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Determination of trace elements in coffee beans and instant coffee of various origins by INAA

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Extensive use of coffee, by one-third of world's population, entails the evaluation of trace element contents in it. Instrumental neutron activation analysis (INAA) was successfully employed to determine the concentration of 20 trace elements (essential, toxic and nonessential) in four samples of coffee beans of various origins and two instant coffee brands most commonly consumed in Pakistan. This study provides the base-line values of certain toxic and essential elements in coffee. The daily intake of essential and toxic elements through coffee was estimated and compared with the recommended values. The cumulative intake of Mn is four times higher than the recommended value and that of toxic elements is well below the tolerance limits.

Introduction

Human body is continuously exposed to a variety of inorganic elements through food, water and air. There has been increasing interest in the evaluation of the amounts of various trace elements in them because of their nutritive importance and toxicological effects.[1,2] Trace elements are vitally important for various metabolic processes, and toxic elements if present in relatively higher amounts adversely affect these processes.[3,4] Therefore, information about trace element distribution is of significant importance in assessing the adequacy with respect to the intake of essential elements and in evaluating the potential health risks arising from exposure to toxic elements from food and related products.[5] Food[6] being the main source of intake of these elements, it becomes imperative to monitor the concentration of toxic and essential elements in various food items and products of daily consumption. Trace element levels have been measured extensively in individual food articles and integrated human diets.[7–9]

The majority of agricultural products are used for human food and animal feed, others have a unique and specific use due to the pharmacologically active constituents in the plants. Boiling or brewing tea leaves (*Camellia sinensis*), coffe beans (*Coffea sp.*) or cacao beans (*Theobroma cacao*) to ingest the stimulant alkaloid caffeine is a worldwide accepted tradition.[10] The drink made from the roasted and ground beans of the coffee tree, is the favourite hot drink in almost every country in temperate or cold climates.

Coffee growing is one of the main agriculture activities on which many tropical and subtropical countries rely on to earn foreign exchange. Coffee is the second most important product in international commerce on the basis of volume traded, and it is estimated to be the first on the basis of value. The value of coffee imports is estimated to be about $2 billion a year, or 1% of total world trade. Most coffee is consumed in the form of a beverage. Two species of the genus coffea (family *Rubiaceae*), coffea arabica (*Arabica*) and coffea canephora (*Robusta*), are raised in quantity for beans.[11,12] Extensive use of coffee, by one-third of world's population,[12] entails the evaluation of trace element contents in it. Little information is available on the levels of trace element contents in coffee beans of different origins in the literature.

The concentration of trace elements in biological materials can be determined using different analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), particle induced X-ray emission (PIXE), photon activation analysis (PAA), charged particle induced activation analysis (CPAA), etc. Neutron activation analysis (NAA), a well established technique for multielement determination at trace level with high sensitivities,[13–15] has been extensively used in our laboratory for the analysis of high purity materials, ores, rocks and biological materials.[16–18] In the present work, an assessment of elemental profile of coffee beans of four different origins and two instant coffee brands has been carried out by instrumental neutron activation analysis (INAA).

Experimental

Sampling and sample preparation

Samples of Brazilian, Caribbean, Indian and Kenyan coffee beans and two instant coffee brands were collected from local markets of a Rawalpindi/Islamabad area at random in sufficient quantities. The samples of coffee beans were thoroughly washed to remove any surface contamination first with distilled water, then

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with deionized water and thereafter dried with hot air blower. The coffee beans were first freeze-dried and then ground to fine powder. The samples were stored in pre-cleaned polyethylene capped bottles. To avoid contamination special care has been taken wherever necessary for the cleansing of the tools used for sample preparation and sample containers. They were washed with trichloroethylene, acetone and deionized water, sequentially. The reagents used were of ultra-pure grade. All the procedures, up to the final sealing of the samples, were carried out in a clean-bench facility to avoid any possibility of external contamination.

Preparation of the standards

The standards were prepared from stock solutions of the respective elements under investigation containing, 1 mg·cm^{-3} ultra pure spectrographically standardized substances (from Johnson, Matthey & Co., Ltd., London). These solutions were diluted accordingly to give a wide range of standards for each element. The solutions were dried on ashless filter papers, and sealed in polyethylene/quartz capsules for irradiations. Blank filter papers were also irradiated to determine their contributions, and necessary corrections were made. Standards of appropriate concentrations for all elements under investigation were prepared, i.e., according to the level of respective elements in the samples.

Neutron irradiation

Samples, each weighing about 150 mg, were taken in triplicate and heat-sealed in pre-cleaned polyethylene and quartz ampoules for short and long irradiations, respectively. The quartz ampoules were then placed in NRX-type aluminum irradiation capsules and cold-welded. Irradiations were carried out in thermal tubes and core of a 10 MW swimming pool-type research reactor (PARR-I). The thermal neutron flux density at the irradiation site of the reactor was of the order of $7 \cdot 10^{13}$ n·cm^{-2}·s^{-1}. Thermal neutron flux monitors, e.g., Au, Co, and Al foils, and the standards to monitor the fluctuations in the thermal neutron flux gradient were inserted between the samples. The samples, along with the appropriate amounts of standards and the CRMs, namely NBS Orchard Leaves (SRM-1571) and IAEA Mixed Human Diet (H-9), were irradiated from 2 minutes to 12 hours, depending on the requirement. The irradiated samples and standards were transferred to preweighed polyethylene vials and reweighed to determine the exact weight.

Gamma-ray spectrometry

The γ-ray spectra of the samples and standards were measured, after appropriate cooling, for varying times ranging from 2 minutes to 24 hours employing a 4k series 85, a Canberra multichannel analyzer coupled to an Eurisys coaxial 245 cm^3 HPGe detector. The system has a resolution of 1.9 keV for 1332.5 keV γ-peak of ^{60}Co and peak/Compton ratio of 70:1. The data, transferred from the MCA to the central computer facility, were processed using locally developed software. The γ-spectrometry was repeated several times to determine the half-life of each indicator radionuclide.

Results and discussion

The optimized conditions and the nuclear data used for the determination of trace elements in coffee beans and ground branded coffee were the same as described in Reference 14 and are listed in Table 1 with the reference nuclear data.[19] Accordingly, the short-lived indicator radionuclides, i.e., ^{38}Cl, ^{116m}In, ^{56}Mn, ^{42}K and ^{24}Na, were measured employing short irradiations. The relatively long-lived indicator radionuclides, i.e., ^{82}Br, ^{122}Sb, ^{131}Ba, ^{86}Rb, ^{51}Cr, ^{169}Yb, ^{141}Ce, ^{59}Fe, ^{203}Hg, ^{46}Sc, ^{75}Se, ^{65}Zn, ^{134}Cs, ^{60}Co and ^{152}Eu, were measured employing long irradiations and appropriate cooling times. The γ-peaks of all radionuclides, except for ^{65}Zn and ^{203}Hg, were well resolved and free from any serious interference. The full energy peak areas of 1115.5 keV and 279.2 keV from ^{65}Zn and ^{203}Hg, respectively, were determined after subtracting contributions from 1120.5 keV of ^{46}Sc and 279.5 keV of ^{75}Se, respectively. The reliability of the method was checked by analyzing NBS Orchard Leaves (SRM-1571) and IAEA Mixed Human Diet (H-9), employing the above-mentioned set of conditions. Our values are in fairly good agreement with the certified values, as shown in Table 2.

Table 1. Optimum experimental conditions and nuclear data[19] employed in the analysis

Isotope	Half-life	Gamma-peak, keV	Irradiation time	Cooling time
^{38}Cl	37.2 m	1642.4, 2167.5	2 m	30 m
^{116}In	54.15 m	1097.3, 1293.6	2 m	30 m
^{56}Mn	2.58 h	846.6	2 m	2 h
^{42}K	12.4 h	1524.7	2 m	2 h
^{24}Na	15.0 h	1368.5	2 m	2 h
^{82}Br	35.4 h	776.5	24 h	2 d
^{122}Sb	2.7 d	564.1	24 h	2 d
^{131}Ba	11.80 d	496.2	24 h	4 d
^{86}Rb	18.6 d	1078.8	24 h	2 w
^{51}Cr	27.8 d	320.1	24 h	2 w
^{169}Yb	32.02 d	177.2, 197.9	24 h	2 w
^{141}Ce	32.38 d	145.4	24 h	2 w
^{59}Fe	44.6 d	1099.3, 1291.6	24 h	2 w
^{203}Hg	46.6 d	279.2	24 h	2 w
^{46}Sc	83.9 d	889.3, 1120.5	24 h	2 w
^{75}Se	120.0 d	264.5, 135.9	24 h	2 w
^{65}Zn	243.8 d	1115.5	24 h	2 w
^{134}Cs	2.04 y	795.8	24 h	2 w
^{60}Co	5.26 y	1173.2, 1332.5	24 h	2 w
^{152}Eu	13.2 y	1408.0	24 h	2 w

Table 2. Analysis of NBS and IAEA reference materials (in μg/g)*

Element	Orchard leaves (SRM-1571)		Mixed human diet (H-9)	
	Our values	NBS values	Our values	IAEA values
Fe	298 ± 15	300 ± 20	32.9 ± 2.0	33.5 ± 2.2
Mn	92 ± 3	91 ± 4	12.1 ± 0.9	11.8 ± 0.8
Co[a]	197 ± 7	(200)	50 ± 6	43 ± 5
Zn	23 ± 4	25 ± 3	27.3 ± 1.5	27.5 ± 1.8
Na	85 ± 4	82 ± 6	8120 ± 580	8100 ± 690
K	14595 ± 400	14700 ± 300	8295 ± 620	8300 ± 664
Hg[a]	149 ± 20	155 ± 15	5.0 ± 1.0	5.0 ± 1.0
Se	0.1 ± 0.01	0.08 ± 0.01	0.12 ± 0.01	0.11 ± 0.01
As[a]	9 ± 2	10 ± 2	90 ± 30	88 ± 32
Br	9.8 ± 1.0	(10)	8.1 ± 0.6	7.5 ± 0.68
Cl	678 ± 30	(690)	12590 ± 1570	12500 ± 1500
Cs	0.04 ± 0.002	(0.04)	0.03 ± 0.002	(0.025)
Rb	11 ± 2	12 ± 1	8.2 ± 0.5	8.0 ± 0.6

* Error quoted is the standard deviation.
Values in parentheses are uncertified.
[a] Concentrations in ng/g.

The concentration of 20 elements were determined and the analytical results, as averages of at least five determinations with standard deviations around mean values, are given in Table 3. Indian coffee beans are comparatively rich in Cr, Fe and Co whereas Brazilian coffee beans are rich in Mn, Zn, Ba and K. Sodium contents in Indian and Kenyan coffee beans are comparable, while the Brazilian beans contain very low amount of Na. Indian beans have exceptionally higher amounts of Se (100 ng/g) as compared to the rest of the varieties of beans ranging from 14 to 27 ng/g. Caribbean beans contain higher amounts of Sb, Hg and Br, whereas Cl is higher in Brazilian beans. Cesium contents are higher in Brazilian and Caribbean beans by a factor of 4–5 as compared to the Indian and Kenyan beans. Indium concentration is higher in Brazilian beans whereas rest of the non-essential elements, i.e., Rb, Eu, Yb, Ce and Sc are almost comparable in all of the four varieties investigated. Comparing the two blended instant coffee brands coded as GBN and MW, GBN has higher concentrations of Cr, Fe, Zn, Na, and K whereas MW contains higher amounts of Mn, Co, Sb and Se. Mercury contents are higher in MW by a factor of >2 as compared to GBN, while the remaining elements are more or less comparable. It may be noted that with the exception of Ba, Sb, Se, Cl, Br, Cs and In, the concentrations of the rest of elements are higher in blended instant coffee as compared to the coffee beans which may be attributed to the treatment steps involved in the processing of raw coffee beans (percolation).

The average/day/person intake values for essential and toxic elements through the consumption of coffee were estimated assuming that the daily intake of coffee beans is 10 g (dry weight). The estimated values are given in Table 4 along with the suggested daily requirement/tolerance limits.[20] The intakes of Zn, K, and Ba from Brazilian coffee beans, Cr, Fe and Co from Indian coffee beans and Mn and Na from Kenyan coffee beans are higher. As far as the toxic elements are concerned, the intake of Se and Hg is maximum through Caribbean coffee beans. However, their daily intake is well below the daily tolerance[20] levels. The intake of most of the essential trace elements is higher through the instant coffee brands as compared to the coffee beans. The intake of Se and Hg through MW instant coffee is higher than the GBN instant coffee brand.

Table 3. Elemental concentrations* in coffee beans of various origins and in instant coffee

Element	Brazilian coffee beans	Caribbean coffee beans	Indian coffee beans	Kenyan coffee beans	GBN instant coffee	MW instant coffee
Cr, ng/g	29 ± 2	19 ± 2	89 ± 8	60 ± 5	152 ± 13	62 ± 5
Mn, μg/g	48.6 ± 3.9	28.3 ± 2.4	24.6 ± 2.1	49.5 ± 4.2	19.1 ± 1.7	23.2 ± 1.9
Fe, μg/g	34.7 ± 2.9	28.9 ± 2.4	72.0 ± 5.9	30.0 ± 2.6	83.2 ± 6.9	62.3 ± 5.1
Co, ng/g	200 ± 17	59 ± 5	241 ± 20	197 ± 16	36 ± 3	322 ± 27
Zn, μg/g	10.7 ± 0.9	4.8 ± 0.4	5.1 ± 0.4	5.3 ± 0.4	37.7 ± 3.2	26.5 ± 2.2
Ba, μg/g	4.4 ± 0.3	3.4 ± 0.3	1.7 ± 0.1	1.6 ± 0.1	2.8 ± 0.2	3.2 ± 0.3
Na, μg/g	7.6 ± 0.6	14.9 ± 1.2	21.3 ± 1.8	26.2 ± 2.3	63.1 ± 5.6	57.2 ± 4.8
K, %	2.4 ± 0.2	2.0 ± 0.2	1.7 ± 0.1	1.9 ± 0.1	3.3 ± 0.3	2.3 ± 0.2
Sb, ng/g	32 ± 3	98 ± 8	87 ± 7	49 ± 4	34 ± 3	52 ± 4
Se, ng/g	14 ± 1	27 ± 2	100 ± 8	15 ± 1	23 ± 2	96 ± 7
Hg, ng/g	6 ± 1	16 ± 2	9 ± 1	7 ± 1	9 ± 1	22 ± 2
Cl, μg/g	198 ± 17	146 ± 12	117 ± 9	49 ± 4	83 ± 7	77 ± 6
Br, μg/g	2.0 ± 0.2	8.5 ± 0.7	4.3 ± 0.4	0.70 ± 0.06	1.4 ± 0.1	1.2 ± 0.1
Cs, ng/g	102 ± 8	93 ± 7	26 ± 2	16 ± 2	56 ± 5	48 ± 4
In, ng/g	81 ± 7	35 ± 3	13 ± 1	24 ± 2	42 ± 4	32 ± 3
Rb, μg/g	12.3 ± 1.1	14.8 ± 1.2	18.3 ± 1.6	17.1 ± 1.5	15.5 ± 1.4	16.5 ± 1.5
Eu, ng/g	9 ± 1	11 ± 1	15 ± 2	8 ± 1	12 ± 1	17 ± 2
Yb, ng/g	10 ± 1	17 ± 2	9 ± 1	22 ± 2	29 ± 3	16 ± 2
Ce, ng/g	50 ± 4	39 ± 3	54 ± 5	31 ± 3	41 ± 3	29 ± 3
Sc, ng/g	8 ± 1	13 ± 1	14 ± 2	10 ± 1	19 ± 2	15 ± 2

* Averages of five determinations and error quoted are the standard deviation.
All values expressed on dry weight basis.

Table 4. Intake values (in μg/day, person) of some trace elements through coffee consumption*

Element	Brazilian coffee beans	Caribbean coffee beans	Indian coffee beans	Kenyan coffee beans	GBN instant coffee	MW instant coffee	D R/T**
Cr	0.29	0.19	0.89	0.60	1.52	0.62	0.01–0.2
Mn	486	283	246	495	191	232	0.5–5
Fe	347	289	720	300	832	623	10–20
Co	2	0.59	2.41	1.97	0.36	3.22	0.14–1.7
Zn	107	48	51	53	377	265	8–15
Na	76	149	213	262	631	572	115–3000
K	24000	20000	17000	19000	33000	23000	300–5000
Ba	44	34	17	16	28	32	50–510
Se	0.14	0.27	1	0.15	0.23	0.96	200
Hg	0.06	0.16	0.09	0.07	0.09	0.22	40
Sb	0.32	0.98	0.87	0.49	0.34	0.52	–
Cl	1980	1460	1170	490	830	770	200–500

* D R/T= Daily requirement/tolerance expressed in mg/day, person.[20]
** Assuming daily/person consumption of coffee = 10 g.
All values expressed on dry weight basis.

Conclusions

This study assessed the content of 20 elements in six coffee varieties. The study provides base-line values of certain toxic and essential elements in four varieties of coffee beans and two most commonly used brands of instant coffee. The estimation of probable intake of the toxic trace elements indicates that their amounts are well below the daily tolerance limits.

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