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Analytical Methods for Determining Metals Concentrations in Coffee (*Coffea arabica L.*) in Ethiopia: A Review

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Abstract: Coffee is a widely consumed beverage and is the second most traded commodity globally after petroleum. The aim of this paper is to provide a comprehensive review of the analytical and instrumental methods employed in Ethiopia to determine the concentrations of essential and toxic heavy metals in coffee. Several studies have been conducted to determine the concentrations of these metals in Ethiopian coffee, using various spectroscopic techniques, namely flame atomic absorption spectrometry (FAAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), direct mercury analyzer (DMA), particle-induced X-ray emission (PIXE), energy dispersive X-ray fluorescence, inductively coupled plasma (ICP), X-ray fluorescence spectroscopy (XRF), and elemental analyzer-isotope ratio mass spectroscopy. The results of these studies indicate that the concentrations of essential metals such as K, Mg, Fe, Zn, Cu, and Mn were within the permissible limits established by international organizations. Conversely, the concentration of nonessential metals, namely Pb, Cd, and Cr, was either below the detection limits or within the maximum permissible limits set by international organizations. Specifically, the concentration of essential and toxic metals present in coffee beans was found to be within the permissible limits established by international organizations, which is crucial for the nutritional value of coffee as well as the safety of consumers. These findings suggest that Ethiopian coffee is generally safe for human consumption in terms of metal content. Furthermore, significant differences were detected in the elemental composition of coffee samples obtained from different regions of Ethiopia. The elemental composition of coffee samples varies among different regions of Ethiopia. indicate that the geographical origin of coffee may be distinguished based on its elemental profile. This information can be useful for the authentication of the coffee origin, which is a critical aspect of maintaining the quality and authenticity of Ethiopian coffee.

Keywords: Coffee, Essential, Ethiopia, Heavy Metals, Non-Essential, Quality, Safety, Toxic

1. Introduction

The coffee bean is a highly significant commodity in the global market, with an annual consumption of approximately 9,997,680 tons and 400 billion cups [1]. It is the second most traded economic product after petroleum, with a production of 10,200 kg and a value of 35 billion dollars annually [1, 2]. Despite the presence of over a hundred coffee varieties, only two types, namely Arabica coffee (Coffea arabica L.) and Robusta coffee (Coffea canephora), are of significant commercial value and are traded globally [3, 4]. Arabica coffee, which accounts for 75% of the world's coffee production, is renowned for its superior aroma and flavor. In contrast, Robusta coffee, which represents about 25% of the world's coffee trading, is more resilient to unfavorable weather conditions and diseases [5, 6].

The origin of Coffee Arabica is Ethiopia, where it grows in large quantities on highland plateaus ranging from 1300m to 1900m [7]. The plant is evergreen, reaching up to 10m tall, with the size and shape of its beans being dependent on various factors such as the environment, crop practices, and variety [7]. Coffee is an essential crop in Ethiopia, contributing the highest export revenue and becoming a brand item within the country [8, 9]. Its sensory attributes, such as aroma and flavor, coupled with its energizing and health-boosting properties, make it an attractive commodity [1-3]. Robusta coffee contains more caffeine, elements, and antioxidants than Arabica coffee, and they differ in their chemical composition and growth conditions [9].

Regular consumption of coffee in the recommended range of 2 to 4 cups per day has been found to be effective in averting the onset of a variety of cancers such as breast, prostate, colorectal, endometrial, liver, and esophageal cancer [9]. Moreover, the beneficial effects of coffee extend to the prevention of obesity, depression in women, insulin sensitivity, diabetes mellitus (type II), hyperglycemia, Alzheimer's disease, Parkinson's disease, brain tumors, and heart diseases, mainly due to the presence of antioxidants [10, 11]. It is, however, postulated that heightened coffee intake (in excess of 5 cups per day) may culminate in several health hazards, such as bone loss and fractures, in addition to anxiety, headache, restlessness, nausea, hypertension, tremulousness, irritability, lethargy, palpitations, insomnia, and the toxic effects of caffeine, plausibly owed to the high caffeine intake [10].

With over 1000 agents having different biological activities, including macronutrients, micronutrients like vitamins, phenolic compounds, and elements such as Iron (Fe), Zn (zinc), Sodium (Na), Bohr (B), Magnesium (Mg), Calcium (Ca), and Potassium (K) [1, 6, 12], coffee is a highly complex product. Metals, a group of heavy metals found in various foods, including coffee beans, are present in minor or trace levels [13]. These metals are classified as either essential or non-essential (toxic) groups [11, 14, 15]. Essential and non-essential (toxic) elements, such as Fe, Cu, Mn, Co, and Zn, play a critical role in the natural functioning of living organisms. However, their elevated concentrations can lead to toxicity in the human body [6, 16-18]. Conversely, toxic heavy metals, such as Pb, Cd, As, and Hg, are not essential for the regular activity of living organisms and are considered toxic elements even at trace levels [1, 4, 17, 19]. These metals pose several health risks, including mutagenic, carcinogenicity, carcinogenicity, and embryo toxic effects [14].

Many reports exist in the literature on the levels of selected essential and non-essential metals in raw and roasted coffee beans from various parts of the world, including Ethiopia. These studies encompass the determination of essential and toxic metals in both raw and roasted coffee in Bule Hora Woreda, Borena Zone, Ethiopia [20]. Grembecka [21] conducted a study aimed at distinguishing market coffee and its infusions based on their mineral composition. According to Gebretsadik [22] analyzed the levels of essential and nonessential metals in roasted coffee beans from Yirgacheffe and Sidama, Ethiopia. Similarly, Berego [23] determined the contents of essential and toxic metals present in coffee beans and soil in Dale Woreda, Sidama Regional State, and Southern Ethiopia. In another study, Nikus [24] analyzed essential and nonessential metal levels in roasted Hararghe coffee bean varieties. Animut [25] conducted a study aimed at determining the levels of selected essential metals in the coffee of the eastern Amhara region using ICP-OES. Ashu and Chandravanshi [26] measured the concentration levels of metals in commercially available roasted Ethiopian coffee powders and infusions. Similarly, Gure [9] assessed metal levels in roasted indigenous Ethiopian coffee varieties. Feleke [27] estimated the elemental concentrations of Ethiopia Coffee Arabica in different coffee bean varieties using energy dispersive X-ray fluorescence. Moreover, Habte [28] conducted an elemental profiling of Ethiopian coffee samples using ICP-OES, ICP-MS, and direct mercury analyzer (DMA). Finally, Worku [29] utilized XRF and ICP-based multi-element and stable isotope profiling to differentiate the geographical origin of Ethiopian coffee.

Coffee plants absorb these elements from their surrounding environment (i.e., soil, water, and air) during their growth stages [10]. The elemental profile of coffee is influenced by many factors, including plant species, soil chemistry, climate, geographic location, agricultural practices, environmental pollution, and water attributes used in cultivation and processing methods [6, 10, 29-31].

The concentration of various elements in the green and roasted Coffee bean can be determined using different analytical techniques such as flame atomic absorption spectrometry (FAAS) [32], high-resolution continuum source (HR-CS FAAS), and solid sampling electrothermal (SS-ET AAS) [33, 34], particle-induced X-ray emission (PIXE) [6] neutron activation analysis (INAA), inductively coupled plasma- optical emission spectrometry (ICP-OES) [1, 35-37] and inductively coupled plasma mass spectrometry (ICP-MS) [3, 6, 36-40], using energy dispersive X-ray fluorescence [27], ICP-OES, ICP-MS, and direct mercury analyzer (DMA) [28]. Finally, Worku [29] utilized multi-element and stable isotope analysis based on XRF and ICP. However, it is worth noting that these methods have their advantages, as well as disadvantages.

In Ethiopia, the effects of various environmental and genetic factors on the metal content of coffee have not been well studied. A broader and more diverse analysis of coffee samples from different regions and coffee types would be beneficial. Alternative analytical techniques could provide more detailed information on metal content. Geographic variations in metal levels and the long-term effects of coffee consumption have not been well studied in Ethiopia. Future studies could investigate harmful substances and the relationship between elemental composition and sensory characteristics. Finally, future research could examine the bio-availability and toxicity of metals in coffee and the impact of various methods. Monitoring the concentration of essential and toxic heavy metals in coffee is crucial due to their importance in human health and the popularity of coffee consumption in many countries, including Ethiopia. This paper provides a comprehensive review of the methods used in Ethiopia to determine the levels of these metals in coffee.

2. Overview of the Concentrations of Essential and Toxic Metals in Coffee

The investigation conducted by Gebretsadik [22] demonstrated that the levels of essential metals such as sodium, calcium, potassium, magnesium, manganese, copper, and zinc were within the recommended thresholds established by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO). In the same study, Gebretsadik [22] observed that the concentrations of iron, zinc, copper, and manganese in the roasted coffee beans were 79.76, 16.48, 7.93, and 8.41 mg/kg, respectively, with mean values.

Animut's [25] findings indicated the concentration ranges of various metals including potassium, calcium, magnesium, iron, zinc, manganese, and chromium to be in the range of 1963-9133, 551-951, 879-1944, 29-79, 11-56, 4.2-6.3, and 1.5-2.7 mg/kg, respectively. The study found significant variations in the mean concentrations of all the metals across the three zones [25]. Ashu and Chandravanshi [26] identified iron as the most abundant trace microelement in coffee powders followed by manganese and zinc. Furthermore, the trend of macro-elements in the infusion was analogous to that of the powder, whereas zinc was the most abundant microelement followed by manganese and iron. The level of cobalt was the lowest in all coffee samples [26]. Getachew and Worku's [20] provides insights into the levels of essential and toxic metals present in raw and roasted coffee samples from Bule Hora Woreda, Borena Zone, Ethiopia. The study stresses the importance of determining mineral nutrients and toxic elements in coffee and offers data on the concentration of six essential metals (calcium, potassium, magnesium, copper, zinc, and manganese) and three toxic metals (chromium, lead, and cadmium) in the coffee samples. The examination carried out by Feleke [27] evinced the existence of four predominant constituents (P, K, Ca, S) and eight minor constituents (Mn, Fe, Cu, Zn, Se, Sr, Rb, Br) in twenty distinct coffee Arabica collected from diverse regions of Ethiopia. The concentration of said constituents varied amongst various subspecies and locations. Habte [28] presented a comprehensive dossier on the ascertainment of mineral content and geographical differentiation of coffee specimens from eleven major regions in Ethiopia.

Another study conducted by Berego [23] investigated the concentration of various metals (K, Na, Ca, Mn, Cu, Zn, Ni) in coffee beans from farmers' farms in Kege, Wenenata, Gane, Wondo, Bera, and Magara, coffee beans from Kege farmers' farms exhibited the highest concentration of micro-elements, with Manganese being the most prominent, followed by Cu, Zn, and Ni. According to Gebretsadik [22], Mn has a higher level when compared to other micro-elements (Mn, Zn, and Cu). As for macro-elements (Mg, Na, and Ca), K has the highest concentration. Notably, roasted coffee powders contained higher amounts of metals than infusions, and they were richer in K to the greatest extent, followed by Mg and Ca, with Na occurring at the lowest level relative to the other essential macro-elements [26]. The study conducted by Berego [23] revealed that the levels of macro- and trace elements in coffee beans from farmlands and washed plants were within permitted levels. Out of all sampling farm land sites, K (Potassium) exhibited the highest concentration among macro-elements in coffee beans, followed by Na and Ca [23]. Conversely, Na was found to have the lowest concentration of the macro-elements analyzed [22]. Gure [9] reported that the essential metals, such as iron, copper, zinc, and manganese, were found to be within the acceptable limits set by the WHO and the FAO.

The investigation conducted by Nikus [24] evinced that the concentrations of various metals including K, Mg, Ca, Zn, Cd, Mn, and Pb in all roasted coffee bean varieties were within the recommended maximum permissible limits. This infers that the consumption of coffee made from Hararghe coffee bean does not pose any health risk with regard to the metals scrutinized in the current study. In a separate investigation by Animut [25], all seven types of metals, namely K, Ca, Mg, Fe, Zn, Cr, and Mn, were discerned in green coffee beans from the three zones of Amhara region, and the mean concentration of each metal differed across the three zones. Habte [28] investigated a total of 45 essential and toxic heavy metals in from different regions of Ethiopian coffee. The authors further analysis divulge that Gojjam coffee samples exhibited the highest concentration levels of arsenic, holmium, lanthanum, thallium, uranium, and yttrium, whereas Jimma samples had high levels of zirconium, cerium, stannum, niobium, iridium, and indium. In contrast, Bale originated samples manifested significantly higher contents of selenium, molybdenum, neodymium, germanium, and silver [28]. Similarly, Worku [29] analyzed the presence of essential and toxic heavy metals in coffee samples from six different in Ethiopia.

Gebretsadik [22] found that the levels of essential metals in all roasted coffee samples were in the order of K > Mg > Ca > Na > Mn > Zn > Cu, while the order of metal levels in coffee bean samples from farmland was K>Na>Ca>Mn>Cu>Ni>Zn and in coffee beans from washed plants was K>Na>Ca>Mn>Cu>Zn>Ni [23]. Correspondingly, the levels of metals in all roasted coffee bean varieties were in the order of K > Mg > Ca > Zn > Cd [24]. Feleke [27] reported that the order of elements concentration from highest to lowest was K > Ca > P > S > Fe > Rb > Mn > Cu > Sr > Zn > Br > Se and posited that the variation in elemental concentration of coffee subspecies could be ascribed to their capacity to absorb minerals from the soil through their roots and transport them to the coffee bean [27].

Nevertheless, there were certain apprehensions regarding the concentrations of Cd, Pb, and Cr in roasted coffee beans, as the mean concentrations of Cd, Pb, and Cr were found to be 0.04, 0.03, and 0.07 mg/kg, correspondingly [22]. In point of fact, some samples of coffee beans from Yirgacheffe exhibited concentrations of Cr that exceeded the maximum allowable limit [22]. Conversely, the metals Mn and Pb were below the method detection limit [24], and according to Getachew & Worku [20], there is no health risk associated with heavy metals during the consumption of coffee beans from Bule Hora woreda.

The toxic metal Cd was not detected in Harar A and B coffee varieties, but a certain concentration of toxic metal Cd was detected in Harar C coffee varieties [24]. The non-essential toxic metals Pb and Cd were not detected in the coffee samples revealing that the commercially available Ethiopian coffee powder contains either very low amounts (< 0.01 µg Cd and < 0.04 µg Pb per gram coffee powder) or may be free from these metals [26]. The concentration of toxic metals in both raw and roasted coffee samples was found to be below the maximum permissible limits set by the World Health Organization (WHO) and the European Union (EU) [20].

The presence of certain metals in coffee bean samples has been a topic of study in recent years. According to Berego [23], the metals Pb, Co, Cr and Cd were not detected in the samples. Similarly, Gebretsadik [22] found that the levels of toxic metals Cd and Pb were below the limit of detection in all samples analyzed, indicating that coffee is generally safe to consume in terms of these metals. However, the cadmium levels in soil samples were found to be higher than the permissible limit for agricultural soil recommended by the WHO and FAO, as reported by Berego [23]. On the other hand, all other metals analyzed were below the permissible limit set by the FAO/WHO (FAO/WHO, 2001) as reported by Gebretsadik [22] and Berego [23]. Additionally, Gure [9] found that the concentrations of cadmium, lead, chromium, and nickel were below the maximum allowable limits set by the WHO and the FAO.

Regarding essential and non-essential metals, the concentration of essential metals in raw coffee samples was found to be higher than in roasted coffee samples, as reported by Getachew and Worku [20]. They found that calcium, iron, zinc, copper, and manganese were the most abundant essential metals, while chromium, nickel, lead, cadmium, and mercury were present at lower concentrations, which suggests that the risk of exposure to these metals through coffee consumption is low [20]. Meanwhile, Nikus [24] found that the toxic metal Cd was not detected in Harar A and B coffee varieties, but a concentration was found in Harar C coffee variety. Ashu and Chandravanshi [26] reported that the non-essential toxic metals Pb and Cd were not detected in the coffee samples, revealing that the commercially available Ethiopian coffee powder contains either very low amounts or may be free from these metals. Furthermore, Getachew and Worku [20] found that the concentration of toxic metals in both raw and roasted coffee samples was below the maximum permissible limits set by the World Health Organization (WHO) and the European Union (EU).

2.1. Analyses of Metals Concentrations in Coffee Using Various Analytical Techniques

Berego [23] investigated the metal concentrations in coffee beans, farmed soil samples, and washed and unwashed coffee. This proposal became a reality through the use of flame atomic absorption spectrometry (FAAS). Niku [24] also used a Flame Atomic Absorption Spectrophotometer to assess the concentrations of K, Mg, Ca, Mn, Zn, Cd, and Pb in various Hararghe coffee bean varietals. Gure [9] did the same thing by using flame atomic absorption spectrometry to measure the levels of several metals (K, Mg, Ca, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, and Zn) in roasted coffee from various Ethiopian locations. Similar to Getachew and Worku [20], who used FAAS to measure the content of three harmful elements (Cr, Pb, and Cd) and six important metals (Ca, K, Mg, Cu, Zn, and Mn) in samples of raw and roasted coffee from Bule Hora woreda, Borena Zone, Ethiopia. Numerous studies have examined the concentrations of both essential and non-essential metals in Ethiopian coffee granules and their infusions [26]. Three commercially available roasted Ethiopian coffee powders (Abyssinia, Alem, and Pride) were sourced from local markets. Ashu and Chandravanshi [26] used flame atomic absorption spectrometry to measure the concentrations of nine essential metals (K, Mg, Ca, Na, Mn, Fe, Cu, Zn, Co) and two nonessential metals (Pb, Cd) in these powders.

Additionally, Animut [25] used inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine the metal concentrations in green coffee beans from the South Wollo, North Wollo, and North Shewa zones of the Amhara region. The Kjelda method was used to digest and extract seven different metal types (K, Ca, Mg, Fe, Zn, Cr, and Mn). Feleke [27] also used Energy Dispersive X-ray Florescence (EDXRF) elements analysis to look at the elements concentrations of coffee Arabica subspecies grown in various parts of Ethiopia. In a different study, Habte [28] used cutting-edge methods like ICP-OES, ICP-MS, and DMA to examine the contents of 45 elements in 129 samples of coffee. Worku [29] used multi-element profiling based on XRF and ICP to show the mean concentrations of important and harmful metals in coffee samples from six different locations of Ethiopia. Overall, Table 1 provides information about the essential and non-essential metals in Ethiopian coffee studies, including the methods used for analysis and their corresponding references for each metal.

Table 1. *Lists various elements and the methods used to analyze the them, along with their references.*

Element	Method	References
Al	ICP-OES, ICP-MS, DMA	[28]
Ba	ICP-OES, ICP-MS, DMA	[28]
Br	EDXRF	[27]
Ca	FAAS, ICP-OES, EDXRF, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[9, 20-29]
Cd	FAAS	[9, 20, 22-24, 26, 28]
Co	FAAS, ICP-OES, ICP-MS, DMA,	[9, 23, 28].
Cr	FAAS, ICP-OES, ICP-MS, DMA,	[9, 23, 28].
Cu	FAAS, ICP-OES, ICP-MS, DMA,	[9, 20, 22, 26-29]

Element	Method	References
Fe	FAAS, ICP-OES, EDXRF, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[9, 25-29]
K	FAAS, ICP-OES, EDXRF, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[9, 20-29]
Mg	FAAS, ICP-OES, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[9, 20, 22, 24-26, 28-29]
Mn	FAAS, ICP-OES, EDXRF, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[9, 20, 22, 23-29]
Na	FAAS, ICP-OES, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[22, 26, 28, 29]
Ni	FAAS	[9, 23, 28-29]
Pb	FAAS, ICP-OES, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[9, 20, 22-26, 28-29]
Rb	EDXRF	[27]
S	EDXRF, ICP-OES-ICP-MS- DMA	[26-27]
Se	EDXRF	[27]
Sr	EDXRF	[27-28]
Zn	FAAS, ICP-OES, EDXRF, ICP-OES-ICP-MS- DMA, XRF-ICP-MS	[9, 22, 29]

These methods include ICP-OES, ICP-MS, DMA, EDXRF, and FAAS, which are used to determine element concentrations in samples. The references provide more information on the studies where these methods were used.

2.2. Comparison Sample Digestion Techniques for Metals Analysis in Coffee

The study conducted by Gebretsadik [22] utilized a closed microwave-assisted wet digestion technique incorporating concentrated (69-70%) HNO_3 and 30% H_2O_2 reagents for the decomposition of ground roasted coffee samples. On the other hand, Berego [23] developed an optimized procedure for coffee sample preparation using HNO_3 and H_2O_2 reagents in a microwave system, and assessed its accuracy by analyzing the digest of the spiked samples. Gure [9] identified that the optimal digestion process involved 4 hours of refluxing at 270°C using a mixture of HNO_3 and $HClO_4$. Nikus [24] carried out the digestion process using an open vessel system with the use of 3 mL HNO_3 (70%), 1 mL $HClO_4$ (70%), 1 mL H_2SO_4 (98%), and 1 mL H_2O_2 (30%) reagents, with three samples of Hararghe coffee bean obtained from the Ethiopian commodity exchange. Meanwhile, Ashu and Chandravanshi [26] developed an optimized digestion procedure utilizing 5 mL of HNO_3 and 1 mL of $HClO_4$ with a total time of 4 hours at a temperature of around 350 ^{o}C for digestion of 0.5 g of powder sample, and 4 mL of HNO^3 and 1 mL of $HClO_4$ with a total time of 4 hours for 25 mL infusion that was evaporated to dryness.

2.3. Validating Methods for Analyzing Metals Concentrations in Coffee

The findings of Gebretsadik [22] revealed that the recoveries of metals in spiked roasted coffee samples ranged from 95%-104% with a relative standard deviation (RSD) of 3-6%. Similarly, Gure [9] reported that the recoveries of metals in spiked samples varied from 90% to 110%. Furthermore, Gure [9] found significant differences in the concentrations of certain metals with variations in the geographical origin of coffee beans. Nikus [24] optimized and validated the digestion procedure using spiking experiments, which showed a variation in the recoveries of spiked samples from 94% to 112% for roasted coffee samples. The validity of the optimized procedure was evaluated by Ashu & Chandravanshi [26] using spiked samples with analyze recoveries ranging from 97−103% for coffee powder and 95−102% for infusion samples.

According to the literature, Gebretsadik [22] and Nikus [24] found the closed microwave-assisted wet digestion method and determination of selected metals by flame atomic absorption spectroscopy to be efficient. Similarly, Ashu & Chandravanshi [26] reported that the wet digestion method and determination of selected metals at trace levels in coffee powders and their infusions by the flame atomic absorption method were accurate, precise, and efficient. Habte [28] demonstrated the validity of the analytical methods used through quality assurance parameters such as analysis of certified reference material, linearity, precision, spike recovery, and accuracy.

However, Worku [29] found XRF-based multi-elements with and without δ13C to be more effective than ICP-based multi-elements with and without stable isotopes in differentiating the geographical origin of coffee. Hence, XRF-based multi-element approach can be a preferred method of choice for determining the geographic origin of Ethiopian coffee as it is more rapid, easier, and cheaper than the ICP-based multi-element approach. The significant differences in the elemental composition of coffee samples from different regions in Ethiopia suggest that the approach used in this study could be useful for coffee authentication and traceability, as well as for establishing geographical indications for Ethiopian coffee.

2.4. Recommended Limits and Safety of Metals Concentrations in Ethiopian Coffee

The recommended limits for essential metals in food, including coffee beans, have been established by the WHO and the FAO, with differing limits for each metal. However, limits for potassium, magnesium, calcium, and sodium have not yet been established. Provisional tolerable weekly intake (PTWI) has been set by the WHO for manganese and copper, but PTWI for zinc has been established by the FAO/WHO Joint Expert Committee on Food Additives (JECFA). According to Gure [9] and Gebretsadik [22] discovered that roasted coffee beans from Yirgacheffe and Sidama contained Fe, Zn, Cu, and Mn concentrations within the recommended limits, while Cd, Pb, and Cr concentrations were below the maximum allowable limits. However, Cr concentrations in some samples of coffee beans from Yirgacheffe exceeded the maximum allowable limit. The concentration levels of essential and non-essential metals in roasted coffee beans were found to be comparable to levels discovered in other parts of the world [22]. Nikus [24] concluded that the metal concentrations found in all roasted coffee bean varieties were within the recommended maximum permissible limits, suggesting that there is no health risk associated with consuming coffee made from Hararghe coffee beans with regards to the metals analyzed in the study. Overall, studies indicate that the consumption of roasted indigenous coffee varieties of Ethiopia is safe from the perspective of metal toxicity [9, 24]. However, these are general recommendations that may vary depending on specific situations or populations, and there are no specific recommended limits for essential metals in coffee beans, but rather for overall dietary intake [9]. The essential macro- and micro-elements were discovered to be present in the coffee infusion prepared from the powder samples, which may also serve as a dietary mineral source depending on the amount consumed [26]. Habte [28] concluded that the elemental profiling of coffee samples collected from different regions of Ethiopia can be used to authenticate the coffee samples and classify them according to their geographical origin. Worku [29] discovered significant variations in the elemental composition of coffee samples from different regions in Ethiopia, with varying concentrations of essential and toxic metals. According to Habte [28], the elemental composition of coffee samples differed greatly depending on their origin. The results of the study have the potential to be useful for the coffee industry in ensuring the quality and authenticity of Ethiopian coffee in both local and export markets [28]. Overall, the study demonstrates the potential of XRF-based multi-element profiling as a relatively fast and low-cost tool to trace the geographical origin of Ethiopian coffee.

2.5. Monitoring Metals Concentrations in Ethiopian Coffee for Safety

The consumption of roasted coffee beans can provide essential dietary metals and introduce trace metals into the food chain, as demonstrated by Gebretsadik [22] and Nikus [24]. It is generally considered safe for adults to drink two cups of coffee, as the metal amounts obtained from two cups are well below the recommended daily values, with no risk of toxicity from cadmium (Cd) and lead (Pb), as noted by Gure [9].

The present study's data could be valuable in supplementing available food composition data and approximating dietary intakes of essential and nonessential metals in Ethiopia through coffee consumption. The concentration of essential and toxic metals in coffee is dependent on the coffee bean's origin, the type of coffee analyzed, and the utilized analytical method. Nevertheless, most studies suggest that the concentration of toxic metals in coffee is generally low and does not pose a significant health risk. While the study examined selected roasted coffee samples from specific Ethiopian regions, a more extensive and diverse sample from various regions and coffee types would prove beneficial. However, continuous monitoring of metal concentrations in coffee beans is crucial to ensure consumer safety, as emphasized by Gure [9]. Therefore, the study highlights the necessity for timely and precise analyses of metal concentrations in coffee to ensure consumer safety.

3. Conclusion

This review paper aims to provide a comprehensive overview of diverse analytical and instrumental methodologies utilized for evaluating the content of essential and toxic heavy metals in coffee in Ethiopia. Among the methods are atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, and X-ray fluorescence spectroscopy, to name a few. In addition, the paper elaborates on the importance of monitoring metal levels in coffee due to the potential health risks associated with excessive amounts of certain metals. Moreover, the discrepancies in the elemental composition of coffee samples from different regions of Ethiopia suggest that the geographic origin of coffee can be identified using its elemental profile. The worth of this knowledge lies in its ability to authenticate the origin of coffee, which is critical for maintaining the quality and authenticity of Ethiopian coffee. In conclusion, the paper offers valuable insights into the techniques utilized for analyzing the metal content of coffee in Ethiopia, which can be of great significance for future research endeavors in this field.

4. Recommendation

Future studies could examine the influence of various factors such as processing, storage, and preparation methods, as well as genetic and environmental factors on the metals contents of coffee. This would provide a better understanding of coffee quality. It would be beneficial to conduct a more thorough and varied analysis of samples from various coffee-producing regions and varieties. Future investigations could also look for potential contaminants by examining the metallic components of unroasted coffee beans and the soil where they were grown. Alternative analytical methods that could offer more thorough information on the metal content of coffee include ICP-MS, ICP-OES, DMA GC-MS, X-ray fluorescence spectrometry (XRF), and elemental analyzer-isotope ratio mass spectrometry.

Future research should examine geographic variations in metal concentrations in coffee, their long-term effects, any potentially harmful substances like mycotoxins or pesticides, and the relationship between elemental composition and sensory qualities. The impact of various brewing, roasting, and processing methods, as well as the bioavailability and toxicity of metals in coffee, could also be examined.

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