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Levels of Selected Essential and Nonessential Metals in Roasted Coffee Beans of Yirgacheffe and Sidama, Ethiopia

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Abstract: The study was conducted to assess the contents of essential and non-essential metals in coffee beans. For this matter, seven essential metals such as K, Mg, Ca, Na, Mn, Cu and Zn and two nonessential metals (Cd and Pb) in four roasted coffee samples (washed Yirgacheffe, unwashed Yirgacheffe, washed Sidama and unwashed Sidama) were determined by FAAS. Closed microwave assisted wet digestion method with addition of concentrated (69-70%) HNO_3 and 30% H_2O_2 were selected for decomposition of ground roasted coffee samples. Generally, the levels of metals in all roasted coffee samples were found: K > Mg > Ca > Na >Mn> Zn > Cu, but the non-essential metals Pb and Cd were found to be below method detection limit. The digestion method was evaluated by spiking roasted coffee samples and their percentage recoveries were in the range of 95 −104 %. It is suggested that the consumption of roasted coffee beans could be a source of dietary essential metals and a possible entrance path way for trace metals to the food chain.

Keywords: Essential and Non-essential Metals, FAAS, Micro-wave Digestion, Roasted Coffee Beans

1. Introduction

Currently, one of the greatest challenges is the production of food, not only in sufficient amounts, but also with adequate nutritional quality, assuring nutritional balanced and a contaminant free food supply. Moreover, the increasing awareness of the important role of trace elements in biological systems has stimulated the extension and refinement of studies in this field which have provided a great deal of information. Accordingly, the content of mineral micronutrients and some other trace elements in coffee beans is of great general and special interest [1].

Over two-thirds of all the research literature on geographic origin commodities involves the analysis of vitamins or other organic molecules (amino acids, triglycerides, volatile aromatic compounds, etc.) [2]. However, a shortcoming of using vitamins (or other organic compounds) is their susceptibility to degradation those organic chemicals including enzymatic changes from the time of harvest through storage to the time of analysis [3]. This is also important because coffee beans are processed and organic chemical profiles are likely to be especially susceptible. The use of minerals and trace elements is therefore powerful because trace elements are significantly more stable in the commodity versus vitamins or some other types of organic compounds [4].

For determination of metals in raw or roasted coffees have used different analytical techniques like flame atomic absorption spectrometry (FAAS) [5], inductively coupled plasma optical emission spectrometry (ICP OES) [6] and neutron activation analysis (NAA) [7], results of these studies have revealed that the levels of metals differs among coffee species and varieties growing in the different parts of the world [8, 9]. This study aimed to determine the levels of essential and non-essential metals in washed and unwashed Yirgacheffe and Sidama roasted coffee beans which grow in Ethiopia.

2. Experimental

2.1. Instruments and Apparatus

Coffee Roasting Machine (PROBAT-WERKE, BRZ-2 type

Emmerich am Rhein, 2006, Germany), Microwave oven (Buck Scientific, inc. Type MWS-1, East Norwalk, USA) equipped with digestion vessels made of Teflon Fluor Modified (TFM), Flame atomic absorption spectrophotometer (FAAS) (Buck Scientific Model 210VGP AAS, East Norwalk, USA) fitted with deuterium background corrector and air acetylene flame atomizer.

2.2. Chemicals and Reagents

All the chemicals used were of analytical grade: 69−70% HNO_3 (Uni-Chem^R, Chemical reagents.), 30% H_2O_2 (Uni-Chem^R, Chemical reagents.), Lanthanum nitrate hydrate, 99.9% (Aldrich, USA), Stock standard solutions of concentration 1000 mg/L in 2% HNO_3 of the metals K, Mg, Ca, Na, Mn, Zn, Cu, Cd and Pb (Inorganic^{TM} Ventures.) and Deionized water chemically pure with <1.5 µs/cm.

2.3. Sample Preparation

Both washed and unwashed coffee samples were collected using plastic bags from Ethiopia Commodity Exchange (ECX, Hawassa, Ethiopia) and Yirgacheffe Woreda marketing and cooperative bureau. The pre-treated (cleaned) green or raw coffee bean samples were roasted in 150 g batches by using coffee roasting machine (PROBAT-WERKE, BRZ-2 type Emmerich am Rhein, 2006, Germany) at the Ethiopian Commercial Exchange (ECX, Hawassa, Ethiopia) Coffee Quality and Flavor Inspection laboratory Center. All the roasting process was carried out by an expert on coffee roasting and the temperature and time needed for roasting of all coffee samples were 180 ^oC and 8-12 min respectively, medium roasting was selected among the degree of roasting coffee beans (light, medium and dark). Finally the roasted coffee samples were ground in to fine powder using mortar and pestle (to protect metal contamination).

2.4. Digestion of Ground Roasted Coffee Samples

In this study a method developed by Oleszczuk*et al.* [14] with a mass of 0.3 g powder of each roasted coffee sample was transferred to TFM digestion vessels followed by addition of 5 mL of concentrated (69-70%) HNO_3 and 3 mL of 30% H_2O_2 was selected for decomposition of ground roasted coffee samples. In the first step the temperature was linearly increased to 145 ^oC in 5 min with power of the rotating 80 W. In the second step the temperature was kept 200 ^oC for 10 min with power of the rotating 90 W and in the third step the temperature was linearly decreased to 50 ^oC in 10 min with rotating power of 0 W. For digestion of blank samples, eight reagent blanks were digested following the same procedure used for the ground roasted coffee samples. Finally, the concentrations of metals (K, Na, Ca, Mg, Mn, Cu, Zn, Cd and Pd) were determined directly in the extract solution by flame atomic absorption spectrometry (FAAS).

2.5. Digestion the Spiked Roasted Coffee Samples

A spiking experiment was done to evaluate the efficiency and accuracy of the the method used. Known amounts of standard metal solutions were added to the roasted coffee samples taking care of the dilution of the final solution. Aliquots of 0.75 mL of 1000 mg/L K, 0.75 mL of 100 mg/L Mg, Ca and Na and 0.3mL of 10 mg/L Mn, Zn, Cu, Pb and Cd were spiked at once in to a 0.3 g of ground roasted coffee samples in the TFM digestion vessel and digested following the same optimized procedure as the unspiked samples.

2.6. Statistical Analysis

The significance of variation between samples was analyzed by student's t-test and one-way ANOVA using Microsoft Excel (Microsoft Excel 13.0 Work Sheet, The Apache Software Foundation, 2007) was used.

3. Results and Discussions

3.1. Method Validation

The method detection limit for the metals in roasted coffee samples (Table 1) were calculated as as given below in equation 1:

$$MDL = t(n-1, 1-\mu = 0.99)(S) \quad (1)$$

Where: MDL = method detection limit t (n-1, 1-µ= 0.99) = students' t value appropriate for a 99% confidence level with (t_7= 2.99, for n= 8) S = standard deviation estimate with n-1 degrees of freedom (for n= 8).

Table 1. *Method detection limit (MDL) for roasted coffee bean samples.*

Elements	K	Mg	Ca	Na	Mn	Zn	Cu	Cd	Pd
MDL(µgg^{-1})	0.07	0.05	0.04	0.06	0.02	0.03	0.02	0.01	0.04

The percentage recoveries were calculated using equation 2 given below.

$$R\,(\%) = \frac{\text{metal conc. in spicked sample} - \text{metal conc. in unspicked sample}}{\text{Conc. of metal spiked}} x\ 100 \quad (2)$$

The percentage recoveries of metals in the spiked roasted coffee samples were found in the range of 95 %−104 % with RSD 3−6% indicated in Table 2.

Table 2. *Recovery test results for the analysis of metals in roasted coffee samples.*

Element	Concentration in the sample (μgg^{-1})[a]	Amount added (μgg^{-1})	Concentration in the spiked sample (μgg^{-1})[b]	Recovery (%)[c]
K	18563	2500	21013±21	98±6
Mg	1992	250	2234±19	97±4
Ca	965	250	1213±12	95±3
Na	446	250	706±20	104±6
Mn	19	10	29±0.8	96±5
Zn	16	10	26±0.6	103±4
Cu	10	10	21±0.5	101±3
Cd	ND	10	10.3±0.3	103±4
Pb	ND	10	10.2±0.2	102±5

[a]Mean concentration of samples, [b]Mean concentration ± SD of spiked samples, [c]Mean recovery ± SD of percentage recoveries, ND= Not detected

3.2. Distribution of Metals in Roasted Coffee Samples

The concentrations of macro-elements (K, Mg, Ca and Na), micro-elements (Mn, Cu and Zn) and non-essential elements (Cd and Pb) determined in four types of roasted coffee samples summarized in Table 3.

Generally, the mean concentration of metals in all roasted coffee samples follows the order: K > Mg > Ca > Na >Mn> Zn > Cu, but the non-essential metals Pb and Cd were found to be below detection limit.

Table 3. *Concentration (mean ± SD, n = 3, μgg^{-1}) of elements in the roasted coffee samples.*

Element	Concentration of metals (μgg-1)a			
	Washed Yirgacheffe roasted coffee	Unwashed Yirgacheffe roasted coffee	Washed Sidama roasted coffee	Unwashed Sidama roasted coffee
K	19610±343	19471±392	18754±462	18563±477
Mg	1970±41	1943±45	2030±98	1992±93
Ca	943±29	931±17	1009±18	976±24
Na	484±85	463±69	475±65	446±73
Mn	23±0.5	21±0.3	20±0.1	19±0.2
Zn	14±0.3	15±0.2	17±0.2	18±0.3
Cu	12±0.3	13±0.2	9±0.3	10±0.1
Cd	ND	ND	ND	ND
Pb	ND	ND	ND	ND

[a]Mean concentration ± standard deviation of each sample analysed.

Washed Yirgacheffe roasted coffee: contains K in highest amount of the macro-elements with concentration 19610±343 μgg^{-1}followed by Mg (1970±41 μgg^{-1}) and Ca (943±29 μgg^{-1}). Na (484±85 μgg^{-1}) was found to be present at the lowest concentration of the macro-elements analyzed (Table 3). Among the concentration of trace micro-elements, Mn (23±0.5 μgg^{-1}) was found in higher amount than others followed by Zn (14±0.3 μgg^{-1}) and Cu (12±0.3 μgg^{-1}).

Unwashed Yirgacheffe roasted coffee: of the macro-elements K with concentration 19471±392 μgg^{-1} was found to be present in the highest level followed by Mg (1943±45 μgg^{-1}), Ca (931±17 μgg^{-1}) and Na (463±69 μgg^{-1}) with the lowest concentration of the macro-elements analyzed (Table 3). Unwashed Yirgacheffe roasted coffee type also contains, Mn with concentration 21±0.3 μgg^{-1}followed by Zn (15±0.2 μgg^{-1}) and Cu (13±0.2 μgg^{-1}).

Washed Sidama roasted coffee: among the macro--elements, K was found in highest amount with concentration 18754±462 μgg^{-1} than Mg (2030±98 μgg^{-1}) and Ca (1009±18 μgg^{-1}). Na with concentration 475±65 μgg^{-1}was found to be present at the lowest concentration of the macro-elements analyzed (Table 3). Washed Sidama roasted coffee also contains Mn with concentration 20±0.1 μgg^{-1}, Zn (17±0.2 μgg^{-1}) and Cu (9±0.3 μgg^{-1}) slightly lower than the micro-elements.

*Unwashed Sidama roasted coffee: t*he fourth which is washed Sidama roasted coffee type also contains K with concentration 18563±477 μgg^{-1} in the highest level followed by Mg (1992±93 μgg^{-1}), Ca (976±24 μgg^{-1}) and Na (446±73 μgg^{-1}) with the lowest concentration of the macro-elements analyzed (Table 3). In this roasted coffee sample Mn with concentration 19±0.2 μgg^{-1}, Zn (18±0.3 μgg^{-1}) and Cu (10±0.1 μgg^{-1}) slightly lower than the microelements.

3.3. Statistical Analysis

The significance of variation in metals concentration between samples was analysed by students t-test and one-way ANOVA. Accordingly, students' t-test shows, for concentration of; K, Mg, Ca and Na no significant difference at p = 0.05 and for concentrations of; Mn, Zn and Cu a significant difference at p = 0.05 was observed between washed and unwashed Yirgacheffe as well as between washed and unwashed Sidama roasted coffee samples respectively.

From one way ANOVA test for significant difference; for concentrations of Mg and Na no significant difference at p = 0.05 and for Mn, Zn and Cu, a significant difference at p = 0.05 was observed between all four roasted coffee samples.

However, for concentrations of K and Ca; a significant difference at p = 0.05 was observed only for both washed Yirgacheffe and Sidama as well as for both unwashed Yirgacheffe and Sidama roasted coffee samples respectively.

3.4. Comparison of the Metal Content of Roasted Coffee Samples with Other Reported Values

In different studies the metal content of roasted coffee samples have been analyzed for both Arabica and Robusta coffee types [9-11]. The composition of Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn have been determined and used as chemical descriptions to differentiate between roasted coffee samples from Arabica and Robusta coffee varieties. According to the report on roasted coffee varieties present in southeast Brazilian market, there is a difference in metal content among the samples of roasted coffee varieties. These variations in metal compositions among samples roasted coffee can indicate the differences in the factors that influence the cultivation of the coffee plant; such as the type of soil, the use of fertilizers with different chemical compositions and the ambient conditions [9].

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. Martin *et al.*[11] have 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 (μgg^{-1}): Ca (970), Cu (13.4), Fe (46.2), K (14930), Mg (1740), Mn (14.1), Na (33.4) and 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) and 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. Ashu and Chandravanshi [13] also determine the concentrations of metals (K, Mg, Ca, Na, Mn, Fe, Cu, Zn, Co, Pb, Cd) in three brands of commercially available roasted Ethiopian coffee powders (Abyssinia, Alem and Pride). The mean concentration of each metal in the three brands of coffee powder samples was (μgg^{-1}): 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) and Co (1.60±0.05) in which both those results are comparable with the present study.

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 macro-elements K > Mg > Ca > Na is in good agreements. Regarding the trace microelements, Mn> Zn > Cu > Co in roasted coffee powder is followed for most reports. Similarly, reports by Ashu and Chandravanshi [13] and Grembecka *et al.* [16-17] shows that toxic elements Pb and Cd were not detectable under their analysis conditions using the FAAS which is in a good agreement with the present study. Generally, the concentration of the macro and micro-elements in both washed and unwashed Yirgacheffe and Sidama roasted coffee samples (present study) were compared to other reported values in Table 4 and 5.

Table 4. *Comparison of the concentrations of macro-elements in roasted coffee beans samples with other reported values.*

Origin	Concentration (μgg^{-1}) of metal in roasted coffee beans				Reference
	K	Mg	Ca	Na	
Ethiopia	18563−19610	1943−2030	931−1009	446−484	Present study
Various origins	11750−15850	800−2840	513−1620	382−459	[16]
Brazil	32500−39800	2120−4150	1110−1890	274−665	[10]
Ivory Coast	14010−14480	1610−1820	940−1220	15.9−21.4	[11]
Ethiopia	14310−19400	5470−6080	500−990	–	[12]
Uganda	14080−14990	1670−1780	1170−1230	11–14	[11]
Ethiopia	14361−14583	1959−1968	843−1045	468−501	[13]

Table 5. *Comparison of the concentrations micro-elements in the roasted coffee bean samples with literature values.*

Origin	Concentration (μgg^{-1})[b] of metal in roasted coffee beans					Reference
	Mn	Zn	Cu	Cd	Pb	
Ethiopia	19−23	14−18	9−13	ND	ND	Present study
Brazil	29−40	3.9−9.8	49−88	0.7−0.9	0.015−0.058	[10]
Ethiopia	22−24	12−19	11−17	ND	ND	[13]
Various origins	16.5−40.6	3.2−16.2	12.1−20.1	ND	ND	[16]
Ethiopia	15−20	6−30	13−28	ND	ND	[12]

[b]Their concentrations were below detection limit, ND = Not detected

4. Conclusions

The closed microwave assisted wet digestion method and determination of selected metals in roasted coffee samples by flame atomic absorption spectroscopic method was found to be efficient. K has high concentration among the macro-elements (Mg, Na and Ca). Moreover, Mn found high level comparing with other micro-elements (Mn, Zn and Cu). In all roasted coffee bean samples the level of toxic elements (Cd and Pb) were avail below the method detection limits. The

levels of both essential and non-essential metals investigated in roasted coffee beans were comparable with that of the rest of the world. It could be suggested that the roasted coffee beans under investigation could be source of dietary minerals and trace metals and 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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