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CONCENTRATION LEVELS OF METALS IN COMMERCIALLY AVAILABLE ETHIOPIAN ROASTED COFFEE POWDERS AND THEIR INFUSIONS

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ABSTRACT. The concentrations of nine essential metals (K, Mg, Ca, Na, Mn, Fe, Cu, Zn, Co) and two non-essential (Pb, Cd) metals were determined in three brands of commercially available roasted Ethiopian coffee powders (Abyssinia, Alem and Pride) obtained from local markets and their infusions using flame atomic absorption spectrometry (FAAS). An optimized digestion procedure was developed using 5 mL of HNO_3 and 1 mL of $HClO_4$ with 4 hours total time at temperature around 350 ^oC for digestion of 0.5 g of powder sample while 4 mL of HNO_3 and 1 mL of $HClO_4$ with 4 hours total time for 25 mL infusion evaporated to dryness. The validity of the optimized procedure was evaluated by the analysis of spiked samples whose recovery of analytes was in the range of 97–103 % for the coffee powder and 95–102 % for the infusion samples. The mean concentration of each metal in the three brands of coffee powder samples was (µg element/g): K (14488±467), Mg (1964±78), Ca (945±65), Na (484±12), Fe (52.0±4.0), Mn (23.0±0.9), Cu (14.0±0.6), Zn (15.0±0.8), Co (1.60±0.05) while that in their infusions (µg element/100 mL): K (37205±1501), Mg (2829±105), Ca (1619±102), Na (591±20), Fe (18.3±1.5), Mn (23.7±1.2), Cu (3.0±0.3), Zn (24.0±1.1), Co (1.8±0.1), respectively. The metal concentrations of the coffee powders were higher than those of coffee infusions, when expressed in the same units. The extraction was highest for K (85.6%), intermediate for Zn (57.5%), Ca (56.6%), Mg (48.0%), Na (40.7%), Co (39.8%), and Mn (33.5%) and lowest for Fe (11.6%) and Cu (6.8%). The concentrations of metals in the Ethiopian coffees were comparable to the values reported in other parts of the world.

KEY WORDS: Coffee, Roasted coffee powder, Coffee infusion, Essential metals, Non-essential metals, FAAS

INTRODUCTION

Coffee is a widely-consumed stimulant beverage prepared from roasted seeds, commonly called coffee beans, of the coffee plant. The popularity of coffee as a beverage is ever increasing, despite the fact that there are reports attesting that it is not necessarily good for health [1].

Coffee is the single most important crop in the Ethiopian economy as it contributes over 60% of the national foreign exchange earnings, 30% of government direct revenue, and subsistence earnings of about 25% of the population [2].

The part of the coffee which is important for household consumption and commercial purposes is the bean, which naturally contains proteins, carbohydrates, vitamins and mineral substances [3-6]. However, the chemical content of the coffee varies with coffee types and environment in which they are cultivated and also in raw and roasted coffee beans of the same coffee type collected from the same environment [3].

Although little information is available on the levels of trace element contents in coffee beans of different origins in the literature, several studies have been carried out on determinations of the level of minerals (major, minor and toxic metals) in green (raw) and roasted coffee varieties in different parts of the world (such as Brazil, Nigeria, India, etc.), using different analytical techniques like flame atomic absorption spectrometry (FAAS) [7], inductively coupled plasma optical emission spectrometry (ICP OES) [8] and neutron activation analysis (NAA) [9]. Results of these studies have revealed that the levels of metals in raw or roasted coffees, differs among coffee species and varieties growing in the different parts of the

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world [10-12]. It has also been shown that there is no health hazard that is associated with exposure to Cd and Pb via coffee consumption [7].

Green coffee samples are observed to contain Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr, and Zn as analyzed by ICP OES, of which P, Mn and Cu showed larger differences for the two varieties (Arabica and Robusta coffee). Consequently, P, Mn and Cu are being used as chemical differentiators [8]. The contents of Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr, and Zn determined in roasted Arabica and Robusta coffee types were used as chemical differentiators for the two varieties [12-14]. The variation in the content of these metals are also known to be linked to differences in the factors influencing cultivation of the coffee plant; like soil, fertilizers and environment.

The concentrations of Ca, Mg, K, Na, P, Co, Mn, Fe, Cr, Ni, Zn, Cu, Cd, and Pb were determined in dry market coffee samples and infusions evaporated to dryness by flame atomic absorption spectrometry (FAAS). The analyzed samples were observed to have quite different concentrations of these elements with the highest values observed for K at concentration range of 1175−1585 mg in 100 g of ground coffee. The highest percentage of leaching (78.5%) in to the infusions was also observed for K [7]. The mineral content in 100 g of Brazilian soluble coffee is on average: Na 0.05 g, K 4 g, P 0.35 g, Ca 0.35 g, Fe 45 mg, Cu 0.5 mg, Zn 5 mg and the Mg content varies from 0.16 to 0.31 g [15].

There is only one report on the determination of concentration of Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn in raw and roasted indigenous coffee varieties in Ethiopia. The report indicated higher concentrations of these metals in roasted coffee than in the corresponding raw varieties [16]. However, there are no literature reports on the determination of levels of metals in the different varieties of commercially available roasted coffee powders and their infusions in Ethiopia.

This study reports the levels of essential and non-essential metals in commercially available roasted Ethiopian coffee powders and their infusions so that the total metal concentration of the coffee powder and that of the infusion/brew can be compared. The results of this study may provide useful baseline data on the levels and temporal variations of some nutrients in commercially available roasted coffee powders and their infusions in the country and may initiate further studies on nutritional, medicinal and toxicological effects of the commercially available Ethiopian coffee varieties.

EXPERIMENTAL

Instruments and apparatus

A blending device (Moulinex, France) was used for mixing and homogenizing the bulk coffee sample. Round bottom flasks (250 mL) fitted with reflux condenser were used in a Kjeldahl digestion block (Gallenkamp, England) apparatus for the digestion of the coffee powder and residue of coffee infusion. An analytical digital balance was used to weigh the coffee samples. Measuring cylinders and micropipettes (Dragonmed, Shangai, China, 100−1000 μL) were used for measuring different volumes of coffee infusion sample, acid reagents and standard solutions. Volumetric flasks (25 mL, 50 mL, 100 mL) were used for the dilution of the sample solutions and the preparation of standards. Flame atomic absorption spectrophotometer (Buck Scientific Model 210VGP AAS, East Norwalk, USA) fitted with deuterium background corrector and air-acetylene flame atomizer was used for the determination of concentrations of the metals (Mg, Ca, Mn, Fe, Cu, Zn, Co, Cd and Pb). Na and K were determined in the emission mode of the instrument.

Chemicals and reagents

All the chemicals and reagents used were of analytical grade: HNO_3 (69–70%, Fine-Chem Mumbai-391780, India) and $HClO_4$ (70%, Aldrich, UK) were used for the digestion of the roasted coffee powder and coffee infusion samples. Lanthanum nitrate hydrate, 99.9% (Aldrich, USA) was used to prevent the chemical interference on Ca and Mg during the analysis of coffee samples. Stock standard solution of concentration 1000 mg/L in 2% HNO_3 of the metals K, Na, Ca, Mn, Fe, Cu, Zn, Co, and Pb (Buck Scientific Puro-Graphic^{tm}) was used for preparing an intermediate standard solution containing 10 mg metal/L. For Fe, $Fe(NO_3)_2$ (99%, Avocado Research Chemicals Ltd., Heysham, Lancs.) standard solution was used. Mixed working standards were prepared from the intermediate standards of each metal. Deionized water (chemically pure: 1.5 μs/cm and below) was used for cleaning of the glassware and dilution of the sample and other purposes.

The FAAS instrument was calibrated using a series of four working standard solutions of each metal prepared by diluting the intermediated standard solutions mentioned previously. Table 1 shows the wavelengths and values of correlation coefficients of the calibration curves.

Apparatus cleaning

All glassware used were washed with tap water using detergent. Strong oxidizing solution of a mixture of potassium dichromate and sulfuric acid was also used for cleaning by soaking the apparatus for about 24 hours. All apparatus were rinsed with deionized water and dried before use. The apparatus were also soaked in HNO_3 and rinsed with deionized water before the next analysis.

Sampling

The coffee powder samples used for the analysis were purchased from the local markets. Roasted powders of different local coffee brands packed in sizes of up to 1 kg are available in the local markets. The analysis was conducted on the three types of commercially available and most commonly used roasted Ethiopian coffee powders (Abyssinia coffee, Alem coffee and Pride coffee). Five samples of each brand were obtained from five different sampling sites.

Sample preparation

Roasted coffee powder samples. A bulk sample for the analysis was prepared for each brand by taking 20 g of coffee powder from the 250 g packages of the 5 coffee samples of each brand and mixed for homogeneity using an electronic blender. Thus, the amount needed for analysis was taken from the 100 g of the bulk coffee powder sample prepared.

Coffee infusion samples. In this study, 6 g (≈ two spoons) coffee powder was added to 200 mL (≈ two cups) of boiled water (for about 5 min) to prepare a coffee based on the estimation of daily consumption of coffee for most people in the country as two cups on average. Finally, the boiled sample was allowed to cool for about 10 min and the pure infusion sample was obtained by filtering.

Digestion of the coffee powder. Literature procedure used for the digestion of coffee powder [16] was used with slight modification. A 0.5 g portion of roasted coffee powder was added to a 250 mL round bottom flask. To this, 4 mL of 70% HNO_3 and 0.5 mL of 70% $HClO_4$ was added and the round bottom flask was fitted to a reflux condenser. The sample mixture was then

digested on a Kjeldahl apparatus for about 2 hours by keeping the temperature to around 350 ^{o}C. After this the sample mixture was removed and 1 mL of 70% HNO_3 and 0.5 mL of 70% $HClO_4$ was added and further digested for another two more hours at the same temperature through slight variation at some time intervals. The digest was removed and allowed to cool for about 25 min. Then 30 mL of dionized water was added to the digest and filtered with Whatman No. 1 filter paper. The filtrate was diluted to 50 mL with deinized water and a clear and colorless solution was obtained.

Digestion of the coffee infusion samples. A slightly modified procedure was used for the case of the coffee infusion samples with less reagent volume consumption and digestion temperature. A 25 mL aliquot of the coffee infusion was taken in a round bottom flask and heated to evaporate to avoid dilution of the acid reagents to be added. Then 3.5 mL of 70% HNO_3 and 0.5 mL of 70% $HClO_4$ was added after cooling to avoid explosion due to contact between the acid reagent and the organic matter contained in the sample. The mixture was digested continuously on a Kjeldahl apparatus for about 2 hours at a temperature of about 300 ^{o}C. The sample mixture was then removed and 0.5 mL of each of the acid reagents was added and digested further for 2 more hours at the same temperature through slight variation at a certain time intervals. The digest was then removed and cooled for 25 min at room temperate in open air. 30 mL of deionized water was added to the digest solution, gently swirled and filtered in to 50 mL volumetric flask using a Whatman No. 1 filter paper. Finally, it was diluted up to the mark and a clear and colorless solution was obtained. Three replicate digestions were made for each brands of the coffee infusion. The digest solutions were kept in a refrigerator until the analysis for the analyte metals.

Digestion of blank samples. Estimation of the metal concentration of the blank is important for the determination of the detection limit of the analytical method used during the study. Thus, six reagent blanks were digested in parallel for each sample type and a total of twelve blanks were digested following the same procedure used for the coffee powder and infusion samples.

Method validation

A spiking experiment was done to evaluate the efficiency of the procedure used. Known amounts of standard metal solutions were added to the coffee samples taking care of the dilution of the final solution. Aliquots of 200 µL of 1000 mg/L Mg, 100 µL of 1000 mg/L of Ca and Na, 50 µL of 100 mg/L Zn, Cu, Mn, Co, Pb, Cd, and 100 µL of 100 mg/L Fe were spiked at once into a 0.5 g of coffee powder samples in one digestion flask and 1400 µL of 1000 mg/L of K was spiked to the same mass of the coffee powder sample in another digestion flask.

Comparatively lesser volumes of the standard solutions were consumed for the case of the coffee infusion samples. 100 µL of 1000 mg/L of Mg, 50 µL of 1000 mg/L of Na and Ca together with 50 µL of 100 mg/L of Zn, Cu, Co, Mn, Cd, Fe and Pb were spiked at once in to the coffee infusion sample in one digestion flask and 1000 µL of 1000 mg/L of K was spiked in to the coffee infusion sample in another digestion flask.

All the spiked samples were digested in triplicate following the same digestion procedure used for the coffee powders and their infusions, as described previously. The digested spiked samples were analyzed for their respective metals contents using FAAS.

Determination of the essential and non-essential metals

An intermediate standard solution of concentration 10 mg/L for each metal was prepared by dilution of the stock standard solution (1000 mg/L) of the metals. A series of four working

standards were prepared for each metal from this intermediate standard solution for each of the analyte metals. Three replicate measurements were used for each brand of the coffee powder and the coffee infusion for the determination of the total metal content.

Statistical analysis

The significance of variation between samples was analyzed using one-way ANOVA and SPSS (SPSS 13.0 for windows, The Apache Software Foundation, 2000) soft ware was used for statistical analysis to know the presence or absence of significant difference in mean concentration of each metal between the analyzed coffee samples.

RESULTS AND DISCUSSION

Figures of merit

The limit of detection is the amount of analyte that gives a signal equal to three times the standard deviation of the blank [17] or it is the minimum concentration of the analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero [18]. The method detection limit for the metals in both the coffee powder and coffee infusion samples was calculated as three times the standard deviations of the six blank determinations. The method detection limits of the metals are given in Table 1. The method detection limits for all the metals were < 0.1 μg/g which clearly indicate that the method is applicable for the determination of metals at trace levels. The percentage recovery lies within the range 97–103% (with RSD 1–5%) for the coffee powder and 95–102% (with RSD 1–7%) for the coffee infusion, which are within the acceptable range for all metals (Table 2 and 3). This confirms that the method is of good precision and accuracy.

Table 1. Analytical wavelengths, correlation coefficients of the calibration curves and method detection limits for coffee powder and coffee infusion samples.

Element	Wavelength (nm)	Correlation coefficient of calibration curves	Method detection limit for coffee powder samples (μg/g)	Method detection limit for coffee infusion samples (μg/100 mL)
Na	589.9	0.9997	0.06	0.1
K	766.5	0.9994	0.07	0.2
Mg	285.2	0.9999	0.09	0.2
Ca	422.7	0.9990	0.08	0.2
Fe	248.3	0.9983	0.04	0.1
Cu	324.8	0.9999	0.07	0.1
Mn	279.5	0.9993	0.03	0.1
Co	240.7	0.9995	0.08	0.2
Zn	213.9	0.9999	0.09	0.2
Cd	228.9	0.9996	0.01	0.05
Pb	283.3	0.9998	0.04	0.1

Distribution of metals in coffee powder samples

The concentrations of macro- and micro-elements determined in the three brands of both the coffee powders and their respective infusions are summarized in Tables 4 and 5.

The concentrations of the metals analyzed vary widely in the coffee powder and coffee infusion samples. Each brand differs from the other in its metal content with slight differences. Generally, the infusions containing soluble components in hot water had lower concentrations of each metal than their respective powder samples. The macroelements were present at higher concentrations than microelements as described below.

Table 2. Recovery test results of metals for the analysis of coffee powder samples.

Metal	Concentration in the sample (μg/g)[a]	Amount added (μg/g)	Concentration in the spiked sample (μg/g)[b]	Recovery (%)[c]
K	14361	2800	17020 ± 20	99 ± 4
Mg	1966	400	2325 ± 10	98 ± 5
Ca	1045	200	1221 ± 9	98 ± 5
Na	468	200	676 ± 3	101 ± 3
Fe	53	20	72 ± 4	99 ± 5
Mn	24	10	33 ± 1	97 ± 3
Cu	14	10	23 ± 1	96 ± 4
Zn	19	10	30 ± 1	103 ± 3
Co	1.6	10	12.0 ± 0.4	103 ± 4
Pb	<MDL[d]	5.0	5.2 ± 0.3	104 ± 6
Cd	<MDL[d]	5.0	5.1 ± 0.2	102 ± 4

[a]Mean concentration of samples analyzed in triplicate.
[b]Mean concentration ± SD of samples spiked in triplicate.
[c]Mean recovery ± SD of percentage recoveries of triplicate analyses.
[d]Their concentration was below method detection limit (0.04 μg/g for Pb and 0.01 μg/g for Cd).

Table 3. Recovery test results of metals for the analysis the coffee infusion samples.

Metal	Concentration in the sample (μg/100 mL)[a]	Amount added (μg/100 mL)	Concentration in the spiked sample (μg/100 mL)[b]	Recovery (%)[c]
K	37182	3999	40689 ± 162	98 ± 7
Mg	2853	399	3150 ± 24	97 ± 5
Ca	1551	198	1794 ± 27	102 ± 6
Na	585	198	759 ± 15	97 ± 4
Fe	20.1	21.0	42.0 ± 1.8	102 ± 3
Mn	27.9	21.0	48 ± 1.5	98 ± 4
Cu	4.2	21.0	24.0 ± 0.9	95 ± 2
Zn	25.2	21.0	45 ± 1.4	97 ± 2
Co	2.4	21.0	22.5 ± 0.3	96 ± 1
Pb	<MDL[d]	15.0	15.6 ± 0.6	104 ± 4
Cd	<MDL[d]	15.0	15.3 ± 0.6	102 ± 4

[a]Mean concentration of samples analyzed in triplicate.
[b]Mean concentration ± SD of samples spiked in triplicate.
[c]Mean recovery ± SD of percentage recoveries of triplicate analyses.
[d]Not detected, concentration was below method detection limit (0.15 μg/100 mL for Pb and 0.03 μg/100 mL for Cd).

Abyssinia coffee powder contains K in highest amount of the macroelements with concentration 14520 ± 428 μg/g followed by Mg (1968 ± 9 μg/g) and Ca (946 ± 48 μg/g). Na (484 ± 48 μg/g) was found to be present at the lowest concentration of the macroelements analyzed (Table 4).

Table 4. Concentration (mean ± SD, n = 3, μg/g) of elements in the three brands of coffee powder samples.

Element	Concentration of metals (μg/g)[a]		
	Abyssinia coffee powder	Alem coffee powder	Pride coffee powder
K	14520 ± 428	14361 ± 478	14583 ± 495
Mg	1968 ± 89	1966 ± 68	1959 ± 76
Ca	946 ± 48	1045 ± 77	843 ± 70
Na	484 ± 13	468 ± 12	501 ± 10
Fe	52.0 ± 4.0	53.0 ± 5.0	52.0 ± 3.0
Mn	24.0 ± 0.6	24.0 ± 1.5	22.0 ± 0.5
Cu	17.0 ± 0.2	14.0 ± 0.8	11.0 ± 0.7
Zn	13.0 ± 0.7	19.0 ± 0.8	12.0 ± 0.8
Co	1.90 ± 0.05	1.60 ± 0.06	1.30 ± 0.03
Pb	<MDL[b]	<MDL[b]	<MDL[b]
Cd	<MDL[b]	<MDL[b]	<MDL[b]

[a]Concentration values are average of three analyzed samples ± standard deviation.
[b]Their concentrations were below the method detection limit.

Table 5. Concentration (mean ± SD, n = 3, μg/100 mL) of elements in the three brands of coffee infusion samples.

Element	Concentration of metals (μg/100 mL)[a]		
	Abyssinia coffee infusion	Alem coffee infusion	Pride coffee infusion
K	37182 ± 1869	35901 ± 1350	38532 ± 1284
Mg	2853 ± 129	2826 ± 84	2808 ± 102
Ca	1551 ± 108	2040 ± 105	1266 ± 93
Na	585 ± 18	528 ± 15	663 ± 27
Fe	20.1 ± 1.5	21.0 ± 1.8	13.8 ± 1.2
Mn	27.9 ± 1.5	24.0 ± 0.9	18.9 ± 1.2
Cu	4.2 ± 0.6	2.4 ± 0.1	2.1 ± 0.1
Zn	24.0 ± 1.2	30.0 ± 1.2	21.0 ± 0.9
Co	2.4 ± 0.1	1.5 ± 0.1	1.8 ± 0.1
Pb	<MDL[b]	<MDL[b]	<MDL[b]
Cd	<MDL[b]	<MDL[b]	<MDL[b]

[a]Concentration values are average of three analyzed samples ± standard deviation.
[b]Their concentrations were below the method detection limit.

Fe (52 ± 4 μg/g) was found in higher amounts than other trace microelements. The concentration of Cu (17.4 ± 0.2 μg/g) was next to Mn (24 ± 0.6 μg/g), which was found in larger concentration than Zn (13 ± 0.7). The trace metal found in the lowest concentration was Co (1.9 ± 0.05 μg/g). Pb and Cd were found to be below the method detection limits (0.04 μg/g and 0.01 μg/g, respectively) in all the coffee powder samples. The level of metals in the Abyssinia coffee powder was found in the decreasing concentration order of metals K > Mg > Na > Ca > Fe > Mn > Cu > Zn > Co.

Of the macroelements K (14361 ± 478 μg/g) was observed to be present in the highest concentration in Alem coffee powder. Ca was found in largest amounts than Mg with concentrations of 1045 ± 77 μg/g and 1966 ± 6 μg/g, respectively. Na (467.6 ± 2.4 μg/g) was found in appreciable amount (Table 4).

Alem coffee powder sample also contained Fe (53 ± 5 μg/g) in larger amounts than other microelements, proceeded by Mn (23.6 ± 1.5 μg/g). In contrast to the Abyssinia coffee powder, Zn (19 ± 0.8 μg/g) was found in larger concentration than Cu (14 ± 0.8 μg/g). Only a small

amount of Co at a concentration of 1.6 ± 0.06 μg/g was detected. The non-essential metals (Cd and Pb) were below the method detection limit. The concentrations of metals determined in Alem coffee powder was in the same decreasing concentration order as in Abyssinia coffee powder, except for the higher concentration of Zn than of Cu: K > Mg > Na > Ca > Fe > Mn > Zn > Cu > Co.

Pride coffee powder was also much rich in its content of K (14583 ± 495 μg/g) than other macroelements followed by Mg (1959 ± 7 μg/g), Ca (843 ± 70 μg/g) and Na (501 ± 10 μg/g) (Table 4).

The concentration of Fe (51.5 ± 3.0 μg/g) was higher than Mn (22 ± 0.5 μg/g). Cu (11 ± 0.7 μg/g) and Zn (12 ± 0.8 μg/g) only slightly differ. Co (1.3 ± 0.03 μg/g) is the least of all metals. The toxic metals (Cd and Pb) were below the method detection limit.

Distribution of metals in coffee infusion samples

The concentrations of metals were also quite variable in the coffee infusion samples (Table 5). Different brands had different concentration of the metals like the coffee powder samples had. The concentration of each metal in each brands of coffee infusion is clearly described below.

K (37182 ± 1869 μg/100 mL) was found to be in highest concentration among the microelements in Abyssinia coffee infusion. Mg was found in larger amounts than Ca with concentrations of 2853 ± 129 and 1551 ± 108 μg/100 mL, respectively. Na (585 ± 18 μg/100 mL) was found in appreciable amounts too.

Less amounts of trace metals were detected in Abyssinia coffee infusion of which Mn (27.9 ± 1.5 μg/100 mL) was present in slightly higher concentration than the other metals. The concentrations of Zn (24.0 ± 1.2 μg/100 mL) and Fe (20.1 ± 1.5 μg/100 mL) were higher than that of Cu (4.2 ± 0.6 μg/100 mL). Co was detected at the lowest concentration of all metals of 2.4 ± 0.1 μg/100 mL. In all infusion samples, the toxic heavy metals (Pb and Cd) were below the method detection limits, 0.1 μg/g and 0.05 μg/100 mL for all coffee infusion samples, respectively.

The highest level of K (35901 ± 1350 μg/100 mL) was observed in Alem coffee infusion followed by Mg (2826 ± 84 μg/100 mL) (Table 5). Similar to the Abyssinia coffee infusion, the concentration of Ca (2040 ± 105 μg/100 mL) is greater than the concentration of Na (528 ± 15 μg/100 mL).

Of the trace metals, Zn (30.0 ± 1.4 μg/100 mL) was found in a higher amount than the other metals proceeded by Mn (24.0 ± 0.9 μg/100 mL). The concentration of Fe (21.0 ± 1.8 μg/100 mL) is higher than that of Cu (2.4 ± 0.1 μg/100 mL), like in the Abyssinia coffee infusion. The concentration of Co (1.5 ± 0.1 μg/100 mL) in this infusion was the least of the samples analyzed. The toxic metals (Cd and Pb) were not detected as they were below the method detection limit. The decreasing concentration order for the macroelements in this infusion is the same as that in the Abyssinia while the order for the microelements is different since the concentration of Zn > Mn unlike the Abyssinia coffee infusion, Zn > Mn > Fe > Cu > Co.

In infusion prepared from Pride coffee powder, out of microelements K (38532 ± 1284 μg/100 mL) was observed to be present in the highest concentration. Table 5 shows that the concentration of Mg (2808 ± 102 μg/100 mL) was found to be more than twice the concentration of Ca (1266 ± 93 μg/100 mL). Na (663 ± 27 μg/100 mL) was also found in more appreciable amounts than other infusion samples.

Pride coffee infusion also contains Zn (21.0 ± 0.9 μg/100 mL) in larger amounts than other microelements proceeded by Mn (18.9 ± 1.2 μg/100 mL). Fe (13.8 ± 1.2 μg/100 mL) was found in larger concentration than Cu (2.1 ± 0.1 μg/100 mL). Only a small amount of Co at

concentration of 1.8 ± 0.1 µg/100 mL was detected. The non-essential metals (Cd and Pb) were again below the method detection limit. The concentrations of metals determined in Pride coffee infusion with decreasing concentration trend confirms the similarity to that of Alem coffee infusion.

Efficiency of extraction of metals from coffee powders into coffee infusions

The percentage of metals extracted from the coffee powder to coffee infusion was found to vary widely. The extraction was highest for K (85.6%), intermediate for Zn (57.5%), Ca (56.6%), Mg (48.0%), Na (40.7%), Co (39.8%), and Mn (33.5%), and lowest for Fe (11.6%) and Cu (6.8%). The low extractability of Fe and Cu is most likely due to strong complex formation of these two metals with caffeine and alkaloids (having N as donor atom) of the coffee powder [19, 20]. The efficiency of extraction of the metals from coffee powder to coffee infusion was in the following order: K > Zn > Ca > Mg > Na > Co > Mn > Fe > Cu. Table 6 presents the percentage extraction of individual metals from the coffee powder of the three brands into coffee infusion.

Table 6. Percentages of metals extracted from coffee powder into coffee infusions[a].

Metal	Abyssinia coffee (%)	Alem coffee (%)	Pride coffee (%)	Average (%)
K	85.4	83.3	88.1	85.6
Mg	48.3	47.9	47.8	48.0
Ca	54.7	65.1	50.1	56.6
Na	40.3	37.6	44.1	40.7
Fe	12.9	13.2	8.8	11.6
Mn	38.7	33.3	28.6	33.5
Cu	8.2	5.7	6.4	6.8
Zn	61.5	52.6	58.3	57.5
Co	42.1	31.3	46.1	39.8
Pb	<MDL[b]	<MDL[b]	<MDL[b]	–
Cd	<MDL[b]	<MDL[b]	<MDL[b]	–

[a]Concentration values are average of three analyzed samples.
[b]Their concentrations were below the method detection limit.

Statistical analysis

For K and Fe, no significant difference ($p \geq 0.05$) at 95 % confidence interval was observed in the mean concentrations between all the three samples of the coffee powder (Abyssinia/Alem, Abyssinia/Pride and Alem/Pride). The mean concentrations of Mn and Mg do not differ significantly ($p \geq 0.05$) for Abyssinia and Alem coffee powders while it differ significantly for Abyssinia compared to Pride and Alem to Pride. Similarly, Zn has a mean concentration that did not differ significantly between the Abyssinia and Alem coffee powders. However, there was a significant difference ($p < 0.05$) at 95 % confidence level in the mean concentration of Cu, Na and Ca between all analyzed coffee powder samples. In addition to this, significant differences in mean concentration were observed for Zn between Abyssinia and Alem coffee powders similar to that of Alem and pride coffee powders.

The coffee infusion samples were also analyzed using the same statistical analysis technique. Except K and Fe, there was significant difference ($p < 0.05$) at 95 % confidence interval in the mean concentration of all the metals between the Abyssinia and Alem coffee infusion samples. A significant difference in mean concentrations was also observed for all

metals between the infusion prepared from the Alem and Pride coffee powders. Similarly, for Abyssinia and Pride coffee infusions, a significant difference was observed for the mean concentrations of all metals except K.

Comparison of the metal content coffee sample with other reported values

Commercial coffee industry uses blends of coffee beans that come from a wide range of geographical areas having different chemical and organoleptic properties depending on different factors. Thus, for the commercial qualification of coffee producers must select among the different varieties to produce the best quality. The percentage of Arabica and Robusta, green coffee processing methods, difference in roasting, treatments in the roasting step and origin of coffee (related to soil conditions) are some of the factors for the difference in the blends and quality of coffee further affecting the distribution of the metal content which could be used as a tool for characterizing coffee varieties [21].

Although various chemical analyses target to a similar objective, there may also be a difference in sampling, sample preparation and analytical techniques. Considering all these, the result of the present study can be compared to the findings of other authors. Grembecka *et al.* [7] have determined the total metal content using FAAS in different market coffee samples collected from different countries and observed that ground coffee samples contain Ca (841 μg/g), Mg (2100 μg/g), Na (420 μg/g), K (13690 μg/g), Fe (41.6 μg/g), Mn (22.4 μg/g), Cu (16.1 μg/g), Zn (5.3 μg/g) and Co (0.4 μg/g) where as Pb and Cd were below their method detection limits which were 0.1 μg/g and 0.03 μg/g, respectively. The results of present study are in good agreement with these values [7].

Martin *et al.* [14] have also determined the metal content of roasted coffee samples of various origin and the concentrations have been used as chemical descriptors to differentiate between roasted coffee samples from the Arabica and Robusta varieties. The Arabica coffee variety from Nicaragua contained (μg element/g): Ca (970), Cu (13.4), Fe (46.2), K (14930), Mg (1740), Mn (14.1), Na (33.4), Zn (19.3) while the Robusta variety from Ivory Cost contained Ca (940), Cu (16.1), Fe (56.1), K (14480), Mg (1610), Mn (12.2), Na (21.4), Zn (13.9) comparable to the values reported in this paper. Furthermore, they used the P, Mn and Cu content to discriminate between the Arabica and Robusta roasted coffee varieties. They observed that roasted coffee mixture which is 20%, 15%, 10% and 5% in its Robusta composition contains μg Mn/g: 22, 22.1, 22.9, 23.6; respectively while the one with 30%, 25%, 10% and 5% in its Arabica composition contains μg Cu/g: 17.5, 17.6, 17.1, 16.1, respectively. This principle with proper statistical application could also help in the identification of the blends of market coffee samples [14].

Zaidi *et al.* [9] have determined the concentration of essential and nonessential metals in coffee beans from four origins namely Brazilian, Caribbean, Indian and Kenyan. The elemental concentrations for Mn, Fe, Co, Zn, Na and K are observed to lie in the range μg element/g: 19.1–49.5, 28.9–83.2, 0.036–0.322, 4.8–37.7, 7.6–63.1 and 17000–33000, respectively. The comparison of concentration of macroelements of the present study with other reported values are given in Table 7.

The results of the present study are in good agreement with the most of reported values. Moreover, the general trend of the metal concentration for macroelements K > Mg > Ca > Na is in good agreements except that K was observed to be less than the reported values which may be attributed to the soil on which the coffee is grown in Ethiopia without fertilizer.

Regarding the trace microelements, Fe > Mn > Cu > Zn > Co in roasted coffee powder is followed for most reports. Co was detected up to very low levels by one study with nearly comparable values to the levels reported here. Similarly, a report by Grembecka *et al.* [7] for the microelements shows that toxic microelements (Pb, Cd) were not detectable under their analysis

conditions using the FAAS as shown previously. The concentration of the microelements in commercially available roasted Ethiopian coffee powder is compared to other reported values in Table 8.

Table 7. Comparison of the concentrations of macro-elements in Ethiopian coffee powder with that reported in the rest of the world.

Origin	Concentration (μg/g) of metal in roasted coffee powder				Reference
	K	Mg	Ca	Na	
Ethiopia	14361–14583	1959–1968	843–1045	468–501	Present study
Various origins	11750–15850	800–2840	513–1620	382–459	[7]
Brazil	32500–39800	2120–4150	1110–1890	274–6665	[13]
India	14000–29000	2000–3100	490–791	–	[22]
Ivory Coast	14010–14480	1610–1820	940–1220	15.9–21.4	[14]
Various origins	17500–19600	2058–2410	934–1234	10–41	[23]
Uganda	14080–14990	1670–1780	1170–1230	11–14	[14]

Table 8. Comparison of the concentrations micro-elements in the Ethiopian coffee powder with that reported in the rest of the world.

Origin	Concentration (μg/g) of metals in roasted coffee powder							References
	Fe	Mn	Zn	Cu	Co	Pb	Cd	
Ethiopia	52–53	22–24	12–19	11–17	1.3–1.9	<MDL	<MDL	Present study
Various origins	20.3–68	16.5–40.6	3.2–16.2	12.1–20.1	0.1–0.9	<MDL	<MDL	[7]
Brazil	14–450	4–39	3–15	0.5–2.3				[13]
India	16–92	7–13	2–9	0.4–16		0.02–0.2	0.001–0.03	[22]
Ivory Coast	56.1–63	12.2–13.1	13.9–15.1	16.8–17.2				[14]
Various origins	12–31	19–39	6.51–8.03	12–18				[23]
Uganda	63–63.7	12.1–13.3	12.9–57.9	15.6–17				[14]

MDL = method detection limit.

The coffee infusion also contains mineral nutrients that are essential for humans. Tables 9 and 10 provide a comparison for the macro and microelement content, respectively per 100 mL of the coffee brew prepared from commercially available roasted Ethiopian coffee powder with coffee powder that originates from other parts of the world. Gillies and Birkbeck [25] have determined mineral concentrations in tea and coffee samples by FAAS and used the data to estimate daily intakes of mineral from these beverages in New Zealand.

The concentration trend for macroelements K > Mg > Na > Ca also goes with most of the reports for the coffee infusions. The value of K in the present study is lower than other reported values. The value for the rest of the metals is nearly comparable despite the factors like different analytical techniques, considerable variation in mineral concentrations in coffee beans itself, difference in water used, gains and losses during processing and different methods of preparation.

Regarding the trace elements, Santos *et al.* [10] determined metal concentration levels in foodstuffs frequently consumed by Rio de Janeiro inhabitants of which one is coffee. The amounts of Cu, Mn, Zn, and Fe extracted from coffee beans in the brewing processes were determined to be (μg element/100 mL): 6–58, 2–16, 17–18, 11–33, respectively. Similarly, Gillies and Birkbeck [25] determined the concentration range of the trace elements Mn, Cu, Zn,

Pb and Cd as (μg element/100 mL): 29–40, 3.9–9.8, 49–88, 0.7–0.9 and 0.015–0.058, respectively in drinking coffee.

Onianwa *et al.* [11] have analyzed several beverages and food drinks available in Nigeria for their contents of the heavy metals like Cd (1.3–10.5 μg/100 mL, Co (0.15–21.3 μg/100 mL, Cu 3.2–14.1 μg/100 mL, Fe (9.45–261 μg/100 mL, Pb 0.135–1.4 μg/100 mL and Zn 5.6–21 μg/100 mL). The levels of the various metals are comparable to the present study as they were generally low and within safe limits.

Overall the results obtained in this work are in good agreement with those reported from other parts of the world implying its acceptability regardless of some factors contributing to the deviation in some ways.

Table 9. Comparison of the concentrations of macro-elements in Ethiopian coffee infusion with reported values.

Origin	Mineral content (μg/100 mL) of coffee infusion*				References
	K	Mg	Ca	Na	
Ethiopia	35000–39000	2800–3000	1300–2000	530–660	Present study
Finland	73000–110000	7300–12000	2500–3900		[24]
New Zealand	74000–85600	4300–5200	2780–2680	800–1290	[25]
USA	42900	8300			[26]

*Concentration in approximately one cup (≈ 100 mL) of coffee.

Table 10. Comparison of the concentrations of micro-elements in coffee infusion with reported values.

Origin	Mineral content (μg/100 mL) of coffee infusion*							Reference
	Fe	Mn	Cu	Zn	Co	Pb	Cd	
Ethiopia	10–20	20–30	2–4	20–30	2–2.4	<MDL	<MDL	Present study
Finland	35–60	48–120	3–101	10–16				[24]
New Zealand	11–33	2–16	6–58	17–18				[25]
Brazil		29–40	3.9–9.8	49–88		0.7–0.9	0.015–0.058	[10]
USA		90	22					[21]
Nigeria	9.45–261		3.2–14.1	5.6–21	0.15–21.3	0.14–1.4	1.3–10.5	[11]

*Concentration in approximately one cup (≈ 100 mL) of coffee. MDL = method detection limit.

CONCLUSIONS

The wet digestion method and the determination of selected metals at trace levels in coffee powders and their infusions by flame atomic absorption method was found to be efficient, precise and accurate.

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. Generally, the roasted coffee powders contained higher amounts of metals than the infusions and were richer in K to the largest extent followed by Mg and Ca with Na occurring at the lowest level relative to the other essential macroelements. The Fe concentration was determined to be the highest followed by Mn and Zn out of the trace microelements in coffee powders. The coffee infusion prepared from the powder samples was found to contain the essential macro- and micro-elements, which could also serve as dietary mineral source depending on the amount consumed. The abundance trend for macro-elements in the infusion was similar to that of the

powder while for microelements, Zn was the highest followed by Mn and Fe. Co was detected at the lowest level in all coffee samples. The values found are in line with previously reported data on other types of coffee samples.

The data obtained in the present study could be valuable in complementing available food composition data and estimating dietary intakes of essential and nonessential metals in Ethiopia through coffee consumption.

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