# Determination of Multiple Elemental Concentrations in Tea from China by Inductively Coupled Plasma Optical Emission Spectrometry

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**Abstract**  The main goals of this study were to determine the best preparation procedure (microwave digestion, infrared digestion, or dry ashing) to analyze 17 elements in ten tea samples from different manufacturers in China with inductively coupled plasma optical emission spectrometry. Elemental measurement accuracy was determined by comparison with certified green tea reference material (GBW10052). Our results showed that a simple, rapid, and reliable microwave digestion was the best procedure preceding spectrometric measurements, resulting in the highest mean content values of K, Ca, Mg, Fe, and Zn in the tea samples, and that Cd, Pb, and As were under permissible limits based on a national standard (NY695-2003). The elemental differences and correlation of samples, as well as the classification and differentiation between the tea samples, were analyzed statistically.

*Keywords:* *determination, tea, inductively coupled plasma optical emission spectrometry, multiple elemental concentrations, China*

**Cite This Article:** Mingjun Huang, Xinhe Yang, Zhonghua Liu, Qingli Mao, Caiqin Qin, and Bangyu Lv, "Determination of Multiple Elemental Concentrations in Tea from China by Inductively Coupled Plasma Optical Emission Spectrometry." *Journal of Food and Nutrition Research*, vol. 4, no. 7 (2016): 471-477. doi: 10.12691/jfnr-4-7-9.

## 1. Introduction

Tea is the second-most popular beverage next to water, consumed by over two-thirds of the world's population [1]. Based on the degree of fermentation, it is classified into non-fermented (green tea), partially fermented (white, yellow, and oolong teas), fermented (black tea), and post-fermented (dark tea) [2,3]. In recent years, many studies reported that tea has numerous health benefits, including a variety of hypolipidemic, anti-obesity, anti-mutagenic, anti-oxidative, anti-tumor, free radical scavenging, and toxicity-suppressing activities [4-16]. A growing number of consumers are drinking tea in light of the health benefits and within the current background of a strong interest in food health and safety.

The benefits from drinking tea are mainly related to characteristic polyphenolic compounds known as catechins, particularly (-)-epigallocatechin gallate, that counteract various activities related to obesity, cancer, oxidants, diabetes mellitus, and hypertension [17,18,19,20,21]. These well-known health benefits are related to the synergistic effects of the whole matrix, rather than just the presence of individual substances. Therefore, the benefits of drinking tea are associated with a variety of ingredients, which are, at their core, composed of elements that play an important role in metabolism regulation and the activation of enzymes. Tea contains all of the essential trace elements, with some in particularly high concentrations. Each element present in tea is variable in its concentration because of differences in geographic areas, raw materials, and manufacturing procedures. People can directly absorb essential trace elements from tea because about 50–60% of the elements are soluble in hot water. Essential trace elements such as Se, Cu, Sr, Fe, and Zn are not synthesized in the human body [22,23]. Therefore, an appropriate intake of these is extremely important for proper growth and development. To date, there have been no comparative studies of the elemental content in different tea to evaluate their essential trace elements for human health. In addition, it is important to regularly monitor heavy metal concentrations in tea to ensure safety and to maintain its health benefits because they are implicated in serious health risks.

Based on the above reasons, the objective of the present study was to accurately and effectively document the concentration of 17 selected elements (K, Ca, Mg, Sr, B, As, Cd, Co, Cu, Fe, Mo, Ni, Pb, Se, V, and Zn) in ten typical tea samples, spanning the range of fermentation degrees, procured from different manufacturers in China. To achieve the study objective, we compared microwave digestion, infrared digestion, and dry ashing to choose a simple, fast, and reliable sample preparation procedure prior to inductively coupled plasma optical emission spectrometry (ICP-OES). The accuracy of the measurements was determined by comparison with certified reference

material (GBW10052, a green tea). A variety of statistical methods was used to analyze elemental differences, produce a correlation of element content, and clarify the differentiation and classification of tea samples.

## 2. Material and Methods

### 2.1. Samples, Reagents, and Solutions

The ten tea samples used in this study were from different manufacturers in China. They included non-fermented (Xinyang green tea (XYGT), Henan), partially fermented (Tieguanyin tea (TGYT); Wulong tea (WLT), Fujian), fermented (Qimen black tea (QMBT), Anhui), and post-fermented (Pu-erh tea (PET), Yunnan; Qingzhuan dark tea (QZDT), Hubei; Fuzhuan dark tea (FZDT) and Qianliang dark tea (QLDT), Hunan; Liubao dark tea (LBDT), Guangxi; Kangzhuan dark tea (KZDT), Sichuan.

Chemical reagents, 30% (m/m) $H_2O_2$ and 65%(m/m) $HNO_3$ (Chinese Medicine Group Chemical Reagent Co., Ltd, Shanghai, China) and Milli Q water (Millipore, Bedford, USA) were used throughout the experiment. All of the plastic and glassware were soaked in 5% diluted nitric acid for 24 h, and rinsed with Milli Q water prior to use.

The ICP multi-element standard solutions containing the analyzed elements (100 mg/L, PerkinElmer, USA) were suitably diluted in 5% diluted nitric acid and a mixed standard solution was prepared. The calibration curve ranges (5 points) were selected to match the expected concentrations (0–6 mg/kg) for all of the studied elements. The correlation coefficient ($r^2$) in all analyses was 0.9999. A certified green tea reference material (GBW 10052, Chinese Academy of Geological Sciences, Beijing, China) was used to determine the accuracy of the method.

### 2.2. Instrumentation

An ICP-OES (Optima 8000; PerkinElmer) with reciprocal observations (axial and radial) and operational software (winLab32) was used for simultaneous multi-element determination of K, Ca, Mg, B, As, Cd, Co, Cu, Fe, Li, Mo, Ni, Pb, Se, Sr, V, and Zn. The operating parameters consisted of a RF power of 1.35 kW, plasma flow rate of 15 L $min^{-1}$, auxiliary gas flow of 0.5 L $min^{-1}$, nebulizer flow rate of 0.8 L $min^{-1}$, and pump flow rate of 1.5 L $min^{-1}$. A concentric nebulizer and a cyclonic-type spray chamber introduced the sample solutions into the plasma; argon (99.999% pure, Wuhan, China) was used to purge the optics and form the plasma.

A microwave digestion system equipped with polytetrafluoroethylene vessels (APL MD6CN-H, Beijing, China), resistance furnace with crucibles (SX2-4-10, Wuhan, China), and an infrared digestion device (LWY84B, Changzhou, China) were used for sample digestion. A pulverizer (QSB-100, Yongkang, China) and a forced convection drying cabinet (XMTD-8222, Shanghai, China) were used for grinding the tea samples and drying them and the vessels, respectively.

### 2.3. Analytical Procedure

#### 2.3.1. Sample Preparation

All samples were dried at 103°C to a constant weight, and then ground in a pulverizer into 80 mesh powder.

Afterwards, the powder samples were stored in labeled and tightly sealed polyethylene sample bags until analysis.

For the microwave digestion, 0.5 g of sample was placed into a 100 mL polytetrafluoroethylene vessel on an electric heating plate, 5 mL of a concentrated $HNO_3$ solution was added and left for 15 min (110°C) as a pre-digestion step. Next, 2 mL of 30% $H_2O_2$ and 2 mL of concentrated $HNO_3$ were added. The sample was then digested in the microwave system at 800 w according to the following temperature program: 120°C for 5 min, 150°C for 10 min, and 180°C for 15 min. Finally, the complete digestion solution was heated almost to dryness to remove the acid, and the remaining colorless aliquot was transferred to a volumetric flask and diluted to 25 mL with ultrapure water. All samples were prepared using the same preparatory and microwave methods.

For the infrared digestion, 0.5 g of the sample was put into a 100 mL digestion tube, added with 5 mL of a concentrated $HNO_3$ solution and left overnight. Additional portions of 5 mL concentrated $HNO_3$ were then added. Under the instrumental operating temperature (380°C), 30% $H_2O_2$ was constantly added to the digestion tube until the solution became clear. The complete digestion solution was heated almost to dryness to remove the acid, and then the remaining aliquot was transferred to a volumetric flask and diluted to 25 mL with ultrapure water.

For the dry asing procedure, we referred to the entry-exit inspection and quarantine industry standards of China and used the tea import and export total ash determination method (SN/T 0925-2000). In this preparation, 0.5 g of a sample was dry ashed in a furnace at 500±25°C for 4 h. Then, the ash was dissolved with 1–2 mL of 5% diluted nitric acid, after which the solution was transferred to a volumetric flask and diluted with 5% diluted nitric acid.

All sample solutions were prepared three times with each method and filtered over 0.45µm mesh for ICP-OES analysis. Procedural blanks were also prepared using each sample preparation procedure.

#### 2.3.2. Statistical Analysis

Variance, correlation, cluster, and principal component analyses were performed with SPSS (version 19.0 for Windows). Variance analysis was used to distinguish the different levels of each element among the tea samples. Correlation analysis demonstrated significant differences among the elemental contents. Principal component analysis (PCA) was used to find and interpret complex relationships between the different elements and samples. Cluster analysis was used to establish the sample clustering based on element concentrations.

## 3. Results and Discussion

### 3.1. Preferred Sample Preparation Procedure

The microwave digestion, infrared digestion, and dry ashing procedures were used to decompose ten tea samples to allow us to choose the best sample preparation procedure prior to elemental determination by ICP-OES. The accuracy of each preparation method was tested by comparing the results after ICP-OES with a certified green tea reference (GBW10052). The results showed that the microwave digestion resulted in the best agreement with

certified values (Table 1). The accuracy of microwave digestion, infrared digestion, and dry ashing was also verified by the recovery test (Table 2), which generally exhibited acceptable mean recovery rates for all three procedures, further demonstrating the suitability of microwave digestion. In addition, factors such as the level of contamination, sample homogeneity, reproducibility and digestion completeness, analysis suitability, sample preparation time, and cost need to be considered when preparing samples for analysis [24]. The microwave digestion is less time consuming, is lower energy consumption and cost, and is performed at lower temperatures than both the infrared digestion and dry ashing. As a final advantage, microwave digestion can completely prevent sample contamination.

**Table 1. Results of the analysis with the microwave digestion, Infrared digestion and dry ashing procedures of GBW 10052 Green tea certified reference material (mg kg⁻¹), n=3**

| Element | Analyzing spectrum line | Certified value | Microwave digestion | Infrared digestion | Dry ashing |
|---|---|---|---|---|---|
| Ca | 317.933 | 12100±30 | 11923.33±32.146[a] | 9697.00±15.100[b] | 11133.33±64.291[a] |
| Mg | 285.213 | 2200±8 | 2034.33±10.693[a] | 1937.20 ±80.763[b] | 1896.43 ±67.666[a] |
| K | 766.490 | 15500±70 | 15456.67±65.064[a] | 15054.00±45.033[a] | 17103.33±35.119[b] |
| B | 249.677 | 14.1±1.2 | 13.38±0.956[a] | 12.42±0.220[b] | 13.61±0.520[a] |
| As | 188.979 | 0.27±0.05 | 0.27±0.022[a] | 0.27 ±0.023[a] | 0.26 ±0.011[a] |
| Cd | 228.802 | 0.076±0.004 | 0.07±0.001[a] | 0.07±0.009[a] | 0.07±0.004[a] |
| Co | 228.616 | 0.30±0.02 | 0.31±0.005[a] | 0.23±0.023[b] | 0.31±0.002[a] |
| Cu | 324.752 | 24±1 | 24.29±0.799[a] | 19.48±2.853[b] | 20.30±0.576[b] |
| Fe | 238.204 | 322±23 | 325.07±2.857[a] | 292.83±6.892[b] | 288.40±7.917[c] |
| Li | 610.362 | 0.52±0.04 | 0.52±0.012[a] | 0.45±0.042[a] | 0.48±0.004[a] |
| Mo | 202.031 | 0.11±0.02 | 0.13±0.009[a] | 0.15 ±0.016[a] | 0.14±0.009[a] |
| Ni | 231.604 | 5.4±0.4 | 5.38±0.132[a] | 5.17 ±0.047[a] | 5.28 ±0.137[a] |
| Pb | 220.353 | 1.6±0.2 | 1.61±0.014[a] | 1.36±0.117[b] | 1.41 ±0.071[b] |
| Se | 206.279 | 0.10±0.03 | 0.11±0.003[a] | 0.08±0.004[b] | 0.07±0.005[b] |
| Sr | 421.552 | 36±2 | 35.24±0.535[a] | 34.50 ±2.070[a] | 30.81±0.656[b] |
| V | 290.880 | 0.60±0.15 | 0.69±0.068[a] | 0.46 ±0.010[b] | 0.47±0.013[b] |
| Zn | 213.857 | 35±2 | 35.72±0.998[a] | 27.53±3.737[b] | 28.31±3.095[b] |

[a] Mean ±standard deviation. Columns with results with superscript letters indicate a significant difference at p≤0.05 level by Duncan's multiple range test.

**Table 2. Recoveries of elements in the certified reference material GBW10052 green tea prepared with the microwave digestion, Infrared digestion and dry ashing procedures (%), n=3**

| Element | Microwave digestion[a] | Infrared digestion[a] | Dry ashing[a] | Element | Microwave digestion[a] | Infrared digestion[a] | Dry ashing[a] |
|---|---|---|---|---|---|---|---|
| Ca | 95.26±2.64 | 104.50±0.61 | 97.77±2.05 | Li | 102.16±5.81 | 100.88±4.78 | 97.05±4.34 |
| Mg | 98.12±1.96 | 100.53±2.01 | 95.04±1.37 | Mo | 94.94±0.28 | 95.08±0.18 | 93.38±1.02 |
| K | 100.12±0.63 | 95.80±1.78 | 103.60±1.33 | Ni | 94.28±0.70 | 102.78±13.65 | 96.14±1.02 |
| B | 96.31±3.35 | 96.93±2.79 | 96.82±2.61 | Pb | 95.84±3.43 | 89.45±3.73 | 96.28±0.49 |
| As | 95.93±1.02 | 97.20±1.04 | 98.25±0.56 | Se | 102.46±1.10 | 98.95±0.49 | 99.75±2.47 |
| Cd | 97.63±0.21 | 99.38±0.62 | 100.09±0.38 | Sr | 98.67±1.83 | 103.96±4.12 | 98.91±0.52 |
| Co | 92.89±0.61 | 93.80±0.99 | 94.14±0.58 | V | 96.60±0.98 | 96.86±0.58 | 95.79±0.27 |
| Cu | 103.21±2.55 | 105.34±2.05 | 99.46±1.21 | Zn | 98.15±0.88 | 97.86±1.44 | 104.87±1.57 |
| Fe | 100.00±0.19 | 99.22±2.03 | 101.44±3.49 | | | | |

[a] Mean ±standard deviation.

From our analytical results, we showed that the use of microwave digestion for preparing tea samples provided a simple, fast, and reliable procedure and was therefore chosen as the preferred preparation procedure in this study.

## 3.2. Element Contents in Ten Tea Samples

The concentrations of the 17 elements are expressed as arithmetic means (n=3) with standard deviations (SDs) shown in Table 3. The mean concentrations (mg kg⁻¹, dry weight) of K (10680.73), Ca (4018.77), Mg (1552.00), Fe (356.13), and Zn (26.30) were the highest elements in the ten tea samples. Lv et al. reported PET contains high concentrations of K, Ca, and Mg [25]. Anna et al. also reported that green and black tea contains abundant Fe, K, and Zn [26]. It is worth noting that the concentrations of toxic elements such as Pb, As, and Cd were lower in all ten tea samples than the permissible limit based on the NY695-2003 PRC National Standard (Pb ≤5 mg kg⁻¹, As ≤2 mg kg⁻¹, and Cd ≤1 mg kg⁻¹. Seham et al. reported that

2–20% of the total Cd concentration is released into tea infusions with boiling water [27]. Hence, the calculated average daily intakes of Pb, As, and Cd in tea infusions from our samples were within the bounds of safety.

Interestingly, Ca, Mg, Sr, B, As, Cd, Co, Mo, Fe, Ni, V, and Li contents were highest in KZDT, which originates from Sichuan Province, the southwestern tea area, while Se and Zn contents in QMBT, K content in LBDT, Cu content in PET , and Pb content in FZDT were highest. Among the ten tea samples, Pb concentrations showed the highest relative difference with a maximum to minimum content ratio of 47.65, followed by Li (24.31) and Sr (8.86); ratios of the other elements ranged from 1.53 to 8.83. Significant differences in element content among the ten tea samples, analyzed by Duncan's multiple range test, were marked using superscript letters. Noticeably, Cd in TGYT, Mo in LBDT, TGYT and WLT, Pb in QMBT, Li in LBDT, QMBT, PET, and WLT, and Se in TGTY and WLT were below detection.

**Table 3. Elemental concentrations of ten tea samples measured with ICP-OES combined with microwave digestion (mg kg$^{-1}$ d.w.)**

| Element | QZDT | KZDT | FZDT | LBDT | QMBT | QLDT | PET | XYGT | TGYT | WLT |
|---|---|---|---|---|---|---|---|---|---|---|
| K | 9817.67 ±97.21[c] | 9968.33 ±27.10[d] | 9758.67 ±96.67[c] | 13583.33 ±108.17[i] | 12630.00 ±134.54[h] | 10395.67 ±60.17[e] | 11613.33 ±65.06[g] | 9510.00 ±85.42[b] | 10626.67 ±56.86[f] | 8903.67 ±85.04[a] |
| Ca | 5405.67 ±22.50[g] | 7012.33 ±32.81[h] | 5465.00 ±25.24[g] | 3916.00 +43.94[e] | 1911.00 ±74.67[a] | 4124.67 ±23.71[f] | 3759.67 ±47.86[d] | 2123.67 ±36.61[b] | 2657.00 ±22.87[c] | 3812.67 ±77.47[d] |
| Mg | 1662.67 ±36.30[d] | 1965.33 ±23.44[f] | 1648.67 ±22.72[d] | 1693.00 ±26.41[e] | 1519.3 3±20.21[c] | 1432.67 ±23.03[b] | 1439.67 ±28.75[b] | 1191.33 ±70.81[a] | 1413.00 ±19.92[b] | 1554.33 ±31.53[c] |
| Sr | 22.27 ±0.79[e] | 37.84 ±0.85[f] | 23.12 ±0.66[e] | 14.12 ±0.85[c] | 6.16 ±0.40[a] | 14.48 ±1.83[c] | 14.03 ±0.77[c] | 4.27 ±0.22[a] | 6.55 ±0.93[b] | 18.88 ±2.64[d] |
| B | 11.24 ±0.87[b] | 16.66 ±0.79[e] | 13.08 ±0.68[d] | 12.55 ±1.07[c] | 10.99 ±0.74[b] | 9.81 ±1.77[b] | 10.25 ±0.71[b] | 6.80 ±0.45[a] | 7.56 ±0.69[a] | 10.49 ±1.18[b] |
| As | 1.28 ±0.19[d] | 1.59 ±0.12[e] | 1.23 ±0.12[d] | 0.55 ±0.04[b] | 0.18 ±0.17[a] | 0.61 ±0.09[c] | 0.32 ±0.04[a] | 0.20 ±0.16[a] | 0.23 ±0.13[a] | 1.35 ±0.30[d] |
| Cd | 0.13 ±0.03[c] | 0.27 ±0.01[e] | 0.231 ±0.01[d] | 0.04 ±0.01[a] | 0.03 ±0.01[a] | 0.10 ±0.01[b] | 0.09 ±0.01[b] | 0.08 ±0.01[b] | < 0.030* | 0.05 ±0.01[a] |
| Co | 0.48 ±0.08[c] | 0.73 ±0.01[d] | 0.50 ±0.02[c] | 0.24 ±0.02[a] | 0.23 ±0.01[a] | 0.35 ±0.08[b] | 0.46 ±0.02[c] | 0.47 ±0.05[c] | 0.21 ±0.01[a] | 0.34 ±0.04[b] |
| Cu | 14.43 ±0.77[b] | 16.6 ±0.43[c] | 22.18 ±0.85[d] | 15.16 ±0.79[b] | 17.59 ±1.09[d] | 15.36 ±2.19[b] | 23.23 ±0.96[d] | 16.35 ±1.07[b] | 6.60 ±0.63[a] | 7.80 ±1.12[a] |
| Fe | 623.63 ±4.39[f] | 776.2 ±18.34[g] | 440.6 ±11.37[e] | 328.77 ±18.20[d] | 111.57 ±10.14[a] | 239.03 ±21.89[c] | 237.80 ±8.47[c] | 125.77 ±8.74[b] | 95.69 ±8.72[a] | 337.70 ±15.59[d] |
| Mo | 0.05 ±0.03[a] | 0.06 ±0.05[b] | 0.04 ±0.01[c] | < 0.0096* | 0.01 ±0.01[c] | 0.01 ±0.02[c] | 0.02 ±0.01[c] | 0.02 ±0.01[c] | < 0.0096* | < 0.0096* |
| Ni | 4.19 ±0.72[b] | 8.80 ±0.19[e] | 5.66 ±0.25[c] | 4.15 ±0.26[b] | 6.63 ±0.42[d] | 4.67 ±1.16[b] | 8.25 ±0.42[e] | 6.14 ±0.44[c] | 1.35 ±0.15[a] | 1.76 ±0.29[a] |
| Pb | 2.67 ±0.55[c] | 4.05 ±0.08[d] | 4.28 ±0.26[d] | 0.16 ±0.06[a] | < 0.0050* | 1.01 ±0.15[b] | 0.17 ±0.15[a] | 1.17 ±0.10[b] | 0.09 ±0.12[a] | 0.21 ±0.14[a] |
| Se | 0.19 ±0.10[a] | 0.75 ±0.12[a] | 0.58 ±0.28[a] | 1.08 ±0.86[b] | 1.40 ±0.12[c] | 0.59 ±0.08[a] | 0.50 ±0.07[a] | 0.51±0.09[a] | < 0.0486* | < 0.0486* |
| V | 1.46 ±0.27[f] | 2.06 ±0.03[g] | 1.04 ±0.24[e] | 0.47 ±0.18[a] | 0.32 ±0.02[a] | 0.58 ±0.06[b] | 0.79 ±0.04[d] | 0.56 ±0.04[a] | 0.33 ±0.03[a] | 0.63 ±0.06[c] |
| Zn | 25.69 ±0.87[b] | 31.58 ±0.93[d] | 31.29 ±2.36[d] | 33.09 ±1.92[e] | 40.34 ±3.60[f] | 23.54 ±2.83[b] | 27.60 ±1.38[c] | 28.60 ±1.70[c] | 16.88 ±1.62[a] | 18.46 ±2.82[a] |
| Li | 0.41 ±0.29[b] | 0.41 ±0.04[b] | 0.15 ±0.02[a] | < 0.0050* | < 0.0050* | 0.16 ±0.02[a] | < 0.0050* | 0.01 ±0.01[a] | 0.17 ±0.04[a] | < 0.0050* |

Note：Columns with results with superscript letters indicate a significant difference at p≤0.05 level by Duncan's multiple range test. * Below the limit of quantification(LOQ, mg kg$^{-1}$ ).
QZDT: Qingzhuan dark tea;      KZDT: Kangzhuan dark tea;      FZDT: Fuzhuan dark tea; LBDT: Liubao dark tea; QMBT: Qimen black tea; QLDT: Qianliang dark tea; PET: Pu-erh tea; XYGT: Xinyang green tea; TGYT: Tieguanyin tea; WLT: Wulong tea.

It is well known that there are differences in the raw material tenderness and the manufacturing procedures between non-fermented tea (XYGT), partially fermented tea (TGYT and WLT), fermented tea (QMBT), and post-fermented tea (PET, QZDT, FZDT, QLDT, LBDT, and KZDT). Previous studies suggested that mineral elements are one of the important reference points for judging the tea-producing area [25,28,29]. Therefore, we conclude that the different element concentrations in our ten tea samples are caused by several factors, including raw material, manufacturing procedures, soil type, and regional climate.

## 3.3. Correlation Analysis

**Table 4. Correlation matrix for the elemental concentrations in ten tea samples**

| | K | Ca | Mg | Sr | B | As | Cd | Co | Cu | Fe | Mo | Ni | Pb | Se | V | Zn | Li |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K | 1.000 | | | | | | | | | | | | | | | | |
| Ca | -0.297 | 1.000 | | | | | | | | | | | | | | | |
| Mg | 0.120 | 0.818** | 1.000 | | | | | | | | | | | | | | |
| Sr | -0.326 | 0.969** | 0.858** | 1.000 | | | | | | | | | | | | | |
| B | 0.111 | 0.821** | 0.952** | 0.872** | 1.000 | | | | | | | | | | | | |
| As | -0.529 | 0.870** | 0.741* | 0.910** | 0.712* | 1.000 | | | | | | | | | | | |
| Cd | -0.409 | 0.860** | 0.606 | 0.849** | 0.729* | 0.719* | 1.000 | | | | | | | | | | |
| Co | -0.509 | 0.749* | 0.437 | 0.771** | 0.559 | 0.634* | 0.899** | 1.000 | | | | | | | | | |
| Cu | 0.241 | 0.226 | 0.091 | 0.172 | 0.336 | -0.051 | 0.488 | 0.438 | 1.000 | | | | | | | | |
| Fe | -0.299 | 0.949** | 0.845** | 0.954** | 0.820** | 0.895** | 0.804** | 0.762* | 0.150 | 1.000 | | | | | | | |
| Mo | -0.383 | 0.772** | 0.544 | 0.752** | 0.611 | 0.635* | 0.888** | 0.890** | 0.448 | 0.823** | 1.000 | | | | | | |
| Ni | 0.168 | 0.294 | 0.236 | 0.332 | 0.465 | 0.024 | 0.567 | 0.647* | 0.828** | 0.301 | 0.582 | 1.000 | | | | | |
| Pb | -0.469 | 0.813** | 0.563 | 0.773** | 0.635* | 0.724* | 0.951** | 0.808** | 0.370 | 0.786** | 0.895** | 0.384 | 1.000 | | | | |
| Se | 0.725 | -0.111 | 0.237 | -0.073 | 0.380 | -0.275 | 0.040 | -0.093 | 0.525 | -0.073 | 0.002 | 0.564 | -0.039 | 1.000 | | | |
| V | -0.392 | 0.898** | 0.716* | 0.913** | 0.735* | 0.791** | 0.872** | 0.901** | 0.252 | 0.946** | 0.928** | 0.481 | 0.827** | -0.095 | 1.000 | | |
| Zn | 0.562 | 0.017 | 0.295 | 0.055 | 0.456 | -0.120 | 0.236 | 0.133 | 0.671* | 0.101 | 0.273 | 0.686* | 0.193 | 0.928** | 0.112 | 1.000 | |
| Li | -0.389 | 0.751* | 0.575 | 0.702* | 0.482 | 0.632 | 0.649* | 0.602 | -0.071 | 0.785** | 0.789** | 0.125 | 0.719* | -0.246 | 0.824** | -0.116 | 1.000 |

Note: Pearson Correlation. (2-tailed):'*'Significant at 0.05 probability level.'**'Significant at 0.01 probability level.

Correlation analysis was used to describe the relationship among the elements (Table 4). Ca showed significant ($P<0.01$) positive correlations with Mg, Sr, B, As, Cd, Fe, Mo, Pb, and V, whereas Mg positively correlated with Sr, B and Fe, and Sr with B, As, Cd, Co, Fe, Pb, and V. Additionally, As was positively correlated with Fe and V, Cd with Co, Fe, Mo, Pb and V, Cu with Ni, Fe with Mo, Pb, V and Li, Mo with Pb, V and Li, Pb with V, Se with Zn, and Zn with Li. K showed a negative correlation with Ca, Sr, As, Cd, Co, Fe, Mo, Pb, V, and Li, but was the only element not significant at $P<0.05$ with other elements. There were some correlations that indicated a very weak or even no relationship; for example, Ca with Zn, and Cu with As and Mg.

## 3.4. Principal Component Analysis

Bartlett's test of sphericity and Kaiser–Meyer–Olkin measure of sampling adequacy were used to determine the suitability of the data for PCA. PCA obtains information on the most meaningful parameters that describe the entire dataset, which enables data reduction with a minimum loss of the original information. In this study, the significance level in Bartlett's test was 0, which showed there were significant relationships among variables, and the Kaiser–Meyer–Olkin value (0.628) indicated that PCA would be useful for our dataset.

The results of the elemental measurements in triplicate were used in the PCA. A clear pattern of loadings is obtained by various rotational strategies, in which varimax rotation is commonly used. The principal components are rotated to ensure that the total sum of squares on the loadings of each new axis is maximized. The variable loading on the first three components and the variance explained by each component are presented in Table 5. The first component explained 97.87% of the total

variance in the dataset with high loading values for K. The loadings were largest for Ca on the second component with an eigenvalue of 0.212, and for Mg on the third component with an eigenvalue of 0.001. According to Kaiser's rule, an eigenvalue greater than one is considered a significant index for retaining the maximum amount of variability present in the data. Therefore, the second and third components are not significant and do not explain 2.117% and 0.009%, respectively, of the total variance, as would have been expected if they had higher eigenvalues.

**Table 5. The loading of three components after varimax rotation.**

| Element | Principal components | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| K | 3.57884 | 1.45309 | 0.33322 |
| Ca | -1.69519 | 3.41546 | 0.64698 |
| Mg | 0.00249 | 0.32409 | -3.70230 |
| Sr | -0.12733 | -0.38582 | 0.21926 |
| B | -0.11636 | -0.40029 | 0.25086 |
| As | -0.11620 | -0.40594 | 0.26317 |
| Cd | -0.11565 | -0.40692 | 0.27197 |
| Co | -0.11565 | -0.40675 | 0.27139 |
| Cu | -0.11327 | -0.40159 | 0.37493 |
| Fe | -0.37840 | 0.05110 | -0.86968 |
| Mo | -0.11558 | -0.40703 | 0.27104 |
| Ni | -0.11513 | -0.40491 | 0.30222 |
| Pb | -0.11748 | -0.40432 | 0.27623 |
| Se | -0.11525 | -0.40711 | 0.27499 |
| V | -0.11614 | -0.40600 | 0.27017 |
| Zn | -0.10799 | -0.40023 | 0.27401 |
| Li | -0.11572 | -0.40683 | 0.27155 |
| Eigenvalue | 9.787 | 0.212 | 0.001 |
| variance(%) | 97.870 | 2.117 | 0.009 |
| Cumulative variance(%) | 97.870 | 99.987 | 99.997 |

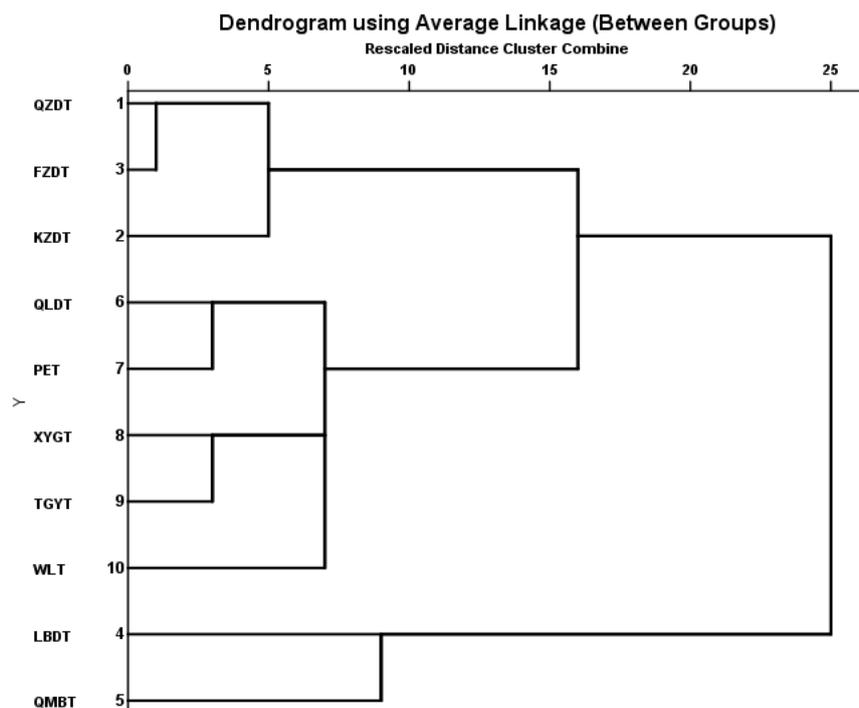## 3.5. Cluster Analysis



**Figure 1.** Dendrogram of cluster analysis

Cluster analysis is an unsupervised classification procedure, involving a measurement of the similarity

between objects. Objects are grouped in clusters according to their nearness or similarity. The measurement of the

similarity is based on the squared Euclidean distance. Ward's method of cluster analysis was applied by using the Statistica package in SPSS. The results indicated that the tea samples can be classified into six groups (Figure 1): (1) QZDT and FZDT; (2) KZDT; (3) QLDT and PET; (4) XYGT and TGYT; (5) WLT; (6) LBDT and QMBT. This means that Group 1, 3, 4, 6 have very similar to elemental concentrations at each intra-group. In addition, Groups 3 and 4 are even closer to each other, Group 5 is nearest to Groups 3 and 4, and group 2 was also a sub-cluster of Group 1 and has some similarities to QZDT and/or FZDT. In spite of the elemental concentrations, whose trends do not completely match each other, Group 1, 2, 3 and 4 are also clustered into a larger group. These results suggest that, to a certain extent, similarities between tea samples exist.

# 4. Conclusion

This study demonstrated that, compared with infrared digestion and dry ashing, microwave digestion to prepare tea samples for ICP-OES possessed analytical advantages, including the best agreement between observed elemental values and certified values of standard samples, and satisfactory standard recovery. It is also less time consuming, is lower energy consumption and cost, is easy to perform, and is safer. The concentrations of 17 elements (K, Ca, Mg, Sr, B, As, Cd, Co, Cu, Fe, Li, Mo, Ni, Pb, Se, V, and Zn) in ten tea samples procured from different manufacturers in China were successfully determined by ICP-OES after microwave digestion. The elemental concentrations in the samples are different, but the mean values of K, Ca, Mg, Fe, and Zn were highest in all of the samples. The results were used to statistically analyze the differences and correlations of the elemental concentrations, as well as to differentiate and classify the tea samples. In addition, Pb, As, and Cd concentrations in all of the samples were under permissible safety limits.

# Acknowledgements

# Conflict of Interest

The authors declare that there are no conflicts of interest.

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