Determination of 16 heavy metal elements and 16 rare earth elements in Ya'an tibet tea by ICP-MS

P W Li¹, J H Li ¹,², S X Chen¹*, X L Meng¹

¹College of Horticulture, Sichuan Agricultural University, Chengdu, Sichuan, China
²National Tea Product Quality Supervision and Inspection Center (Sichuan), Ya’an, Sichuan, China

*Corresponding author. P W Li and S X Chen contributed equally to this work.

Abstract. The contents of 16 heavy metal elements such as As, Be, Co, Cr, Cu, Ga, Li, Ni, Sr, V, Zn, Ag, Cd, Cs, Bi, Pb and 16 rare earth elements such as Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu were analyzed, simultaneously and effectively by inductively coupled plasma-mass spectrometry (ICP-MS) method with high pressure digestion and Rh, Re as the internal standard elements. The linear correlation coefficient of each element standard curve was 0.9919 - 0.9999; the detection limit of each element is 0.0003 µg/L - 0.2164 µg/L; the daily and daytime deviation of each element was lower; the average recoveries were between 93.39% - 110.99%, RSD was less than 7.49%. The results showed that the average content of Zn was the highest to be (32.833±0.993) mg/kg, followed by Cu, Sr and Ni, which were significantly higher than those of other 28 elements. The total amount of rare earth in Ya'an was 0.588 mg/kg - 3.161 mg/kg, The average content of Ce was the highest, followed by La, Sc, Nd and Y, the total amount of rare earth total 83.16%-86.15%, the average content of Lu was the lowest. The proportion of each element in the soil, different tea varieties on the absorption and enrichment of various elements, application of fertilizer and pesticide in tea garden resulted in the great differences of each element content.

1. Introduction

Tea contains many kinds of nutritional components, such as tea polyphenols, amino acids and so on. It also contains a variety of trace metal elements. These elements may bring beneficial effects. For example, Zn, Cu, an excess free radical remover in the body, can effectively increase immunity and delay aging [1]. At the same time, they may also threaten the life and health of humans [2]. Excessive intake of heavy metals such as Cd, Cr, Pb, As and Se in diet will increase the risk of cancer to some extent [3]. Rare earth elements in tea enter human body through food chain, and trace rare earth can play a role in health care. However, excessive intake will accumulate in different parts of the body and lead to lesions, and may lead to acute myocardial infarction, leukemia and so on [4-5]. Therefore, human health problems caused by heavy metals and rare earth elements are attracting more and more attention. ICP-MS is a multi-element rapid detection technology. Because of its high sensitivity and simple and effective advantages, it is used for the determination of trace metal elements, especially rare earth elements in tea [6-8]. It is mainly applied to the identification of origin and safety application of tea [9-11]. Ya’an Tibetan Tea is a famous black tea in Sichuan South Road side tea. It uses the processing technology of south side tea and innovates the characteristic tea that is suitable for domestic sale, overseas sale and export tea products according to market demand. In recent years, the upsurge of Tibetan tea drinking has sprang up, and the tea industry of domestic sales has made great
progress. At present, there is no systematic study on the safety detection of heavy metals and rare earth elements in Ya'an Tibetan tea. In this experiment, Ya'an Tibetan tea was taken as the research object, with high pressure digestion for sample pretreatment, Rh and Re as internal standard elements. A rapid and effective method was established by ICP-MS, at the same time, 16 kinds of heavy metal elements such as As, Be, Co, Cr, Cu, Ga, Li, Ni, Sr, V, Zn, Ag, Cd, Cs, Bi, Pb etc. and 16 rare earth elements such as Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu etc. were quickly and effectively measured. It provides technical support for Ya'an Tibetan tea quality and quality detection and comprehensive benefit and its sustainable development.

2. Materials and Methods

2.1. Materials and reagents
Ya'an Tibetan tea was provided by the main tea producing enterprises in Ya'an, Sichuan Province, all of which were spring tea. The sample was fully grated and spare. 16 kinds of heavy metal storage solution and mass spectrum tuning solution were purchased from PerkinElmer company of the United States. Rare earth and In, Re and Rh internal standard storage solutions are purchased from the national nonferrous metals and electronic materials analysis and testing center. Nitric acid was purchased from Merck company in Germany. The experiment water was ultra pure water. The glassware used was soaked in 20% nitric acid solution for more than 24 h and rinsed clean with ultra pure water.

2.2. Instrument and equipment
NexION 300Q ICP-MS is from PerkinElmer United States. HPA-S high pressure ashing apparatus is from Anton Paar company in the Austria. ALC-110.4 electronic balance is from Sartorius company in the German. Arium Comfort water purifier is from Sartorius company in the German.

2.3. Experimental method

2.3.1. Sample digestion
The dried tea powder was accurately weighed 0.35g in the quartz digestion tank, adding 3 mL of concentrated nitric acid. After, the seal was put into the high pressure ashing apparatus. Dissolve according to the following procedures: The temperature was first heated to 70 degrees, and raised temperature to 120℃within 20 min, then warmed up to 180℃and held at 180℃for 60 minutes. After cooling, the treatment solution was taken out of the digestion tank, and the volume was adjusted to 25 mL volumetric flask with ultrapure water, shaken for use, and after appropriate dilution, it was measured on the machine. At the same time, a blank control was made.

2.3.2. ICP-MS working parameters
By using the standard detection mode, the performance state of the instrument and the parameters of the instrument are optimized by inhaling mass spectrometry tuning liquid. The sensitivity, oxide, double charge and resolution of the instrument meet the requirements of measurement. The specific parameters were as follows: ICP RF power: 1050W, Atomizer flow: 0.89 L/min, Auxiliary gas flow: 1.2 L/min, Plasma gas flow: 16 L/min, Atomizer: Concentric Nebulizer, Scanning times: 20, Number of readings: 1, Repetitions: 3, Detector: Double mode, Acquisition mode: Jump peak, Detection method: automatic, Integral time: 36s, Be>3000 cps, Mg>20000 cps, In>50000 cps, U>40000 cps, CeO/Ce≤ 3%, Mass number 220 background≤ 5%.

2.3.3. Standard solution and internal standard solution
The 1% nitric acid solution was used to dilute the mixed storage liquid of 10 ug/mL and 16 kinds of the heavy metal mixed standard storage liquid such as As, Be, Co, Cr, Cu, Ga, Li, Ni, Sr, V, Zn, Ag, Cd, Cs, Bi, Pb, etc. step by step to the standard solution of different gradient. Among rare earth
solution: 0, 0.5, 1.0, 2.0, 5.0, 10.0 ug/L. The other 16 kinds of heavy metal mixed standard solutions: 0, 1.0, 2.0, 5.0, 10.0, 20.0 ug/L. The 100 ug/mL In, Re and Rh mixed internal standard storage solution was diluted to 1 ug/L by 1% nitric acid solution.

2.4. Data analysis
All the results were expressed in mean value of ± SD (n=3), and Excel 2003 was used to analyze the significance of variance.

3. Results and Analysis

3.1. The selection of the internal standard elements and the number of the elements to be measured
This study involved 32 different metal elements, so on the basis of the satisfactory results of the internal standard stability test, the mass fraction of the elements with large abundance, high sensitivity and small disturbance should be selected. Comparing the three internal standard tests of In, Re and Rh, in this experiment, Rh102.905 was finally chosen as the internal standard of Sc 44.956, Y88.905, As74.922, Be9.012, Co 58.953, Cu 62.930, Ga 68.926, Li 7.016, Ni 57.935, Sr 87.906, V50.944, Zn 63.929, La138.906, Ce139.905, Pd140.907, Nd145.913, Sm 146.926, Eu152.929, Gd156.934

3.2. Selection of sample digestion methods
Samples preparation is the key to affect the accuracy of element content. At present, most of the metal elements digestion use microwave digestion[12]. But the consumption of reagents is large. When completing the resolution, it is necessary to remove the acid from the digestion solution to avoid the interference of measuring signals and instrument damage to ICP-MS. In this experiment, tea standard substance GBW 10016 was used as sample for microwave digestion and high pressure digestion respectively. The results showed that the content of 32 metal elements, recovery rate, etc. can meet the simultaneous determination of 32 elements. However, microwave digestion can reduce reagent consumption, reduce environmental pollution and do not need to run sour. Therefore, high pressure digestion method was adopted.

3.3. The standard curve, linear range and detection limit of each element
The standard curve is obtained by taking the element concentration as the abscissa and the ratio of the response value of the measured element to the internal standard element as ordinate. The detection limit of the method is 3 times the standard deviation of blank value of 11 samples[13].

| element | regression equation | r | LOD/ (ug·L⁻¹) | element | regression equation | r | LOD/ (ug·L⁻¹) |
|---------|---------------------|---|---------------|---------|---------------------|---|---------------|
| Sc      | y = 0.8428 x - 0.0374 | 0.9999 | 0.0354 | Nd      | y =0.2546 x + 0.0025 | 0.9999 | 0.0018 |
| Y       | y = 1.2959 x +0.0349 | 0.9999 | 0.0017 | Sm      | y = 0.2174 x +0.0038 | 0.9999 | 0.0043 |
| As      | y = 0.0734 x +0.0064 | 0.9999 | 0.0094 | Eu      | y = 0.7596 x +0.0203 | 0.9999 | 0.0006 |
| Be      | y = 0.0743 x +0.0008 | 0.9999 | 0.0023 | Gd      | y = 0.2719 x +0.0012 | 0.9999 | 0.0009 |
| Co      | y = 0.6732 x +0.0372 | 0.9999 | 0.0010 | Tb      | y = 1.3664x + 0.0400 | 0.9999 | 0.0006 |
| Cr      | y = 0.5384x +0.0310 | 0.9999 | 0.0762 | Dy      | y = 0.3401 x +0.0063 | 0.9999 | 0.0006 |
| Cu      | y = 0.3081x +0.0624 | 0.9999 | 0.0196 | Ag      | y = 0.4650 x +0.0359 | 0.9999 | 0.0113 |
| Ga      | y = 0.5815 x +0.0460 | 0.9999 | 0.0100 | Cd      | y = 0.1945x + 0.0119 | 0.9999 | 0.0006 |
| Li      | y = 0.3130 x +0.0220 | 0.9999 | 0.0100 | Cs      | y = 1.1620 x +0.1036 | 0.9999 | 0.0013 |
| Ni      | y = 0.3590 x +0.0344 | 0.9999 | 0.1356 | Ho      | y = 3.3012 x +0.6304 | 0.9990 | 0.0007 |
| Sr      | y = 1.0534 x +0.0945 | 0.9999 | 0.0039 | Er      | y = 1.0833 x + 0.2101 | 0.9991 | 0.0010 |
| V       | y = 0.6380 x +0.0222 | 0.9999 | 0.0060 | Tm      | y = 3.2495 x +0.5665 | 0.9992 | 0.0003 |
As can be seen from Table 1, the 32-element standard curve had a good linear relationship and the correlation coefficients were mostly 0.9999. The detection limit of the 32 elements was very low, from 0.0003ug/L to 0.2164ug/L. Zn had the highest detection limit, and the detection limit of Ni and Tm was the lowest. The correlation coefficient and detection limit of each element can meet the requirements of quantitative analysis.

3.4. Repeatability, stability and recovery of the method

Within-day precision is measured the same tea reference material which is GBW10016 GSB-7 five times in a row on the same day. The inter-day precision is measured on the same sample for 3 consecutive days, measured 3 times a day, and averaged. The results showed that the RSD of within-day precision and inter-day precision were 0.12~3.85% and 1.21%~6.65% respectively. The within-day precision RSD of each element was less than the inter-day precision (Table 2). Each element had a low within-day and inter-day deviation, and the within-day deviation was less than the inter-day deviation. It showed that the stability and reproducibility of the method was good.

The recovery rate was the tea standard substance GBW10016 GSB-7 with known content, adding 3 different concentration of standard liquid. When completing the resolution, the sample was determined and the recovery rate of each component was calculated. The results showed that the recovery rate was between from 93.39% to 110.99%. The recovery rate of RSD was less than 7.49% (Table 2).

| element | within-day precision/% | inter-day/% | recovery | recovery RSD/% | element | within-day precision/% | inter-day/% | recovery | recovery RSD/% |
|---------|------------------------|------------|---------|--------------|---------|------------------------|------------|---------|--------------|
| Sc      | 0.68                   | 3.78       | 105.83  | 2.48         | Nd      | 1.80                   | 6.62       | 105.46  | 1.08         |
| Y       | 0.85                   | 2.46       | 107.61  | 5.71         | Sm      | 1.12                   | 5.85       | 110.99  | 1.58         |
| As      | 1.02                   | 4.26       | 101.43  | 4.52         | Eu      | 1.52                   | 3.30       | 108.35  | 6.37         |
| Be      | 1.49                   | 2.34       | 95.37   | 0.55         | Gd      | 1.54                   | 1.21       | 107.91  | 7.30         |
| Co      | 1.09                   | 1.79       | 104.85  | 3.21         | Tb      | 0.61                   | 5.00       | 103.19  | 3.12         |
| Cr      | 0.87                   | 6.65       | 93.49   | 5.25         | Dy      | 1.07                   | 2.81       | 104.67  | 1.38         |
| Cu      | 0.25                   | 3.75       | 99.59   | 4.14         | Ag      | 3.85                   | 3.51       | 103.88  | 4.08         |
| Ga      | 1.26                   | 2.54       | 107.63  | 1.41         | Cd      | 0.51                   | 3.61       | 93.39   | 7.49         |
| Li      | 1.68                   | 3.77       | 100.17  | 4.56         | Cs      | 0.49                   | 4.44       | 101.95  | 1.60         |
| Ni      | 0.13                   | 6.22       | 97.24   | 4.01         | Ho      | 0.57                   | 3.89       | 104.24  | 3.93         |
| Sr      | 0.84                   | 5.84       | 96.80   | 5.41         | Er      | 1.02                   | 3.36       | 104.88  | 2.27         |
| V       | 0.75                   | 3.31       | 104.55  | 6.76         | Tm      | 1.17                   | 1.42       | 105.67  | 3.27         |
| Zn      | 0.12                   | 2.78       | 99.28   | 3.31         | Yb      | 0.27                   | 2.79       | 104.65  | 0.82         |
| La      | 0.12                   | 3.46       | 101.51  | 2.94         | Lu      | 0.24                   | 2.16       | 102.97  | 6.12         |
| Ce      | 0.57                   | 1.61       | 98.60   | 5.37         | Bi      | 1.00                   | 5.57       | 94.57   | 4.41         |
| Pr      | 0.36                   | 5.13       | 103.57  | 5.59         | Pb      | 0.44                   | 2.33       | 93.68   | 4.29         |

3.5. Simultaneous determination of 32 elements in Ya'an Tibetan tea by ICP-MS

The content of 32 elements in Ya'an Tibetan tea was shown in Table 3. The results showed that the average content of Zn was the highest (32.83±0.993) mg/kg, followed by Cu (16.143±0.658)mg/kg, Sr (12.571±0.659)mg/kg and Ni (9.155±0.210)mg/kg. They were significantly higher than those of the other 28 elements ($P<0.010$). At present, NY/T 288-2012 requires Cu is less than 30 mg/kg. GB 2762-2017 requires that the lead is less than 5 mg/kg, and deletes the requirements for the limit of rare earth. NY 659-2003 requires that the chromium is less than 5 mg/kg. Cadmium is less than 1 mg/kg.
Arsenic is less than 2 mg/kg. It shows that the chromium, cadmium and arsenic in Ya'an Tibetan tea have not exceeded the standard. There is no limit on other elements in the current tea standards.

The total amount of rare earth elements in Ya'an Tibetan tea was from 0.588 mg/kg to 3.161 mg/kg, with an average of (1.699±0.016) mg/kg. Rare earth elements included 16 elements: light rare earth (La, Ce, Pr, Nd, Sm, Eu, Gd) and heavy rare earth (Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc). As shown in Table 3, the total amount of light rare earth elements Ce, Eu, La, Nd, Pr, Sm accounted for 56.77~70.07% of the total content of 16 rare earth elements, which was significantly higher than the total amount of heavy rare earth elements Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y (P < 0.01). This conclusion was consistent with the previous research [13]. The average content of Ce in Ya'an Tibetan tea was the highest among all rare earth elements (0.546±0.012) mg/kg, followed by La (0.257±0.004) mg/kg, Sc (0.48±0.004) mg/kg, Nd (0.195±0.008) mg/kg and Y (0.193±0.003) mg/kg. The total amount of Ce, La, Sc, Nd, and Y accounted for 83.16% ~ 86.15% of the total amount of rare earths.

Table 3. Contents of 32 elements in Ya'an Tibetan tea (mg/kg)

| element | 1    | 2    | 3    | 4    | 5    | 6    | average content |
|---------|------|------|------|------|------|------|-----------------|
| Sc      | 0.363±0.029 | 0.174±0.025 | 0.617±0.014 | 0.137±0.010 | 0.160±0.016 | 0.48±0.012 | 0.248±0.004     |
| Y       | 0.337±0.005 | 0.110±0.003 | 0.084±0.003 | 0.074±0.002 | 0.101±0.002 | 0.45±0.009 | 0.193±0.003     |
| As      | 0.131±0.007 | 0.078±0.003 | 0.075±0.002 | 0.060±0.001 | 0.118±0.007 | 0.377±0.023 | 0.140±0.001     |
| Be      | 0.047±0.004 | 0.018±0.002 | 0.012±0.001 | 0.009±0.000 | 0.017±0.002 | 0.060±0.001 | 0.027±0.000     |
| Co      | 0.621±0.023 | 0.610±0.006 | 0.567±0.014 | 0.398±0.010 | 0.588±0.018 | 0.686±0.004 | 0.578±0.011     |
| Cr      | 2.381±0.086 | 0.988±0.021 | 1.577±0.072 | 0.805±0.048 | 1.180±0.042 | 3.724±0.083 | 1.776±0.059     |
| Cu      | 13.096±0.718 | 16.968±0.974 | 15.967±0.822 | 16.251±0.382 | 17.894±0.533 | 16.684±0.517 | 16.143±0.658   |
| Ga      | 1.009±0.052 | 0.513±0.012 | 0.584±0.011 | 0.300±0.011 | 0.502±0.011 | 1.440±0.035 | 0.725±0.022     |
| Li      | 0.461±0.039 | 0.307±0.030 | 0.259±0.020 | 0.310±0.027 | 0.262±0.023 | 0.661±0.032 | 0.377±0.005     |
| Ni      | 7.718±0.536 | 9.169±0.425 | 11.191±0.243 | 8.494±0.359 | 9.880±0.372 | 8.476±0.399 | 9.155±0.210     |
| Sr      | 16.483±0.299 | 9.653±1.136 | 11.008±0.766 | 4.755±0.417 | 7.855±0.402 | 24.771±0.932 | 12.571±0.659   |
| V       | 0.631±0.010 | 0.263±0.007 | 0.318±0.005 | 0.218±0.006 | 0.284±0.003 | 1.000±0.006 | 0.452±0.004     |
| Zn      | 22.357±0.636 | 30.139±0.686 | 36.220±2.269 | 46.158±1.904 | 35.376±1.022 | 26.745±0.714 | 32.833±0.993   |
| La      | 0.483±0.027 | 0.131±0.015 | 0.113±0.011 | 0.079±0.009 | 0.120±0.015 | 0.618±0.021 | 0.257±0.004     |
| Ce      | 1.158±0.025 | 0.234±0.027 | 0.191±0.019 | 0.153±0.012 | 0.218±0.009 | 1.323±0.028 | 0.546±0.012     |
| Pr      | 0.097±0.002 | 0.028±0.002 | 0.021±0.003 | 0.018±0.001 | 0.023±0.005 | 0.144±0.020 | 0.055±0.002     |
| Nd      | 0.362±0.013 | 0.103±0.008 | 0.079±0.010 | 0.063±0.002 | 0.093±0.008 | 0.468±0.036 | 0.195±0.008     |
| Sm      | 0.070±0.003 | 0.021±0.001 | 0.017±0.001 | 0.012±0.002 | 0.020±0.001 | 0.096±0.011 | 0.039±0.003     |
| Eu      | 0.046±0.002 | 0.018±0.000 | 0.019±0.000 | 0.010±0.000 | 0.018±0.001 | 0.057±0.001 | 0.028±0.000     |
| Gd      | 0.090±0.006 | 0.025±0.001 | 0.019±0.002 | 0.015±0.001 | 0.023±0.001 | 0.138±0.027 | 0.052±0.005     |
| Tb      | 0.012±0.001 | 0.004±0.000 | 0.003±0.000 | 0.002±0.000 | 0.004±0.000 | 0.017±0.000 | 0.007±0.000     |
| Dy      | 0.059±0.002 | 0.018±0.000 | 0.013±0.000 | 0.011±0.001 | 0.016±0.000 | 0.083±0.006 | 0.033±0.001     |
| Ag      | —     | 0.027±0.007 | 0.067±0.008 | 0.016±0.004 | 0.004±0.001 | 0.018±0.007 | 0.021±0.004     |
| Cd      | 0.063±0.005 | 0.080±0.009 | 0.063±0.005 | 0.088±0.007 | 0.067±0.009 | 0.147±0.020 | 0.085±0.008     |
4. Conclusion

In this experiment, Rh and Re were internal standard elements and the samples were digested by high pressure digestion. An ICP-MS method was established to simultaneously detect the contents of 16 heavy metals and 16 rare earth elements in Ya’an Tibetan tea. This method is simple, reproducible, stable and high recovery rate. This method is suitable for rapid and effective detection of multi element pollutants in tea, providing technical support for quality quality testing and comprehensive benefits of Ya’an Tibetan tea, which is of great significance for the sustainable development of Ya’an Tibetan tea industry.

References

[1] SALAHINEJAD M and AFLAKI F 2010 Toxic and essential mineral elements content of black tea leaves and their tea infusions consumed in Iran Biological trace element research vol 134 pp 109–117

[2] LI X, ZHANG Z, LI P, Zhang W and Ding X 2013 Determination for major chemical contaminants in tea (Camellia sinensis) matrices: a review Food research international vol 53 pp 649–658

[3] BOWER J J, LEONARD S S and SHI X 2005 Conference overview: molecular mechanisms of metal toxicity and carcinogenesis Molecular and cellular biochemistry vol 279 pp 3–15

[4] WANG L, HUANG X and ZHOU Q 2008 Effects of rare earth elements on the distribution of mineral elements and heavy metals in horseradish Chemosphere vol 73 pp 314–319

[5] GOMEZ-ARACENA J, Riemersma R A, Gutiérrez-Bedmar M, Bode P, Kark J D, Garcia-Rodríguez A and Martin-Moreno J M 2006 Toenail cerium levels and risk of a first acute myocardial infarction: The EURAMIC and heavy metals study Chemosphere vol 64 pp 112–120

[6] WANG Q S, CHEN D, CAO J X and WU H L 2017 Evaluation of heavy metals and rare-earth elements in famous black teas at home and abroad Journal of Food Science and Technology vol 35 pp 87–94

[7] YI P 2017 Content of Rare Earth and Heavy Metal Elements in Xinyang Maojian Tea and their Risk Assessment Guizhou Agricultural Sciences vol 45 pp 128–131

[8] CHEN X, FANG X Q, DAI X, CHEN T B, LIU X W and LI W Y 2016 Determination of 5 heavy metal elements and 15 rare-earth metal elements in dark tea Food and Machinery vol 32 pp 55–57

[9] MA G, ZHANG Y, ZHANG J, Wang G, Chen L, Zhang M and Lu C 2015 Determining the geographical origin of Chinese green tea by linear discriminant analysis of trace metals and rare earth elements: taking Dongting Biluochun as an example Food Control vol 59 pp 714–720

[10] GUO Y, ZHANG S, LAI L and WANG G 2015 Rare earth elements in Oolong tea and their human health risks associated with drinking tea Journal of Food Composition and Analysis 44 pp 122–127

[11] PARVIZ M, ESHGHI N, ASADI S, Teimoory H and Rezaei M 2015 Investigation of heavy metal contents in infusion tea samples of Iran Toxin Reviews vol 34 pp 2944–2950
[12] WANG Bin, XU Yin-feng, LI Guo-qiang and GUAN H S 2009 Determination of 27 Inorganic Elements in Limonium bicolor by ICP-MS Using Microwave Digestion for Sample Preparation *Spectroscopy and Spectral Analysis* vol 29 pp 3138–3140

[13] NING P, GONG C, ZHANG Y and GUO K K 2010 La, Ce, Pr, Nd and Sm concentrations in Pu'er tea of Yunnan, China *Journal of Rare Earths (English Edition)* vol 28 pp 636–640.

[14] WANG Q Q, XUE Z H, LI W D, CHEN Z D and SUN W J 2017 Study of Accumulation and Distribution of the Rare Earth Elements in Different Tea Cultivars *Acta Horticulturae Sinica* vol 44 pp 1198-1206

[15] LIN R X, CHEN L, XIE C C, ZHOU Z N, CAI Y B and FAN S X 2010 Study on rare earth sources of Oolong tea in Fujian *China Tea* vol 32 pp 10–11

[16] NING P B, GONG C M, ZHANG Y M and GUO K K 2010 Analysis of Rare Earth Elements in Pu'er Tea of Yunnan by ICP-AES *Spectroscopy and Spectral Analysis* vol 30 pp 2830–2833