Simultaneous determination of multiple elements of tea garden soil using inductively coupled plasma mass spectrometry

Z T Gan1, T Yao2*, X S She3, P Q Zhang2, S Q Wang2, Y Wang2, Y Y Tan2 and N Qi2

1School of Tourism, Huangshan University, Huangshan 245041, China
2Analysis and Test Center, Huangshan University, Huangshan 245041, China
3College of Life and Environment Science, Huangshan University, Huangshan 245041, China

*yting@hsu.edu.cn. telephone number: (+86) 0559-2546502

Abstract. Established a method of simultaneous determination of multiple elements of tea garden soil, the inductively coupled plasma mass spectrometry (ICP-MS) was used to test. The soil samples were decomposed by the fully automatic microwave with hydrogen nitrate (HNO3) and hydrofluoric acid (HF). The kinetic energy discrimination (KED) mode, the correction equation and the internal standard method were adopted to eliminate matrix effect interference within the testing process by ICP-MS. Moreover, contents of twenty-six soil elements were calculated with the corresponding standard curve at different content levels of standard solution. The results indicated that the curves of twenty-six elements which the contents were in the range of 0~200μg/L were all approximately linear with correlation coefficients ($R^2$)> 0.990. The ranges of the limits of detection (LOD), the limits of quantification (LOQ) and the average recoveries (AR) of twenty-six soil elements were 0.0038~3.6198μg/L, 0.0127~12.0660μg/L and 84.04 %~121 %, respectively, and the relative standard deviations (RSDs) were less than 7 %. The RSDs of standard substances of soil composition analysis were all < 5 % with ICP-MS in our experiments.

1. Introduction

The tea plant, a perennial evergreen shrub, is widespread in Southern provinces in China. The quality and yield of tea production is significantly affected by soil environment. This was demonstrated in a number of studies that heavy metals in soil were the source of heavy metals in tea production [1]. It is very important to diagnose the quality of soil elements for tea plants management and the quality safety of tea production.

Methods for quantitative determination of soil elements like spectrophotometry [2], atomic absorption spectrometry (AAS) [3], inductively coupled plasma emission spectrometry (ICP-OES) [4] have been generally applied. However, all of them have several disadvantages, which are not suitable for measuring a large number of soil elements such as complexity in pretreatment, non-simultaneous measurement of multiple elements and widely detection limit [5].

The inductively coupled plasma mass spectrometry (ICP-MS) [6] is an analytical instrument combining the advantage of high temperature ionization for the inductively coupled plasma
spectrometer (ICP) and sensitive and rapid scan for the mass spectrometer (MS). Soil elements can be measured quickly, accurately and synchronously with multiple elements with ICP-MS [9]. But the method of ICP-MS still has a few shortcomings such as the interference by mass spectrometry and/or non-mass spectrometry, which affects the accuracy of the results.

Appropriate methods and modes of interference correction should be used to improve the measuring accuracy of soil elements, according to different measurement objects by ICP-MS [10]. For this purpose, soil samples were dissolved with nitric acid and hydrofluoric acid first, next the kinetic energy discrimination (KED) mode, the calibration equation and the internal standard method to correct the interference were selected, and then a simultaneous determination method of ICP-MS was established, last this method was used to determine and analyze twenty-six elements of tea garden soil. It is expected to provide a fast and accurate quantitative analysis method for soil quality detection in tea garden and a basis for the investigation and control of soil elements in tea garden.

2. Materials and Methods

2.1 Reagents and Chemicals

All the reagents and chemicals were of analytical grade (Merck, Darmstadt, Germany) and used as received. A Milli-Q direct water purification system (18.2 MΩ cm, Millipore Corp., Bedford, MA, USA) was used to produce ultra-high purity (UHP) water.

2.2 Stock Standard Solutions

The internal standard solution is a standard solution at 10.0 μg/mL which contains six elements of Sc, Ge, Y, In, Tb and Bi, and the external standard solution is a standard solution at 10.0 μg/mL which contains twenty-six elements of Li, Be, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, (Rb, Sr, Ag, Cd, Sn, Sb, Cs, Ba, Hg, Tl, and Pb (National Analysis and Testing Center, General Research Institute for Nonferrous Metals, China). The tuning Solution is a standard solution at 1.0 μg/L which contains seven elements of Ba, Bi, Ce, Co, In, Li, (Thermo Fisher Scientific, Inc. USA).

2.3 Soil Sampling and Digestion

2.3.1 Soil Sampling. The tea gardens in this experiment are located at Luxi Town, in the south of Qimen County, Anhui Province, China. Soil samples were collected from two kinds of typical tea gardens at the sloping land and the flat land. Four sloping tea gardens were set at levels of 100 m, 90 m, 80 m and 70 m according to the elevation gradient, which were labeled A, B, C and D, respectively. Similarly, taken the abandoned and flat grassland as the control (CK), two flat tea gardens are between a vehicle road and a river labeled E and F at the distance of 5 m and 10 m from the road. The soil samples were collected by using soil auger (φ=6cm). Two hundred and ten soil samples were collected at 10 cm intervals from 0 cm to 100 cm in each tea garden. Three sampling points were randomly selected in each tea garden. After being put into the self-sealed polyethylene bags and transferred to the Laboratory of the Analysis and Test Center, Huangshan University, the soil samples were made by air drying, grinding and sifting 200 mesh sieve for testing.

2.3.2 Standard Substance of Soil Composition Analysis. Soil in the study area is divided into nine types, thirty-three soil genera and forty-five species. The four representative soil types of standard substance of soil composition analysis, namely limestone soil (GBW07404), yellow earths (GBW07405), yellow-brown earths (GBW07406) and latosol (GBW07407), were chosen among them to do comparison tests.

2.3.3 Sample Digestion. The soil samples and four types of standard substances of soil composition analysis were taken 0.1g each, and 4 mL HNO₃ and 1 mL HF (v/v=4:1) were added respectively, and then placed in the dissolving tank of the microwave digestion instrument (PreeKem Scientific
Instruments Co., Ltd, China), which was set up as automatic digestion according to Table 1. After being cooled, the solution was transferred to a volumetric flask, and 2% HNO₃ was added to set the volume at 50ml. They were placed for 24h to clarify, and the supernatant was centrifuged for determination.

Table 1. Methods and conditions of sample digestion in the microwave digestion instrument.

| Steps | T/℃ | Pressure/MPa | t/min |
|-------|------|--------------|-------|
| 1     | 150  | 15           | 3     |
| 2     | 180  | 25           | 3     |
| 3     | 200  | 30           | 3     |
| 4     | 220  | 35           | 15    |

2.4 Preparation of Standard Solution
The internal standard solution (10.0 μg/mL) was taken 2 mL and the external standard solution (10.0 μg/mL) was taken 1 mL, both of which were added with 2% HNO₃ to reach a constant volume to prepare 200μg/L internal standard solution and 400 μg/L external standard stock solution respectively. The series of external standard solutions with the concentration of 1, 2, 5, 10, 20, 50, 100 and 200 μg/L were prepared with 400 μg/L external standard stock solutions.

2.5 ICP-MS

2.5.1 Working Parameters Setting. Soil samples were analyzed for elements of Li, Be, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Sn, Sb, Cs, Ba, Hg, Tl and Pb using ICP-MS (ICAP-Q, Thermo Fisher Scientific, Inc. USA) equipped with the fully automatic microwave and HNO₃ and HF. The working parameters of ICP-MS was set as per Table 2.

Table 2. The working parameters of ICP-MS.

| Working parameters | Conditions | Working parameters | Conditions | Working parameters | Conditions |
|--------------------|------------|--------------------|------------|--------------------|------------|
| RF power           | 1500 W     | Cooling water flow rate | 3.73 L/min | Flow rate of cooling gas | 13 L/min |
| Flux of atomize    | 1 L/min    | Vacuum sampling depth | 10 mm      | Vacuum             | 3.078E-7 MPa |
| Assistant gas flow | 0.8 L/min  | Peristaltic pump speed | 40 RPM     | Times of repetition | 6         |

2.5.2 Determination Method. The isotopes of ⁷Li, ⁹Be, ²⁴Mg, ²⁷Al, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷¹Ga, ⁷³Ge, ⁷⁵As, ⁷⁷Se, ⁸⁸Sr, ⁸⁹Y, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹³³Cs, ¹⁵⁷Ba, ¹⁵⁹Tb, ²⁰⁵Hg, ²⁰⁵Tl, ²⁰⁸Pb and ²⁰⁹Bi were determined by ICP-MS. In addition, ⁴⁵Sc, ⁷³Ge, ⁸⁹Y, ¹¹⁵In, ¹⁵⁹Tb and ²⁰⁹Bi were internal standard substances. Other determined elements were measured by the interpolation method.

The internal standard solutions were drawn through the internal standard injection tube into ICP-MS. The sample solutions were drawn in the order of blank solutions, standard solutions (the concentration is from low to high), the standard soil sample solutions and the soil sample solutions through the sample injection tube into ICP-MS.

2.5.3 Calibration Curve. The calibration curves were chosen to calculate the soil element contents according to the concentration levels of them. For example, at the lower content level of elements like Pb, Cd and As, the calibration curves calibrated from the gradient of 0 ~ 20 μg/L were chosen, and at higher content level like elements of Mn, Fe, the calibration curve calibrated from the gradient of 10 ~ 200 μg/L were chosen.
2.6 Experimental Progress
Firstly, the soil samples were collected, crushed and sieved to acquire the soil power. Secondly, the standard substances of soil composition analysis and the soil power were digested by microwave. Finally, multi-elements were assayed by ICP-MS.

3. Results and Discussions

3.1 Interference Correction

3.1.1 Types of Interference. The quantitative determination of ICP-MS will be affected by interference, especially in the simultaneous determination of multiple elements in soil. Due to the great difference in concentrations among elements to be measured, interference effects will be further intensified. Mass spectrum interference and non-mass spectrum interference are two kinds of interference factors which affect the quantitative determination results of ICP-MS. For different interference, the degree of influence varies, and there are many ways to correct the interference. Different correction methods should be chosen according to the nature of interference in the experiment.

3.1.2 Correction of Mass Spectrum Interference. The interference, which is caused by the overlap of the mass spectra of the interfering components and the mass spectra of target isotope to the measurement results, is called mass spectra interference (or mass interference). It usually displays a positive error of measurement results. Mass spectrum interference mainly comes from the overlap of polyatomic molecule ions, isobars, multiple charge ion/double charge ion or the background noise of external ions, photons, stray light, and detector random electrons, etc. [11].

The interference caused by the overlap of polyatomic molecular ions is the most important interference source in the known mass spectrum interference. In the analysis of soil samples, the polyatomic molecule ion mainly came from the gas components that supply plasma (such as the gas Ar in the experiment), oxygenated chemicals and other matrix elements in soil samples. In addition, the reagent added in the process of soil sample preservation and digestion may be also the source of matrix composition. Due to the most serious interference of chlorine, two kinds of acids, namely hydrogen nitrate and hydrofluoric acid were selected to treat soil samples in the experiment.

ICP-MS introduces a reaction or collision cell technique to overcome the overlapping interference for polyatomic ions, which can remove or minimize the molecular ions generated by ICP ion source. In the operation of ICP-MS, interference correction can be achieved by using standard mode (STD), collision cell technique mode (CCT) or kinetic energy discrimination mode (KED). The mode of STD refers that no gas pipes into the collision cell. The determination of elements like potassium (K) and sodium (Na) will have high sensitivity at the mode of STD. But for the determination of elements at high concentration level, it will cause the overflow of signal and the result cannot be displayed. Therefore, the mode of STD is not suitable for the determination of elements at high concentration levels in soil samples. The mode of CCT refers to the introduction of inert gas such as Helium (He) into the collision cell, and then the inert gas He collides with the interference ion leading to the rupture of the interference ion. But it requires the collision energy of inert gas must be higher than the dissociation energy of polyatomic interference ion, or the collision and dissociation are not going to occur, so the types of interference that can be eliminated by collision and dissociation are limited. Moreover, the mode of CCT cannot solve the problem that the double/polyatomic ion’s kinetic energy will fall sharply after collision and cooling. The mode of KED applies a proper positive potential difference between hexapole and quadrupole on the basis of collision cell. Therefore, the resulted effect of kinetic energy discrimination can inhibit the passage of
multi-atomic ions, while the high-energy ions to be measured can pass through, so as to eliminate the interference. The collision kinetic energy discrimination mode is a physical process, which has nothing to do with the chemical nature of substances, not a reaction process. It has no specific reaction mechanism, and only filters out the multi-atom interference ions through the filter. The kinetic energy discrimination is effective for any ion with different radius, regardless of the type, amount or chemical nature of the interfering substance. As a result, the KED mode is especially suitable for simultaneous analysis of multiple elements in soil samples containing complex and variable unknown matrix [12].

The overlaps of isobars are referred that the targetable isotopic atom has the same mass number as an atom or has the same mass-to-charge ratio (m/z) as an ion. Most of the atoms and ions are from the matrix in the soil sample or acid used to digest soil. Others are from the carrier gas of ICP-MS and impurities produced by the collision/reaction of gases, such as krypton (Kr), xenon (Xe), etc. The interference caused by the overlap of isobars can be corrected by selecting the non-superposing isotope of the target element, and the mathematical method can also be used to eliminate the interference. The formula to correct the overlapping interference of isobars is:

$$I_i = I_z - I_w A_g (A_w)^{-1}$$ (1)

When the mass-to-charge ratio is m/z, $I_i$ refers to the net ion current intensity of determined isotopes, and $I_i$ is the gross ion current intensity of them. $I_w$ is the ion current intensity of the interference element without interference. $A_g$ is the abundance value of the isobar, $A_w$ is the abundance value of another interference isotope.

Taking the determination of $^{75}$As as an example, $^{40}$Ar$^{35}$Cl will interfere with the determination of $^{75}$As, and the content of $^{40}$Ar$^{35}$Cl needs to be determined through $^{40}$Ar$^{37}$Cl as equation (2). While $^{77}$Se will interfere with $^{40}$Ar$^{37}$Cl. It is needed to calculate the content of $^{82}$Se as equation (3). Then using $^{83}$Kr which has no interference of isotope to calculate $^{82}$Kr’s content as equation (4), at last the content of $^{75}$As can be determined. The calculation process is:

$$^{77}ArCl=Int(77)-^{77}Se = Int(77) - ^{82}Se\times0.875$$ (3)

$$^{75}As=Int(75)-^{77}ArCl = Int(75) - ^{82}Kr\times11.56\times(11.55)^{-1}$$ (4)

The overlap of multi-charge ions or doubly charged ions is more related to the alkaline earth metal, some rare earth elements and a few transition metal elements. Under most circumstances, the overlap of multi-charge ions or doubly charged ions rarely occurs, and the probability of occurrence is less than 1 %. At the same time, ICAP-Q has already effectively eliminated the interference of background noise.

3.1.3 Correction of Non-mass Spectrum Interference. Despite many sources to non-mass spectrum interference, it is mainly caused by matrix effect or physical effect. Some non-spectral interference can be eliminated by the promotion of computer hardware technology of ICP-MS. It can also be resolved by eliminating the matrix effect using the internal standard method. Most of soil samples are high-salt matrices, whose components are easy to deposit in the sampling cone, skimmer cone and ion lens of ICP-MS, leading to the drift of the analysis signal. The internal calibration can well compensate the matrix effect and obtain high precision results of ICP-MS. Since many kinds of trace elements are rich in soil, and the influence of complex ions in reagents and samples formed by these soil elements should be considered in the determination of elements. Thus, the internal standard elements should be selected elements with high sensitivity and relative abundance. Meanwhile the elements used as the internal standard must not be the same as the elements of the sample, otherwise, the internal standard signal will be enhanced with extra irregular signals, resulting in the low concentration of the target element after the software correction. In this study, the method of on-line adding internal standard solution was used to reduce the interference of matrix effect and correct the sensitivity of ICP-MS.
3.2 Accuracy and Precision

Blank solution and standard solution were determined using ICP-MS (Table 2), and all experiments were carried out in 11 times repeated. The limits of detection (LOD) and the limits of quantification (LOQ) were set with the concentration corresponding to the standard deviation of 3 times and 10 times, respectively. The results showed that the range of LOD and LOQ are 0.0038 ~ 3.6198 g/L and 0.0127 ~ 12.0660 μg/L, respectively (Table 3). The determined value of elements in the standard solution have a significant linear correlation with element standard value \((R^2 \geq 0.9903)\). Soil samples were determined using ICP-MS in six times repeated. The results show the average recovery rate (AR, %) and the relative standard deviation (RSD, %) of soil samples are 84.04 % ~ 121.68 % and <7 %, respectively (Table 3).

| Serial number | Isotope | Linear equation | \(n=11\) | LOD | LOQ | AR | RSD |
|---------------|---------|----------------|--------|-----|-----|-----|-----|
| 1             | \(^7\)Li | \(f(x)=78.2595*x+62.7069\) | 0.9998 | 3.6198 | 12.066  | 99.68 | 5.16 |
| 2             | \(^9\)Be | \(f(x)=62.0107*x+0.8356\) | 0.9997 | 0.0700 | 0.2333 | 102.23 | 2.83 |
| 3             | \(^{24}\)Mg | \(f(x)=304.2755*x+102.4539\) | 0.9978 | 1.3233 | 4.4110 | 109.33 | 4.75 |
| 4             | \(^{27}\)Al | \(f(x)=94.9132*x+26.1449\) | 1.0000 | 2.6711 | 8.9037 | 121.68 | 6.97 |
| 5             | \(^{51}\)V | \(f(x)=3556.2841*x+187.4257\) | 0.9995 | 0.0149 | 0.0497 | 101.94 | 0.60 |
| 6             | \(^{52}\)Cr | \(f(x)=5343.3240*x+1819.5078\) | 0.9997 | 0.0179 | 0.0597 | 98.23 | 0.72 |
| 7             | \(^{55}\)Mn | \(f(x)=2739.4033*x+827.4585\) | 0.9997 | 0.3399 | 1.1330 | 102.74 | 2.66 |
| 8             | \(^{57}\)Fe | \(f(x)=118.6302*x+16.2169\) | 0.9998 | 2.9912 | 9.9707 | 93.20 | 5.36 |
| 9             | \(^{59}\)Co | \(f(x)=9225.9357*x+283.8570\) | 0.9989 | 2.9912 | 9.9707 | 93.20 | 5.36 |
| 10            | \(^{60}\)Ni | \(f(x)=360.7354*x-21.2449\) | 0.9996 | 0.0038 | 0.0127 | 101.58 | 0.79 |
| 11            | \(^{63}\)Cu | \(f(x)=7240.1934*x+3601.5674\) | 0.9999 | 1.1563 | 3.8543 | 95.12 | 3.84 |
| 12            | \(^{65}\)Zn | \(f(x)=1203.1202*x+814.3189\) | 0.9992 | 1.2460 | 4.1533 | 85.47 | 0.55 |
| 13            | \(^{71}\)Ga | \(f(x)=1499.9865*x+39.9850\) | 0.9996 | 0.0038 | 0.0127 | 101.58 | 0.79 |
| 14            | \(^{73}\)As | \(f(x)=640.7354*x-21.2449\) | 0.9996 | 0.0038 | 0.0127 | 101.58 | 0.79 |
| 15            | \(^{77}\)Se | \(f(x)=13.5778*x+0.8184\) | 0.9968 | 0.3132 | 1.0440 | 91.90 | 6.89 |
| 16            | \(^{85}\)Rb | \(f(x)=1975.4257*x+276.3862\) | 0.9992 | 0.0193 | 0.0643 | 102.84 | 0.82 |
| 17            | \(^{88}\)Sr | \(f(x)=2951.4380*x+876.2586\) | 0.9998 | 0.1076 | 0.3587 | 103.80 | 0.79 |
| 18            | \(^{107}\)Ag | \(f(x)=13487.6149*x+321.2963\) | 0.9959 | 0.0137 | 0.0457 | 89.40 | 0.69 |
| 19            | \(^{111}\)Cd | \(f(x)=2190.5957*x+430.8533\) | 0.9966 | 0.0519 | 0.1730 | 88.28 | 0.60 |
| 20            | \(^{118}\)Sn | \(f(x)=4062.5140*x+852.2403\) | 0.9970 | 0.0497 | 0.1657 | 96.12 | 0.58 |
| 21            | \(^{121}\)Sb | \(f(x)=4939.1173*x+1948.1938\) | 0.9965 | 0.0453 | 0.1510 | 107.54 | 0.64 |
| 22            | \(^{133}\)Cs | \(f(x)=8637.2554*x+163.2911\) | 0.9997 | 0.0038 | 0.0127 | 106.87 | 0.76 |
| 23            | \(^{137}\)Ba | \(f(x)=1794.8058*x+1048.7987\) | 0.9997 | 0.0918 | 0.3060 | 105.35 | 1.10 |
| 24            | \(^{202}\)Hg | \(f(x)=10153.5741*x+82.5190\) | 0.9903 | 0.0045 | 0.0150 | 84.04 | 7.92 |
| 25            | \(^{208}\)Tl | \(f(x)=42607.5479*x+599.1657\) | 0.9991 | 0.0048 | 0.0160 | 100.40 | 0.53 |
| 26            | \(^{208}\)Pb | \(f(x)=30497.4678*x+12205.2521\) | 0.9997 | 2.5713 | 112.10 | 5.64 |

3.3 Determination of Standard Substances of Soil Composition Analysis

The multi-elements (V, Mn, Co, Se, Sr, Cs, Ni, Cu, Zn, As, Cd, Hg, Pb) of four kinds of standard substances of soil composition analysis are determined using ICP-MS, and the results showed that the RSDs of soil of national standard soil samples substances are all < ±5 % (Figure 1). The RSD ranges of GBW07404, GBW07405, GBW07406 and GBW07407 are -3.06 ~3.3 %, -4.5~3.95 %, -
3.27~3.02 % and -2.92~3.17 %, respectively. Which indicated that ICP-MS is very suitable for simultaneous determination of multiple elements of soil samples, even if they have complex components, variable and unknown matrices.

![Figure 1. The RSDs of four kinds of standard substances of soil composition analysis.](image)

### 3.4 Analysis of Samples

Soil elements are the main source of the tea plant elements. They are absorbed into the tea plant through root systems, and can promote or inhibit tea plants’ growth and physiological activities. Some elements may also be enriched in tea plants, such as Se-enriched tea is the result of the enrichment of Se in the tea plant [13]. Many kinds of elements have been detected in the soil, some of which will be beneficial to human body, like As, V, Mn, Fe, Co, Se, Sr, Cs, and so on. Others can cause irreversible toxic effects if they are enriched in human body through tea, such as As, Cr, Ni, Cu, Zn, As, Cd, Hg and Pb. In this experiment, mean contents of the elements like V, Fe, Co, Sr in tea garden were higher than that in CK, on the contrary, Mn, Se and Cs in tea garden less than that in CK (Table 4). Elements like Mn, Fe and Co can affect tea plants on the absorption of other heavy metal elements through changing physical and chemical properties of soil directly and forms of heavy metals in tea garden soil indirectly. Moreover, they can enhance anti-reversibility of tea plant, and reduce the toxicity of heavy metals on tea plant directly. Beneficial elements like Se and Fe in teas could be obtained and utilized by tea drinkers to increase the ability of disease resistance, especially to improve the antioxidant capacity, cancer treatment and anemia treatment.

| Sample plot | V     | Mn    | Fe     | Co     | Se     | Sr     | Cs     |
|-------------|-------|-------|--------|--------|--------|--------|--------|
| A           | 66.7±5.23 | 94.96±5.35 | 17498.35±1843.51 | 2.74±0.54 | 0.29±0.05 | 3.32±0.48 | 6.90±1.78 |
| B           | 71.49±1.75 | 225.81±68.21 | 17558.22±1095.50 | 6.63±3.04 | 0.34±0.02 | 6.87±2.69 | 7.19±0.57 |
| C           | 67.01±5.86 | 255.82±60.21 | 18180.79±1591.98 | 8.66±1.00 | 0.36±0.09 | 3.53±0.80 | 8.03±0.27 |
| D           | 53.46±3.89 | 419.55±32.62 | 15730.15±1447.20 | 8.47±0.53 | 0.21±0.02 | 6.33±0.57 | 5.48±0.91 |
| E           | 53.05±7.91 | 379.43±33.58 | 15965.14±2316.87 | 8.37±0.97 | 0.12±0.03 | 4.53±0.50 | 4.45±0.06 |
| F           | 55.72±1.70 | 331.51±4.37 | 16981.45±1417.64 | 8.70±0.37 | 0.15±0.02 | 3.26±0.47 | 4.74±0.20 |
| Mean        | 61.23±8.07 | 284.51±118.03 | 16985.68±926.99 | 7.26±2.35 | 0.25±0.10 | 4.64±1.59 | 6.13±1.45 |
| CK          | 58.56±3.88 | 316.98±83.22 | 15175.40±1064.97 | 6.86±1.09 | 0.25±0.06 | 3.70±1.43 | 6.76±0.30 |

Heavy metal elements of tea garden soil like Cr, Ni, Cu, Zn, As, Cd, Hg and Pb are determined in this experiment (Table 5). The results show that mean contents of all elements in the tea garden were higher than that in CK. In the soil situation with higher contents of elements like Cr and Ni, the growth and yield of tea plant could be depressed [13]. Higher contents of element Cu can affect the growth and development of roots, and result in dysplasia of tea leaves [14]. Higher Zn can inhibit the enzyme activity and the synthesis of chlorophyll, and then affect
the photosynthesis of tea trees [13]. Element Cd would easily cause intoxication for tea trees. It is specially noticed that Cd will cause cancer, malformation and genic mutation for human body. Pb would inhibit tea plants’ growth and interfere with absorption of Fe from soil [15]. Hg and As also have severe toxicity, and tea plants and human could be poisoned by them [16].

Table 5. The content of heavy metal elements of tea garden soil (mg/kg).

| Sample plot | Cr      | Ni      | Cu      | Zn      | As      | Cd      | Hg      | Pb      |
|------------|---------|---------|---------|---------|---------|---------|---------|---------|
| A          | 45.86±4.70 | 11.75±1.09 | 14.33±0.06 | 99.36±80.43 | 47.03±36.30 | 0.37±0.03 | 0.07±0.02 | 41.50±11.4 |
| B          | 49.75±0.38 | 15.38±2.09 | 14.54±1.48 | 94.49±37.85 | 23.98±1.94 | 0.24±0.01 | 0.10±0.01 | 32.81±1.57 |
| C          | 65.65±14.60 | 31.50±19.92 | 21.20±1.50 | 127.27±31.49 | 27.54±2.75 | 0.19±0.08 | 0.13±0.08 | 25.82±3.53 |
| D          | 60.86±13.12 | 32.15±28.09 | 16.46±0.97 | 133.67±25.22 | 17.03±2.58 | 0.18±0.03 | 0.18±0.13 | 22.59±2.03 |
| E          | 40.76±4.09 | 28.96±21.13 | 16.22±2.18 | 123.1±15.62 | 16.55±2.50 | 0.14±0.05 | 0.21±0.26 | 21.6±5.54 |
| F          | 42.72±2.24 | 55.90±64.96 | 18.16±186 | 65.79±11.30 | 17.43±0.90 | 0.12±0.01 | 0.22±0.08 | 20.73±1.54 |
| Mean       | 50.94±10.13 | 29.27±15.64 | 16.82±2.56 | 107.28±25.67 | 24.93±11.70 | 0.21±0.09 | 0.15±0.06 | 27.51±8.15 |
| CK         | 40.55±1.60 | 23.8±17.44 | 11.61±0.25 | 49.83±6.61 | 15.79±0.72 | 0.13±0.01 | 0.07±0.03 | 22.92±1.75 |

In general, soil elements are the same initial content in tea garden and CK in the same regions. On non-extraneous elements condition, the elements with lower contents should be transferred or absorbed more through roots to plants. The average contents of V, Fe, Se, Co and Sr are all higher than those in CK, which are 61.23, 16985.68, 0.25, 7.26 and 4.64 mg/kg, respectively (Table 4). But the average contents of Mn and Cs are 284.51 and 6.13 mg/kg, lower than in CK (316.98 and 6.76 mg/kg), respectively. It is also found that Mn and Cs are more absorbed by plants and there was no obvious losses due to less absorption. The trend of Mn decreased with the increase of the altitude. The content of Mn is 419.55, 225.82, 255.81 and 94.96 mg/kg at the elevation of 70, 80, 90 and 100 m, respectively.

The contents of 8 heavy metals are listed in Table 5. Contents of Cr, Cu, Zn, As, Cd, Hg and Pb in tea garden are higher than in CK, but Ni was lower. Contents of Cr, Zn, As, Cd and Pb in sloping tea garden are higher than in flat tea garden and CK. The trend of Cr, Cu, Hg decreased and Cd, Pd rise with the increase of the altitude. The downtrend of Zn, Cd contents was more evident than other elements with increase road distance. Nonetheless, there is generally a significant impact on Cd due to terrain, altitude and road. Ni absorption by tea tree incurs major losses under the same initial soil state. The downtrend of Ni is similar to Mn with the increase of the altitude.

4. Conclusion

The soil samples were eliminated using HNO₃ and HF by the fully automatic micro-wave. The matrix effects were perfectly restrained adopting ⁴⁵Sc, ⁷³Ge, ⁸⁸Y, ¹¹⁵In, ¹⁵⁹Tb and ²⁰⁹Bi as interior label elements and KED mode decreased mass spectrum interference. Meanwhile, element contents were calculated based on the different gradient standard curves by a subsection method. The result shows that the linear correlation coefficient was higher, 84.04 % ~ 121.68 % of AR, 0.0038 ~ 3.6198 μg/L of LOD and 0.0127 ~ 12.0660 μg/L of LOQ. The standard substances were well validated and verified from four representative soils adopting this method. Therefore, the faster synchronous method using ICP-MS was feasible and accurate to evaluate 26 elements of tea garden soil. In addition, this method was simple, convenient, accurate, highly sensitive and precise. These investigations will provide scientific evidences and technical supports for evaluating the soil quality and amending the soil.

Acknowledgements

This research was financially supported by Natural Science Foundation of Colleges and Universities in Anhui Province (KJ2017A400), Natural Science Basic Research Plan in Shaanxi Province (2015JM4136), Research on Science Platform for Tourism Management of Huangshan University
References

[1] Dong L K and Fang B 2017 Analysis on spatial heterogeneity of soil heavy metals in tea plantation: case study of high quality tea garden in Jiangsu and Zhejiang. Geographical Research. 36 391-404

[2] Zhang J, Huang J A and Liu Z H 2017 Progress in understanding inhibitory effects of tea functional components on protein aggregation and misfolding diseases. Food Science. 38 277-84

[3] Liu Z M 2013 Direct determination of lead in soil by slurry-sampling graphite furnace atomic absorption spectrometry using STPF technique. Chinese journal of health laboratory technology. 23 1395-96, 1401

[4] Kilbride C, Poole J and Hutchings, TR 2006 A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses. Environmental Pollution. 143 16-23

[5] Jantzi SC and Almirall J R 2014 Elemental analysis of soils using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS) with multivariate discrimination: tape mounting as an alternative to pellets for small forensic transfer specimens. Applied Spectroscopy. 68 963-74

[6] Stroud J L, McGrath S P and Zhao F J 2012 Selenium speciation in soil extracts using LC-ICP-MS. Int J Environ Anal Chem. 92 222-36

[7] Chen S Z, Zhu S P and Lu D B 2014 Solidified floating organic drop microextraction for speciation of selenium and its distribution in selenium-rich tea leaves and tea infusion by electrothermal vapourisation inductively coupled plasma mass spectrometry. Food Chemistry. 169 156-61

[8] Yang H X, Zhao L H, Gao J X, Liu W and Li B 2014 Distribution of Cd, P, S, K, Ca, Cu and Zn elements in Indian Mustard by LA-ICP-MS. Chinese Journal of Analytical Chemistry. 42 355-59

[9] D’Illo S, Violante N, Majorani C and Petrucci F 2011 Dynamic reaction cell ICP-MS for determination of total As, Cr, Se and V in complex matrices: still a challenge? A review. Analytica Chimica Acta. 698 6-13

[10] Zhao X X, Zhang L L and Zhang J P 2014 Spectrum interference and elimination of environmental analysis with ICP-MS. Environmental Monitoring in China. 30 101-6

[11] Zhao M, Cai K, Ren Y, Sun Y H, Wang W J, Chen J M and Chen Z D 2010 Bioaccumulation and transformation of Cu, Zn, Pb, Cd and Cr in different peanut. Journal of Peanuts Science. 39 1-7

[12] Tang D M, Wu J, Tang Y, Zong G Y and Zeng R 2008 The research advance in toxic hazard of heavy metal stress on plant and its resistance mechanism. Sichuan environment. 27 79-83

[13] Makino T, Takano H, Kamiya T, Itou T, Sekiya N, Inahara M and Sakurai Y 2008 Restoration of cadmium-contaminated paddy soils by washing with ferric chloride: Cd extraction mechanism and bench-scale verification. Chemosphere. 70 1035-43

[14] Solanki R and Dhankhar R 2011 Biochemical changes and adaptive strategies of plants under heavy metal stress. Biologia. 66 195-204