption of IR light. The development of Fourier Transform Infrared (FTIR) spectrometers in the late nineteen-sixties has gained immense popularity in a broad range of IR spectroscopy applications [22–30] since it provides chemical information from samples in a fast and non-destructive way with instrumentation that is not expensive. Among other types of IR sampling approaches, the attenuated total reflection (ATR) mode is ideal when the samples under study are neither transparent nor reflective for IR radiation. Therefore, the ATR-FTIR mode has become the standard FTIR technique for the analysis of different materials including foodstuff.

One of the most popular accelerator-based techniques is radiocarbon dating, also referred to as Accelerator Mass Spectrometry – Radiocarbon Analysis or, for short, AMS-^{14}C. Besides the traditional applications of ^{14}C dating in geochronology, its applicability in forensics and related sciences has been widely established for applications including studies in anthropology [31], pharmacology [32], contemporary art [33–36] and illicit trade of organic material from endangered species [37]. These applications are based on the so-called *bomb peak dating* method, i.e. the measurement of the anthropogenic ^{14}C produced in the atmosphere by nuclear detonation tests carried out in the middle of the last century and absorbed by the living organism under study [38]. Chronology resolution on the order of a few years or better has been achieved through this method [38].

In a recent work, Romolo and co-workers demonstrated how the combination of PIXE, Secondary Ion Mass Spectrometry with MeV ions (MeV-SIMS) and INAA results help discriminating authentic pharmaceuticals from counterfeit ones and therefore be useful for the forensic community [39]. The aim of the present work is to extend the work of Romolo and collaborators [39] by demonstrating the combined potentialities of PIXE, FTIR and AMS-^{14}C techniques to forensic scientists. A popular Brazilian coffee brand was chosen as the study case. The same batch of coffee was analyzed by PIXE, FTIR and AMS-^{14}C in five laboratories in different countries. The PIXE results were compared to analogous results from the world-famous Blue Mountain region in Jamaica, while the FTIR results for coffees of different brands were compared. Finally, the date of production of the Brazilian coffee was established by the AMS-^{14}C technique. The results obtained through standard statistical analysis of data demonstrated that these techniques are suitable for forensic studies. Overall, the approach adopted in this work provides a straightforward way to assess the potentialities and advantages these techniques can offer for the forensic community and how they could be used in forensic caseworks.

2. Materials and methods

2.1. Samples

Several 500 g packages of a popular Brazilian regular roasted ground coffee from Melitta brand (*Tradicional*) were bought at the same time and distributed among all laboratories participating in this project. All packages come from a single batch and therefore they share the same properties, including date of production, packaging and expiration date. This coffee has no certification of origin since several farms across different states in Brazil supply coffee to processing plants for production of packed roasted ground coffee, which is, in turn, distributed for all Brazilian retail markets.

Three regular roasted premium coffees from the same Melitta brand labeled *Cerrado*, *Mogiana* and *Sul Minas* and three brands of Blue Mountain coffees from Jamaica (*Jablum, Island Blue* and *JBMC*) were analyzed as well at a single laboratory (Ion Implantation Laboratory, LII, Brazil) for comparison purposes. While *Island Blue* and *JBMC* are regular roasted coffees, no information on the roasting degree of the *Jablum* coffee was provided by the manufacturer. These Brazilian and Jamaican coffees bear the names of the regions where the respective crops were cultivated and harvested. Therefore, these coffees were produced in particular regions and their origins were controlled for superior quality, thus achieving a higher market value.

Finally, several coffees found in the retail market in Singapore (*Best Western*, *Boyd*, *Colombian*, *Mandheling*, *Moccona*, *Nescafe* and *Robert Timms*) were analyzed at the Singapore Synchrotron Light Source (SSLS). It is important to note that *Boyd* and *Robert Timms* are decaffeinated coffees obtained through a water immersion process [40], while all the others are regular roasted ground coffees.

2.2. PIXE

The PIXE experiments were carried out at LII. The coffee samples were homogenized with a mortar and pestle and pressed into 2 mm thick pellets. The samples were irradiated with 2.0 MeV protons with typical currents on the order of 2 nA. The beam spot size on the samples was 4 mm^2. The characteristic X-rays generated during the irradiations were detected by a Si(Li) detector placed at −135° with respect to the beam direction. The energy resolution of the detector is about 150 eV at 5.9 keV. Charge buildup effects on the samples was minimized through the use of an electron flood gun place next to the sample holder. The X-ray spectra were analyzed with the GUPIXWIN software developed at the University of Guelph [41]. Further details of the experimental setup and data analysis can be found elsewhere [42,43].

For the PIXE analysis, *N* samples of the same material are irradiated one at a time, thus generating *N* X-ray spectra. While systematic uncertainties were minimized, each X-ray spectrum can be affected by random experimental factors, like e.g. possible inhomogeneities probed by the proton beam and intrinsic variability of the material itself (organic by nature in the present case). These uncertainties constitute the major contributors for the overall uncertainty associated with each X-ray spectrum. Since the number of samples analyzed by PIXE is relatively high, a traditional statistical analysis based on the variance of the X-ray spectra was carried out.

2.3. AMS-^{14}C

The carbon dating experiments were carried out at CEDAD (Italy), ICER (Hungary) and ETHZ (Switzerland) laboratories, each using similar procedures to chemically process the coffee samples prior to analysis. At CEDAD, two different processing procedures were applied to two aliquots of the sample. One sample portion underwent conventional AAA (Alkali, Acid, Alkali) processing to remove possible contaminants, while another equal portion underwent no chemical processing at all. The ^{14}C/^{12}C isotopic ratio was then measured at the AMS beamline of the 3 MV Tandetron™ accelerator. Further details can be found in [44].

At ETHZ and ICER about 2 mg of roasted ground coffee were prepared for graphitization [36,45–47], and the resulting graphite were pressed into aluminum cathodes for the ^{14}C/^{12}C analysis using the MICADAS (Mini Carbon Dating System) AMS system [48,49].

2.4. ATR-FTIR

A Bruker Vertex 80 v FTIR spectrometer coupled to a PIKE MIRacle universal ATR sampling accessory was employed in the IR experiments for the analysis of coffee. The spectral range and resolution were set between 4000 and 525 cm^{-1} (mid-IR region) and 4 cm^{-1}, respectively. A diamond/ZnSe crystal was used during the experiments, since it is a perfect choice for the analysis of soft, hard and abrasive types of powders. The beam penetration depth is about 2 µm assuming an IR beam incidence angle of 45° and refractive indexes of 2.4 for the crystal and 1.5 at 1000 cm^{-1} for the sample. After several tests, 67 scans were found to be an adequate compromise for collecting good quality spectra within a reasonable time (1 min).

Coffee samples were placed on the surface of ATR crystal (1.8 mm in diameter) and pressed against it using manual clamp. Three independent samples from each brand were analysed, yielding six spectra, each collected at the same experimental conditions at room temperature. In total, 18 FTIR spectra were collected in the ATR mode for the Melitta *Tradicional*. Finally, other coffee brands were analysed in the same manner as well, in order to make a comparison between different brands.

Table 1
Elemental concentrations of different coffees from Melitta brand. The results are expressed by the mean and the respective standard deviations (SD) obtained from the analysis of (n) samples whose results were above the limit of detection (LOD). The total number of samples analyzed for each group is represented by N. The frequency of occurrence F shown in the table stands for the relative number of times (n) that a particular element was positively detected above the LOD with respect to the total number of samples (N). Concentration values are given in mg/kg dry weight. Different superscript letters (a-d) within the rows represent statistically significant differences ($p < 0.05$). The elements Sc and Co were not detected (ND) in any of the *Tradicional* coffee samples.

	Cerrado (N = 50) Mean ± SD (n) F = (n/N)* 100	*Mogiana* (N = 50) Mean ± SD (n) F = (n/N)* 100	*Sul Minas* (N = 50) Mean ± SD (n) F = (n/N)* 100	*Tradicional* (N = 70) Mean ± SD (n) F = (n/N)* 100
Mg	1122^{a} ± 74 (46) 92%	1124^{a} ± 70 (49) 98%	1112^{a} ± 82 (49) 98%	1108^{a} ± 62 (70) 100%
Al	97^{a} ± 55 (7) 14%	101^{a} ± 26 (19) 38%	78^{a} ± 17 (10) 20%	80^{a} ± 19 (24) 34%
Si	81^{ab} ± 59 (22) 44%	95^{a} ± 48 (35) 70%	70^{b} ± 19 (41) 82%	95^{a} ± 45 (61) 87%
P	1030^{a} ± 108 (46) 92%	962^{b} ± 120 (49) 98%	942^{b} ± 126 (49) 98%	1040^{a} ± 82 (70) 100%
S	1364^{a} ± 79 (46) 92%	1435^{b} ± 76 (49) 98%	1325^{c} ± 87 (49) 98%	1268^{d} ± 53 (70) 100%
Cl	174^{a} ± 34 (46) 92%	198^{b} ± 25 (49) 98%	182^{ab} ± 36 (49) 98%	233^{c} ± 36 (68) 97%
K	14,593^{a} ± 565 (46) 92%	14,711^{a} ± 677 (49) 98%	14,678^{a} ± 835 (49) 98%	16,366^{b} ± 582 (70) 100%
Ca	1154^{a} ± 286 (46) 92%	1005^{bc} ± 184 (49) 98%	1121^{ab} ± 372 (49) 98%	968^{c} ± 166 (70) 100%
Sc	19.4^{a} ± 4.7 (5) 10%	16.6^{b} ± 1.9 (4) 8%	14.9^{c} ± 2.7 (8) 16%	ND
Ti	5.3^{a} ± 1.4 (8) 16%	4.8^{ab} ± 1.6 (12) 24%	3.9^{ab} ± 0.7 (7) 14%	4.8^{b} ± 1.5 (38) 54%
Mn	27.1^{a} ± 4.8 (46) 92%	26.3^{a} ± 5.3 (49) 98%	33.3^{b} ± 9.5 (49) 98%	28.0^{a} ± 4.4 (69) 98%
Fe	56^{a} ± 32 (46) 92%	45^{ab} ± 11 (49) 98%	39.7^{b} ± 8.9 (49) 98%	74^{c} ± 32 (68) 97%
Co	2.8^{a} ± 0.2 (4) 8%	< LOD	< LOD	ND
Ni	1.9^{a} ± 0.5 (7) 14%	1.3^{a} ± 0.5 (10) 20%	1.7^{a} ± 0.6 (6) 12%	1.5^{a} ± 0.3 (19) 27%
Cu	15.3^{a} ± 2.9 (46) 92%	14.3^{a} ± 2.8 (49) 98%	14.9^{a} ± 2.8 (49) 98%	15.4^{a} ± 2.9 (70) 100%
Zn	7.7^{a} ± 2.7 (43) 86%	5.5^{b} ± 1.7 (49) 98%	5.5^{b} ± 1.7 (47) 94%	5.4^{b} ± 1.7 (70) 100%
Br	6.5^{a} ± 0.2 (2) 4%	4.8^{a} ± 0.6 (4) 8%	5.6^{a} ± 1.8 (2) 4%	6.2^{a} ± 1.3 (2) 3%
Rb	29^{a} ± 11 (21) 42%	20.8^{b} ± 5.3 (38) 76%	24.5^{ab} ± 7.4 (42) 84%	25.4^{a} ± 7.7 (62) 89%
Sr	23.8^{a} ± 2.2 (5) 10%	17.8^{a} ± 2.7 (3) 6%	21.3^{a} ± 8.9 (7) 14%	15.7^{a} ± 2.1 (6) 9%

3. Results and discussion

3.1. Elemental chemical profile – PIXE

3.1.1. Classification and provenance of Brazilian coffees

The elemental composition of four varieties of Melitta roasted ground coffee were characterized with PIXE, in order to elucidate differences that might correlate with their origin. Three of the coffees, known as *gourmet coffees*, are certified by the producer regarding their region of crop origin (*Cerrado*, *Mogiana* and *Sul de Minas*), while the fourth one (*Tradicional*) corresponds to one of the most popular coffees in the country produced in different farms and regions of Brazil. The elements Mg, Si, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn and Rb were detected in most of the samples. Table 1 shows the mean elemental concentrations found above the LOD in the respective number of samples for the four types of coffee. The mean concentrations are reported in mg/kg and account only for a small fraction (about 2%) of the total mass. The remaining ~ 98% of the mass is comprised of the light matrix elements (carbon, nitrogen and oxygen),which are not detectable by the PIXE setup used. In less than half of the samples, the elements Al, Sc, Ti, Co, Ni, Br and Sr were detected above the LOD. The mean concentrations of these elements varied from 1.3 ± 0.5 mg/kg for Ni up to 101 ± 26 mg/kg for Al. Sc and Co were not detected in the *Tradicional* coffee. In order to compare different coffees, the analytical results in Table 1 were subjected to one-way analysis of variance (ANOVA) and Tukey's post-hoc tests (significance level of 0.05). The concentrations of all elements but Mg, Al, Ni, Cu, Br and Sr were found to be statistically different from at least one of the other coffee varieties. It is important to note that only Mg and Cu were detected in all analyzed samples. Moreover, S and Sc were the only elements whose concentrations differ for all varieties of coffee, although Sc has been detected in a few samples only.

Rubidium is a recurrent element in Brazilian soil [50] and therefore it is usually found in Brazilian foodstuffs and beverages, like wine, coffee and mate tea leaves [50–53]. For this reason, Rb has been suggested as an potential chemical marker for Brazilian foodstuff [52]. The Rb concentrations found in the Brazilian coffees studied here varied from 21 mg/kg up to 29 mg/kg, which are compatible with concentrations found in previous studies of the Melitta *Tradicional* coffee [42,52]. However, a recent study of Melitta *Tradicional* showed a much larger concentration range for Rb, varying from 22 mg/kg up to 58 mg/kg [54]. In that study different batches were analyzed, which were produced 2 and a half years apart, thus proving that the data variance is influenced by several factors, including the crop region and harvesting date which, in turn, reflect on differences found in different batches of the same brand [42]. It is also interesting to observe that the concentration of Rb was found above the LOD in 42% of the *Cerrado* coffee samples.

The concentrations of Mg and Cu are the same for all coffees, while the concentration of S is different for all coffees. In this way, S could be a potential chemical marker for the distinction of the coffees shown in Table 1. Considering only those elements with relatively high frequency of occurrence, the concentrations found in *Mogiana* and *Sul Minas* coffees are the same for 7 elements (P, K, Cl, Ca, Fe, Zn and Rb) besides Mg and Cu. It is worth to mention that these two coffees were produced in regions that are geographically close to each other, which might be the reason.

Potassium, which is the main minor element present in coffee, has similar concentrations (about 15,000 mg/kg) in the gourmet coffees. Comparatively, these concentrations are smaller than those found for the *Tradicional* coffee here and in previous studies [42,52,54–56]. The differences in K content could be related to the type of coffee, since the gourmet coffees are 100% Arabica while the *Tradicional* coffee corresponds to a blend of Arabica and Robusta coffee beans and it has been shown that Arabica coffee has lower concentrations of K than Robusta coffee [57–59].

Other elements like Cl and Fe present in the gourmet coffees have different concentrations from those found in the *Tradicional* coffee. The concentration of Cl found in the *Tradicional* coffee (233 mg/kg) is lower than those found in previous investigations of this coffee [42,54,55]. The presence of Cl in in coffee [60] and wine [61] has been associated with moldy odor and musty taste. This observation could be related to factors linked to field and processing practices, in addition to the region of production. For instance, roasting and grinding of the coffee beans with leaves and twigs collected during harvesting could increase the presence of Cl in the coffee [55]. Extra care taken for the gourmet coffees could explain the lower concentration of Cl in their coffees, since a better control in the whole process from harvesting through packaging to the final consumer avoids contact of the beans with potential sources of Cl. Finally, the Fe concentration determined for the Melitta *Tradicional* agrees well with results from previous studies of this coffee [55,56].

Table 1 shows the frequency each element was detected above the LOD with respect to the total number of samples analyzed for each group of coffee in percent (F in Table 1). Comparison of the frequencies for elements between the coffee types can help identify potential discriminators of these coffees. Many elements including Al, Sc, Ti, Co, Ni, Br and Sr were present in less than 20% of the samples for at least one of the coffees; trace elements like Br and Sr have frequencies below 10%; and other elements have frequencies close to 100%. Both Sc and Co are absent from Melitta *Tradicional* coffee and Co was positively detected in *Cerrado* coffee only. This suggests that Sc and Co may be good potential markers to discriminate these coffees.

3.1.2. Classification and provenance of Jamaican coffees

PIXE analysis of Jamaican Blue Mountain coffees (Table 2) identified the presence of the following elements: Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, and Sr. Although Sc, Co and Br were

Table 2
Elemental concentrations of different Blue Mountain coffees from Jamaica. The results are expressed by the mean and the respective standard deviations (SD) obtained from the analysis of (n) samples whose results were above the limit of detection (LOD). The total number of samples analyzed for each group is represented by N. The frequency of occurrence F shown in the table stands for the relative number of times (n) that a particular element was positively detected above the LOD with respect to the total number of samples (N). Concentration values are given in mg/kg dry weight. Different superscript letters (a-c) within the rows represent statistically significant differences ($p < 0.05$).

	Island Blue N = 15 Mean ± SD (n) F = (n/N)* 100	*Jablum* N = 18 Mean ± SD (n) F = (n/N)* 100	*JBMC* N = 16 Mean ± SD (n) F = (n/N)* 100
Mg	914^{a} ± 91 (15) 100%	977^{a} ± 68 (18) 100%	821^{b} ± 109 (16) 100%
Al	55^{a} ± 30 (4) 27%	57.4^{a} (1) 6%	106^{a} ± 21 (3) 19%
Si	61^{a} ± 14 (8) 53%	68^{a} ± 21 (4) 22%	120^{a} ± 112 (8) 50%
P	985^{ab} ± 142 (15) 100%	1018^{a} ± 124 (18) 100%	864^{b} ± 176 (16) 100%
S	1301^{a} ± 82 (15) 100%	1460^{b} ± 76 (18) 100%	1287^{a} ± 104 (16) 100%
Cl	95^{a} ± 25 (15) 100%	194^{b} ± 44 (18) 100%	116^{a} ± 37 (16) 100%
K	$13,443^{ab}$ ± 775 (15) 100%	$13,878^{a}$ ± 1419 (18) 100%	$12,587^{b}$ ± 700 (16) 100%
Ca	1200^{a} ± 249 (15) 100%	1578^{b} ± 498 (18) 100%	993^{a} ± 135 (16) 100%
Ti	4.11^{a} ± 0.65 (7) 47%	6.2^{a} ± 4.6 (9) 50%	< LOD
Mn	24.4^{a} ± 4.4 (15) 100%	25.6^{a} ± 7.2 (18) 100%	23.8^{a} ± 4.8 (16) 100%
Fe	42.3^{a} ± 5.0 (15) 100%	47.1^{a} ± 8.1 (18) 100%	43.5^{a} ± 9.9 (16) 100%
Ni	1.8^{a} ± 0.6 (5) 33%	2.0^{a} ± 0.8 (7) 39%	1.1^{a} ± 0.1 (4) 25%
Cu	14.6^{a} ± 2.0 (15) 100%	16.5^{a} ± 3.7 (18) 100%	16.3^{a} ± 3.6 (16) 100%
Zn	6.7^{a} ± 2.0 (15) 100%	8.2^{ab} ± 1.5 (17) 94%	10.1^{b} ± 3.5 (16) 100%
Rb	< LOD	13.5^{a} ± 0.4 (3) 17%	15.0^{a} ± 2.3 (6) 38%
Sr	18.4^{a} ± 1.3 (3) 20%	25.2^{a} ± 9.6 (4) 22%	22.9^{a} ± 8.0 (2) 12%

included in the analysis, their concentrations were below the LOD for all samples analyzed. Statistical analyses indicate that the concentrations of Al, Si, Ti, Mn, Fe, Ni, Cu, and Sr are the same or similar for these coffees, suggesting a high degree of resemblance among them. The elements Al, Rb and Sr were detected with an occurrence frequency less than 20% for at least one of the coffees and the concentrations of Al and Sr are much higher than those found in the literature for Jamaican coffees [5,62]. The concentrations of Ca, Mn, Ni, Cu, and Zn in the *Jablum* coffee are compatible with those measured by Antoine and collaborators [5], while the concentrations of Al, Fe, Rb and Sr are higher than those reported in [5]. Only the concentrations of Mg and K reported in [5] were higher those in Table 2. These differences can be attributed to different *Jablum* batches used for both studies, since varying factors such as weather and field practices from crop to crop can influence the final elemental composition of the foodstuff.

Concerning Rb, Table 2 shows that this element was detected in just few samples of the Jamaican Blue Mountain coffees (Table 2) and with relatively lower detection frequencies compared with the Brazilian coffees (Table 1). Lower concentrations of Rb seems to be a characteristic of Blue Mountain coffees and not for coffees grown in other parts of Jamaica. The average concentration of Rb for all coffees from Blue Mountain measured in the present study is 14.5 mg/kg, while Jamaican coffees other than Blue Mountain can reach up to 35 mg/kg [5].

Unlike Brazilian coffees (Table 1), where distinct concentrations for two elements (S and Sc) were observed for all studied coffees, the Blue Mountain coffees bear a relatively high degree of similarity among them. Indeed, the concentrations of Al, Si, Mn, Fe, Ni, Cu and Sr are statistically the same for all Blue Mountain coffees shown in Table 2. Moreover, the results reveal that *Island Blue* and *Jablum* coffees exhibit the same or similar concentrations for most elements. This similarity likely stems from the fact that these coffees are grown in a relatively small area, the Blue Mountain.

3.1.3. Comparison between Melitta Tradicional and Blue Mountain coffees

The elemental concentrations of Melitta *Tradicional* and of Blue Mountain coffees are compared in Table 3. The results for the *Tradicional* coffee are from Table 1, while the results for the *Blue Mountain* coffee in Table 3 are the average of all Jamaican coffees in Table 2. The PIXE spectra (averaged over all spectra) of Melitta *Tradicional* and of *Blue Mountain* coffees are compared in Fig. 1. Despite the similarity of both spectra in terms of elemental profile, some differences are clearly visible, particularly for Fe and Rb.

Most of the elemental concentrations in Table 3 are statistically different between the coffees, suggesting that the coffees are distinct. The only elements present in these coffees with statistically equal concentrations are Al, Si, Ni and Cu.

The concentrations of Mg, P, Cl, K, Mn, Fe, and Rb are higher in the Brazilian coffee than the Jamaican coffees. In particular, the concentrations of Cl, Fe and Rb found in the Brazilian coffee are about 1.7 times higher. The differences in Fe and Rb content are also clearly visible in the PIXE spectra in Fig. 1. Not only is the concentration of Rb higher in the *Tradicional* coffee, its frequency reaches 89%, i.e. much higher than that found for the *Blue Mountain* coffees. This result contrasts that obtained by Liu et al. for Jamaican coffee [62], where a Rb concentration about three times larger than the value of 14.5 mg/kg shown in Table 3 for the Blue Mountain coffees is reported. On the other hand, the Fe results obtained in this work for all Jamaican coffees (Table 2&3) are similar to the value of 49 mg/kg reported by Liu and collaborators [62]. Note that Liu and collaborators analyzed green coffee beans identified only as “Jamaican coffee”, thus not necessarily representing Blue Mountain coffees.

Table 3

Elemental concentrations of Melitta *Tradicional* and *Blue Mountain* coffees. The results of Mellita *Tradicional* were extracted from Table 1, while the *Blue Mountain* coffee results represent the overall average of the concentrations shown in Table 2. The results are expressed by the mean and the respective standard deviations (SD) obtained from the analysis of (n) samples whose results were above the limit of detection (LOD). The total number of samples analyzed for each group is represented by N. The frequency of occurrence F shown in the table stands for the relative number of times (n) that a particular element was positively detected above the LOD with respect to the total number of samples (N). Concentration values are given in mg/kg dry weight. Different superscript letters (a-b) within the rows represent statistically significant differences ($p < 0.05$).

	Tradicional N = 70 Mean ± SD (n) F = (n/N)* 100	*Blue Mountain* N = 49 Mean ± SD (n) F = (n/N)* 100
Mg	1108^{a} ± 62 (70) 100%	907^{b} ± 110 (49) 100%
Al	80^{a} ± 19 (24) 34%	75^{a} ± 35 (8) 16%
Si	95^{a} ± 45 (61) 87%	86^{a} ± 74 (20) 41%
P	1040^{a} ± 82 (70) 100%	957^{b} ± 160 (49) 100%
S	1268^{a} ± 53 (70) 100%	1355^{b} ± 118 (49) 100%
Cl	233^{a} ± 36 (68) 97%	138^{b} ± 56 (49) 100%
K	$16{,}366^{a}$ ± 582 (70) 100%	$13{,}323^{b}$ ± 1158 (49) 100%
Ca	968^{a} ± 166 (70) 100%	1271^{b} ± 418 (49) 100%
Ti	4.8^{a} ± 1.5 (38) 54%	< LOD
Mn	28.0^{a} ± 4.4 (69) 99%	24.6^{b} ± 5.7 (49) 100%
Fe	74^{a} ± 32 (68) 97%	44.4^{b} ± 8.1 (49) 100%
Ni	1.5^{a} ± 0.3 (19) 27%	1.7^{a} ± 0.7 (16) 33%
Cu	15.4^{a} ± 2.9 (70) 100%	15.8^{a} ± 3.3 (49) 100%
Zn	5.4^{a} ± 1.7 (70) 100%	8.4^{b} ± 2.8 (48) 98%
Rb	25.2^{a} ± 7.8 (62) 89%	14.5^{b} ± 2.0 (9) 18%
Sr	15.7^{a} ± 2.1 (6) 9%	22.4^{b} ± 7.3 (9) 18%

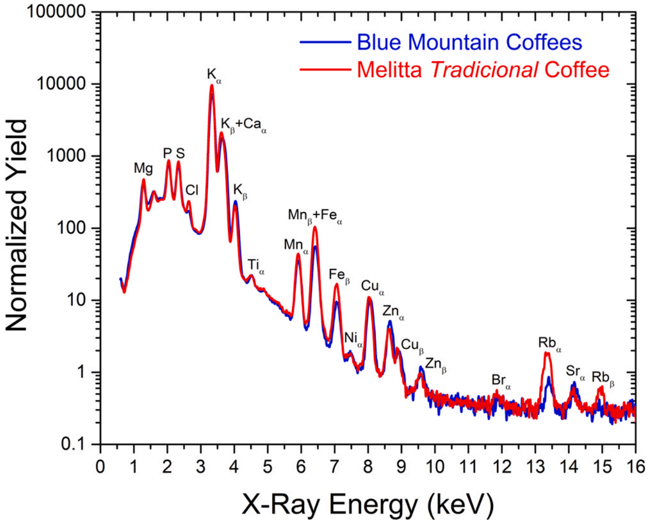

Fig. 1. X-ray yield as a function of the X-ray energy. The yields of all measurements were normalized by the charge accumulated during the experiments. Each spectrum represents an average over all measurements carried out for the Melitta *Tradicional* (red line) and for *Blue Mountain* (blue line) coffees. The elements are identified by the respective atomic transitions (alpha or beta).

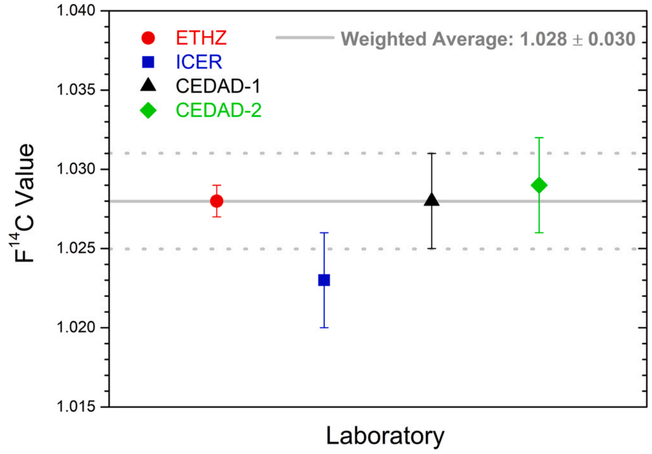

Fig. 2. ^{14}C/^{12}C ratio expressed as the fraction modern F^{14}C value obtained at ETHZ, ICER and CEDAD laboratories. The ETHZ result represents the average obtained from the analysis of 5 subsamples. The results represented by CEDAD-1 and CEDAD-2 refer to the analysis of unprocessed and AAA chemically processed samples respectively. The full gray line stands for the weighted average of all measurements, while the dotted gray line delineates the one standard deviation region. See text for further explanation.

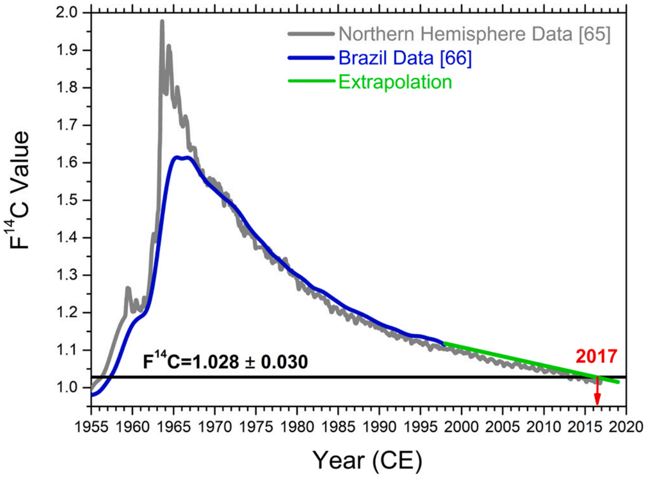

Fig. 3. ^{14}C/^{12}C ratio as a function of the year (Common Era). The ratio is expressed as the fraction modern F^{14}C value. The data from the Northern Hemisphere (gray line) was obtained from the work of Hammer and Levin [65] and is shown as a reference. The Brazilian data (blue line) [66] was extrapolated (green line) after 1997. The red arrow indicates the interception between the extrapolated Brazilian data and the F^{14}C value of 1.028. See text for further explanation.

3.2. *Determination of the harvesting time with AMS-^{14}C*

The AMS-^{14}C results for the Melitta *Tradicional* coffee samples obtained in three different laboratories are shown in Fig. 2, expressed as a carbon fraction modern (F^{14}C). The results for the ^{14}C/^{12}C isotopic ratio take into account corrections due to the calibration of the equipment, to the sample processing background and to the isotopic mass fractionation. The fraction modern F^{14}C is adequate for the assessment of post-bomb ^{14}C samples since it expresses the ratio between the normalized sample activity and its normalized specific activity [63]. The results from the three laboratories are comparable within one standard deviation. A F^{14}C value of 1.028 ± 0.030 was derived from the weighted average of the results obtained in the three laboratories as shown in Fig. 2. The two CEDAD results indicate that processing the samples does not introduce significant contamination in the coffee samples, as the ^{14}C concentration obtained from unprocessed material is undistinguishable from the results obtained from processed samples.

The available database of the atmospheric ^{14}C concentration in the terrestrial atmosphere is used to obtain the time when the coffee was harvested and processed [64]. Since the calibration of "post-bomb" dates are influenced by the intra- and inter-hemisphere differences in ^{14}C concentrations, different curves must be used, depending on the hemisphere under scrutiny. Brazil falls in the SH3 (Southern Hemisphere zone 3) hemisphere as defined by Hua and collaborators [38] and therefore the Northern Hemisphere calibration [65] cannot be used for dating purposes. Since Brazil spans more than 4000 km in the longitudinal direction, differences in calibration from north to south is expected. The calibration curve of the ^{14}C level measured in a Paraná pine tree from Southern Brazil [66] is about 1% higher than the Southern Hemisphere level.

As these organic samples are of young age, proper calibration using a local database extending up to the present is necessary; however, the current available database for Brazil covers a period of time before 1997 only. In order to obtain information corresponding to the present day, the Northern hemisphere data were extrapolated through a least squares linear fit to the data in the range between 1998 and 2017. The obtained straight fit line (R^2 = 0.97) was then shifted along the y-axis by 1%, in order to take into account the deviation of the Brazil data from the global average. The results of the extrapolation procedure are shown in Fig. 3. The first intercept with the curve in the late 1950s was discarded based on the fact that the present samples stemmed from relatively fresh organic material. The second intercept of the extrapolated curve, with weighted F^{14}C value of 1.028 ± 0.030, indicates that the present samples were harvested in 2017 with an uncertainty of about 1.5 years. This result is in agreement with the information of the product provided by the manufacturer, a fabrication date of March 1st 2018 and the expiration date September 2nd 2018.

3.3. *Determination of organic compounds with FTIR*

Since FTIR spectroscopy probes intrinsic molecular vibrational and rotational frequencies of bonds between atoms of molecules present in the samples under study, these absorption bands are generally represented as a function of the wavenumber given in units of cm^{-1}. Eighteen spectra were collected for eight different coffee brands: *Boyd*, *Best Western*, *Colombian*, *Mandheling*, *Moccona*, *Nescafe*, *Robert Timms,* and Melitta *Tradicional*. Unlike the other coffees, *Boyd* and *Robert Timms* are decaffeinated coffees. Each spectrum was corrected for any interference from atmospheric water vapor and carbon dioxide.

The spectral datasets were pre-processed for baseline correction and normalization procedures. Two spectral regions were tested for their ability to distinguish *Mellita Tradicional* coffee from the others:. The first one corresponds to the entire mid-IR range between 4000 cm^{-1} and 525 cm^{-1}. The second one referred to as the fingerprint region focused on much narrower mid-IR region between 1900 cm^{-1} and 525 cm^{-1}. Spectral signatures were interpreted using multivariate analysis with principal component analysis (PCA) and hierarchical cluster analysis (HCA).

Fig. 4 depicts the averaged spectra collected for all eight coffees brands analysed in this work covering the IR range between 4000 cm^{-1} and 2400 cm^{-1}. As can be seen, the ATR-FTIR spectra are quite complex displaying several broad and narrow bands. Such complexity might be connected to several variables including cultivation practices, harvesting, storage and roasting time among others. Eventually, all these parameters determine the coffee sensory profile. The broad band at 3308 cm^{-1} is present in all spectra and corresponds to O-H stretching related to hydroxylated compounds such as sugars, carboxylic acids, phenols, and adsorbed water. The small band located at 3008 cm^{-1} corresponds to the H–C= stretching vibration such as in unsaturated fatty acids. Three coffees (Melitta *Tradicional*, *Best Western* and *Boyd*) have similar FTIR patterns with

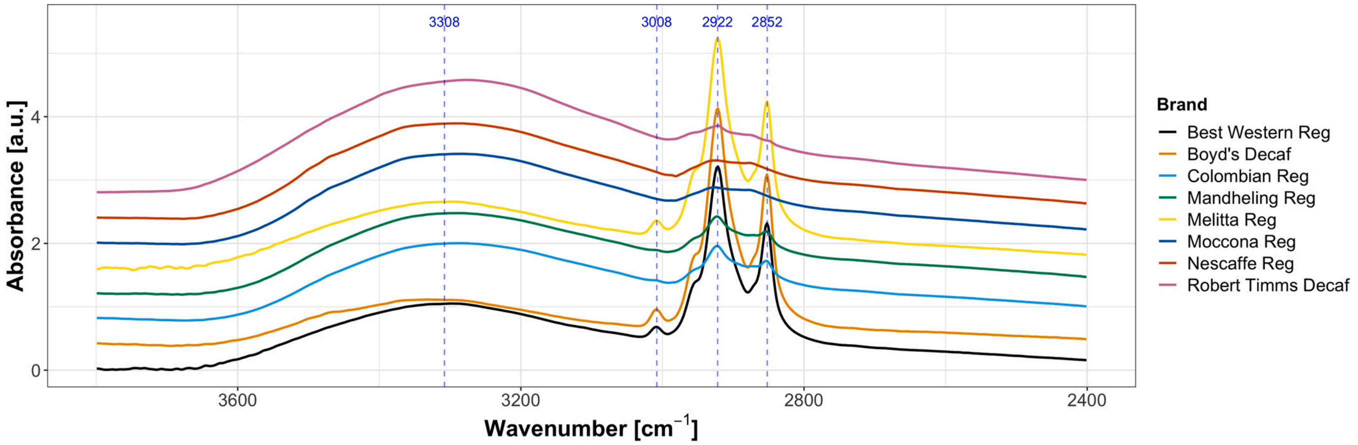

Fig. 4. ATR-FTIR spectra covering the mid-IR range between 3800 cm^{-1} and 2400 cm^{-1} collected for coffee samples bought in the Singapore retail market. The absorbances (given in arbitrary units) were normalized for comparison purposes. Every spectrum is an average profile of 18 spectra collected for every type of coffee. See text for further information.

prominent bands at 2922 cm^{-1} and 2852 cm^{-1} corresponding to the antisymmetric and symmetric vibrations of aliphatic CH$_2$ molecules, such as fatty esters and long-chain alcohols.

Fig. 5 displays the averaged spectra in the fingerprint region between 1900 cm^{-1} and 525 cm^{-1}. The FTIR spectra of Melitta *Tradicional*, *Best Western* and *Boyd* coffees all exhibit another large peak at 1743 cm^{-1} belonging to the stretching vibration of the C=O bond in esters and is attributed to coffee lipids, which affect the aroma quality of the coffee. These three coffees, or the ‘Melitta-like group’, must have a lipid composition that is different from the rest of the analysed samples. The band related to peptide linkages in proteins appears around 1650 cm^{-1} with different amplitudes for each of these coffees. Bands for OH bending of adsorbed water, free fatty acids, and chlorogenic acids are present between 1650 cm^{-1} and 1625 cm^{-1}. IR bands associated with chlorogenic acid occur also in the 1300 cm^{-1} - 800 cm^{-1} region, whereas those for caffeine is found in the region from 1700 cm^{-1} to 745 cm^{-1}, with the most prominent bands at 1655 cm^{-1}, 1549 cm^{-1}, 1239 cm^{-1}, and 762 cm^{-1}. As can be seen in Fig. 4, bands related to caffeine are also observed in spectra for samples labeled as decaffeinated, which indicates that the process of decaffeination was not 100% complete. It is worth mentioning that Robert Timms acknowledges that their decaffeinated coffee may contain up to 0.3% caffeine.

The spectral region between 1900 cm^{-1} and 525 cm^{-1} was chosen as the fingerprint region for the multivariate analysis since it is rich in IR bands for many compounds present in coffee. This spectral region is quite complex, and its complexity might well be connected to several variables including cultivation practices, harvesting, storage, and roasting time among others. HCA and PCA were carried out with the open-source *R Environment* software (R version 4.1.1 and RStudio version 2021.09.0 Build 351). HCA was used to identify similarities among the coffee samples' FTIR spectra. The HCA dendrogram depicted in Fig. 6 shows the hierarchical relationship between spectra. Ward's aggregation algorithm used in HCA partitioned sample spectra into two main groups. Spectra collected for *Tradicional* coffee are linked together at low height with *Boyd* and *Best Western* coffee samples, thus suggesting that these coffees are quite similar. This corroborates the qualitative observations of the FTIR spectra. Finally, the PCA results from the same spectral region indicate that the first four principal components account for 86% of the system variability and provide a good degree of differentiation of the coffees studied in this work. Fig. 7 illustrates the projection of the spectra data onto the two first principal components. Although the *Boyd* and *Best Western* coffees show similarities with Melitta *Tradicional* coffee in the qualitative interpretation, leading to our grouping them into a Melitta-like group, these two coffees still cluster differently, thus allowing a clear distinction.

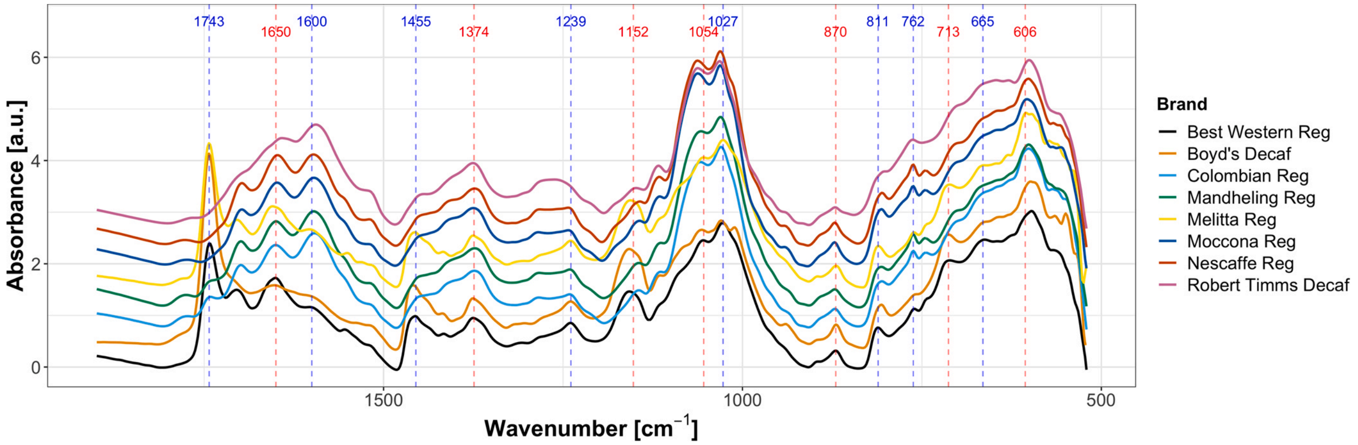

Fig. 5. ATR-FTIR spectra covering the mid-IR range between 1900 cm^{-1} and 525 cm^{-1} collected for eight coffee samples bought in the Singapore retail market. The absorbances (given in arbitrary units) were normalized for comparison purposes. Every spectrum is an average profile of 18 spectra collected for every type of coffee. See text for further information.

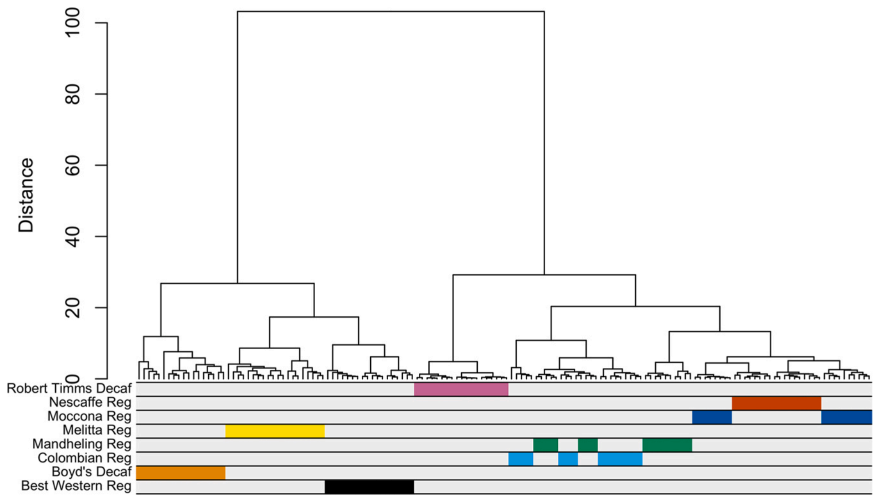

Fig. 6. Dendrogram of the hierarchical clustering analysis (HCA) referring to the mid-IR fingerprint region depicted in Fig. 5. See text for further explanation.

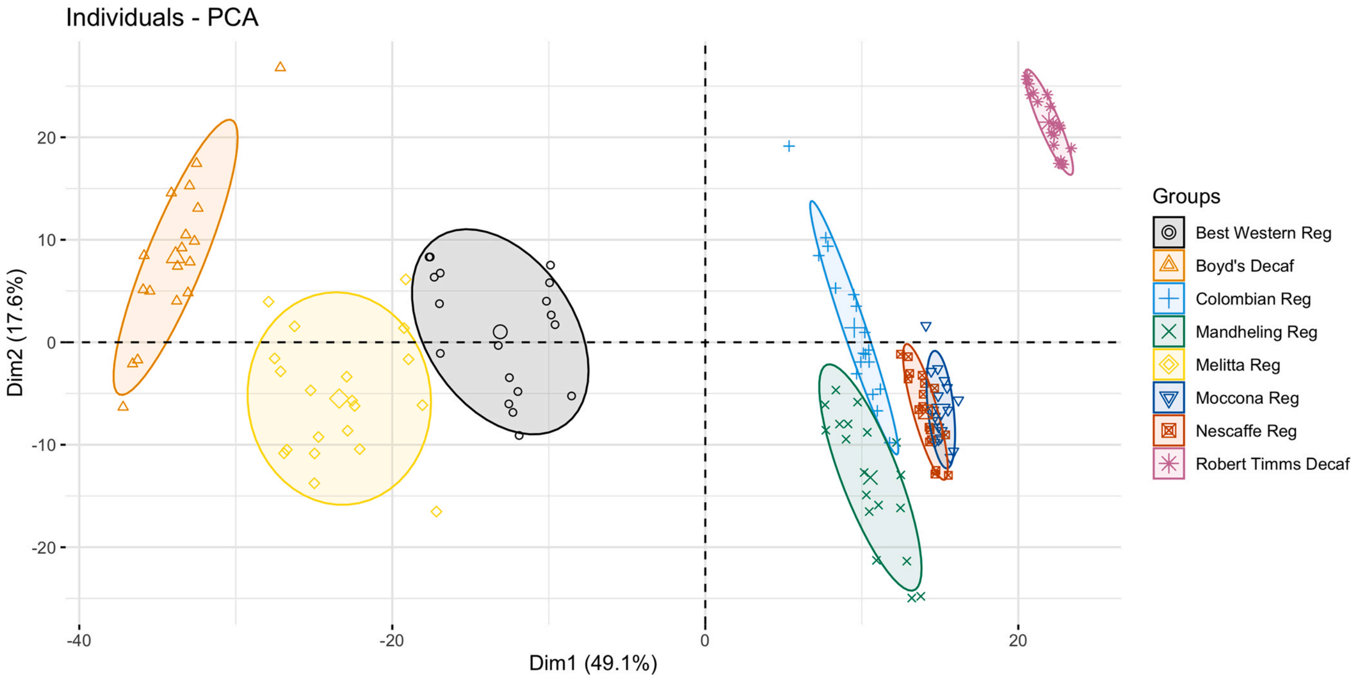

Fig. 7. Graphical presentation of the principal component analysis (PCA) referring to the mid-IR fingerprint region depicted in Fig. 5. The results show the first (49.1%) and second (17.6%) principal components. See text for further explanation.

4. Concluding remarks

In this work, the potentialities of ATR-FTIR and accelerator-based techniques like PIXE and AMS-^{14}C for identifying food fraud were demonstrated through the analysis of an important commodity, namely coffee. This beverage has been targeted for counterfeiting and adulteration due to its importance in the world trade market. The techniques applied can reveal important information regarding a coffee's authenticity and thus might be valuable for forensic scientists.

PIXE provides quantitative information on the elements present in the samples in a straightforward manner. ATR-FTIR probes the molecular compounds of the samples which, in this case, consists of organic material. Both PIXE and ATR-FTIR are non-destructive, which is an important asset as far as forensics is concerned. In order to obtain a complete picture on the quality and authenticity of ground roasted coffee, the AMS-^{14}C technique can pinpoint the time organic materials were produced, in this case, the year the coffee was harvested.

For this study, four Brazilian coffees from the same brand (Melitta) were chosen. Three of them (*Cerrado*, *Mogiana* and *Sul Minas*) are production-origin certified and consist of 100% Arabica beans. The fourth one (*Tradicional*) corresponds to a blend of unknown proportion of Arabica and Robusta coffee beans with no information about its provenance. The Melitta *Tradicional* coffee was analyzed by PIXE, AMS-^{14}C and ATR-FTIR in order to bring a broad perspective of their analytical capabilities to the forensic community. Finally, Jamaican Blue Mountain coffees were analyzed by PIXE as well for comparison purposes.

The PIXE results illustrate the selectivity and individualization power of this technique. Among the factors that have an impact on the final elemental composition of the roasted ground coffee are the coffee bean species, soil, environmental conditions and field practices. PIXE could pinpoint whether coffees are similar or not as far as elemental concentrations are concerned. For instance, similarities were found between *Mogiana* and *Sul Minas* coffees, which are produced in neighboring regions of Brazil. A high degree of similarity was also found among the coffees produced in the Blue Mountain region. Moreover, since Melitta *Tradicional* and the Blue Mountain coffees were produced in different countries with different field practices and different coffee types, it is not a surprise that they differ in their PIXE results for elemental concentrations. Moreover, PIXE can detect elements like Rb, Sc and Co, which could be potential markers helping to identify the origin of coffee based on the soil composition.

The AMS-^{14}C results obtained from three independent laboratories (CEDAD in Italy, ICER in Hungary and ETHZ in Switzerland) demonstrate the inter-laboratory reproducibility of results using this technique. The radiocarbon concentration of the Melitta *Tradicional* coffee was then used to date the sample to the period between 2016 and 2018 which is fully consistent with the expected harvesting year.

FTIR experiments performed in ATR mode are fast and generally cost-effective, which makes it a very attractive technique. When FTIR spectroscopy is combined with multivariate techniques, including HCA and PCA, it becomes a powerful tool for discriminating various type of materials, including coffee. Although coffee is a relative complex material containing over 800 compounds, including carbohydrates and proteins, among others, FTIR spectroscopy was capable of discriminating and pinpointing small differences in the vibrational spectra of different coffees. In this way, ATR-FTIR could detect similarities and differences among coffees thanks to its discrimination power.

Overall, the results presented here illustrate how different cutting-edge techniques can be combined synergistically in order to provide a multi-perspective view of a given problem. We have demonstrated that forgery of organic materials related to the date of production can be easily detected by AMS-^{14}C. This information can also be used to discourage retail of products beyond their expiration date. Moreover, deliberate adulteration of a product can be tested from the elemental and molecular information of PIXE and ATR-FTIR techniques, respectively, in a non-destructive manner, thus preserving samples for further scrutiny and even for use in a court of law. The present work suggests that a worldwide network of laboratories can be quite effective for the elucidation of real cases and may boost forensic science to a new level of expertize.

Finally, it is advisable that research laboratories pursue ISO accreditation, in order to merge synergistically with the forensic community, thus bringing credibility to science-based forensic efforts in legal systems.

CRediT authorship contribution statement

On behalf of all co-authors, I declare that all coauthors participated equally in the present manuscript.

Declaration of competing interest

On behalf of all co-authors, I declare that there are no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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