Brazilian Journal of Analytical Chemistry
2025, Volume 12, Issue 48, pp 37-85
doi: 10.30744/brjac.2179-3425.RV-165-2024

REVIEW

Analytical Techniques for the Determination of Elemental Composition of Coffee

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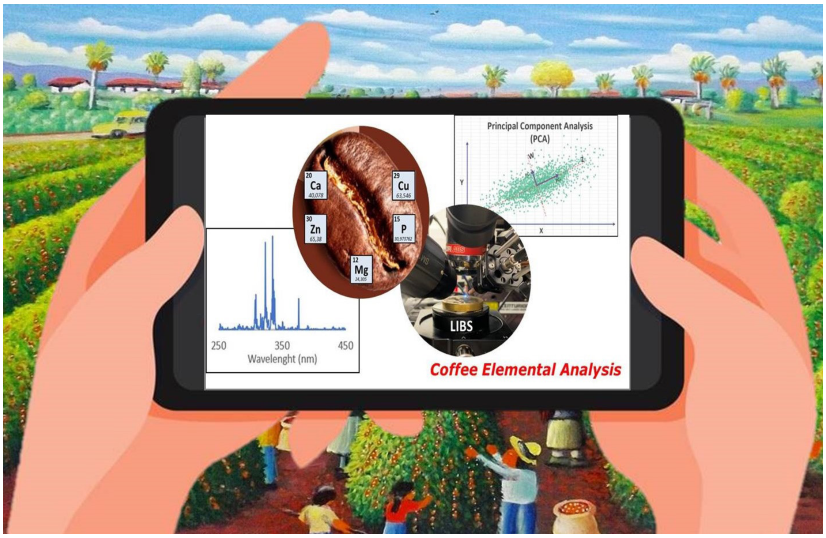


According to the Coffee Market Report (2024) of the International Coffee Organization, the annual worldwide production of coffee increased 5.82% achieving 178 million bags between 2023 and 2024. South America is the coffee production leader accounting for 50.17% of the global production with Brazil playing a central role on it. To sustain the high quality standards under such a high demand, it is important to ensure the consumer health safety, while preserving the good flavor and aroma of coffee (*terroir*). Some key factors are required to allow the proper evaluation of crops and shipments using reliable parameters, which is the case of the determination of the elemental composition of coffee. Coffee organoleptic properties depend on several chemical elements of its composition, while accessing and monitoring their concentrations is challenging, since they might vary considerably according to some agronomical and climatic conditions that plantations are subjected. Yet, the analytes might not be homogeneously distributed throughout samples, demanding both refined solid sampling strategies and laborious sample preparation

Cite: Vilela, T. M.; Almeida, T. C. R.; de Souza, A. L. M.; Joca, J. F. S.; Oliveira, R. S.; Batista, B. L.; Baccaro, A. L. B.; Gaubeur, I.; Felix, F. S. Analytical Techniques for the Determination of Elemental Composition of Coffee. *Braz. J. Anal. Chem.* 2025, *12* (48), pp 37-85. http://dx.doi.org/10.30744/brjac.2179-3425.RV-165-2024

Submitted October 30, 2024; Resubmitted February 22, 2025; Accepted March 9, 2025; Available online May 8, 2025.

This review was submitted to the BrJAC special issue celebrating the achievement of Journal Impact Factor.

and pretreatment. Finally, several analytical techniques are available for researches and analysts to investigate the elemental composition of coffee samples, each one with their own advantages, limitations and particularities. Sometimes it is not a trivial task to choose a proper technique according to the aimed data. Therefore, an overview of the analysis of coffee elemental composition is herein presented, covering selected references from the last two decades. The selected works discuss the determination of elements affecting the quality of coffee in terms of terroir, toxicity, nutritional content, and geographical origin.

Keywords: elemental analysis, ICP OES, ICP-MS, AAS, XRF, LIBS, voltammetry

INTRODUCTION

Coffee is a fruit used to produce the worldwide appreciable stimulant drink from its roasted beans and is implemented in the compounding of many products, as pharmaceuticals and cosmetics. According to the US Department of Agriculture,[1] Brazil is the global leader of coffee production, accounted for 33.61%, followed by Vietnam (18.90%), Colombia (8.24%), and Indonesia (6.31%). Data from 2021/2022 suggest the increase of the global coffee consumption from 1.5 million to 164.8 million bags, highlighting the increase for EU, US, and Brazil.[1,2] More recent data reported by the International Coffee Organization[3] in 2024 show that the worldwide coffee production expanded, reaching 178 million bags in a 5.82% moderate growth. From that, 102.2 million of bags are from the *Coffea arabica* type (57.41%) and 75.8 million bags from the *Coffea canephora* type (42.59%). The global accumulated consumption achieved 177 million of bags, representing an increase of 2.25% in relation to the previous year. The Europe continent occupies the first position in consumption with 53.7 million bags, followed by Asia and Oceania with 45.7 million bags, and the U.S. with 30.9 million bags. The South America occupies the fourth position, with 28 million bags or 15.82% of the overall consumption.

Considering both the high global production and consumption, it is almost a public health issue to preserve the coffee quality in terms of controlling the levels of toxic elements concentrations, while creating reliable parameters associated with the concentration of some essential elements that confer good organoleptic properties to the product, and participate as a good nutritional intake for a healthy diet.[4] The good taste and smell of coffee infusions are usually associated with several elements and compounds, like minerals, acids, aldehydes, carbohydrates, proteins, metals, vitamins, water, and caffeine. The tuning of the concentrations of all these compounds and elements is dictated by many agronomical aspects, such as the planting, harvesting, fertilization, and further production technologies,[5] while other environmental characteristics of plantation fields like the weather, soil composition, and topography might affect it as well.[6,7] Even the microbiota grown during the storage cycles of crops might alter the coffee bean composition and form some detrimental toxins.[8,9] The sugars content is very important for the coffee quality, once they contribute to a natural sweet flavor, a very appreciable characteristic for a coffee to be well valued and classified as *gourmet*. However, the type or even the concentration of carbohydrates to favor the properties of the raw coffee bean is still a subject of major discussion in the food literature, as well as how they impact the coffee flavor, bitterness, color, acidity, and scent.[10] A well-known consensus is the correlation between the coffee organoleptic quality and the reducing and non-reducing sugars content. During the roasting, these carbohydrates undergo reactions with proteins forming furan and other volatile compounds that are responsible for the highly appreciated coffee scent.[11,12] Fructose, glucose and sucrose are the most abundant carbohydrates in coffee beans,[13] with sucrose predominance in the range of 6 to 9% pp. (w/w) under dried basis for Robusta and Arabica species, respectively.[11]

Phenolic compounds are a wide group of substances that might present complex or simple chemical structures, as tannins or lignins, and they are highly present in the coffee composition, particularly as the chlorogenic acids.[14] According to some authors[15–18] chlorogenic acids undergo thermal degradation during the processing of the coffee bean, forming low molecular-weight compounds that are ascribed to scents with different sensorial designations, as spices, clove, and tobacco, besides the bitterness and astringency flavors. The phenolic compounds in coffee act as antioxidant agents to protect aldehydes from their oxidation. Inasmuch the coffee beans are subjected to adverse conditions such as an inappropriate harvest or some processing and storage issues, the *polyphenol oxidases* act over the polyphenols (mainly true for caffeic and chlorogenic acids), diminishing their reducing power and allowing the oxidation of aldehydes, directly interfering in the after-roast flavor and scent of coffee.[19] According to Vignoli, Bassoli and Benassi[14] chlorogenic acids loss are in average between 86% and 93% for soft and intense roasting of Robusta coffee (100-230 ºC). The remaining portion is easily solubilized in hot water, participating of the coffee infusion composition and being the main chlorogenic acids source for the human nutrition.[14] Therefore, the major composition sugars, the caffeoylquinic acid, and its 3–, 4– and 5–isomers are very important precursors of the good coffee terroir. Most works deal with the quantification of total carbohydrates and chlorogenic acids in coffee, while very few make the individual and specific quantifications.[10] Moreover, few scientific papers report the effect of production parameters, such as the harvest waiting time, over the sugars and chlorogenic acids concentrations.[10] Nevertheless, it is important to note that the content of some key macroelements are usually ascribed to the regulation of (or at least, are correlated with) these compounds in the growing plant.

For instance, the nitrogen (N) elemental content is an important parameter to be controlled since its levels are ascribed to the facilitation of the synthesis of chlorogenic acid.[6,10,20] The concentration of potassium (K) is usually ascribed to regulate the sugar natural content at coffee, considering its influence over the starch metabolization by the plant, hydrolyzing it into soluble carbohydrates.[10,20] The boron (B) levels are associated with the accumulation of phenolic compounds, besides the increasing concentrations of caffeine, trigonelline, and sucrose.[20] Copper (Cu) levels affect the aftertaste and body of the coffee beverage[21,22] while Zinc (Zn) enhances the aftertaste and acidity note perception.[7,22] Potassium (K), magnesium (Mg), phosphorus (P), and Nitrogen (N) are the most abundant macroelements found in coffee beans (Figure 1). The sequence of micronutrient uptake by coffee plants decreases typically in the following trend: iron (Fe) > manganese (Mn) > boron (B) > zinc (Zn) > copper (Cu) > molybdenum (Mo).

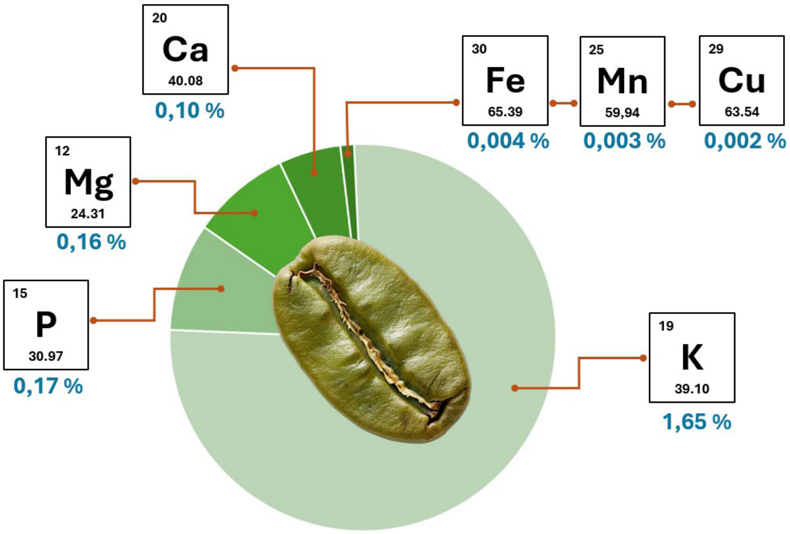


Figure 1. Concentrations (%, dry weight) of some elements in green coffee beans from different regions of Ethiopia.

Values were obtained from: Characterization of the Cultivation Region of Ethiopian Coffee by Elemental Analysis. Authors: Bewketu Mehari, Sandra Combrinck, Bhagwan Singh Chandravanshi, et al. *Anal. Lett*. **2016**, *49* (15), 2474-2489. https://doi.org/10.1080/00032719.2016.1151023. Reprinted by permission of the publisher (Taylor & Francis Ltd, http://www.tandfonline.com).

Besides the essential elements for the good human diet and the regulation of compounds responsible for the organoleptic characteristics of coffee, there are the so-called “non-essential heavy metals” that are highly toxic even at very low concentrations. They are not biodegradable and pose great risk to the living organisms and human health due, *e.g.*, to their carcinogenic effects.[23] Even the essential heavy metals, *i.e.*, zinc (Zn), copper (Cu), iron (Fe) and cobalt (Co), show some unexpected hazardous effects depending on their dosage intake. Dissolved forms of heavy metals are polluting the soil, water and air, which make them naturally entering into the coffee production chain. According to the reports of the International Agency for Research on Cancer, among the known non-essential heavy metals, that are chromium (Cr), lead (Pb), arsenic (As), mercury (Hg), and cadmium (Cd), the arsenic, cadmium and chromium are the major cancer-causing agents.[23] Heavy metals are present in coffee either as free ions or organic complexes (*e.g.* phenolate-metal complexes), representing health risks depending on the element, its speciation, concentration, time of exposure, and intake route.[24,25] It is of utmost importance to constantly monitor the heavy metals content in coffee, even at the trace level, since they present a cumulative character in the living organisms, gradually increasing levels in the food chain and silently posing risks to life.[26] In this sense, the development of analytical methods based on sensitive enough techniques is of great importance to globally sustain the human health and life quality.

According to the broad analytical chemistry literature, the benchmark techniques used to determine the elemental composition of several kinds of samples are the anodic or cathodic stripping voltammetry (ASV or CSV, respectively), the atomic absorption spectroscopy (AAS), the inductively coupled plasma optical emission spectroscopy (ICP OES), the inductively coupled plasma mass spectrometry (ICP-MS) and, more recently, the x-ray fluorescence (XRF), and laser-induced breakdown spectroscopy (LIBS).

The flame atomic absorption spectrometry (F AAS) has been frequently used for the determination of coffee macroelements (Ca, K, Mg, and Na), microelements (Cu, Fe, Mn, and Zn), and trace elements (Cd, Co, Cr, Ni and Pb).[27–33] The High-resolution continuum source flame atomic absorption spectrometry (HR CS-F AAS) is used as well for the determination of Ca, Fe, K, Mg, Mn, and Na.[34] Considering the limited sensitivity of F AAS for the determination of some important trace elements, as Pb, Cd, Cr, Ni, and Pb,[31] the ICP OES[33] or the differential pulse anodic stripping voltammetry (DP-ASV) are rather used under such circumstances.[35] The electrothermal atomic absorption spectrometry (ET AAS) with the same deuterium[36] or Zeeman corrections[37] is more rarely applied, which is the same for the high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GFAAS).[34] Both are used for the quantification of trace microelements in coffee samples, such as Al, Co, Cr, Cu, Fe, Ni, Mn, and Sr.

Among the aforementioned techniques, ICP OES is one of the most applied for the elemental analysis of coffee, since it allows the fast and sensitive determination of several elements at once, including macroelements (Ca, K, Mg, Na, P, S), microelements (Al, B, Co, Cu, Fe, Mn, Sn, Zn) and trace elements (As, Ba, Cd, Cr, Ni, Pb, Sb, Se, Si, Sr).[36,38–49] Although rarely used in the past,[50] studies of the application of inductively coupled plasma mass spectrometry (ICP-MS) for elemental quantifications in coffee are growing in the literature, as will be seen below. It has been used for the determination of Cd, Cr, Cu, Mn, Ni, Pb, U, Zn in coffee samples after the brewing and mineralization of infusions.[51]

The X-ray fluorescence has been used for the multielemental analysis of Br, Ca, Cr, Cu, Fe, K, Mn, Ni, Rb, Sr, and Zn in coffee and this technique is particularly appealing due to the exemption of a lengthy sample preparation.[52] Finally, the Laser-induced Breakdown Spectroscopy is a more recent analytical technique based on the plasma emission of analyte spectral lines from the irradiation of samples with a laser. It is non-destructive, fast and versatile, holding good promise for both qualitative and quantitative analysis of coffee samples without substantial sample preparation too.[53] LIBS instrumentation is relatively simple, robust and even compact, potentially allowing the remote analysis.

So herein, we selected prominent papers from the literature aiming the elemental analysis of coffee from the last two decades (2004-2024), giving emphasis to all these aforementioned analytical techniques. Sample pretreatment and recent applications are also herein covered. Using the advanced search from the google scholar database, we found a sum of 8,724 published papers regarding to the following pattern of keywords: “coffee”, “technique abbreviation” (*e.g.,* “ICP OES”), and “elemental analysis”. For voltammetry, specific keywords were “coffee”, “metal analysis”, and “voltammetry”, excluding – “coffee grounds” to avoid computing papers with non-elemental analytes, and recent applications of spent coffee grounds as an electrode modifier for determinations in other kinds of samples than coffee. The descriptive distribution of reports for each technique is represented as a pie chart at Figure 2.

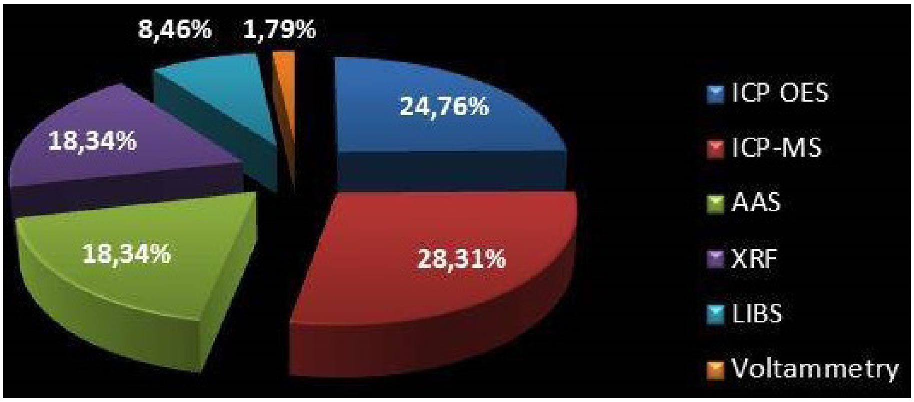


Figure 2. Descriptive pie chart of analytical techniques reported in the literature for the elemental analysis of coffee between 2004 and 2024 years (Google Scholar database).

SAMPLE PRETREATMENT AND CONDITIONING

As the coffee beans are introduced in the lab, they are washed to remove the soil particles and dust using tap water and neutral detergent. Then, they are immersed in diluted hydrochloric acid solution and finished with deionized water.[32] After that, coffee beans are roasted and ground until a fine powder is achieved.[33,54] Alternatively, they might be dried with the help of desiccating agents as silica, or in ovens under thermal treatments between 60 and 103 ºC prior to the pulverization in cryogenic mills or rotor-type mills/grinders.[27,30,36,39,45,55] Considering that roasted coffees are available in the market, the powdered or ground solid coffee samples can be analyzed without further treatments.[48] It is important to mention that some initial stages of the sample washing and pulverization might vary from author to author. An alternative is to issue coffee beans or powdered coffees to manually or mechanical grinding with pestles and mortars or even different types of mills (*e.g.* ball, knife or cryogenic mills), followed by the sieving for the particle size fractioning.[29,37,40,41,46,47,56,57] As a last option, coffee beans can be initially washed simply with distilled and/or deionized waters to remove surface contaminants, subjected to oven or freeze drying, and finally ground to the desired particle size under 0.5 mm.[57–59]

Digestion procedures for coffee solid samples

One first premise for the determination of the total concentration of elements by most of the instrumental techniques is that coffee samples must be solubilized and digested by even the dry ashing in air or the wet oxidative digestion. These last preparation steps are used to reduce the matrix effects and release elements into their free ionic form.[30,47] Sample pretreatment must accomplish the digestion of dissolved organic compounds at least to an extent which they lose their ligand capability with elements or stop interfering with their determination.

The dry ashing comprises the insertion of samples with unities of grams into quartz or platinum crucibles to be heated in muffles, first to 200 ºC and then in the range between 350 ºC and 550 ºC for incineration.[28,35] The ashes are then subjected to an acidic digestion in small portions with a mixture of concentrated nitric and perchloric acids,[35] or concentrated hydrochloric[45] or nitric acids,[28] individually. This digestion step can be performed in open or closed microwave-assisted vessels. After the digestion of ashes and the drying of sample aliquots, the residues are diluted with deionized water or a diluted nitric acid solution.[28,31,35,45] Silicon interference is usually eliminated by adding concentrated hydrofluoric acid during the dry ashing step.[45]

For the wet digestion samples with unities of grams are digested in pressurized closed vessels with the assistance of microwave irradiation,[30,33,36,44,46–48,60] Parr bombs,[47] Berghof apparatus,[27] or open systems with hot plates or heating blocks,[30,37,39,42,43] or even a Kjeldahl apparatus.[61] The digestion with pressurized microwave-assisted closed vessels and controlled temperatures (Figure 3) is frequently associated with a quicker and complete decomposition of coffee samples, avoiding losses of volatile or semi-volatile elements and the undesirable contamination of samples, saving time, reagents and money.[30,33,36,46,47]

Figure 3. Microwave digestion procedure in closed pressurized vessel.

Nevertheless thermal treatments in open systems of hot plates and heating blocks are still viable, considering some drawbacks with possible sodium and zinc contaminations, the iron release or the determination of systematic lower concentrations of calcium.[30] Samples are usually heated in the range of 80 to 180 ºC for 1 to 12 h long.[30,37,42,43,47] Mixtures with several ratios of concentrated nitric acid and 30% pp. (w/w) hydrogen peroxide,[30,33,36,38,43,44,46,47] nitric acid and perchloric acid,[32,61,62] nitric acid and sulfuric acid[39] and, finally, nitric and hydrofluoric acids[27] have been used for the digestion of coffee samples. The effect of catalysts as V_2O_5 in the digestion of coffee samples with nitric acid and hydrogen peroxide has been investigated[30] in several mass-to-volume ratios as well.[27,30,32,33,36–38,42,44,46,47,60,62] Finally, the alkaline solubilization with 25% (m/v) tetramethylammonium hydroxide (TMAH) has been accomplished in heating block systems with open vessels aiming to facilitate the complete disintegration of samples, consuming small amounts of reagents with lower contamination and loss of volatile elements.[43]

Direct analysis of coffee samples

The direct analysis of ground and dried green coffee is possible and might be carried out by the introduction of solid samples[36] or slurries[37] in ET AAS graphite furnace tubes. For the solid samples, small aliquots with 30 to 300 µg are usually weighted on graphite platforms and directly introduced in graphite tubes. Curiously enough, Oleszczuk *et al.*[36] found out that the reliability of their results showed independence from the particle size of solid samples, indicating that elements were homogeneously distributed through different particle size fractions of sifted materials. For the introduction of coffee slurry samples, slurries are prepared by the suspension of 30 to 50 mg portions of the material (< 105 µm) in diluted 0.2% (v/v) nitric acid solutions. Slurries are then heated to 80 or 90 ºC for the element extraction with 25% (v/v) Triton X-100 and sonicated to ensure the homogenization of particles.[37] Flow-injection systems (FIA) have been used for the automation of the slurries constitution and their on-line insertion into the ICP OES nebulizer.[49] Slurries were prepared with 5-50 mg samples (> 70 µm) that were placed in a flow chamber and mixed by a magnetic stirrer with a 1.0% (v/v) nitric acid and 0.5% (v/v) Triton X-100 dispersant solution. The stable slurries were directly pumped by the FIA-system to the nebulizer.

Brewing and digestion procedures for coffee infusions

Different mass-to-volume ratios of coffee and water have been used for brewing either natural or instant coffee samples, varying from 1:5.5[51] until 1:200.[62] Usually, hot deionized or distilled water close to 100 ºC is added to a mass portion of coffee and after some minutes the resulting infusions are filtered or centrifuged.[31,34,44,48,60–62] Coffee maker systems can be used to prepare infusions through percolation of hot water into coffee beds,[51] or by pressurized espresso machines.[57] After the adequate prepare of the beverage, aliquots of the infusions are evaporated to dryness and incinerated at 540 ºC. The resulting residues are digested with small amounts of concentrated hydrochloric or nitric acid and finally diluted to the required volumes.[31,51] Alternatively, infusions aliquots might be evaporated until near dryness and digested with a mixture of concentrated nitric and perchloric acids in a Kjeldahl apparatus.[61] Nevertheless, sometimes coffee infusions can be directly analyzed without any special sample pretreatment besides dilution, acidification for stabilization, or simply both.[34,40,41,44,48,60,62]

ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Theoretical background

Atomic absorption spectroscopy (AAS) is a widely applied analytical technique used to the determination of elemental concentrations of metals in different samples. It is based on the measurement of the radiation absorption by atoms in gaseous state. The extension of the radiation attenuation is directly proportional to the element concentration in the sample, according to Lambert-Beer law.[63] Figure 4 shows the schematic diagram of an atomic absorption spectrometer. Essentially, it contains a radiation source, an atomization system, a monochromator, and a detector. The most common radiation sources are hollow cathode lamps (HCL) and the electrodeless discharge lamps (EDL). Recently, the use of Xe short arc lamps led to the development of the so-called high-resolution continuum-source atomic absorption spectrometry (HR-CS AAS).[64]

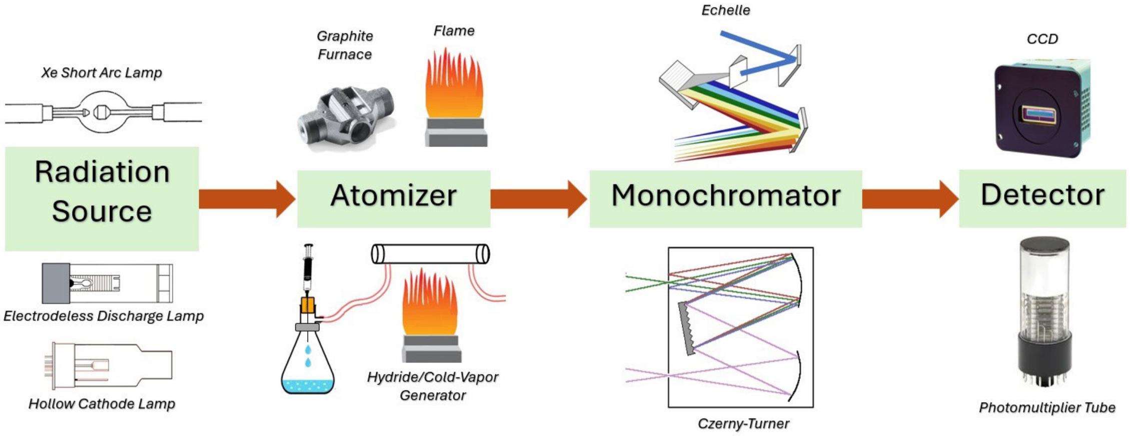


Figure 4. Schematic diagram of an atomic absorption spectrometer.

The most common atomizers are the flame (with air/acetylene and nitrous oxide/acetylene fuel mixtures being the most widely used) and graphite furnace, with specific applications involving the hydride-generating atomizer (for As, Sb, Sn, Se, Bi, and Pb determinations), and the cold-vapor atomizer (for Hg determination).[65]

AAS determinations strongly rely on the sample introduction procedure. In flame atomizers, the most common system is based on the formation of an aerosol by pneumatic nebulizers. In electrothermal atomizers, sample aliquots ranging from 10 to 100 µL are generally inserted into the graphite furnace without expressive sample loss. In addition, it is even possible to directly insert solid samples into the graphite furnace and, consequently, perform a direct solid sampling analysis.[66] For these reasons, electrothermal atomization shows significantly lower LODs for a wide variety of analytes compared to the flame atomization.[67] The sequence of events that leads to the formation of gaseous atoms for analytical determinations by Flame Atomic Absorption Spectrometry (F AAS) and Graphite Furnace Atomic Absorption Spectrometry (GF AAS) is shown in Figure 5.

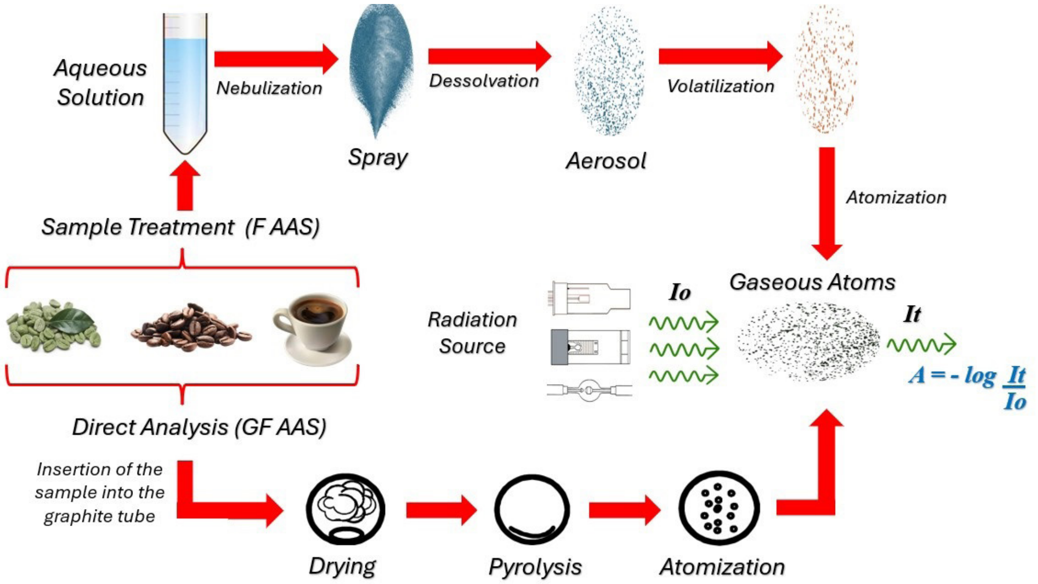


Figure 5. Sequence events of sample preparation, introduction, and atomization for Flame Atomic Absorption Spectroscopy (F AAS) and Graphite Furnace Atomic Absorption Spectroscopy (GF AAS).

The atomization by hydride generation is based on the analyte volatilization by adding sodium borohydride into the acidified aqueous sample. It is applied for the analysis of As, Sb, Sn, Se, Bi, and Pb. Generation of volatile hydrides improves the detection limits between 10 and 100 times, and enables the determination of potentially toxic elements at trace (sometimes ultra-trace) levels.[63] Similarly, the generation of Hg vapor is based on the reduction of Hg^{2+} ions (or organic compounds containing Hg) by a suitable reducing agent. $SnCl_2$ is commonly used. In both cases, vapors are generated in closed systems and are led to a flame burner, where both undergo atomization, as shown in Figure 5. Regardless of the type of atomization, the absorption of the radiation generated by the source occurs anyway.

AAS applications

The applications of AAS techniques for coffee analysis will be categorized into three groups: coffee discrimination (*e.g.*, origin and bean type), coffee food safety, and analytical method optimization.

Flame atomic absorption (F AAS) was employed by Grembecka *et al.*[31] to determine Ca, Mg, K, Na, Co, Mn, Fe, Cr, Ni, Zn, Cu, Cd, and Pb in commercial coffee samples. Based on the mineral composition, it was possible to differentiate coffee varieties chemometrically, distinguishing Arabica coffee from Robusta coffee, grounded coffee from instant coffee, and their respective infusions. Amorim Filho *et al.*[30] determined Ca, Mg, Fe, Cu, Mn, and Zn, as well as Na and K by flame atomic emission photometry, and N by the Kjeldahl method. Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) showed that Na, K, Ca, Cu, Mg, and Fe were the main elements that allowed the distinction between green and roasted coffee samples.

Dos Santos *et al.*[33] evaluated the availability of K, Na, Ca, Mg, Cu, Fe, Mn, Zn (by F AAS), and Cd, Cr, Ni, and Pb (by ICP OES) in coffee and soil samples from traditional, technological, and organic agricultures. Results suggested that Cd, Cr, and Zn (and other toxic elements) from inorganic fertilizers of traditional and technological agricultures; and Cu, Zn (and other metals) from fertilizers of organic coffee cultivations, can cause an increase in these metals content in soil, causing subsequent absorption by plants.

Szymczycha-Madeja *et al.*[68] determined Al, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr and Zn by ICP OES and Ca, Fe, K, Mg and Na by F AAS. Besides demonstrating good analytical performance in terms of accuracy and precision, ultrasound-assisted solubilization of roasted ground and instant coffees in aqua regia enabled the successful classification of 18 coffee samples based on the concentrations of selected elements, using principal component analysis (PCA) and hierarchical cluster analysis (HCA).

Baqueta *et al.*[69] analyzed 100 Canephora coffee samples of different geographical origins from Brazil. All samples were analyzed for their essential mineral content by F AAS using acid digestion in a digester block with diluted HNO_3 and H_2O_2 for four hours to characterize their content of Fe, Ca, Zn, Mg, Mn, Cu, and K. The chemometric tool Independent Components-Discriminant Analysis (IC-DA) was applied to analyze the mineral composition data, discriminating the samples according to the predetermined classes (geographical origins and species) and identifying the minerals responsible for the discriminations.

Stelmach, Pohl, and Szymczycha-Madeja[70] used HR-CS F AAS to determine the total concentrations of Ca, Cu, Fe, Mg, and Mn in 12 green coffee infusions. According to the authors, drip or Turkish coffee methods extracted a higher concentration of elements compared to mug coffee preparations. The same authors[71] also employed HR-CS F AAS to determine the concentration of Ca, Fe, Mg, and Mn in 18 instant coffees, directly employing the prepared brews without additional treatment. *In vitro* simulated gastrointestinal digestion revealed that only a small fraction of total Fe was potentially bioaccessible in instant coffees. Among the studied metals, Mg was found to be highly bioaccessible.

Kalschne *et al.*[72] also used microwave-assisted digestion with HNO_3/H_2O_2 mixture to determine the concentrations of Cu, Ca. Mn, Mg, K, Zn, and Fe in 21 commercial Brazilian coffee brands. PCA analysis allowed the segmentation of traditional coffees from extra-strong coffees based on the mineral composition and the determined organic compounds.

Using HR-CS F AAS and HR-CS GF AAS, Oliveira *et al.*[34] determined Ca, Mg, K, Na, P, Fe, Mn, Cr, and Ni in 49 samples of commercial instant coffees and substitutes. According to the authors, ingestion of two instant beverages per day (a total of 4.0 g instant powder) with or without coffee cannot be regarded as an important source of minerals in the human diet, although it may provide some mineral supplementation. HR-CS F AAS was employed by Özdestan[73] to determine the concentrations of K, Mg, Mn, Na, and Zn in both grounded and brewed coffee (Turkish coffee). Samples were prepared by dry ashing, followed by HCl solubilization of ashes and final dilution. For all samples K was the most abundant element.

Szymczycha-Madeja, Welna and Pohl[74] also validated a method for multi-elemental analysis of dialyzable and non-dialyzable fractions of coffee brews by F AAS and ICP OES. Bioacessibility studies were carried out and the highest bioaccessible fraction was found for Ni. Prescha *et al.*[75] determined the total and soluble silicon contents in different instant food products including 4 coffee drinks by GF AAS. Instant coffee also contained low amounts of soluble silicon and the values comprised only 7.3% of total silicon in these sample. Jeszka-Skowron *et al.*[76] evaluated the relationship between antioxidant capacity, chlorogenic acids, and elemental composition of Arabica and Robusta green coffee from different origins. The concentrations of Cd, Cu, Mn, Pb, and Se were determined by GF AAS after microwave-assisted acidic digestion with HNO_3/H_2O_2 and the authors reported the direct influence of the decaffeination and steaming processes on the changes in the Se, Cu, and Mn concentrations in green coffee beans.

A similar procedure was applied by Windisch *et al.*[77] for Al determination in 10 different samples of coffee beans and their water-extractable fractions, aiming to test the influence of different brewing methods on the concentration of Al extracted into the final drink. According to the authors, the main influence on the Al content in brewed coffee was the respective brewing method and the material of the cookware. The highest content of total Al was recorded in brewed coffee made with a device entirely made of Al alloy. Aiming to determine potentially toxic elements (PTEs - Pb, Cd, As, Ni, Cu, and Fe) in rapid coffee products, Alipour *et al.*[78] heated 0.5 g of each sample at 600 °C for 24 hours and subsequently used 25 mL of *aqua regia* for microwave-assisted digestion. After digestion, the concentrations of PTEs were determined by GF AAS. According to the authors, the concentrations of Fe and Pb were higher than those of the other PTEs, and consuming instant coffee does not endanger the health of consumers. Espinelli Junior *et al.*[79] conducted a study on the fractionation of manganese in commercial coffee samples from conventional and organic cultivation systems. The authors employed microwave-assisted acid digestion for the determination of total Mn content, followed by detection using F AAS. Principal component analysis showed clear differences in manganese fractionation, highlighting the influence of cultivation methods on manganese metabolism and storage. Despite these differences, there was no significant variation in manganese levels in coffee infusions or the fraction available for absorption between the conventional and organic cultivation.

In a recent study, Berego *et al.*[80] determined essential metals (Na, K, Ca, Zn, Mn, Cu, Co, Cr, Ni) and toxic elements (Pb and Cd) in coffee beans and soil samples using microwave-assisted digestion with HNO_3/H_2O_2, followed by detection by F AAS. The authors observed acceptable levels of the analyzed elements in coffee beans, as defined by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO).

Stelmach, Pohl, and Szymczycha-Madeja[70] developed a simple method for determining the content of Ca, Cu, Fe, Mg, Mn, and Zn in coffee by acidification of its infusions with HNO_3, before F AAS determinations. Moreover, it has been demonstrated that Ca, Cu, Mg, and Mn can be determined directly in the infusions without any acidification. Additionally, it has been shown that the preparation conditions, such as water temperature and brewing method, can affect the content of these elements. They[81] also accessed the chemical and physical fractionation patterns of Mn in coffee infusions using solid-phase extraction and ultrafiltration-based procedures, followed by determination by F AAS. Pohl, Stelmach and Szymczycha-Madeja[82] determined concentrations of Ca, Fe, Mg, and Mn, followed by the chemical fractionation patterns, in 18 soluble coffees using a two-column solid-phase extraction method. In these studies, elemental determinations were also performed using F AAS after acidification of the infusion (or aqueous solution obtained from the soluble coffees) with HNO_3. In contrast, Ashu and Chandravanshi[61] and Gure *et al.*[83] adopted traditional procedures for the sample pretreatment of roasted coffees. Four-hour acidic digestions using HNO_3 and $HClO_4$ were employed for both coffee powder samples and infusions.

The slurry sampling was proposed by Trindade *et al.*[84] for the determination of Ca, Fe and Zn by F AAS in industrialized and handcrafted coffee. The slurry optimization was carried out using a constrained mixture design. No significant differences were found between results generated by the proposed new method and the conventional acidic digestion. Trace Ni was determined by Saylan *et al.*[85] in chamomile tea and coffee samples by slotted quartz tube-flame atomic absorption spectrometry (SQT-DLLME-F AAS) after preconcentration with dispersive liquid-liquid microextraction (DLLME) using a Schiff base. A 66,4-fold detection power enhancement was obtained for SQT-DLLME-F AAS over the conventional F AAS system. In this sense, Tışlı *et al.*[86] determined low Mn concentrations using liquid-phase microextraction with choline chloride-phenol mixture as extraction solvent, and tetrahydrofuran as emulsifier agent. A 92.9-fold detection power enhancement was obtained.

Dasbasi *et al.*[87] synthesized a new ternary polymer composite, polystyrene/polyacrylonitrile/polyindole (PSt/PAN/PIN) that has been applied as an adsorbent for the extraction and preconcentration of Cr(III), Cu(II), Fe (III), Mn(II), Pb(II), and Zn(II) ions in coffee and tea samples. Solid phase extraction was successfully used for separation, preconcentration and determination of ions by F AAS, even leading to lower LODs.

Qiu *et al.*[88] proposed a simple procedure involving in-situ digestion of the coffee drinks (called *in-furnace digestion*) for the determination of Pb by GF AAS. Samples were diluted with HNO_3 and Triton X-100 before direct analysis. Results showed good agreement with parallel determinations performed under wet digestion of samples. Direct solid analysis of powdered stimulant plants, including *Coffea arabica* powder, was carried out by de Gois *et al.*[89] The authors determined concentrations of Mn, Ni, Rb, and Sr using HR-CS-GF AAS. Calibration with aqueous standards proved itself to be adequate for Mn, Rb, and Sr. However, for Ni, calibration demanded solid reference materials, considering that the difference in sensitivity was as high as 20%. Comparison of values with those obtained by ICP-MS with acidic microwave-assisted digestion of samples revealed agreements between 88% and 115%.

Direct solid sample analysis and internal standardization were proposed by de Babos *et al.*[90] for the determination of Mo and Ni in plant materials using HR-CS GF AAS. Cobalt was used as an internal standard to minimize matrix effects during Ni determinations, enabling the use of aqueous standards for calibration. Different samples, including coffee pods, were analyzed and the concentrations of Mo and Ni ranged from 0.08 to 0.63 ng mg^{-1}, and from 0.41 to 6.92 ng mg^{-1}, respectively.

A method based on flow injection analysis and atomic absorption spectroscopy with hydride generation (FI-HG AAS) was developed[91] and applied to determine As in fish and coffee beans. The accuracy of the proposed method was evaluated using certified reference materials of biological samples. Coffee samples were spiked with known amounts of the analyte before FI-HG AAS determinations. The obtained results for coffee beans corresponded to 100–105% of the added arsenic.

Using a single-purpose atomic absorption spectrometer for Hg determination, Várady *et al.*[92] determined Hg in specialty coffee beans. They evaluated the effect of various methods of processing on the contents of heavy metals, included Hg, in green and roasted specialty coffees. Table I summarizes main discussed applications and some new details.

Table I. Applications of AAS techniques for coffee analysis, the detected analytes, and a summary of the sample preparation methods used

Technique	Sample	Analytes	Sample Preparation	Reference
F AAS	Coffee Beans	Na, K, Ca, Zn, Mn, Cu, Co, Cr, Ni, Pb and Cr	Microwave-assisted digestion with HNO_3/H_2O_2	80
F AAS	Coffee Infusions	Ca, Cu, Fe, Mg, Mn, and Zn	Acidification of its infusions with HNO_3, before F AAS determinations	70
F AAS	Roasted grounded and instant coffees	Ca, Fe, K, Mg and Na	Ultrasound-assisted solubilization using *aqua regia*	68
F AAS	Green coffee samples	Fe, Ca, Zn, Mg, Mn, Cu, and K	Green coffee samples were roasted to a medium degree and submitted to a mineralization process in a digester block with diluted HNO_3 and H_2O_2 for four hours	69
HR-CS F AAS	Green Coffee Infusions	Ca, Cu, Fe, Mg, and Mn	Overnight pre-digestion with HNO_3 followed by digestion on a hot plate using HNO_3 and H_2O_2	70
GF AAS	Coffee Drinks	Si	Microwave-assisted digestion with HNO_3/H_2O_2 for total Si determinations and extraction with HCl solution at pH 2.5 for soluble Si.	75
GF AAS	Coffee Beans	Al	Microwave-assisted digestion with HNO_3/H_2O_2	77
GF AAS	Coffee Drinks	Pb	In-Situ Digestion (called *in-furnace digestion*). Samples were diluted with HNO_3 and Triton X-100 before analysis	88
GF AAS	Rapid coffee products	Pb, Cd, As, Ni, Cu, and Fe	microwave-assisted digestion with *aqua regia*	78
HR-CS GF AAS	Instant coffees	Cr and Ni	2.0 g of powder were dissolved in hot ultrapure water, centrifuged, and diluted with ultrapure water before analysis	34
HR-CS GF AAS	*Coffea arabica* powders	Mn, Ni, Rb, and Sr	Direct solid analysis	89

INDUCTIVELY COUPLED PLASMA (ICP): Optical Emission Spectroscopy (ICP OES) and Mass Spectrometry (ICP-MS)

Theoretical background

Use of ionic emission frequencies: ICP OES

Nowadays, the inductively coupled plasma techniques (ICP) represent the most popular methodologies for metal analysis.[93] They allow the recording of good emission spectra for plenty of elements under the same excitation conditions simultaneously, with a lower chemical interference due to the high temperatures of operation. Their wide concentration intervals comprising several magnitude orders can determine low levels of metals (even those which form refractory compounds), besides halides and sulfur. Figure 6 presents a schematic of ICP OES instrumentation.

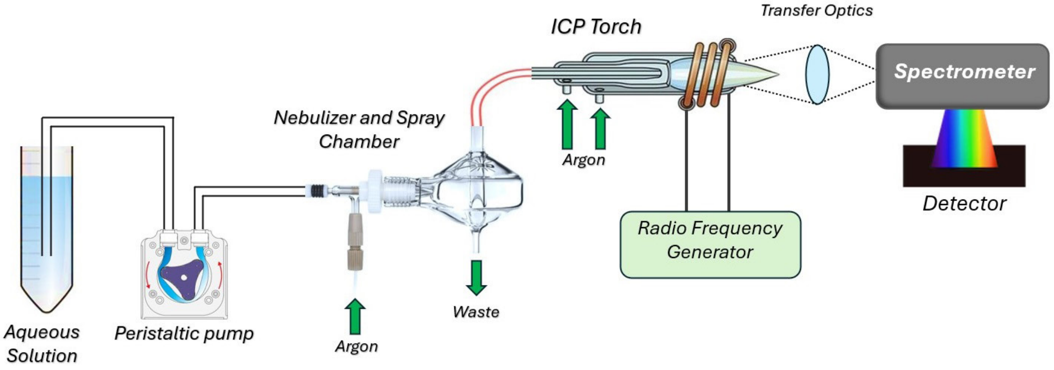


Figure 6. Schematics of an ICP OES instrumentation.

Plasma is an electrically conductive gaseous mixture with considerable concentrations of cations and electrons. The Argon plasma is the most commonly applied at ICP instruments. Argon cations and electrons are the main plasma charge carriers. They can absorb outer energy from different types of sources to achieve and keep temperatures as high as 10,000 K, where an additional ionization is capable to sustain the plasma on, indefinitely. Besides the Inductively Coupled Plasma (ICP), there are still other types of mechanisms to generate the plasma, like the Direct-Current Plasma (DCP) and the Microwave Induced Plasma (MIP).[94,95] Herein we will focus discussions on the ICP instrumentation.

The plasma is generated in the "torch" (three concentric quartz tubes), which the argon flux passes through with common rates of 5 to 20 L min^{-1}. The upper part of tubes is wrapped by a water-cooled inductive coil, ruled by a radiofrequency generator that irradiates between 0.5 to 2.0 kW in 27.12 or 40.68 MHz. Initial ionization of argon is attained by a Tesla coil spark. The resulting ions and electrons interact with the flowing magnetic field from the coil, travelling through closed ring paths. The plasma is maintained by the magnetic field generated by the coil.[96]

Atoms are atomized and ionized during their residence time in the plasma. They are submitted to plasma during about 2 ms prior to achieve the observation point, undergoing temperatures between 550 and 8,000 K (two to three times higher than absorption flames). As a result, atomization is much more efficient in plasma with less interference (even for ionization), since the high electron concentration from argon ionization keep itself constant throughout the whole experiment. Other plasma atomization/ ionization advantages include the chemical inert medium that avoid oxide formations, the almost uniform temperatures throughout its whole section, with low self-absorption and self-reversion ratios, promoting linear calibration curves for wide concentration intervals, and the significant amount of generated ions, which allows it to be used as a source for mass spectrometry.[63,96]

Most manufacturers assemble the ICP torch set up to allow its 90º turn, aligning the radiation source axially to the spectrometric detection system. The axial set up is interesting for mass spectrometry detection, besides the considerable gain of sensitivity observed for the optical detection. The vertical configuration is called “radial” and this set up confers more selectivity to methods, allowing emission height adjustments.[97,98] The use of axial or radial torch setup should be decided according to the chemical behavior of the analyte in the plasma, the selected working spectral line, the demanded validation parameters, and the experimental character.

Samples are introduced in the ICP OES under a flow rate of 1.0 L min^{-1} in the inner central quartz tube. They can be aerosols, thermally generated vapors or thin powders that are inserted by the sample introduction system, which can vary in set up and performance. In most cases, it is constituted by a glass concentric nebulizer that operates under the Bernoulli principle (Meinhard nebulizer). There are still other types of nebulizers, such as the crossed-flow configuration, Babington nebulizer and ultrasonic nebulizers.

Other sampling methods include electrothermal vaporization, which the sample is vaporized in a furnace very alike to those of atomic absorption but herein used merely to introduce the sample. It allows the micro sampling with lower limits of detection (LOD), a wide linear working range, good precision, absence of major interferences and multielemental capacity.[99,100] Finally, the ablation devices for solids are used by many ICP OES manufacturers, since vapor plume and particulate material produced by the sample interaction with an electric discharge arc/spark or a laser beam, can be carried to the plasma by the argon flow to produce the emission signal.[101,102]

For good performances during analysis, it is desirable that ICP OES spectrometers show: (*i*) high resolutions (0.01 nm), (*ii*) fast signal acquisition and recovery, (*iii*) low levels of spurious radiation, (*iv*) wide dynamic range (> 10^6), (*v*) good precision and accuracy to identify and select wavelengths, (*vi*) good precision to measure emission intensities (RSD < 1% under 500 x LOD), (*vii*) high environment stability, (*viii*) easy background radiation correction, and (*ix*) fully computerized operation. There are tens of ICP OES manufactures, with a wide variety of typical performances, configurations and working wavelength windows. Most of them are adjusted to operate between 170 and 800 nm, with few achieving the vacuum UV at 150-160 nm, important for the determination of, *e.g.*, phosphorus, sulfur and carbon.[63,103] The main types of ICP OES spectrometers are: sequential, simultaneous multichannel and Fourier-Transform (rarely used in emission spectroscopy). Sequential equipment is programmed to change from different element lines, keeping a few seconds at each to measure the line intensity with reasonable signal/noise ratio. Multichannel equipment measures almost simultaneously the intensity of lines for several elements (usually, tens of elements).

For the determination of several elements, the sequential ICP OES needs significantly higher sample introduction times than other instruments, consuming more sample volumes and time (higher operation expenses). Both sequential and multichannel ICP OES equipment can be classified according to its optics: those using classical diffraction granting, and other using the Echelle optics. Echelle optics combines the spectral resolution power of both Echelle grating (with lower density of surface grooves) and prism optical lens, resulting in an improved two-dimensional wavelength separation, detected, *e.g.*, by charge-coupled device detectors (CCD) instead of traditional photomultiplier tubes.

Coupling the plasma with a mass spectrometer: ICP-MS

Another important application of the ICP is its coupling with a mass spectrometer (Figure 7). Among the main advantages of this hyphenation are the very low LODs for most elements, the high selectivity of methods (the fingerprint of the element: the isotope), and their reasonable precision and accuracy. In this case, the ICP is applied as an ionization source. Solutions are introduced by conventional or ultrasonic nebulizer, while solids by electric discharge spark, laser ablation, or light discharge vaporization. Gases are also allowed such as the use of ICP-MS as the detector of Gas Chromatography (GC-ICP-MS). This hyphenation strategy allows the determination of different chemical species of target elements (speciation).[104]

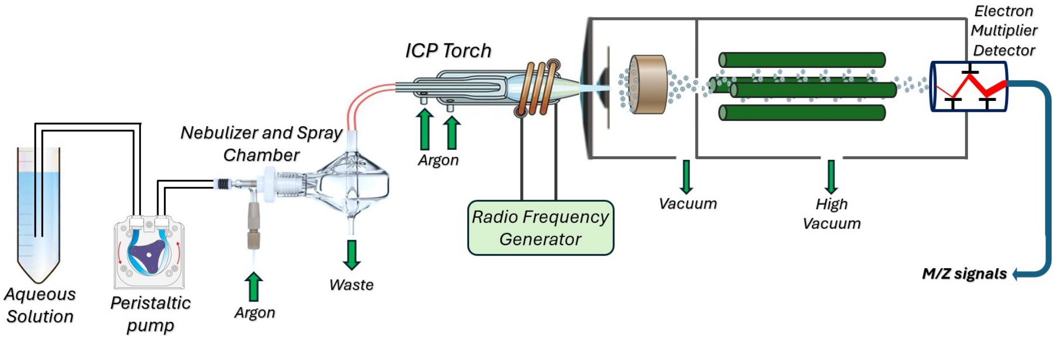


Figure 7. Schematic diagram of an ICP-MS instrumentation.

The positive metal ions are produced by the ICP, sampled by a differentially pumped interface usually connected to a quadrupole mass spectrometer.[105] The spectra are simpler than those of ICP OES, consisting of a series of mass/charge relation counts, corresponding each for one or more isotopes from the interest analytes. They might be used for elements identification and quantification, the last using the internal standard calibration or the isotopic dilution method.

Usually, ICP-MS technical specifications include a mass range between 3 and 300, ionic resolution capacity of 1 *m/z* (using a quadrupole as mass spectrometer), and a dynamic operation range of 6 magnitude orders. About 90% of the periodic table might be determined by ICP-MS with average measuring time of 10 s per element, LODs between 0.1 and 10 ppb, and RSD between 2 and 4% for interpolations in calibration curves.

Regarding the mass analyzer, it is worth noting that the most widely used is the quadrupole, considered to have low resolution (~1 amu). High-resolution analyzers have the advantage of separating ions into better fractions of the m/z ratio, resulting in more accurate measurements. ICP equipment can be listed in relation to resolution using the following acronyms: ICP-MS or ICP-QMS (Q, single quadrupole), ICP-MS/MS (tandem mass spectrometry) or TQ ICP-MS (TQ, triple quadrupole), HR-ICP-MS (HR, generic representation of high resolution) that includes: ICP-TOF-MS (TOF, time of flight), SF-ICP-MS (SF, sector field), and MC-ICP-MS (MC, multicellested). The multicollector is typically used to accurate and simultaneous isotope ratio measurements. It is worth noting that many acronyms are used for the same resolution representation.[105]

One of the major ICP-MS drawbacks is its severe problems with interferences that are divided in spectroscopic and non-spectroscopic interferences. Spectroscopic interferences happen when an ionic species in the plasma presents the same *m/z* ratio than the analyte, being still divided in four types: (*i*) isobaric ions, (*ii*) polyatomic ions, (*iii*) doubly charged ions, and (*iv*) refractory oxide ions.[105,107] To remove isobaric ions and polyatomic interferences some strategies have been proposed: alternative analyte isotopes, mathematical correction equations, cool plasma conditions, high resolution equipment (previously mentioned), collision cell technology (CCT), dynamic reaction cell (DRC), and collision-reaction interface (CRI).[107] The use of a collision/reaction cell has been an alternative for the elimination of spectroscopic interferences in ICP-MS. Meija *et al.*[104] using among other strategies a reaction cell were able to determine low concentrations of volatile Se species in coffee samples. The authors comment that the use of He in the reaction cell made it possible to eliminate the interference of the Ar_2^+ species at *m/z* 78 and 80, allowing the analysis of the most abundant selenium isotope, ^{80}Se.

Non-spectroscopic interferences or matrix effect are known to suppress (or increase) the analytical signal for interfering matrix constituents above 500 mg mL^{-1}. The problem with them might be minimized by diluting solutions, altering the sample introduction procedure, or by the separation of the interfering component from the sample. Still, the internal standardization can help to significantly reduce these effects, choosing an appropriate internal standard with mass and ionization potential close enough to the analyte.[108]

ICP OES and ICP-MS applications

The applications of analytical techniques will be categorized into groups: coffee origin discrimination, coffee food safety, and analytical method optimization. All the articles mentioned below performed a calibration procedure. The most common were: external standard calibration (EC), and internal standardization calibration (IS). Moreover, certified reference materials (CRM) with similar characteristics to the samples (such as peach, citrus, tea and apple leaves, and rice flour) are used to analytical quality control (sample preparation and/or determination of elements).[109–113]

Valentin and Watling[109] demonstrated the promising potential of using the elemental composition of coffee altogether with statistical classification methods for provenance establishment. Coffee samples from 15 countries across five continents were investigated using the statistical interpretation of data from 59 elements concentration determined by ICP-MS and ICP OES. Little effects were observed over the elemental composition of coffee caused by harvest year, ripeness degree or green/roasted condition. Linear discriminant analysis and principal component analysis of elemental concentrations allowed correct classification of 96.9% of samples for their continent origin and, for continent-separated samples, up to 100% of correct classification was obtained into their countries and plantations origin. Ca, Ti, Mn, Co, Ni, Se, Rb, Sr, Mo, Cs and Ba were the most expressive elements for origin differentiation. Recently, a similar report was made by also applying the ICP-MS/MS system.[110]

Muñiz-Valencia *et al.*[114] determined Ca, Cu, Fe, K, Mg, Mn, Na and Zn from Mexican roasted coffee bean by ICP OES. The proposed study combined minerals content with chemometrics for differentiating the geographical origin of Mexican coffee beans. The mineralization of coffee samples was carried out using a microwave digestion system. Chemometrics calculation, such as Kruskal-Wallis test, principal component analysis (PCA), and linear and non-linear pattern recognition techniques (LDA and MLP-ANN) was applied and obtained results show that major elemental composition can be used to geographically differentiated Mexican coffee.

To discriminate Yemeni against Ethiopian coffee, Mohammed *et al.*[115] combined elemental analysis by ICP OES, and statistical analysis using multivariate statistical treatments, hierarchical agglomerative clustering (HAC), and principal component analysis (PCA). Were collected a total 16 coffee samples from different regions of Yemen and the samples mineralization were accomplished by combustion in concentrate HNO_3 and H_2O_2. Using elemental results and chemometric tools the authors proposed Ca-content to differentiate Yemeni and Ethiopian coffees.

Albals *et al.*[116] compared the elemental composition of different coffee varieties to check the toxic elements content, and the consumption safety according to health organizations. Coffee samples constituting of green and toasted beans from Brazil, Ethiopia, Kenya, Columbia, and India were studied. 22 elements including those essential and toxic were determined by ICP-MS. The detected metals and their concentrations per 1 cup intake did not exceed the upper limit of daily intake (TULD) for 80 kg adults or largely contribute to the recommended daily intake (RDI). ICP-MS data were validated *versus* the flame atomic absorption spectrometry (F AAS) by linearly fitting both results in plots for model elements Fe, Mn and Cu, with correlation coefficients better than 0.95. Still, no statistical meaningful difference ($p > 0.05$) was found between results of the two techniques, except for Cr, Co and Zn in green and roasted beans, estimated by ANOVA. Metal profile distribution within closer geographical origins was similar. Although authors conclude that the coffee consumed in Jordan did not contain toxic levels of heavy elements and is safe for consumption, some samples showed Pb concentrations higher than recommended on the local regulations.

Barbosa *et al.*[111] determined 38 elements in organic and non-organic coffee samples. The authors carried out microwave-assisted digestion on 54 coffee powder samples. They evaluated the levels of macro- and microelements to establish reference ranges and identify differences in the patterns of chemical elements in both crop procedures. The use of data mining algorithms, such as Multilayer Perceptron (MLP), Support Vector Machine (SVM) and Naïve Bayes (NB), to determine the type of coffee cultivation made it possible to make this determination with an accuracy of 96.3%.

Anissa *et al.*[112] reported a study to determine metal and metalloids content in coffee to assess the associated health risks, including the evaluation of different packing systems on the final metal concentrations. Forty-four samples were analyzed from different origins, forms, and packaging types. Commercial instant coffee brands of Italy, France, UK, USA, Sweden, Switzerland and Poland were herein used without specification. Determinations were performed by ICP-MS after digestion pretreatment, with data analysis carried out by principal components analysis (PCA) and ANOVA, and health risk assessment determined by the estimated daily intake (EDI), target hazard quotient (THQ), and hazard index (HI). From 44 elements, findings showed a wide variation of levels, with higher concentrations attributed to Al, Mn, Cu and Cd. Considering the packaging, significant differences were found for I, Zn, Co, Cu, Mn and Al content, with highest EDI for Al in grounded coffee packaged in capsules. Cd and Al levels were found above the reference dose for the chronic daily intake (CDI), with THQ and HI greater than 1.0 for different forms of coffee. Products stored in glass bottles showed regular metal levels. Authors claim that more research on the relationships between the metal concentrations in coffee samples and those in feed, water, and soil are interesting for future studies. A similar report was made by Yüksel *et al.*[117] evaluating the potential adverse health effects using THQ, HI, cancer risk (CR), and EDI from elemental profiling of the non-alcoholic beverage samples (ice coffee, iced tea, and energy drinks) from Istanbul. Potentially toxic elements (PTEs) Mn, Fe, Zn, Ni, Cu, Cr, Pb, Cd, Sb, As, Ti, and Hg were determined by ICP-MS.

Concerned about the large amount of waste generated by the production and consumption of coffee, Ninčević Grassino *et al.*[113] reported a study to evaluate the use of coffee silver skin (CSS) and spent coffee grounds (SCG) as mineral sources to improve their status and help recognizing them as novel foods. Metal and metalloid content in both sub-products was validated and a comparative study of green and roasted beans was conducted in parallel. Twenty-nine elements were determined by High Resolution ICP-MS (HR-ICP-MS), showing high levels of the macro essential elements: K, Mg, and Na. Essential trace elements showed Fe predominance, while Mo, Cr, Co and Se were detected in the ultratrace range between 0.02 and 2.42 mg kg^{-1}. Toxic elements Pb, As, Cd and Sn were found in a range below the maximum levels ruled in foodstuff by the EU Commission. Nevertheless, Rb, Ba, Sr, Ti and Al were found in higher levels, ranging from 2.33 to 764 mg kg^{-1}. Authors conclude that the high content of essential elements in CSSs might be useful for daily human needs, which encourages its potential use, but not prior to meet the requirements for the use of novel foods, which demands the strict monitoring of the potentially toxic elements.

Gois *et al.*[118] proposed a sample preparation method for the elemental determination of Ba, Ca, Cu, Fe, K, Mg, Mn, P, Sr, Sc, and Zn in samples of 35 different green coffee beans from various coffee cultivars, geographical regions (Espirito Santo, São Paulo, and Minas Gerais). The sample preparation strategies were microwave-assisted digestion and ultrasound-assisted extraction (UAE). The results obtained by both sample preparation methods were in agreement, showing the possibility of a fast and simple sample preparation by UAE.

Meija *et al.*[104] investigated the volatile selenium species contained in green coffee beans, roasted beans, and brewed coffee drink using the GC-ICP-MS technique with sample preconcentration by solid phase microextration (SPME). Trace level selenium species were detected in roasted coffee beans and in the steam from brewed beverages, with no detectable selenium found in the headspace of green beans, indicating their formation during the roasting process, just like observed for sulfur volatiles. Matching standards were also used to identify the selenium-compounds in coffee, and the artificial supplementation of green coffee beans was attained before the roasting to characterize the formation of the volatile selenium compounds. Among other strategies that allowed the determination of volatile Se species, at low concentrations, the authors used a reaction cell with H_2 to eliminate Ar_2^+ (at *m/z* 78 and 80) interference and chose the ^{78}Se isotope, which is not the most abundant, but allowed results with good precision and sensitivity.

A method for the determination of total inorganic arsenic and selenium in slim instant coffees using hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP OES) was proposed by Welna, Szymczycha-Madeja, and Pohl.[119] Six different accomplished preparations were evaluated. For the total As and Se determinations, previously, any As(V) form present was pre-reduced to As(III) with KI (in ascorbic acid medium) and HCl, and any Se(VI) form present was pre-reduced to Se(IV) by heating with HCl. As and Se hydrides were generated using reductant solution $NaBH_4$ in NaOH medium. Obtained results show that the As and Se hydride generation is dependent of sample preparation strategy and reducing conditions. Solubilization in aqua regia followed by ultrasonication of sample slurries, previously formed, proved to be the best strategy for the sample preparation. Total As and Se concentrations in analyzed instant coffees using the developed methodology ranged from <LOD to 0.282 μg g^{-1} (As) and <LOD to 0.240 μg g^{-1} (Se).

Gonçalves *et al.*[120] developed a method for determination of Al, Co, Cr, Cu, Mn, Ni, and Zn in coffee and other drinks by MIP OES. Coffee samples were prepared by infusion followed by filtration and a simple dilution in HNO_3 1% (v/v). The main goal of the work was to compare standard dilution analysis (SDA) obtained results with traditional calibration strategies, including external calibration (EC), internal standard (IS), and standard additions (SA). For SDA calibrations[121] only two solutions are required: the first containing 50% sample and 50% of a standard mixture, and the second containing 50% sample and 50% solvent (blank solution). Comparing the average recoveries of SDA (97%) with the other calibration strategies EC (95%), IS (102%), and SA (101%) for coffee samples, for example, they proved that SDA is a suitable strategy when using MIP OES for metal determination in this type of sample. Finally, Table II highlights details of some studies that used ICP techniques for elemental coffee analysis.

Table II. ICP OES and ICP-MS coffee samples elemental analysis

Technique	Samples	Analytes	Sample preparation	Reference
ICP OES	Coffee beans	Ba, Ca, Cu, Fe, K, Mg, Mn, P, Sr, Sc, and Zn	300 mg were submitted to MAD[a] using concentrate HNO_3 and H_2O_2 and 200 mg UAE[b] submitted to ultrasound energy for 15 min in 0.6 mol L^{-1} HNO_3. Than samples were centrifuged for 10 min at 3000 rpm.	118
ICP OES and ICP-MS	Green and roasted coffee	59 elements	1 g was submitted to acid digestion using concentrate HNO_3 and H_2O_2. Residue obtained after evaporation was dissolved at HNO_3 20%. A solution of iridium–rhodium was used as internal standard.	109
HG-ICP OES	Instant slim coffee	As and Se	0.5 g was submitted to (i) open vessel hot-plate heating digestion using a mixture of concentrate HNO_3 and H_2O_2, (ii) MAD concentrate HNO_3+H_2O_2 (6+1 mL), (iii) solubilization in aqua regia, (iv) solubilization in tetramethyl ammonium hydroxide, and 1,0 g was submitted to (v) 2.0% (v/v) HNO_3, and (vi) water.	119
HR-ICP-MS	Green and roasted coffee, coffee silver skin (CSS) and spent coffee grounds (SCG)	Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn	0.05 g previously homogenized in an agate mill was submitted to MAD using a mixture of concentrate HNO_3 and HF. A solution of indium was used as internal standard.	113

[a]Microwave-assisted digestion; [b]Ultrasound-assisted extraction.

LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

Theoretical background

LIBS is a type of optical emission spectroscopy that utilizes plasma generation by focusing a high-energy laser beam on a material. The laser induces the ablation of a small portion of the material, generating a high-temperature microplasma that emits spectral lines characteristic of the chemical elements present, enabling their identification and quantification.[122] The phenomena occurring during the laser ablation process in a material[53,123] are illustrated in Figure 8 and the schematic diagram of a LIBS system is shown at Figure 9.

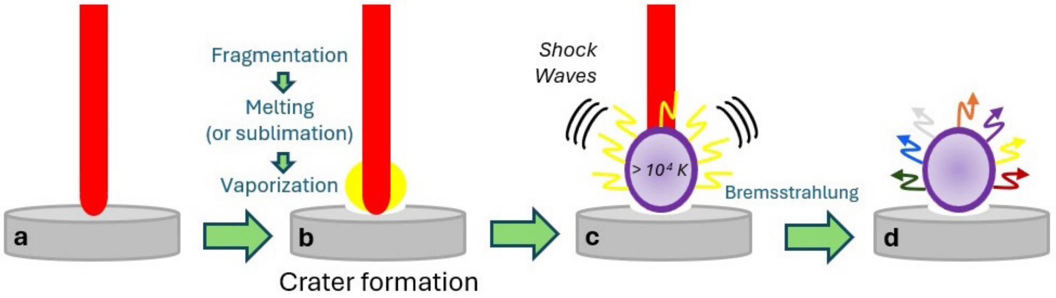


Figure 8. Schematic diagram of surface plasma lifetime: (a) plasma ignition, (b) thermal vaporization, (c) plasma expansion, and (d) elemental specific emissions.

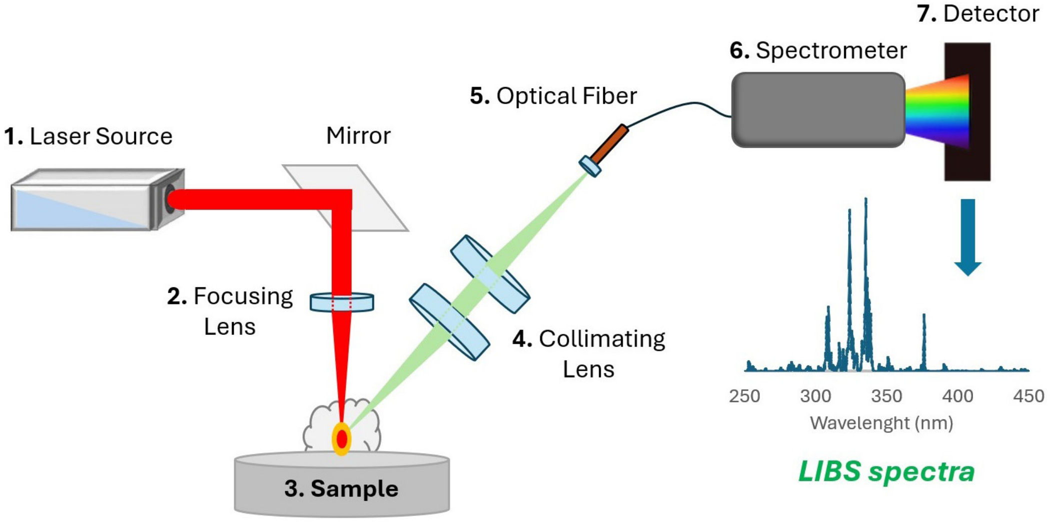


Figure 9. Schematic diagram representing the optical elements of the LIBS instrumentation.

LIBS quickly performs multi-elemental analysis with relatively simple instrumentation.[124] Analysis can be performed on complex matrices, such as petroleum products,[125,126] cosmetics,[127,128] plant materials,[129,130] biological fluids,[131] and food samples,[132,133] with few steps of sample pretreatments. Portable instruments are available for field or remote analysis.[134,135] Main limitations lies in its lower sensitivity and accuracy once compared to other spectroscopic techniques, such as F AAS and ICP OES.

The laser source is responsible for the laser beam emission, comprising the steps of absorption, stimulated and spontaneous emissions. Lasers are emitted by the stimulation of energetic decays of excited species, doubling generated photons that confer high intensity, directionality, monochromaticity, and coherence to the radiation.[122] The most commonly applied lasers for LIBS are the Nd:YAG (1064 nm) due to their capability of supplying high density laser pulses with focalized power, achieving millions of Watts.[122,136]

LIBS optical components are used to focus the laser pulse on the sample surface, and to collect and conduct the plasma radiation through an optical fiber cape, until the spectrometer. The simpler LIBS configuration uses the sample holder positioned at 90º from the laser source. Other adjustments are made to better focus the laser on the sample, to improve the data acquisition from plasma, and to select the proper working wavelength. Optical fibers are used to improve the harvesting of plasma radiation in cases which the detector should be positioned relatively far from the sample, allowing the analysis of hot samples. Focus lens should be used to direct the light to the collecting fiber cape, which improves detection sensitivity.[122,136]

The spectral detection system collects, resolves and measures the plasma emissions from the sample. It is formed by a wavelength selector followed by an optical detector. LIBS spectra are usually complex, formed by multiple non-resolved emission lines prone to spectral interferences, which demands the use of a spectrometer prior to the detector. The spectrometer should show a high spectral resolution in the range of 0.003 to 0.1 nm, to properly disperse the plasma radiation, organizing spectra in terms of radiation intensity *versus* each wavelength.[53,122,136]

The Echelle spectrometer is the most applied for LIBS, since its 2D spectral resolution surpasses $\lambda/\Delta\lambda > 10{,}000$ that is high enough to resolve the overlapping of plasma emission lines.[136] As the main detectors, photomultipliers (PMT), photodiode arrays (PDA), intensified PDAs, charge-couple devices (CCD), and intensified CCDs are the most common used. The coupling of Echelle spectrometer with ICCDs is often applied due to its wide spectral range (165 to 1000 nm) with high 2D resolutions that allows multielemental analysis with high sensitivity.[136]

LIBS spectra are inherently complex due to signal-to-noise issues, including fluctuations in laser energy, sputtering rate, laser-sample coupling, and other intrinsic plasma characteristics. Sample homogeneity and its analyte distribution play important role on that matter too. Therefore, chemometrics is an important tool to treat data,[136,137] meanwhile the data normalization is an important procedure to minimize undesirable variations associated with signal acquisition in LIBS.[137,138]

Regarding the calibration, in recent years different strategies have been proposed, mainly due to the absence of calibrating material with characteristics like the samples, which could minimize the effect of laser-sample interaction. Among other calibration strategies, the following stands out: matrix-matching calibration (MMC), multi-energy calibration (MEC), one-point gravimetric standard addition (OP GSA), one-point and multi-line calibration (OP MLC), slope ratio calibration (SRC), two-point calibration transfer (TP CT), single-sample calibration (SSC), multiple linear regression (MLR), principal component regression (PCR), partial least squares (PLS), and artificial neural networks (ANN) (SRC-LIBS).[130,138,139]

Pattern supervised recognizing methods, such as SIMCA, partial least squares discriminant analysis (PLS DA), k-nearest neighbor (KNN), and linear discriminant analyses (LDA) are highly used for the proposition of classifying models for spectral information.[140] Pattern non-supervised recognizing methods, as principal component analysis (PCA), and hierarchical cluster analysis (HCA) are commonly used too, starting with PCA.[122,140] Finally, the multivariate calibration is an important chemometrics tool, mainly, the partial least squares (PLS) and the multiple linear regression (MLR).[141]

LIBS applications

The following studies propose the application of LIBS for identifying the type of bean and its quality control, fraud detection, and determining the mineral composition of coffee samples.

Abdulmadjid *et al.*[142] used LIBS to make rapid identification of elements in coffee, showing its potentiality for lineage authentication. ND-YAG laser at 10 Torr surrounding atmosphere was used, intending the elemental detection of Arabica and Robusta green beans. K (766.49 nm), Na (588.9 nm), Ca (393.3 nm), CN band (388.3 nm), N (337.13 nm), and C (247.8 nm) were detected in both coffee types, following the decreasing concentration trend: Ca > K > CN > Na > N > C for Arabica; and K > Ca > CN > Na > C > N for Robusta. The potassium emission intensity was almost the same for both coffees, but sodium was lower for Arabica. To differentiate both, the ratio intensities K/C, Na/C, CN/C, and Ca/C were used, finding that

CN/C and Ca/C in Arabica beans were significantly different from those in Robusta. These ratio intensities were indicated by authors as potential markers for proper chemical discrimination.

Zhang *et al.*[143] used LIBS combined with chemometrics to identify coffee varieties to help improving the coffee trading and consumption. Wavelength transform was applied to reduced spectra noise, while partial least squares-discriminant analysis (PLS-DA), radial basis function neural network (RBFNN), and support vector machine (SVM) were used to build classification models. PCA was used to select differentiable spectral variables to the coffee identification: 20 wavelengths were chosen, corresponding to C I, Mg I, Mg II, Al II, CN, H, Ca II, Fe I, K I, Na I, N I, and O I, and PLS-DA, RBFNN, and SVM pointed the acceptable results on the corresponding wavelengths. Authors claim the feasibility of identifying coffee varieties using LIBS combined with chemometrics, but pointed out the necessity of further studies using more samples to produce more robust classifications models. Using a pulsed nanosecond laser (Nd:YAG laser at 1064 nm). Alkallas *et al.*[144] determined the qualitative elemental compositions (C, O, H, CN groups, Fe, K, Ca, and Mg) of eight different cultivars of roasted coffee beans. Combining LIBS and chemometrics tools (PCA) the authors showed the potential of the proposed method for the elemental identification and classification of coffee samples.

An objective quantitative LIBS methodology to quantify the chemical contents of coffee beans has been reported by Wirani *et al.*[145] laser energy of 120 mJ and delay time of 1 µs was used, allowing the detection of Ca, W, Sr, Mg, Na, H, K, O, Rb, and Be. Calcium was the main element found in coffee beans, and the roasting process decreased the Ca emission intensity by more than 40%. Furthermore, discriminant analysis helped to distinguish between Arabica and Robusta lineages, either in green or roasted conditions, using the Ca, W, Sr, and Mg as identifier elements. Authors affirmed that the overall chemical composition of roasted coffee beans were affected by factors as the soil composition, location, climatic conditions in the area, and the post-harvesting procedures that green beans are submitted to (*e.g.,* drying, storage, fermentation, and roasting). The methodology shall complement the organoleptic-quality testing of coffee, usually performed by experienced testers.

The combination between LIBS and Raman spectroscopy was proposed by Shin *et al.*[146] for the authentication of food samples, including brands of Arabica coffee beans. The authors propose that class detection and classification were accomplished through the use of multivariate feature selection and machine-learning procedures. The accuracy of classification was observed to improve by approximately 10% when utilizing the hybrid Raman/LIBS spectra, as opposed to the analysis of spectra from the individual methods.

To monitor the so-called black, immature and sour beans (BIS), a type of defective bean, Silva *et al.*[147] used LIBS with spectral processing and variable selection to fit linear regression models for predicting defective BIS in coffee blends. The high prediction capacity of models was proved by low root mean square error of prediction (RMSEP < 3.8%), and relatively high determination coefficients (R-square > 0,8), leading to reliable chemical-guided responses, less susceptible to visual indistinguishability than the current quality-control methodology based on manual inspections.

Sezer e*t al.*[148] proposed the use of LIBS with chemometrics to evaluate coffee adulteration with chickpea, corn, and wheat. Methods were used to classify and quantify the adulteration ratio in Arabica coffee, with coefficients of determination (R-square) and limits of detection (LOD) of 0.996, 0.995, 0.995 and 0.56%, 0.52% and 0.45%, respectively, for chickpea, corn and wheat adulterations. According to authors, the methodology helps to prevent the market unfair competition, protects customers, and is a novelty to ensure the coffee quality-control.

The semi-quantitative analysis of mineral composition was performed by LIBS in Harari coffee, with and without herbal additives, such as clove, ginger, and cardamom.[149] Fe, Ca, K, Mg and Na were observed in all types of samples, with an increase of mineral content due to the herb-enrichment. Authors claim that the semi-quantitative LIBS analysis is rapid and effective to monitor changes in the elemental composition of food samples, pointing out the possibility of enriching coffee with essential mineral nutrients by simply adding natural herbs.

Gondal *et al.*[150] used a refined LIBS detection system with a 266 nm wavelength pulsed Nd:YAG laser, 500 mm spectrograph and gated ICCD camera with built-in delay generator, to study the elemental composition of coffee available in Saudi Arabia. The elements Mg, Ca, Al, Cu, Na, Ba, Br, Co, Cr, Ce, Mn, and Mo were observed in LIBS spectrum and, sodium line was used to study the parametric dependence of the LIBS signal, which shows a linear dependence with the laser pulse energy. The dependence of LIBS signal still showed a typical increase with the time delay between the excitation and data acquisition, with optimum acquisition at 400 ns.

Khalil and Labib[151] developed a fast detection system based on dual-pulsed LIBS to estimate the content of micro-toxic elements in commercial coffee brands. Thirteen coffee brands were analyzed by the developed DP-LIBS, and the ICP OES benchmark technique. Elements such as Al, Pb, Zn, and Cr were identified and, standard calibration for each element was attained by the preparation of standard matrices with known elemental concentrations. The intensity of line emissions was used as the quantitative calibration parameter. Precision of DP-LIBS data was compared and validated with ICP OES parallel analysis of samples, showing good agreement. Authors affirm that the suggested new DP-LIBS protocol demonstrated excellent analytical benefits for the detection of micro-toxic elements in coffee or other food products, ensuring their safety and quality. Table III shows some LIBS applications for the classification and identification of fraud in different coffee samples.

Table III. LIBS applications used to identify and classify fraud occasions for several coffee brands and samples

Sample	Application	Reference
Green Coffee Beans	Differentiation of Robusta and Arabica coffee beans based on the signal intensities of K, Na, Ca, C, N, and the molecular band CN.	142
Green Coffee Beans	Use of different chemometric tools to identify coffee varieties based on various emission lines in the LIBS spectra	143
Roasted coffee beans	Determination of the qualitative composition aimed at the classification of diferente roasted coffee samples	144
Coffee Blends	Prediction of defective BIS (black, immature, and sour beans), using fit linear regression models	147
Arabica Coffee	Evaluation of coffee adulteration with chickpea, corn, and wheat	148
Harari Coffee	Employment of semiquantitative analysis by LIBS to identify herb enrichment in Harari coffee samples with clove, ginger, and cardamom	149
Commercial coffee brands	Estimate the content of micro-toxic elements using double-pulse LIBS.	151

X-RAY FLUORESCENCE (XRF)

Theoretical background

The X-ray fluorescence (XRF) is a distinctive analytical technique used for the fast determination of elements with the atomic number above the oxygen (> 8), allowing the qualitative identification of elements and the (semi)quantitative elemental analysis. Differently from other elemental analysis techniques, it allows the development of non-destructive analytical methodologies with few or even no sample pretreatment. The XRF is based on the analysis of energy dispersion of fluorescence emitted by an X-ray irradiated sample. It is an absorption/emission technique,[152,153] which is different from the X-ray diffraction (XRD) that works with the scattering of incident radiation without absorption/emission events. The XRF analysis (Figure 10) is initiated by the absorption of incident X-ray by electrons in the sample, shifting them to more energetic layers of the atom or even promoting its ionization, leaving intern vacant orbitals in K or L layers. Electrons from outer or more energetic layers decay to this bottom vacant orbital, emitting the so-called fluorescence radiation with lower energies than the original one absorbed.

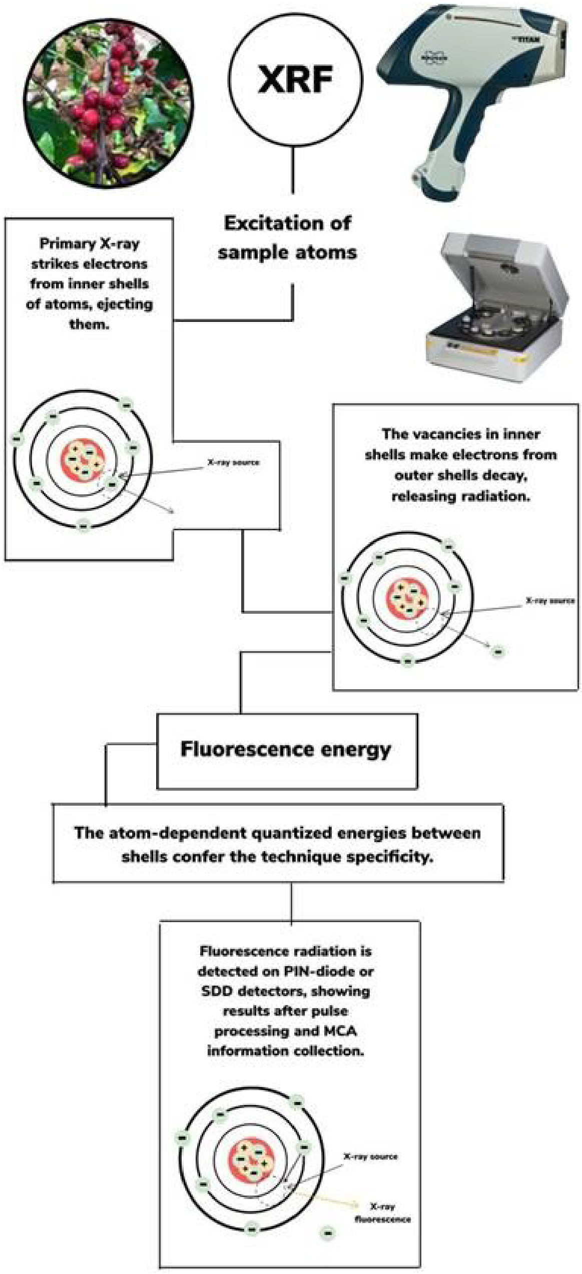
The selectivity of XRF method is coffered by the discrete energy between layers and orbitals that are atomically-dependent. So, the frequency of absorbed and emitted radiation is resonant to the corresponding orbital transitions and particular to the parental atom,[153] allowing the determination of different elements. The emitted signals are transduced in a multichannel analyzer, resolving with high performance the X-ray radiation individually. Modern XRF detectors can process about 1 million counts per second, providing reliable information about the sample elemental compounding.

Historically, the XRF has been associated with geological analyses and only solid samples were studied. Nowadays, with the instrumental improvements it is even possible to investigate, *e.g.*, alloys, powders, liquids, and filtering materials. Most of XRF applications are situated in environmental, chemical, metallurgic, archeological, soil, and agronomical analysis.[154] Its main advantages to other techniques besides the non-destructive analysis of solid samples is the multielemental capability, simple and fast sample preparation, the wide dynamic range of quantitative analysis, relatively low LODs, high precision, fast data processing, and low-cost.[155]

For instance, Hernández *et al.*[156] demonstrated the viability of using XRF to quantify the elemental concentrations in samples of fresh and used ground coffee, as well as instant coffee, trying to obtain information about possible differences in several elements to use that as markers of coffee provenance. Calibration was performed using NIST certified reference materials 1547 (peach leaves), 1570a (spinach leaves), and 1573a (tomato leaves), determining accuracy by the analysis of a NIST reference 1571 (orchard leaves). Complex spectra were deconvoluted with the open-access computer code QXAS. They found that the XRF analysis were accurate, the elemental content was similar to other works, and significant differences in the concentration of elements as P, K, and Ca were observed among roasted ground coffee, used ground coffee, and instant coffee specimens due to the water dragging during the brewing. It was not possible to differentiate origin of samples by the difference of elemental concentrations, and authors even assumed the need of using multivariate statistical analysis (as Principal Component Analysis) in wider sample sets to better establish the coffee origin.

Tezzoto *et al*.[157] used the XRF as an alternative technique to evaluate the simultaneous multielemental quantification of essential elements in *Coffea arabica L.* plants. The ICP OES technique paired with certified reference materials from leaves were used for the calibration and the accuracy of the XRF method for the determination of the concentration of several nutrients in coffee leaves and branches. Authors claimed that the XRF proved to be advantageous with low costs using loose powder samples. Spiked collected samples with excess of Ni and Zn were used, showing good relationships between certified values and XRF data, with recoveries ranging from 82 to 117%.

Weinberger *et al.*[158] made a critical evaluation of the use of XRF to determine the elemental composition of coffee, starting with the sample pretreatment procedure that was tested by the use of pellets or loose powder samples, passing through the quantification strategies testing different fundamental parameters and empirical calibrations, and finishing with the test of explorative principal component analysis (PCA) and partial least square regression (PLS) to discriminate the different types of coffee samples among pure, instant, and with additives. The raw XRF spectra without the software fitting and quantification procedure were used for the first time in the literature. Results were used to establish a reliable and simple method for the multielemental analysis of coffee by XRF, providing a good basis for future XRF spectra applications as sample fingerprints for coffee traceability and authentication.



Excitation of sample atoms

Primary X-ray strikes electrons from inner shells of atoms, ejecting them.

The vacancies in inner shells make electrons from outer shells decay, releasing radiation.

Fluorescence energy

The atom-dependent quantized energies between shells confer the technique specificity.

Fluorescence radiation is detected on PIN-diode or SDD detectors, showing results after pulse processing and MCA information collection.

Figure 10. The X-ray fluorescence of a hypothetical atom.

Although it is even possible to generate an X-ray emission spectrum by simply introducing the sample in the target of an X-ray tube, this approach shows many drawbacks that limit the technique application for many kinds of materials. So, the excitation is usually accomplished by the irradiation of the sample with an X-ray beam from an originating tube in two main types of equipment: the wavelength dispersive X-ray fluorescence (WDXRF) that resolves wavelength lines by prisms with diffraction or geometrical dispersion; and the energy dispersive X-ray fluorescence (EDXRF), which resolves wavelength lines based on the electronic dispersion of photon energy with a pulse height analyzer. WDXRF analyzers present higher spectral resolutions (mainly, at lower energy regions), lower background residual signals, wider dynamic ranges, and capacity to measure ultralight element signals, despite of its higher instrumental complexity, lower detection efficiency, and the operation demand for high power X-ray sources.[159]

Portable XRF (pXRF) field analyzers are from EDXRF category,[155,160,161] comprising not only hardware and software improvements, but still new accessories and peripherals that extent its application. Despite of some advantages, many literature works have pointed out the ambient humidity as a problem to the analysis. It decreases the incident X-ray intensity and disperses the generated fluorescence, underestimating the sample content of lighter chemical elements.[160,161] Among other disadvantages of pXRF are the interference of high organic content in the sample, sample granulometry[162] and the lengthier time of analysis.[162,163] Therefore, to avoid these drawbacks, it is highly recommended to standardize samples prior to analysis, so as to diminish the negative influence of these factors.

Most applications reside in the environmental analysis field, in such areas which *in situ* fast and practical measurements are required: accidental contaminations after industrial activities, pollution and natural disasters, as hurricanes and earthquakes. As an example, after Katrina hurricane disaster, the pXRF device was frequently used to territorially chart the Pb and As soil contamination, detecting large excessive amounts of Pb.[164] Agronomical uses (*e.g.* Figure 11) are very common too for investigating the chemical elements during plant tissues studies. Samples as corn, cotton, and soy were analyzed with the pXRF to investigate Ca, Co, Cr, Fe, K, Mn, Ni, P, S, Si and Zn.[165] Proximal sensors have been usually used for this and other soil science studies: rocks, sediments, plant tissues, water and other types of natural matrices.[166] Considering the non-destructive nature of determinations, the XRF is a promising technique for elemental compounding determinations in coffee-plant leaves using, *e.g.*, pulverized samples in a dispersive EDX spectrometer, avoiding lengthy acidic digestion pretreatments.[157]

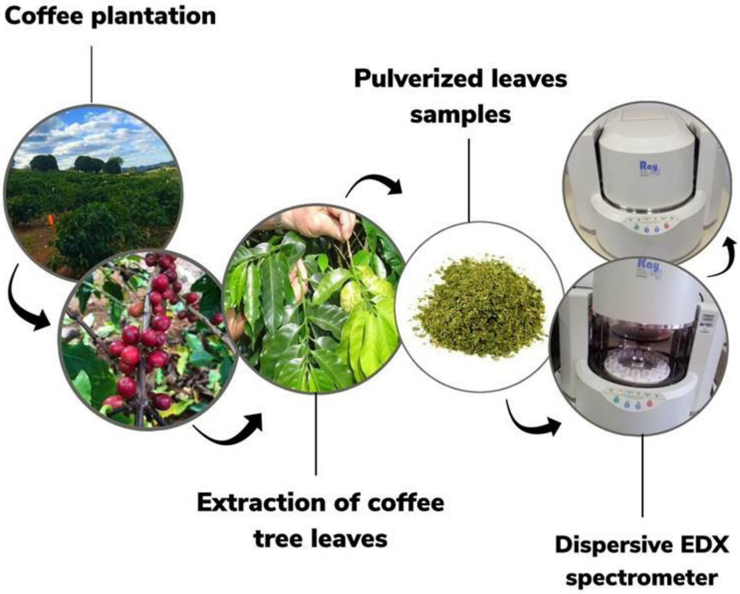


Figure 11. EDXRF procedure for determinations in coffee-plant leaves.

XRF applications

The chemical composition of both roasted and ground coffee is strongly related with the soil conditions in the coffee cultivation.[32,33,42] The elemental content in coffee plants is highly influenced by the growing environment, something associated with the characteristics of the planting soil as the lime content, the organic content, pH, and drainage status conditions.[27,42,45] And, as earlier discuss, the concentration of certain macroelements is regarded to the modulation of the total sugar and phenolic content (chlorogenic acids) in coffee, regulating the coffee sensory attributes. Considering that, Teixeira *et al.*[167] reported the use of portable X-ray fluorescence (pXRF) to characterize the effects of the soil management on its elemental compounding. Math models were drawn for fertility predictions. The pXRF data were used to correlate and validate the soil fertility attributes determined through laboratory analysis and the lime application, with or without area management distinction. Management on coffee crops increased levels of Sr, CaO, P_2O_5, Cu and Zn. The general models were able to predict the exchangeable Ca(II), pH and base saturation parameters, losing effectiveness for unmanaged areas.

pXRF has been used[168] to measure elemental concentrations to characterize parent material (PM) for understanding the soil distribution across landscapes. The mapping of *phyllite* variations was accessed using the pXRF data, and evaluating each of three soil horizons of Brazilian Cerrado, divided in a total of 120 soil samples. Chemometrics was used to model and predict the PM through pXRF data to the entire area, consolidating nine maps (3 horizons data for 3 algorithms) that were validated for overall, producer's, and user's accuracy, and kappa coefficient. Authors found out that best results were obtained by support vector machine algorithm, with optimal performance for V, Ni, Sr, and Pb, regardless of land use.

Worku *et al.*[169] showed a standardization method to check the coffee provenance authentication using multielemental analysis (X-ray fluorescence, spectrometry-based techniques, and ICP) and $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$ determinations by elemental analyzer-isotope ratio mass spectrometry. 103 green Arabica coffee samples from four regions of Ethiopia were tested to determine their geographical origin. XRF-based multi-elements with and without $\delta^{13}C$, using linear discriminant analysis, seemed to be the most effective method for the geographical discrimination of coffee with higher accuracy classification than ICP-based multi-elements, despite of stable isotopes usage.

Assis *et al.*[170] developed a multivariate model to characterize Robusta-Arabica coffee blends using the NIR spectroscopy and total reflectance TXRF. Eighty blends were herein tested as samples, with green dried and peeled beans from different Brazilian regions and harvests. The TXRF was used to determine 14 elements: P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Rb and Sr. Duplicate measurements were performed under random sequences in relation with the blend compounding. Both molecular and atomic data were fused in a quantitative model to allow the determination of samples authenticity. The interpretation of partial least squares (PLS) for the simultaneous detection of multiple adulterants was the key factor to correlate atomic/molecular data, pointing out Arabica coffee with higher contents of lipids, saccharose, Mn, and Br, while Robusta coffee showed higher Rb, Fe, Sr and Cu contents.

EDXRF has been proposed by Almeida *et al.*[171] as a simple approach to quickly quantify Cd, Pb, Mn and Fe in milled samples of coffee from Salvador, Bahia, Brazil. The methodology showed LODs of 62, 55, 86 and 76 µg kg^{-1} for Cd, Pb, Fe and Mn, respectively, with reasonable linear correlation coefficients. It was validated by the execution of parallel determinations using ICP OES with acidic digestion sample preparation. Both methodologies showed no meaningful statistical difference on their results. Therefore, EDXRF proved itself to be a valid alternative to lengthy ICP OES determinations, skipping the sample pretreatment with lower reagent costs, and an equally practical multielemental detection. Table IV summarizes main applications and brief analytical details.

Table IV. XRF analysis for coffee environmental samples

XRF Technique	Samples	Analytes	Analytical procedure	Ref.
pXRF	Soil from coffee and eucalyptus cultivation	V, Al_2O_3, Pb, Sr, Cl, Zn, Cu, Ni, Fe, Mn, CaO, P_2O_5 and K_2O	Soil samples were air-dried, passed through a 2 mm sieve and subjected to laboratory analyses: pXRF featuring a Rh X-ray tube of 4W, 15-50 keV, and 5-100-µA, silicon drift detector (SDD) with a resolution <145 eV.	167
pXRF	Soil from coffee cultivation	V, Sr, Cu, P, Fe, Pb, Y and Zn	Soil samples were air-dried and passed through a 2 mm sieve prior to pXRF analysis. Elemental analyses were performed using directly pXRF, using Trace dual soil mode (60 s dwell time). Spectrometer contained a 50-keV and 100-µA X-ray tube.	168

(continues on next page)

Table IV. XRF analysis for coffee environmental samples (continuation)

XRF Technique	Samples	Analytes	Analytical procedure	Ref.
WD-XRF	Green Arabica coffee beans	K, Ca, Mg, Al, Si, P, S, Cl, Fe, Mn, Cu, Zn, Rb, Sr, Ni, K_2O, CaO, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3 and Fe_2O_3	Freeze-dried coffee beans were grounded prior to mixing with polypropylene wax binding agent at a ratio of 1:4 (binder:sample). The sample materials were then pressed into 40 mm diameter pellets at 150 kN. Tube settings ranged from 25 kV, 160 mA for low atomic weight elements up to 60 kV, 66 mA for high atomic weight elements.	169
TXRF	Dried and peeled green coffee beans	P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Rb and Sr	Coffee beans were roasted, grinded and sieved (40 mesh). Extraction: 1 g of sample + 10 mL of deionized water for 20 min at 90 °C. Then, mixture was centrifuged for 10 min at 3000 rpm and filtrated. The TXRF was equipped with a molybdenum tube - Kα 17.5 keV excitation source (600 µA, 50 kV, 50 W), a multi-layer onochromator and a silicon drift detector with an active area of 10 mm². For sample preparation, 250 µL of the coffee extract were mixed with 200 µL of deionized water and 50 µL of the internal standard (10 mg L^{-1} gallium solution)	170
EDXRF	Milled coffee beans	Cd, Pb, Mn, and Fe	Coffeee beans were milled with a granulometric control of particle size less than 150 µm. Each sample was analyzed as a pellet disk (3 mm in thickness and 36 mm in diameter).The operational conditions of the equipment were: tube tension, 40 kV; tube current, 2 mA; and irradiation time, 100 s.	171

VOLTAMMETRIC ANALYSIS

Theoretical background

Since the early days of the analysis of toxic metals in food, analytical determinations have been carried out by atomic absorption spectroscopy (AAS) using the flame atomization (F AAS), or the electrothermal mode (ET AAS) for samples with trace level concentrations.[172] Comparatively, voltammetry is rarely used for the elemental analysis of coffee samples. Mostly, it is considered an option when the F AAS is recognized to be not sensitive enough for the determination of trace elements and both the ICP OES and ET AAS are unavailable. Nevertheless, voltammetry technique offers electrochemical approaches with high sensitivity and selectivity using inexpensive instrumentation for the simultaneous determinations. For instance, Suseela *et al.*[35] studied the daily intake of trace metals from the coffee ingestion in India. They used the F AAS for the determination of Ca, Cr, Fe, K, Mg, Mn, Ni, Sr, Zn, and the differential pulse anodic stripping voltammetry (DPASV) for Pb, Cd, and Cu. Limits of detection (LODs) reported by authors were at least 38 times lower for DPASV than for F AAS. Considering the low concentrations encountered in coffee samples in the ppb magnitude order, the differential pulse anodic stripping voltammetry (DPASV for Cd, Pb, Cu, and Zn) or the adsorption differential pulse voltammetry (ADPV for Co and Ni) are required to make the *in situ* preconcentration of analytes to achieve low enough limits of quantification (LOQs) for analytical determinations.[173] Therefore, voltammetry can provide an alternative for F AAS and ICP OES for the trace element analysis in coffee, enabling the quality control of these spectrometric techniques or the creation of routine low-cost methodologies.

Now starting from the basics, voltammetry is an analytical technique that measures the current that flows through a working electrode (WE) immersed into a three electrochemical cell. A potential referenced against a reference electrode (RE) is applied by an auxiliary electrode (AE) over this working electrode (WE) to ensure that an oxidation or reduction reaction happens on its surface with negligible consumption of the analyte in the bulk electrolyte.[174] This potential (independent variable) is a time-dependent excitation signal responsible to generate the measured current (dependent variable), which is used as the analytical response. There are four common waveforms of excitation signals (Figure 12): linear sweep (LSV), which the potential increases linearly with time; pulsed forms, which are the square-wave (SWV) and differential pulse (DPV), where the current is measured in different times during the pulse lifetime and; the triangular wave, which the potential varies linearly between two threshold values and then returns. The rate of the linear excursion of potential is called scan rate, usually reported in mV s^{-1}. [63]

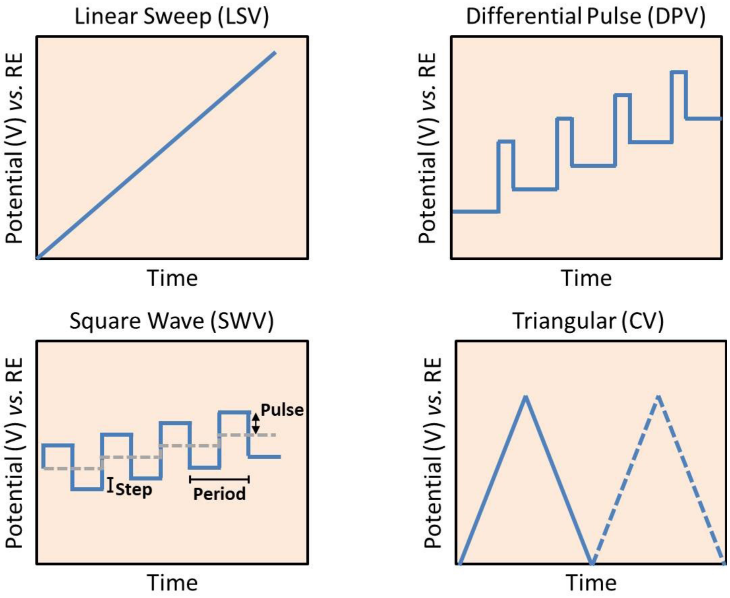


Figure 12. Schematically diagram of signal excitation waveforms according to the related voltammetric technique.

The types of voltammetric methods are classified according to the excitation waveforms: LSV is ascribed to the hydrodynamic voltammetry (or even the polarography in the past), SWV to the square-wave voltammetry, DPV to the differential-pulse voltammetry, and the triangular wave to the cyclic voltammetry (CV).[174] The device responsible for the applied potentials and the current measurement is called potentiostat. It comprises a signal source as a tension generator[175] capable of supplying all the signals observed at Figure 12.

As important as the excitation signals are the WE materials: there is a great variety of them. Usually, WE are assembled by a small planar disc from a cylindrical conductor material embedded in a cylindrical inert polymer (as Kel-F or Teflon) and connected by a conductive wire. Noble metals are often used (as Ag, Au and Pt), as well as carbon-based materials like carbon paste electrodes,[176] carbons fibers,[177] glassy carbon,[178] pyrolytic carbon,[179] boron-doped diamond,[180] carbon nanotubes,[181] and reduced graphene-oxide.[182,183] Semiconductors as metal oxides can be used as well.[184] The WE materials are chosen accordingly to the application, which is mainly dictated by both the electrode material and the solution compounding. The positive working potential threshold is usually determined by the water-to-oxygen oxidation (O_2/H_2O), and the negative threshold by the water-to-hydrogen reduction (H_2/H_2O).[174]

For many years, the hanging-drop mercury electrode (HDME) has been widely applied to the determination of the concentration of metals due to the wide range of negative potentials achieved, besides the facility of renewing its surface and reducing metallic ions to amalgams.[185] Due to toxicity issues[186] the HDME have been gradually substituted, firstly, by amalgam electrodes[187] and now for carbon-based electrodes.[188] Some other types of electrodes include the ultramicroelectrodes (UME), which are metallic wires or carbon fibers with small diameters (5-100 μm) embedded in tempered-glass cylinders,[189] and the sandwich electrode, mostly used for voltammetric flow analysis.[190] The commercially available sandwich electrode is made of a conductive disc embedded in a polyetheretherketone (PEEK) block, and can be used in several flow-cell setups for, *e.g.*, flow injection analysis (FIA),[191] batch injection analysis (BIA),[192] and (ultra)high performance liquid chromatography (u-HPLC).[193]

Finally, the surface modification of conductive substrates is a very important research area of electroanalysis. Modified electrodes show a myriad of applications, starting with electrocatalysis (*e.g.* oxygen and hydrogen reduction reactions,[194,195] electrochromic devices,[196] molecular electronic devices as diodes and transistors,[197] enzymatic biosensors,[198] and immunosensors).[199] Most studies use modifications to impart sensitivity and selectivity to the electrochemical sensor, specifically detecting dissolved species or certain molecular functional groups.

Stripping voltammetry analysis

Considering the determination of metals in aqueous solutions, the most common strategy used is the anodic stripping voltammetry (ASV). The analyte is electrodeposited onto the WE surface under the application of a cathodic biasing potential simultaneously to the stirring of the solution. After a strictly controlled elapsed time of electrodeposition, both the electrolysis and the stirring are interrupted, and analytes are determined by their stripping using one of the potential scan programs of Figure 12. The potential is scanned to positive values and the analytes are reoxidized to their original ionic forms.[200,201] The electrodeposition step is actually an electrochemical preconcentration and, as an interesting result, it improves the methodology sensitivity, conferring the lowest LODs to ASV among the voltammetric methods. For instance, the differential pulse anodic stripping voltammetry (DPASV) achieves nM LODs for analytes of environmental importance, as Pb(II), Cd(II) and Tl(II).[202] The potential program of a typical DPASV is shown below with a hypothetical resulting voltammogram and calibration curve (Figure 13).

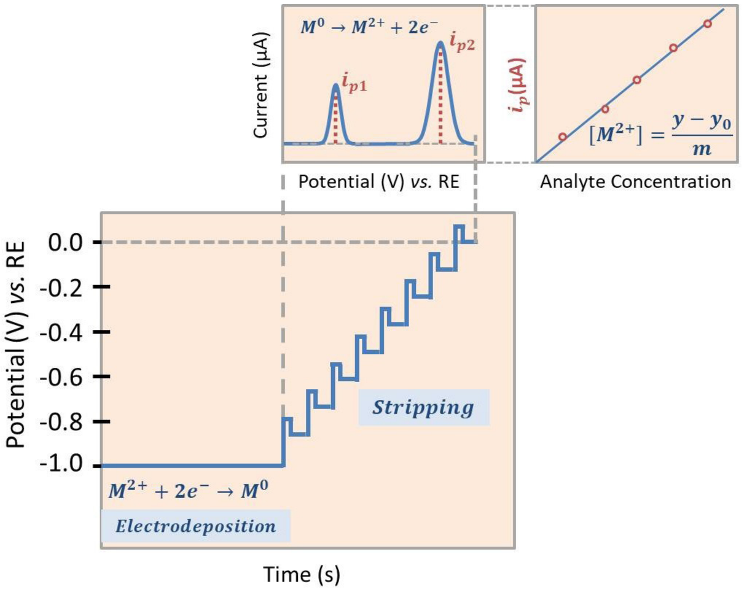


Figure 13. Diagram of hypothetical potential program developed for differential pulse anodic stripping voltammetry (DPASV) with the preconcentration electrodeposition and the stripping steps. Insets show the DPASV resulting voltammogram for the stripping of two generic metallic ion analytes, and the calibration curve based on the stripping peak current (i_p).

Initially, a very low potential (as –1 V *vs.* Ag/AgCl) is applied at the WE for several minutes, under solution stirring, to promote the concomitant electrodeposition of metal ions (as Zn(II), Cd(II), Pb(II), Ga(II) and Cu(II)), until a reasonable amount of them is accumulated on the WE surface. Then, the stirring is interrupted, and the potential is sustained at the initial low value for some few seconds. Finally, DP potential scan is applied while the current is recorded during the stripping step. The voltammogram is the plot of measured currents in function of the applied potential (determined by the product of stripping time by the scan rate).[202] Interpreting the resulting voltammogram, the oxidation process for each metal starts on the onset potential, from where the current starts to pronounceably increase until the peak value in the formal half-wave potential ($E'_{1/2}$). As the electrodeposit is gradually stripped, the current peak decreases to achieve back the baseline. Different metals are detected according to their $E'_{1/2}$, and the technique resolution is dictated by the striping kinetics of each metal from the WE electrode surface.[175,202] For the quantitative determination, the current peak height is frequently used as the analytical signal parameter (y) to plot the linear calibration curve, which is proportional to the mass of the electrodeposited metal. Therefore, the quantitative performance of the methods depends, among other factors, on the potential control, the deposition time, the stirring fluid-dynamics, and the standard solutions used for the signal acquisition. [200-202]

Voltammetric stripping methods are particularly interesting for trace metal analysis from micro- to nmol L^{-1} concentrations, since the preconcentration step allows analyte quantifications with reasonable accuracy, agility and simplicity. The electrodeposition time should vary from a few seconds to a single minute for 0.1 μmol L^{-1} analyte concentrations, until 30 min or even more for nmol L^{-1} concentrations. Still, the preconcentration electrodeposition times depend on the sensitivity of the stripping method, favoring pulsed methods that are much less affected by capacitive non-faradaic background currents.[203]

Besides the metals electrodeposition, there is another very usual type of stripping voltammetry: the adsorptive stripping analysis.[204] It is quite similar to the original one despite of the analyte deposition that happens through the physical adsorption on the WE surface. After accumulation, the stripping occurs by the potential scan by LSV, DP or SW. Many organic molecules with clinical or pharmaceutical interest can be anchored on the Hg or carbon electrodes[205,206] mainly, once close to the zero-charge potential. Under proper stirring, the adsorption happens quickly with 1 to 5 min of accumulation time for a 0.1 μmol L^{-1} solution, and 10 to 20 min for nmol L^{-1} samples. Low concentration cations have been widely determined by adsorptive stripping voltammetry, with complexation of the metals with a ligand as the o-phenanthroline[207] or aminopolycarboxylic acids.[202] Very low LODs can be reported for these methodologies.

Dissolved organic matter (DOM) interference in voltammetric analysis

One major drawback of the voltammetric analysis of metals is the direct interference of dissolved organic matter. Among the most common voltammetric interferences caused by the dissolved organic matter are the analytical signal distortion, the half-wave potential displacement, and the partial or total wave suppression.[208] Still, the irreversible adsorption of organic molecules on the working electrode surface can lead to a progressive response blocking[209] that can only be reactivated by the scanning to elevated potentials, surface irradiation, or even by mechanical/thermal treatments, something much more expensive and lengthier than the aqueous sample pretreatment itself.

Considering the context of the coffee analysis, the solid sample pretreatment must be accomplished as for any other analytical technique that demands dissolved homogeneous samples, *i.e.*, the coffee surface washing, the coffee dry ashing followed by the acidic dissolution, or the coffee oxidative wet digestion, as previously discussed. Unfortunately, usual pressurized wet digestion methodologies used for the trace metal analysis by AAS leave some dissolved organic breakdown byproducts in the digested sample.[174,175] That is not a problem for spectroscopic methodologies with a matrix destruction stage, but it is for voltammetric approaches that need a further treatment to oxidize these residual organic byproducts, if not until complete mineralization, to a minimal extent which they stop poisoning the electrode surface or interacting with the dissolved ionic metals.[174]

Besides, highly acid concentrations lead to several drawbacks for the voltammetric determination of trace metals, such as the sample contamination (solved by the use of expensive ultrapure reagents) and the high residual background currents. They compromise the method detectability demanding the post digestion dilution, reducing analytes trace to ultratrace concentrations and making the quantification impossible. The closed vessel microwave-assisted digestion (MAD)[210] with inner temperature and pressure control during the digestion can help solving the problem, allowing the use of diluted HNO_3 acid (with or without associations). However, for some authors the used of MAD seems to be excessive and milder sample pretreatments have been reported over the years.

The UV photolysis[211] is a classic solution that uses the UV emission lines from a medium-pressure mercury lamp to irradiate samples with high DOM content or with low DOM content in the presence of a photosensitizer.[212] Chromophore sensitizing groups in organic species or photosensitizers absorb the incident UV radiation, promoting the formation of reactive oxidative species that reacts with DOM, releasing the ionic metals. The classic Fenton[213] or Photo-Fenton[214] reactions can be used to oxidize DOM,[215] as the Fe(II)/Fe(III) and H_2O_2 reactants (under UV irradiation or not) lead to the hydroxyl radical formation, a highly oxidative and reactive radical regarded to the so-called advanced oxidation processes (AOPs).

And regarding to AOP, the UV TiO_2 photocatalytic oxidation process have been used to oxidize DOM for the voltammetric determination of metals, even in the suspended form in a flow-injection system,[209] or immobilized over the surface of electrodes[190,216] in photoelectrocatalytic approaches.[217] TiO_2 is a photocatalyst that forms photoholes and electrons under UV irradiation. Those charge carriers can be transferred to dissolved species in an interface electrolyte, forming oxidative reactive species (as the hydroxyl radical) that can oxidize dissolved organic compounds and release the coordinated ionic metals in solution.[217] The UV/TiO_2 photocatalytic sample pretreatment is very appealing for the voltammetric determination of metals, since it spares the consumption of acids and opens the perspective to work with safer UVA wavelengths (~ 370 nm), emitted from low-power sources (as UV-LEDs) in small portable photoelectrochemical flow cell devices to treat very small volumes of sample (from nano- to microliters).

Voltammetric applications

Although not a nowadays study, when it comes to the determination of heavy metals in environmental samples by DPASV (as coffee itself), the work in memory of Prof. H. W. Nurnberg is an interesting stop. In 1987, his group reported: *"A reliable procedure for the determination of the trace metals Cd, Cu, Ni, Pb and Zn in liquid and solid environmental samples by an advanced voltammetric method"*,[173] namely the differential pulse anodic stripping voltammetry (DPASV). They performed a sample pretreatment by the wet digestion with $HNO_3/HClO_4$ mixture, and the determination of Cd(II), Cu(II), Pb(II) and Zn(II) was accomplished at pH 2 by DPASV, while the determination of Ni(II) and Co(II) was performed at pH 9 after their adsorptive accumulation at the electrode with dimethylglyoxime, under the so-called adsorption differential pulse voltammetry (ADPV). By the time, authors pointed out as the main advantages of the methodology the high sensitivity, good precision and accuracy, the determination of groups of metals (in contrast to the electrothermal atomic absorption spectroscopy – ETAAS, which only a single metal per run was determined), and the low cost of the instrumentation in general. For the elemental concentration profile in coffee, authors[173] found Cd(II) and Pb(II) at ppb magnitude order, even lower than the concentrations in some drinking water samples. Instant coffee presented Cu(II) concentrations 50 times lower than in coffee grain, while an enrichment was observed for Ni(II) and Co(II). Still, they concluded that coffee grain concentrations fail to provide valid information about the intake of these metals by drinking the infused beverage, since all the metals concentrations found were below the tolerable limits for the metals in drinking water for the time. Metal components should be soluble in hot water to allow the direct correlation between grains and the drinking beverage concentrations.

Pohl *et al.*[50] reviewed important topics about the determination of elemental composition of coffee by instrumental methods. They reported that the elemental content in coffee is about 5% pp., and is an interesting indicator of its authenticity, according to the metal's concentration patterns regarding to its origin at the growing soils, in addition to cultivation and environmental conditions. Besides, the instrumental measurements can prove the quality and safety of raw beans, characterize byproducts and the final product. They reviewed the use of atomic absorption and emission spectrometry techniques, and the instrumental neutron activation analysis to determine the concentration in green, roasted, ground, and instant samples of coffee. Some sample preparation and pretreatment is addressed as well, covering the digestion processes. The DPASV is rapidly mentioned as a tool for the determination of trace Pb(II), Cd(II) and Cu(II), in recognition of the lack of sensitivity of flame atomic absorption spectroscopy (F AAS).

Magnier *et al.*[218] reported a competitive ligand exchange–adsorptive stripping voltammetry (CLE–AdSV) for the speciation of Al(III) in several consumed beverages (coffee among them), discussing the Al bioavailability. Determinations involved the adsorption of Al-complexes with the ligand cupferron onto a HMDE at pH 6.5, during accumulation step at –0.60 V *vs.* Ag/AgCl for 60 s, and final cupferron concentration of 0.4 mM. These conditions were used to determine the concentration of electro-labile Al, the range of ligand concentration, and the conditional stability constants of complexes by titration procedures, with overall relative uncertainties lower than 15%. Hevia *et al.*[219] presented an adsorptive stripping voltammetric method for the determination of trace-levels of Cu(II) in food samples (including coffee), based on the metal complexation with α-lipoic acid (LA), and subsequent adsorptive accumulation on HDME. Experimental conditions included an accumulation potential of -0.3 V *vs.* Ag/AgCl during 30 s, at pH 3.6 and 0.6-1.2 μmol L^{-1} concentrations of LA, with resulting Cu-LA complex signal at -0.55 V. The linear range of operation was determined between 0.33–65.0 μg L^{-1}, with LOD of 0.1 μg L^{-1}, and RSD of 2.1% for 12 replicates measured for 5.0 μg L^{-1} Cu(II) solution. The method was still validated using certified reference wastewater (SPS–WW1), and water samples spiked with 18 foreign metal ions.

Palisoc *et al.*[220] fabricated graphene paste electrodes modified with gold nanoparticles, used to determine trace concentrations of Cd(II) and Pb(II) by ASV. Calibration curves showed linear relation between metals concentration and peak current, showing LODs of 256 ppb and 267 ppb for Pb(II) and Cd(II), respectively. Traces of them were determined in coffee samples, which were confirmed by AAS analysis. Filik and Avan[221] developed a microextraction methodology with magnetic dextran for the speciation study of chromium ions. Cr(VI) ions were retained on the magnetic dextran sorbents, eluted and then detected by LSV at screen-printed carbon electrodes modified with gold nanoparticles. Linear operation range, LOD, LOQ were determine as 0.5-10 μmol L^{-1}, 0.01 μmol L^{-1}, and 0.1 μmol L^{-1}, respectively. Cr(III) concentration was determined after their oxidation to Cr(VI) by H_2O_2 in ammoniac alkaline medium. Food samples (tea, coffee and mineral water) were used as real samples, and determinations were carried out by calibration with the standard addition method. Recovery tests showed the method applicability to real food samples, yielding values between 92 and 102%. Authors still claim that the method may also be extended to the determination of trace Cr species in biological, pharmaceutical and environmental samples.

There are many other interesting applications of voltammetric methodologies involving the coffee that are worthwhile mentioning, regarding not exactly the determination of metals on its compounding. As an example, Estrada-Aldrete *et al.*[222] quantified Pb (II) and Cd (II) trace levels by DPASV, using carbon paste electrodes modified with 50% of spent coffee grounds (SCG) in aqueous solution samples. Experimental design was used to optimize the intensity of oxidation current according to the accumulation time and the reduction potential factors, finding best conditions at 76 s and -1.2V *vs.* Ag/AgCl, respectively, for Cd (II); and 120 s and -1.2V *vs.* Ag/AgCl for Pb (II). LOD found was less than 0.3 mM, which made authors claim their electrode as a viable and sustainable alternative. Zribi *et al.*[223] used an amperometric sensor based on boron-doped diamond (BDD) modified with transition metal nanocatalysts by physical vapor deposition sputtering (Pt, Ir, Au, and Ru) for coffee discrimination in real samples. A broadly selective electrode array was assembled from the bare BDD with its metal-modified variations to detect electroactive species in coffee samples, so as chemometric tools could be adopted to determine relevant parameters to classify four different coffee capsule samples, according to the artificial prediction of taste.

Finally, CV technique has been currently used to determine antioxidant properties of infused beverages, such as green coffee samples.[224] Components of green coffee bean extracts and their properties were determined by a myriad of analytical techniques: gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis) spectroscopy; and the voltammetric role was to determine the mixture antioxidant properties, capable of reducing transition metal ions (as iron and copper) by polyphenolic compounds, that are oxidized in a potential range according to CV thresholds implemented. Authors claim that the performed electroanalytical measurements proved to be rapid and appropriate for the evaluation, and they can still be expanded to other food sources with noted high antioxidant activity. Table V summarizes main applications and brief analytical details.

Table V. Voltammetric analysis for coffee environmental samples

Voltammetry	Samples	Analytes	Analytical procedure	Reference
CLE-AdSV	Beverages (water, tea, infusion, coffee, orange juice, tomato juice, beer and red wine)	Al (III) speciation	Adsorption of Al-complexes with the ligand cupferron onto a HMDE at pH 6.5, with accumulation step at -0.60 V vs. Ag/AgCl for 60 s and final cupferron concentration of 0.40 mM.	218
AdSV	Food Samples (sweeteners, sugar, tea, coffee, and mate infusions)	Cu (II) trace levels	Adsorptive accumulation of α–lipoic acid (LA) metal complex on HDME at -0.30 V vs. Ag/AgCl during 30 s at pH 3.6 and 0.6-1.2 μM LA, with Cu-LA complex signal at -0.55 V vs. Ag/AgCl.	219
ASV	Coffee	Cd (II) and Pb (II)	Gold nanoparticles (AuNP) modified graphene paste electrodes (GPE) used as working electrode in anodic stripping voltammetry (ASV) for the determination of cadmium (Cd^{2+}) and lead (Pb^{2+}).	220
Me-LSV	Food samples (tea, coffee and mineral water)	Cr speciation	Retention of Cr (VI) ions on magnetic dextran sorbents followed by elution and LSV detection at screen-printed carbon electrodes modified with gold nanoparticles. Cr (III) determined by H_2O_2 oxidation to Cr (VI) in ammoniac alkaline medium.	221

CONCLUSIONS AND PERSPECTIVES

Unlike other food markets, consumers are usually aware of high quality varieties of coffee, demanding special tastes and good aroma from beans with a known origin. It is not an option to avoid determining the provenience of coffee in the coffee trade. So, to assure the quality stated in labels and protect the health of consumers, different parameters are drawn using analytical methods to prove the wholesomeness of green and roasted beans, prepared coffee, and infusions. The organoleptic analysis of coffee beans relies on the evaluation of their odor and taste, besides some additional information about their size, shape, color, and cross-section. To assess the quality of infusions, the flavor of prepared beverages is described accordingly to standardize conditions of individual notes that, unfortunately, are stained by the subjective character of evaluations, even when they are carried out by specialized coffee testers. Thus, chemical methods based on the determination of different compounds are very important for the coffee analysis aiming the discrimination of coffee varieties, brands or origin. It should be noted that during the production stages, the composition of coffee changes and among all the compounds, only caffeine is stable enough to stand the high roasting temperatures. In this context, elements and their concentration are stable during all the production stages and subsequent storage, and for that reason the elemental composition is so relevant for the coffee quality control and bromatological evaluation.

Concerning the quality control, for a long time no standard reference material (CRM) was available for coffee. The reliability of results had to be tested using CRMs of other plants and food samples. Ultimately, results could be verified by the analysis of a special quality control standard traceable to NIST. Satisfactory accuracy results were achieved in a 73 –103% compliance of measured values with certified values for different elements. Some attempts in the past to produce CRMs for organic green coffee[58] led to the conclusion that coffee matrix can only be homogeneous for Ca, Co, Cs, K, and Sc. However, Lee *et al.*[225] recently developed a novel coffee bean matrix-certified reference material (KRISS CRM 108-10-023) for elemental analysis of eight elements: Mg, Ca, Fe, Cu, Zn, Cd, Hg, and Pb. This CRM was prepared by freeze-drying the raw coffee beans and grounding them until a homogeneous powder was obtained. Once purified with irradiation, the elements mass fractions were measured using the double isotope dilution inductively coupled plasma mass spectrometry (double ID-ICP-MS), achieving excellent stability and homogeneity. Most certainly, this new CRM will contribute for the enhancement of quality control of coffee and coffee products by improving the measurement reliability, and drive new research in the development of standardized methods worldwide.

Regarding to the traceability of coffee origin, the statistical analysis of data from elemental composition of samples plays a major role in the assessment of the coffee genuineness. By treating coffee samples as objects and elemental concentrations as variables, it is possible to draw individual patterns within the objects and classify them according to the geographical origin, the variety or the type of coffee using different chemometric tools. For instance, the principal component analysis (PCA),[30,68] the hierarchical cluster analysis (HCA),[30,68] the factor analysis (FA),[31] the canonical discriminant analysis (CDA),[42] and the linear discriminant analysis (LDA)[226] have been used for the reduction and exploratory visualization of data for dry coffee and infusions for a given origin, variety, and type of cultivation. PCA and HCA are particularly helpful to determine the performance of the discrimination of analyzed samples according to the selected variables,[44] while discriminant function analysis (DFA) and the Neural networks (NN)[42] are useful to classify unknown samples into predetermined classes. Data mining and knowledge discovery databases (KDD)[56] may lead the way to the discrimination between organically and conventionally cultivated coffees using the content of Br, Ca, Cs, Co, Mn, and Rb as chemical markers. Analysis of Variance (ANOVA)[34] is usually applied to confirm the statistical difference between mean concentrations of elements among different coffee samples. And, finally, the partial least squares regression (PLS)[54] has been used to analyze the composition of arabica and robusta blends in terms of the elemental content.

It is important to mention that elements alone do not offer reasonable discrimination capacity for coffee samples.[45] Better results can be obtained by combining the concentration of several elements and, the higher the number of variables, the better.[42] The elements K, Mg, and Zn have been established as the best descriptors for the differentiation of the type of coffee, between roasted or instant soluble.[44] Meanwhile, Al, Na, and Zn have been successfully used to distinguish coffees from organic to conventional production modes.[44] Unfortunately, the direct correlation between the elemental composition of coffee samples and the geographical origin is somehow challenging, considering that many marketed coffees are blends from cultivations of different global regions. Additionally, when classifying coffee samples, one should bear in mind that several factors affect the elemental composition of coffee beans and the quality of roasted and ground coffees.[25,30,31,33] The coffee planting requires the use of fertilizers as a source of macro- and micronutrients, inorganic fertilizers and organic residues that may contaminate the crop soil with trace elements, achieving coffee beans and the final product.[33,57] The use of pesticides and agrochemicals can contaminate the roasted coffee beans and infusions too.[57] The simple contact of coffee beans with the soil during the harvest, the processing, and the classification stages are enough for the contamination, finally achieving the infusion. Environmental parameters,[36,48] production processes and batch sample workup, and even the packing of the coffee product can lead to higher concentrations of certain elements. Researchers should be aware of the contamination sources compromising their coffee samples and choose wisely the most appropriate combination of elements for each kind of classification with the most suitable chemometric tool.

Concerning the sample pretreatment, there is a considerable variation between the initial stages of sample washing for the removal of surface contaminants and sample pulverization. The difference of steps varying from authors should be deeper studied to investigate their influence over the overall elemental analysis. Despite of the choice between dry ashing and wet oxidative digestion, small portions of coffee samples should undergo the acidic digestion, and that step is usually better carried out by the closed vessel microwave-assisted acidic digestion (MAD) than by open vessel thermal treatments. MAD saves time, avoids contamination, and allows the digestion using diluted acids in the smallest volume as possible, prioritizing the analyst safety and the lower consumption of reagents. Since the sample preparation is often the slowest and most laborious step in the analytical sequence, exploring other forms of sample preparation using, for example, ultrasound-assisted extraction (UAE) may be an interesting alternative in the future to MAD.

As described, the elemental analysis of coffee by F AAS require the digestion and mineralization of the organic matrix prior to the determination, which is usually carried out by simple standard solutions, with some exceptions for the K and Na measurements that requires the use of CsCl in standards and samples as a chemical suppressor,[31,34] or the quantification of Ca and Mg that demands the addition of $LaCl_3$ to standard and sample solutions to avoid chemical interferences.[31] As observed for F AAS, coffee samples are usually digested for the analysis by ET AAS,[34] despite of some determinations by the direct analysis of solid samples[36] or slurries.[37] The latter, once compared to the digested sample analysis, offer higher sensitivities for trace elements considering the absence of dilutions, besides the low risk of contamination or loss of elements usually acomiting samples during the preparation step. The external calibration curves with aqueous standard solutions usually are used for determinations with ET AAS[34] and, for solid direct analysis or slurries, calibrations are carried out with aqueous solutions or solid CRMs[36] applying chemical modifiers to stabilize elements, and modify the matrix of coffee samples at high pyrolysis temperatures.[31,34]

ICP OES might be considered the “gold-standard” for the elemental analysis of coffee, allowing the simultaneous sensitive determination of tens of elements at the same run, with lower detection limits, higher sensitivities, wider linear ranges and faster measurements than F AAS and ET AAS.[50] Samples should be digested for the ICP OES determinations, which might be accomplished by calibration with simple standard solutions due to the virtual absence of spectral chemical and ionization interferences. For the sampling of slurries, the standard addition method[49] has been successfully used for the calibration and to control possible matrix effects. Further signal fluctuations can be addressed by adding an internal standard[50] to sample and standard solutions. The major drawbacks for the ICP OES include the spectral complexity and high emission backgrounds, something that is much better for the ICP-MS that shows even higher sensitivities and additional selectivity due to the high mass resolution with very alike sample pretreatment procedures. In the past, the ICP-MS use was limited by its cost, maintenance and complex operation, besides the severe drawbacks with spectroscopic (*m/z* ratio coincidence), and non-spectroscopic interferences (matrix effect, also a concern in ICP OES). With the development of electronics and instrumentation, ICP-MS instruments are becoming more accessible, with automatic corrections of spectroscopic isobaric interferences using inner libraries of isotopic abundance. For the non-spectroscopic interference, matrix effects are being reduced simply using more diluted solutions, changing the procedure for the sample introduction, separating the interfering species, or even adopting internal standards.

Voltammetry is the main classical technique in the literature for the determination of total metal concentrations. It is simple, cheap, fast, sensitive, portable, robust to analyze turbid samples, and highly versatile to hyphenate with separation techniques as the chromatography. However, voltammetric techniques are susceptible to interferences of organo-mineral complexes, they are not totally compatible with acidic wet digestions, can determine only a few metals by each analytical run, and suffer from electrode surface poisoning. X-ray fluorescence (XRF) is a non-destructive technique for the analysis of solid samples. It is the best choice to field determinations with multielemental capability, low costs, simple and fast sample preparation, reasonable sensitivity, and high precision. Portable XRF (pXRF) field analyzers suffer from interferences by ambient humidity, high organic content, and sample granulometry, demanding the standardization of coffee samples to avoid major problems. LIBS is a relatively-recent technique that can quickly perform multi-elemental analysis on complex matrices with few or none sample pretreatment steps even for solid samples. That includes field or remote analysis by portable equipments. Nevertheless, LIBS spectra are complex with lots of signal-noise issues that, altogether with sample homogeneity and sample analyte distribution, lead to poor precisions. The lack of reference material that allows obtaining calibration curves is perhaps one of the greatest difficulties encountered to widen the use of LIBS in quantitative analysis. Therefore, the development of new calibration strategies and even calibration standards are challenges that must be overcome to expand the use of LIBS for the elemental analysis of coffee.

Conflicts of interest

The authors declare no conflicts of any possible nature.

Acknowledgements

The authors thank the support of FAPEMIG [BPD-01048-22 - Finance code 001], CAPES [Finance code 001], EMBRAPA-CAFÉ [Notice 20/2018 and code 145].

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