Elemental Profiling of Indian Tea by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

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INTRODUCTION

Tea (*Camellia sinensis*), black and green, is one of the most popular beverages. Drying and roasting produces green tea, whereas black tea is obtained after a fermentation process. The economic and social interest in tea is clear since about 20 billion cups of tea are consumed daily around the world (1-2). The medicinal value of tea for prevention and treatment of many health problems has also become more and more commonly known (3). Tea contains flavonoids, minerals, and trace elements that are essential to human health. Current studies show that tea has specific antioxidants and health-promoting ingredients. Studies on green tea have shown that it possesses antioxidative, antimutagenic, and anticarcinogenic activities (4-7). Polymeric polyphenols are the most abundant pigments in black tea. Studies on isolation and chemical characterization of these polyphenolic compounds are carried out for their chemopreventive effects (8). The main sources of heavy metals in plants are their growth media, nutrients, water, and soil. Consequently, differences in the elemental content are expected. Other sources may include pesticides and fertilizers. Elevated heavy metal levels cause damage to plants such as delayed flowering, lower chlorophyll con-

ABSTRACT

Fourteen elements (Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, and Zn) in 56 tea samples from different geographical regions of India (Assam, Darjeeling, Munnar, and Kangra) were quantitatively determined using inductively coupled plasma optical emission spectrometry (ICP-OES) after microwave digestion. Validation of the analytical methodology was carried out using Certified Reference Material GSB-7 Tea Leaves.

The tea samples were found to contain Al (0.421–4.139), Ca (3.513–9.495), Fe (0.096–453), K (9.046–34.967), Mg (0.414–3.868), and Mn (0.157–1.021) in mg/g levels, while B (2.7–39.0), Ba (29.0–72.9), Cr (3.7–10.5), Cu (2.5–31.9), Na (10.2–80.4), Ni (2.6–11.4), Sr (10.9–47.3), and Zn (16.4–50.7) were at µg/g levels.

The analytical data for the tea leaves from Assam and Darjeeling agreed with those reported in the literature. To the best of our knowledge, the data on the elemental content of tea samples from Kangra (Himachal Pradesh) are reported for the first time. Significant differences in the metal concentrations of virgin tea leaves vs. the processed tea leaves were observed. A correlation analysis of the elemental data was also carried out.

tent and reduction in the number and quality of shoots (9). Along with essential elements, tea may contain some non-essential elements, e.g., heavy elements such as As and Pb which have toxicological effects.

In India, tea is planted in Assam and Darjeeling (both in the north-east), Nilgiris and Munnar (southern parts), and Himachal Pradesh (north-west). Since these locations are geographically distinct, there could be differences in the elemental profiling of the tea samples due to the geochemistry of the soil and other factors. Tea grown in Darjeeling is of great demand worldwide due to its unmatched flavor and taste, its market price is very high and chances of adulteration and fraud are possible. Therefore, determination of the elemental composition and geographical origin of food and related products is essential. To the best of our knowledge, no systematic geochemical studies of soils and water samples in the mentioned areas of India are available for comparison. Several researchers have carried out analyses of different tea samples grown in their country, using analytical techniques such as atomic absorption spectroscopy (AAS) (10), inductively coupled plasma optical emission spectrometry (ICP-OES) (11), inductively coupled plasma mass spectrometry (ICP-MS) (12), total reflection X-ray fluorescence spectrometry (TXRF) (13).

In the present work, the quantitative determination of 14 elements (Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, and Zn) in different

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tea samples was carried out using ICP-OES analysis due to its simplicity, speed of analysis, as well as its capability to provide multi-elemental data. Virgin tea leaves as well as processed tea samples were collected from the different tea plantation regions in India. The organic content of the Kangra tea leaves has been reported previously (14-15) while, to the best of our knowledge, the elemental content of Kangra tea samples are reported for the first time in the present study.

EXPERIMENTAL

Instrumentation

The digested samples were analyzed using a Model ULTIMA - IITM (M/s. Jobin Yvon, France) inductively coupled plasma optical emission spectrometer having a resolution of 5 picometer. A multi-element standard solution was introduced into the ICP for auto-searching of the analytical lines. Profiling of the spectral lines was checked using the tea reference standard and taking into account sensitivity and spectral interferences; the analytical lines were chosen for analysis of the samples. The analytical lines selected for the quantification of the different elements, and the ICP-OES operating conditions are listed in Table I.

Calibration curves were obtained in the concentration range of 0.1 µg/g to 10 µg/g for the 14 elements (Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, and Zn) using the ICP-OES multi-elemental standards. Ca, K, and Mg were determined after a 100-fold dilution of the sample solutions. The digested solution of each sample was analyzed three times by ICP-OES. The analysis of the certified reference material was performed in a similar manner in order to validate the analytical method.

Samples

Fifty-six tea samples of different origin were collected from the different tea plantations in India. For comparison purposes, tea samples were also procured from the supermarket. Details of the different samples, such as sample origin, are shown in Table III.

Standard Solutions and Reagents

Multi-elemental ultrapure ICP standard solutions (1000 µg/L, Merck, Darmstadt, Germany), digested samples, and standard stock solutions were diluted, when necessary, using 1M HNO₃. Suprapur[®] grade 65% HNO₃ and 50% H₂O₂ (Merck) were used for the quantitative digestion and dissolu-

tion of the tea samples. Ultrapure water (18 MΩ.cm⁻¹, Milli-QTM purification device, Millipore Corporation, Bengaluru, India) was used for preparing the dilute acids. The certified reference material (CRM) GSB-7 Tea Leaves was obtained from the Bureau of Analyzed Samples (Middlesbrough, UK).

Sample Preparation

A Multiwave[®] 3000 microwave digestion system (Anton Paar, Graz, Austria), equipped with a temperature and pressure regulator, was used for digestion of the tea samples. The dried samples were digested in duplicate. Around 250 mg of each sample was taken into pre-cleaned PTFE vessels. Microwave digestion was carried out using a

TABLE I
ICP-OES Operating Parameters

Power	1000 W
Normal speed of pump	20 rpm
Plasma gas flow rate	12 L/min
Auxiliary gas flow rate	1 L/min
Cooling gas flow rate	0.2 L/min
Nebulizer	Concentric, Quartz
Nebulization flow rate	0.02 L/min
Nebulizer pressure	1 bar
Calibration range	0.1-10 µg/g

Element	Detection Wavelength (nm)	Detection Limit (µg/L)
Al	309.2	6.4
B	249.7	7.6
Ba	455.4	2.3
Ca	317.9	4.5
Cr	283.5	2.1
Cu	324.7	2.2
Fe	259.9	2.0
K	766.4	54
Mg	279.5	1.5
Mn	257.6	2.0
Na	589.0	9.4
Ni	221.6	2.0
Sr	407.7	1.8
Zn	213.9	2.0

mixture of 3 mL HNO₃ and 1 mL H₂O₂. For digestion, maximum power of 500 watts was used, which yielded a maximum temperature of 190 °C and a pressure of 25 bars. The total run time for the program was about 105 minutes. After digestion, the sample vessels were cooled, vented, and opened. The clear solution was then transferred into pre-leached polypropylene bottles. All sample preparation steps were carried out in a cleanroom environment lab of Class -100 in order to avoid any contamination. The samples were then diluted to 25 mL with 1 M HNO₃ for ICP-OES analysis. Validation of the analytical procedure was performed using CRM GSB-7 Tea Leaves.

Data Analysis

For statistical analyses, Single Factor Analysis of Variance (ANOVA), Student's *t*-test, and correlation analysis were applied to the obtained data to establish the significant relation between two variables. Single Factor Analysis of Variance, a statistical tool, performs a simple analysis of variance on data for two or more samples and compares the mean of two or more than two sets of samples. (16)

The Student's *t*-test is used to establish whether the means are statistically different or not. When comparing two sets of data, where *s*₁ and *s*₂ are dissimilar according to the F test, *t*_{cal} is calculated by using the following equations (Eq.):

$$t_{cal} = \frac{|x_1 - x_2|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \quad \text{Eq. (1)}$$

where *x*₁ = mean of data set 1,
*x*₂ = mean of data set 2,
*n*₁ = number of data in set 1,
*n*₂ = number of data in set 2,
*s*₁ = standard deviation of set 1,
*s*₂ = standard deviation of the data

Set 2, applicable number of the degrees of freedom, *df*, is calculated as:

$$df = n_1 + n_2 - 2 \quad \text{Eq. (2)}$$

The correlation analysis is a statistical tool particularly useful when there are more than two measurement variables for each of the *N* subjects. The output, correlation coefficient (*r*), is a measure of the extent to which two measurement variables "vary together." The value of the correlation coefficient must be between -1 (indicates negative correlation) and +1 (indicates positive correlation), while the '0' value of the correlation coefficient indicates no correlation. The correlation coefficient is calculated by using following formula:

$$\text{Corr}_{X,Y} = \frac{\text{Cov}(X,Y)}{\sqrt{\text{Var}(X) \text{Var}(Y)}} \quad \text{Eq. (3)}$$

In Equation 3, *Corr*_{X,Y} = correlation

coefficient (*r*), *Cov* (*X*,*Y*) = Covariance between two variables, *Var* (*X*) and *Var* (*Y*) = Variance of the data for variable *X* and *Y*.

RESULTS AND DISCUSSION

The analytical results of the present work for CRM GSB-7 Tea Leaves are given in Table II listing the mean elemental concentrations, standard deviations, certified/information values, and percentage RSD. High precision in the data are suggested by the RSDs (%) which are <10% for most of elements, except for Ba and Fe. The concentrations of the major and trace elements (Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, and Zn) in 56 samples from different locations in India (Assam, Darjeeling, Munnar, and Kangra) are listed in Table III. This table presents the concentration ranges, average concentrations, and standard deviations obtained for the different elements in the tea samples. It can be seen that large standard deviations are obtained, which

TABLE II
Elemental Concentrations of CRM GSB-7 Tea Leaves

Element	GSB-7 Tea Leaves (n =3)*		
	Observed Value (µg/g), (<i>x</i> ± <i>σ</i>)	Certified Value (µg/ g), (<i>μ</i> ± <i>σ</i>)	RSD (%)
Al	0.085±0.001	0.094±0.009	1.1
B	11±1	14±1	9
Ba	7.6±1.1	9.6±0.5	14
Ca	2414±126	3260±80	6
Cr	ND	0.45±0.1	-
Cu	17.1±0.2	18.6±0.7	1.1
Fe	262±51	242±18	19
K	16181±553	16300±700	4
Mg	1556±180	1860±110	1.1
Mn	510±8	500±20	2
Na	65±7	90±10	10
Ni	ND	3.4±0.3	-
Sr	4.3±0.4	9.1±1.2	8
Zn	51±0.3	51±2	0.5

Concentration in mean value ± S.D.

*Values in parentheses indicate the number of samples analyzed.

ND = Not determined.

indicates that there are large differences in the samples originating from the same geographical origin.

The elements K, Ca, Mg, Mn, and Fe were found in mg/g levels of dried samples, while the other elements were in trace concentration ($\mu\text{g/g}$) levels. Highest average concentration of Al was found in Kangra tea samples followed by Munnar, Darjeeling, and Assam. Kangra tea samples were found to be rich in Al, B, Mn, and Na compared to other regions, but depleted in K content as compared to those from Assam Darjeeling and Munnar. Among all four regions, the Assam tea samples were found rich in K content. Calcium content was highest in the Munnar tea samples, followed by Kangra, Assam, and Darjeeling. Regular variations were observed for Ba, Cu, Fe, Ni, and Zn from all four regions. The magnesium concentration did not show significant variation. Strontium concentration was found in the order Munnar > Assam > Kangra > Darjeeling. Chromium was found in the Munnar and Assam samples only, but was below the detectable limit of the ICP-OES for the Darjeeling and Kangra tea samples.

Table IV shows a comparison of the elemental concentrations found in the present work with those reported in the literature (2, 9, 17-19). It can be seen that the values reported in the present work are in general agreement with those reported in the literature.

It was considered worthwhile to compare the differences between virgin tea leaves and processed tea leaves. In general, only processed tea samples are available for analysis. Considerable variation in the elemental concentrations between the virgin tea leaves and processed tea leaves were observed. Table V shows the data on the average concentrations and the related standard deviation of 14 elements

in fresh and processed Indian tea samples. The processed tea samples showed a considerable increase in Al, Ba, Fe, Mn, and Na concentration in comparison to fresh tea leaves from all regions. No considerable change in concentration was observed for B, Ce, K, Mg, Ni, Sr, and Zn. Chromium was found in processed tea samples from Assam and Munnar, while virgin tea samples from these regions and processed tea samples from Darjeeling and Kangra did not show any Cr. Kangra fresh tea samples showed higher concentrations of Al, B, Fe, and Sr in comparison to processed tea samples.

A comparison was also made between two types of teas (black and green) because there is a significant difference in the production methods employed. Green tea is produced by drying or firing plucked tea leaves without fermentation, while black tea production involves plucking of the leaves, withering in a tray, rolling in machinery, followed by fermentation in large-sized containers and subsequent drying (20).

A study of the differences in concentrations of elements in black tea and green tea from Munnar was carried out. It was found that the concentrations of Al, Fe, Mn, and Sr were significantly higher in black tea in comparison to the green tea samples. The calculated values of t for Al (3.4), Fe (4.2), Mn (3.2), and Sr (3.0) is higher than the t -critical value of 2.44 ($P = 0.05$).

In the Munnar black tea samples, Al ($1367 \pm 124 \mu\text{g/g}$) was found to be higher than in the green tea samples ($840 \pm 306 \mu\text{g/g}$). Similarly, boron (B) was found to be higher in the black tea samples ($17.3 \pm 1.7 \mu\text{g/g}$) in comparison to the green tea samples ($14.9 \pm 1.1 \mu\text{g/g}$). Krejčová and Černohorský reported higher concentrations of B ($9.2 \pm 0.42 \mu\text{g/g}$) in black tea than in green tea ($5.5 \pm 0.15 \mu\text{g/g}$)

(21). The concentration of Mn in green tea samples was $283 \pm 124 \mu\text{g/g}$, while in black tea it was twice as high ($499 \pm 60 \mu\text{g/g}$). The concentrations of Fe, Na, and Sr in black tea samples were $243 \pm 64 \mu\text{g/g}$, $41.5 \pm 8.4 \mu\text{g/g}$ and $42.5 \pm 4.3 \mu\text{g/g}$, respectively, whereas the green tea samples showed a decrease in the concentrations of these elements ($180 \pm 7 \mu\text{g/g}$ Fe, $30.3 \pm 8.1 \mu\text{g/g}$ Na, and $28.5 \pm 8.3 \mu\text{g/g}$ Sr).

Chromium was detected only in Assam black tea ($11.9 \pm 8.4 \mu\text{g/g}$), while for the black tea from Darjeeling Cr it was $14.2 \pm 10.5 \mu\text{g/g}$. The increase in elemental concentrations found in black tea and processed black tea may be due to the machinery used during processing such as cutting of the leaves, drying, roasting, grinding, fermenting, and converting it into CTC (Crushed Torn and Curled) granule form (22).

The concentration data obtained for tea leaves samples from Assam, Darjeeling, Munnar, and Kangra were subjected to statistical analysis and correlation coefficients were determined. With the exception of Mg, single factor analysis of variance (ANOVA) showed statistically significant differences in the mean concentrations of Al, B, Ba, Ca, Cu, Fe, K, Mn, Na, Ni, Sr, and Zn for the Assam, Darjeeling, Munnar and Kangra tea samples ($F_{\text{calculated}} > F_{\text{critical}}$, $p < 0.05$).

Table VI shows the correlation coefficients observed for the different element pairs of the tea leave samples. Strong correlation was observed among different elements. For instance, Al is strongly positively correlated with B, Na, and Mn ($r = 0.76-0.89$) and negatively correlated with K ($r = -0.75$). Barium is correlated with Fe and Ni ($r = 0.75-0.90$). Potassium-manganese and potassium-sodium pairs show negative correlations ($r = -0.57$ to -0.84). Iron shows positive correlation with Ni and Sr

TABLE III
Observed Concentration Range and Average Values (µg/g) in Tea Samples
From Assam, Darjeeling, Munnar, and Kangra Regions of India

Element	Assam (n=18)		Darjeeling (n=15)		Munnar (South India) (n=9)		Kangra (n=14)	
	Observed Range	Mean Conc. ± S.D.	Observed Range	Mean Conc. ± S.D.	Observed Range	Mean Conc. ± S.D.	Observed Range	Mean Conc. ± S.D.
Al	421-915	678±162	530-1410	801±264	517-1646	1105±395	803-4139	2176±1330
B	4.8-16.3	10.1±3.6	2.7-13.3	8.3±3.1	11.5-19.2	16.0±2.2	14.6-39.0	21.1±7.1
Ba	39.3-65.6	47.7±7.1	29.0-53.3	39.3±9.3	32.2-72.9	51.4±13.9	31.0-54.4	42.3±6.7
Ca	4290-8704	5809±1122	4316-9334	5528±1344	3513-9125	7478±1669	4862-9495	6074±1349
Cr	3.7-8.2	4.8±1.90	ND	ND	8.0-26.3	14.22±10.5	ND	ND
Cu	7.3-29.7	16.2±4.8	5.8-30.1	19.2±7.7	14.2-31.9	21.8±6.6	2.5-18.6	10.4±5.8
Fe	100-279	152±54	96-453	289±106	111-318	196±72	109-356	187±64
K	16922-34967	21875±3751	16706-23159	19470±1898	15354-19219	17682±1450	9046-18879	14402±3904
Mg	1711-3868	2516±467	414-2861	2267±596	1940-2353	2203±172	2150-2696	2490±164
Mn	273-934	650±175	229-543	396±75	157-547	367±139	429-1021	801±190
Na	21.0-54.6	31.1±11.1	10.2-43.5	18.4±10.1	22.9-48.0	34.1±9.0	76.4-80.4	78.1±1.4
Ni	3.7-11.4	7.2±2.2	1.3-8.0	4.6±1.9	4.2-11.4	6.3±2.2	2.6-5.7	4.4±1.5
Sr	15.5-33.4	24.3±4.8	10.9-27.5	17.8±5.2	14.6-47.3	34.4±9.7	13.0-24.9	18.5±3.7
Zn	22.6-35.9	28.1±4.1	19.1-50.7	35.9±9.1	24.5-37.1	31.0±4.2	16.4-44.9	27.9±8.5

N.D. = Not detected by ICP-OES.

Note: Types of samples analyzed: Assam = Black tea (16) + Green tea (2) = 18, Darjeeling = Green tea (15), Munnar = Black tea (4) + Green tea (5) = 9, Kangra = Green tea (14), Total number of tea samples analyzed = 56.

TABLE IV
Comparison of Elemental Concentrations (µg/g) in Tea Samples with Data Reported by Other Researchers

Element	Assam Region				Darjeeling Region				Southern India	
	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	GFAAS
	Present Work (18)*	Pedro et al. (2001) (2)*	Malik et al. (2008) (2)*	Lamble et al. (1995) (3)*	Present Work (15)*	Pedro et al. (2001) (1)*	Malik et al. (2008) (5)*	Lamble et al. (1995) (3)*	Present Work (9)*	Seenivasan et al. (2008) (15)*
Al	678±162	492±25	249.5±54.4	687	801±264	465	176±42	619	1105±395	NA
B	10.1±3.6	NA	19.5±0.8	NA	8.3±3.1	NA	19.6±7.4	NA	16.0±2.2	NA
Ba	47.7±7.1	6.3±1.5	NA	33.3	39.3±9.3	10.2	NA	35.1	51.4±13.9	NA
Ca	5809±1122	4201±479	6577±142	4249	5528±1344	3844	4303±458	4486	7478±1669	NA
Cr	4.8±1.90	NA	NA	NA	NA	NA	NA	NA	14.22±10.5	11.4±2.6
Cu	16.2±4.8	15.9±0.57	34.9±2.1	28.4	19.2±7.7	24.4	38.6±16.8	21.0	21.8±6.6	26.9±1.5
Fe	152±54	99.3±12.7	833±114	NA	289±106	17.9	85.7±14.5	NA	196±72	NA
K	21875±3751	16838±1153	20647±2975	NA	19470±1898	16359	21985±1596	NA	17682±1450	NA
Mg	2516±467	2016±156	2306±252	2171	2267±596	1872	2413±229	2433	2203±172	NA
Mn	650±175	479.0±67.6	445±202	734	396±75	460	398±68	551	367±139	NA
Na	31.1±11.1	57.1±27.2	NA	NA	18.4±10.1	54.5	NA	NA	34.1±9.0	NA
Ni	7.2±2.2	NA	4.5±2.3	NA	4.6±1.9	NA	6.2±1.6	NA	6.3±2.2	1.9±0.4
Sr	24.3±4.8	17.2±1.8	NA	NA	17.8±5.2	10.7	NA	NA	34.4±9.7	NA
Zn	28.1±4.1	25.1±1.7	28.0±0.9	31.3	35.9±9.1	37.7	31.9±7.2	32.8	31.0±4.2	NA

Concentration in mean value ± S.D.

*Values in parentheses indicate the number of samples analyzed.

TABLE V
Observed Mean Concentration in Fresh and Processed Tea Samples ($\mu\text{g/g}$)
From Assam, Darjeeling, Munnar, and Kangra Regions of India

Element	Assam		Darjeeling		Munnar (South)		Kangra	
	Virgin Tea (n=2)*	Processed Tea (n=16)*	Virgin Tea (n=2)*	Processed Tea (n=13)*	Virgin Tea (n=2)*	Processed Tea (n=7)*	Virgin Tea (n=6)*	Processed Tea (n=8)*
Al	461 $\pm$ 56	762 $\pm$ 199	634 $\pm$ 20.7	803 $\pm$ 319	526 $\pm$ 12	1271 $\pm$ 255	1847 $\pm$ 1399	1061 $\pm$ 188
B	6.1 $\pm$ 1.7	10.5 $\pm$ 3.5	8.30 $\pm$ 1.1	8.6 $\pm$ 2.8	15.9 $\pm$ 1.8	16.0 $\pm$ 2.4	18.7 $\pm$ 8.5	16.4 $\pm$ 1.3
Ba	46.1 $\pm$ 6.5	61.0 $\pm$ 5.2	29.27 $\pm$ 3.8	41.7 $\pm$ 10.5	43.1 $\pm$ 7.7	53.8 $\pm$ 14.7	37.80 $\pm$ 13.3	39.8 $\pm$ 4.3
Ca	5158 $\pm$ 1197	5890 $\pm$ 1125	4628 $\pm$ 364.8	5528 $\pm$ 1732	7358 $\pm$ 338	7514 $\pm$ 1921	5293 $\pm$ 2334	5317 $\pm$ 397
Cr	ND	11.9 $\pm$ 8.4	ND	ND	ND	14.22 $\pm$ 10.5	ND	ND
Cu	21 $\pm$ 12.2	15.5 $\pm$ 3.6	3.8 $\pm$ 0.8	18.2 $\pm$ 6.0	14.3 $\pm$ 0.18	23.9 $\pm$ 5.8	12.7 $\pm$ 8.0	15.1 $\pm$ 2.9
Fe	125 $\pm$ 35	205 $\pm$ 108	196 $\pm$ 8.8	321 $\pm$ 101	166 $\pm$ 5	206 $\pm$ 83	191 $\pm$ 96	184 $\pm$ 82
K	19384 $\pm$ 3481	22186 $\pm$ 3770	18381 $\pm$ 2959	20453 $\pm$ 1910	15624 $\pm$ 381	18271 $\pm$ 982	12856 $\pm$ 6043	17670 $\pm$ 797
Mg	2489 $\pm$ 236	2520 $\pm$ 493	2414 $\pm$ 44.0	2591 $\pm$ 165	2383 $\pm$ 103	2152 $\pm$ 155	2214 $\pm$ 852	2502 $\pm$ 145
Mn	312 $\pm$ 85	692 $\pm$ 131	229 $\pm$ 1.4	413 $\pm$ 58	157 $\pm$ 10	428 $\pm$ 84	752 $\pm$ 312	760 $\pm$ 224
Na	22.3 $\pm$ 0.6	32.8 $\pm$ 11.3	25.98 $\pm$ 0.8	28.5 $\pm$ 36.8	38.9 $\pm$ 0.4	32.7 $\pm$ 9.8	65.1 $\pm$ 33.8	77.5 $\pm$ 1.2
Ni	ND	7.2 $\pm$ 2.1	3.46 $\pm$ 0.5	3.4 $\pm$ 1.0	4.9 $\pm$ 0.4	6.7 $\pm$ 2.3	4.7 $\pm$ 2.4	5.1 $\pm$ 0.6
Sr	20.8 $\pm$ 7.6	24.7 $\pm$ 4.3	17.53 $\pm$ 3.2	19.7 $\pm$ 5.9	28.8 $\pm$ 5.3	35.9 $\pm$ 10.3	22.1 $\pm$ 9.4	18.3 $\pm$ 4.2
Zn	28.4 $\pm$ 6.1	27.9 $\pm$ 4.1	19.15 $\pm$ 5.0	35.9 $\pm$ 7.7	28.7 $\pm$ 1.8	31.6 $\pm$ 4.5	25.5 $\pm$ 10.4	29.5 $\pm$ 3.6

Concentration in Mean Value $\pm$ S.D.

N.D. = Not detected by ICP-OES.

*Values in parentheses indicate the number of samples analyzed.

TABLE VI
Inter-elemental Correlation Coefficient Matrix for Virgin Indian Tea Samples

Element	Al	B	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Ni	Sr	Zn
Al	1.00	0.89	-0.30	0.16	-0.11	0.15	-0.75	0.40	0.81	0.76	-0.22	0.21	-0.12
B		1.00	-0.32	0.14	-0.21	0.03	-0.62	0.37	0.61	0.67	-0.16	0.26	-0.25
Ba			1.00	-0.40	-0.12	0.75	-0.09	-0.28	0.18	-0.21	0.90	0.38	0.28
Ca				1.00	-0.35	-0.28	-0.47	0.22	0.16	-0.14	-0.31	-0.02	-0.02
Cu					1.00	0.01	0.29	0.47	-0.32	0.29	-0.26	0.06	0.71
Fe						1.00	-0.49	-0.20	0.44	0.36	0.75	0.66	0.41
K							1.00	-0.30	-0.84	-0.57	-0.17	-0.45	-0.10
Mg								1.00	0.21	0.35	-0.43	-0.03	0.34
Mn									1.00	0.47	0.23	0.17	-0.09
Na										1.00	-0.14	0.40	0.17
Ni											1.00	0.34	0.11
Sr												1.00	0.52
Zn													1.00

The numbers in bold indicate good correlation between the elements (i.e., correlation coefficient greater than or equal to ± 0.5).

($r = 0.66-0.75$). Similarly, boron-potassium, boron-sodium, boron-manganese, and copper-zinc pairs showed correlations.

CONCLUSION

In this study, 14 elements (Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, and Zn) were determined in 56 tea leave samples grown in different regions of India (Assam, Darjeeling, Munnar, and Kangra). It was found that all tea samples are a good source of the essential elements Ca, K, Mn, and Fe. Tea leave samples from Kangra were analyzed for the first time in the present work. Significant variation in the concentrations of most elements (Al, B, Ba, Ca, Cu, Fe, K, Mn, Na, Ni, Sr, and Zn) were observed, except for Cr and Mg which showed no significant variation for teas from any of the regions.

The tea samples were found to contain the following elements:

•Al (0.421–4.139), Ca (3.513–9.495), Fe (0.096–453), K (9.046–34.967), Mg (0.414–3.868), and Mn (0.157–1.021) at mg/g levels.

•B (2.7–39.0), Ba (29.0–72.9), Cr (3.7–10.5), Cu (2.5–31.9), Na (10.2–80.4), Ni (2.6–11.4), Sr (10.9–47.3), and Zn (16.4–50.7) at $\mu\text{g/g}$ levels.

Inter-element correlation coefficients were also calculated. A significant difference was observed between the virgin tea samples and the processed tea samples. Along with a multivariate statistical analysis, the elemental data generated for the tea samples from the different regions of India will be useful to establish the origin of the given tea samples (23–25). However, elemental data along with geochemical soil database from these regions will be useful to arrive at definite conclusions about the origin of a given tea sample.

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