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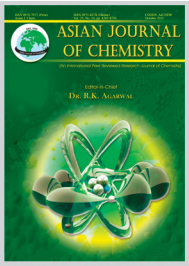

Determination of Fifteen Rare Earth Elements in Green Tea Leaves and Their Tea Infusions Consumed in Zhejiang Province, China

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Using the inductively coupled plasma mass spectrometer (ICP-MS) determined the contents of 15 rare earth elements in 28 green tea samples and 6 tea infusions which collected in Zhejiang province, China. La, Ce, Nd and Y are the dominants elements amongst 15 rare earth elements, the maximum of rare earth elements in the 28 green tea samples is 2.0 μg g^{-1}, the content of Ce. Total rare earth elements oxide of 28 samples range from 0.4 to 7.3 μg g^{-1}, the total rare earth elements oxides of 6 samples exceed the national standard of maximum levels. Otherwise the rare earth elements in the infusion of those 6 green tea samples are far more below the permission concentration in drinking water. The extraction efficiency of rare earth elements into the infusion is 3.4 % in average. The contradiction between the standards of green tea leaves and their infusion concentrations can be contribute to the low extraction efficiency of rare earth elements in the green tea samples into their infusions.

Key Words: Rare earth elements, Green tea, Infusion.

INTRODUCTION

Rare earth elements have similar chemical properties and tend to be present naturally as a group rather than alone. China has the largest reserves of rare earth elements (REEs) in the world[1]. Rare earth elements are abundant in Chinese soil, especially in the southern China[2]. Since 1972 using the fertilizers of rare earth elements in the agricultural fields becomes popular in China. Such as the application of rare earth fertilizers *nongle*[3,4], *changle*[5] to the tea plants can promote the yield of tea. Those rare earth fertilizers contains the nitrate or chloride of rare earth elements, with the application of the fertilizers it can induce accumulation in the soils and plants[6]. The contents of rare earth elements in tea sample became a focus for the reason above. Lin *et al.*[6] tested 30 samples from two main production region of oolong teas in Fujian province, the results showed that the contents of rare earth elements in 26.7 % of samples exceeded 2.0 μg g^{-1}.

Up to now, no evident proved that the rare earth elements are the essential elements to human being. The half live of rare earth elements in body from one year to tens of years. The rare earth elements can permeate the blood brain barrier then ingress the brain tissue, impact the excretion of insulin and induce hepatic adipose infiltration[7].

Zhejiang province is the main production region of green tea in China, determination the rare earth elements in the green teas and their infusion can provide the information about the security of drink the green teas. In this article, 28 green tea samples and 6 green tea infusions were determined by inductively coupled plasma mass spectrometer (ICP-MS).

EXPERIMENTAL

ICP-MS: The instrument used was Xseries II ICP-MS (Thermo fisher, United States) equipped with quartz torch, nickel sampler and skimmer cones, a peristaltic pump (maintaining a 1 mL min^{-1} sample uptake rate), a concentric nebulizer and a double pass Scott-type spray chamber. Operating conditions are summarized in Table-1.

TABLE-1
ICP-MS OPERATING CONDITIONS

Auxiliary (L/min)	0.74
Nebuliser (L/min)	0.85
Forward power (W)	1223.5
Analogue detector (V)	2060
PC detector (V)	1300
Resolution	Standard
Dwell (ms)	100
Number of replicates	3
Peri-pump (r/min)	20

Microwave digestion system: For the dissolution of samples, a microwave digestion system (MARS™ digestion

and Extraction System, CEM, USA) was used with TFM (tetrafluormethaxil) vessels.

Reagent and standard solution: Deionized distilled water 18 MΩ cm^{-1} (Milli-Q Element, Bedford, MA) was used throughout the work to prepare all standard and sample solutions. Concentrated nitric acid (65 % -70 %) and hydrogen peroxide (30 %) were used for the digestion of samples.

Rare earth elements working standard resolution were prepared by serial dilutions of the stock solution (100 mg L^{-1}, GSB 04-1789-2004, national center of analysis and testing for nonferrous metals and electronic materials).

The internal standard solution of 10 µg L of In and Bi in 1 % HNO_3 was prepared from the stock solution (100 mg L^{-1}, GBW (E) 080178 and GBW (E) 080644, Beijing research institute of chemical engineering and metallurgy).

Sampling and pre-treatment of samples: Twenty eight green tea samples were collected from the place of origin in the Lishui city, South-West of Zhejiang Province. The samples were dried in the baking oven under 105 ºC for 6 h, then smashed as powder for analysis. Those 28 green tea samples were named as HMQ, LGLRQ, MFQ, JGYQ, YCQ, XGXHQ, BSHCQ, XDSFQ, XC1Q, XC2Q, XC3Q, BLCQ, HMC, YH1C, YH2C, YH3C, LGLRC, MFC, JGYC, FYCC, YCC, BLCC, BSHCC, XDSFC, XC1C, XC2C, XC3C and BLCC as well according to their Chinese names.

Analytical method was according to the Chinese national standard GB/T 23199-2008. About 0.5 g tea sample was accurately weighed and transferred into TFM vessel, followed by adding 4 mL 65 %-70 % HNO_3, cold digestion over night, then added 2 mL 30 % H_2O_2. The vessels were capped and placed in the microwave system and digested using the parameters listed in Table-2. At the end of the program, the vessels were cooled to room temperature in a fume hood and the pressure inside the vessels slowly released. After cooling the digested samples were transferred to 50 mL graduated polypropylene centrifuge tubes, washed three times with double-deionized water to a volume of 50 mL and filtered by filter paper to remove any remaining undissolved solid particles that might block the nebulizer. Process a reagent blank in the same way.

TABLE-2
OPERATING PARAMETERS, TEMPERATURE PROGRAMS AND DIGESTION REAGENTS FOR MICROWAVE SYSTEM

Power (W)	0- 1, 200
No of vessels	40
Vessel volume (mL)	55
Sensors control	Temperature
Ramp time (min)	10
Hold time (min)	30
Hold temperature (ºC)	185
HNO_3/H_2O_2 digestion mixture (mL)	4 mL conc. HNO_3 and 2 mL 30 % H_2O_2

The tea infusions were prepared by adding 100 mL 85 ºC DWW in 150 mL glass beakers with 2.0-2.5 g tea samples. After 15 min of infusion, the solutions were filtered. When the solutions reached room temperature, imbibed 20 mL solution with pipette into 50 mL glass beakers, then evaporated the solutions on electric hot plate until about 1 mL volume left over, cooled down and 5 mL HNO_3 were added. The digestion was carried out for *ca.* 1 h at 150 ºC until the solution became transparent, 1 mL H_2O_2 was added, the digestion was continued until the volume of solution reached about 1 mL. Finally the solutions were transferred into 25 mL graduated polypropylene centrifuge tubes, washed three times with double-deionized water to a volume of 25 mL and filtered by filter paper. Process a reagent blank in the same way.

Measurements: An inductively coupled plasma mass spectrometry was used for rare earth elements determination; the operating parameters are shown in Table-1. Sample solution and internal standard were injected simultaneously through a three-way pipe. The precision of method was evaluated in 10 replicate determinations on each of 5 different randomly chosen samples. The reliability of the method was confirmed by using a certified reference material (GBW 10016, National research centre for certified reference materials, CRM Tea).

To evaluate the analytical characteristics of the method for each element, the detection limits were calculated according to IUPAC rules[8]. The detection limits of 15 rare earth elements are listed in Table-3.

TABLE-3
DETECTION LIMITS OF 15 RARE EARTH ELEMENTS IN THE TEA (ng g^{-1})

Y	0.11	Sm	0.16	Ho	0.024
La	0.3	Eu	0.096	Er	0.066
Ce	0.19	Gd	0.12	Tm	0.011
Pr	0.067	Tb	0.018	Yb	0.024
Nd	0.36	Dy	0.045	Lu	0.0083

RESULTS AND DISCUSSION

Characteristics of rare earth elements in 28 green tea samples: As rare earth elements are divided into light rare earth elements (LREE, La-Gd and Sc) and heavy rare earth elements (HREE, Y and Tb-Lu)[9]. The contents of 15 rare earth elements were listed in Table-4, it showed that the La, Ce, Nd, which belong to the LREE and Y one of HREE were the main rare earth elements in the tea leaves, the per cent of total rare earth elements of these four elements were 23.7, 31.8, 15.8 and 12.0 % respectively. The contents of 15 rare earth elements in the green tea samples were significant difference. The maximum and minimum contents were 2 µg g^{-1} and below detection limits respectively.

Except Y the other HREE contents in the tea samples were 1 or 2 order of magnitude lower than that of LREE especially that of Tb, Tm and Lu, usually lower than 10 ng g^{-1}.

Rare earth elements are not only non-essential elements to human being, but also may result in damage to the health of body. Consequently the maximum levels of rare earth elements, by oxides of rare earth elements, in the tea are 2.0 µg g^{-1} according to mandatory national standards GB 2762-2005 maximum levels of contaminants in food. The total rare earth elements oxide (TREO) of 15 elements in the 28 green tea samples ranged from 0.4 to 7.3 µg g^{-1} and the contents of total rare earth elements oxide in 6 green teas, such as LGLRQ, JGYQ, BSHCQ, XC3Q, YH1C, JGYC, were exceeded the maximum level in GB 2762-2005. The results of contents of total rare earth elements oxide in green tea samples are showed in Fig. 1.

TABLE-4
RESULTS OF RARE EARTH ELEMENTS CONTENTS OF 28 GREEN TEA SAMPLES IN ZHEJIANG PROVINCE /(μg·g^{-1})[a]

Samples	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
HMQ	0.29 ± 0.0056	0.38 ± 0.0077	0.41 ± 0.011	0.060 ± 0.0014	0.24 ± 0.0056	0.040 ± 0.0012	0.021 ± 0.0001	0.051 ± 0.0019	0.006 ± 0.0002	0.037 ± 0.0009	0.008 ± 0.0002	0.031 ± 0.0005	0.006 ± 0.0002	0.043 ± 0.0004	0.007 ± 0.0002
LGLRQ	0.18 ± 0.0025	0.44 ± 0.011	0.66 ± 0.0087	0.062 ± 0.0002	0.25 ± 0.010	0.043 ± 0.0002	0.015 ± 0.0002	0.057 ± 0.0002	0.006 ± 0.0002	0.031 ± 0.0025	0.006 ± 0.0002	0.018 ± 0.0002	0.003 ± 0.0002	0.019 ± 0.0012	ND[b]
MFQ	0.035 ± 0.0035	0.098 ± 0.0077	0.15 ± 0.0047	0.015 ± 0.0005	0.063 ± 0.0012	0.011 ± 0.0017	0.011 ± 0.0005	0.014 ± 0.0010	ND	0.007 ± 0.0002	ND	0.004 ± 0.0005	ND	0.003 ± 0.0007	ND
JGYQ	1.0 ± 0.039	1.3 ± 0.040	1.8 ± 0.049	0.22 ± 0.0038	0.84 ± 0.023	0.15 ± 0.0026	0.063 ± 0.0031	0.20 ± 0.0045	0.026 ± 0.0012	0.16 ± 0.0062	0.035 ± 0.0007	0.12 ± 0.0064	0.019	0.13 ± 0.0014	0.018 ± 0.0002
YCQ	0.072 ± 0.0053	0.061 ± 0.0090	0.097 ± 0.0063	0.013 ± 0.0007	0.056 ± 0.0041	0.010 ± 0.0010	.0093 ± 0.0007	0.013 ± 0.0010	ND	0.010 ± 0.0012	ND	0.007 ± 0.0002	ND ± 0.0002	0.007 ± 0.0002	ND
XGXHQ	0.11 ± 0.0042	0.18 ± 0.0026	0.27 ± 0.0065	0.036 ± 0.0007	0.14 ± 0.0072	0.027 ± 0.0033	0.017 ± 0.0002	0.031 ± 0.0012	0.003 ± 0.0002	0.017 ± 0.0005	0.003 ± 0.0005	0.010 ± 0.0007	ND	0.009 ± 0.0002	ND
BSHCQ	0.35 ± 0.0038	0.43 ± 0.018	0.38 ± 0.0041	0.088 ± 0.0007	0.37 ± 0.012	0.074 ± 0.0026	0.024 ± 0.0010	0.081 ± 0.0007	0.011 ± 0.0002	0.059 ± 0.0010	0.012 ± 0.0002	0.039 ± 0.0002	0.006 ± 0.0002	0.044 ± 0.0002	0.007 ± 0.0002
XDSFQ	0.11 ± 0.0010	0.19 ± 0.0046	0.22 ± 0.0019	0.034 ± 0..0005	0.14 ± 0.0005	0.022 ± 0.0005	0.015 ± 0.0005	0.029 ± 0.0007	0.003 ± 0.0002	0.017 ± 0.0014	0.003 ± 0.0002	0.010 ± 0.0007	ND	0.010 ± 0.0005	ND
XC1Q	0.076 ± 0.0026	0.22 ± 0.0029	0.28 ± 0.0010	0.023 ± 0.0012	0.086 ± 0.0024	0.015 ± 0.0011	0.011 ± 0.0005	0.021 ± 0.0014	ND	0.010 ± 0.0007	ND	0.006 ± 0.0007	ND	0.006 ± 0.0002	ND
XC2Q	0.18 ± 0.012	0.26 ± 0.018	0.44 ± 0.028	0.039 ± 0.0018	0.15 ± 0.0081	0.027 ± 0.0014	0.017 ± 0.0016	0.038 ± 0.0011	0.004 ± 0.0002	0.022 ± 0.0022	0.005 ± 0.0002	0.015 ± 0.0007	ND	0.014 ± 0.0002	ND
XC3Q	0.18 ± 0.0011	1.3 ± 0.0014	2.0 ± 0.015	0.25 ± 0.0025	0.94 ± 0.013	0.13 ± 0.0011	0.024 ± 0.0018	0.16 ± 0.0014	0.011 ± 0.0005	0.036 ± 0.0025	0.006 ± 0.0002	0.021 ± 0.0005	ND	0.016 ± 0.0005	ND
BLCQ	0.054 ± 0.0010	0.23 ± 0.0026	0.41 ± 0.0007	0.031 ± 0.0014	0.096 ± 0.0002	0.015 ± 0.0002	.0066 ± 0.0001	0.026 ± 0.0002	ND	0.008 ± 0.0005	ND	0.005 ± 0.0002	ND	0.004 ± 0.0002	ND
HMC	0.18 ± 0.004	0.25 ± 0.0020	0.18 ± 0.0052	0.043 ± 0.0007	0.17 ± 0.0045	0.032 ± 0.0043	0.010 ± 0.0007	0.037 ± 0.0004	0.005 ± 0.0002	0.026 ± 0.0002	0.005 ± 0.0002	0.018 ± 0.0005	0.003 ± 0.0002	0.023 ± 0.0002	0.004 ± 0.0002
YH1C	0.16 ± 0.0061	0.56 ± 0.018	0.53 ± 0.014	0.12 ± 0.0017	0.46 ± 0.0028	0.069 ± 0.0007	0.010 ± 0.0012	0.081 ± 0.0097	0.007 ± 0.0002	0.029 ± 0.0017	0.005 ± 0.0005	0.016 ± 0.0002	ND	0.012 ± 0.0002	ND
YH2C	0.044 ± 0.0012	0.066 ± 0.0012	0.16 ± 0.0016	0.017 ± 0.0002	0.073 ± 0.0037	0.013 ± 0.0007	0.005 ± 0.0001	0.017 ± 0.0016	ND	0.008 ± 0.0002	ND	0.004 ± 0.0002	ND	0.004 ± 0.0002	ND
YH3C	0.080 ± 0.0015	0.21 ± 0.0054	0.37 ± 0.0049	0.040 ± 0.0005	0.16 ± 0.0059	0.027 ± 0.0007	0.006 ± 0.0007	0.035 ± 0.0007	0.003 ± 0.0002	0.014 ± 0.0002	ND	0.008 ± 0.0002	ND	0.006 ± 0.0002	ND
LGLRC	0.033 ± 0.0005	0.082 ± 0.0012	0.14 ± 0.0023	0.014 ± 0.0007	0.057 ± 0.0002	0.009 ± 0.0001	0.005 ± 0.0001	0.013 ± 0.0009	ND	0.005 ± 0.0007	ND	0.004 ± 0.0002	ND	0.003 ± 0.0002	ND
MFC	0.088 ± 0.0055	0.31 ± 0.013	0.26 ± 0.013	0.050 ± 0.0043	0.20 ± 0.0053	0.027 ± 0.0031	0.021 ± 0.0022	0.036 ± 0.0005	0.003 ± 0.0002	0.014 ± 0.0002	ND	0.008 ± 0.0002	ND	0.006 ± 0.0002	ND
JGYC	0.75 ± 0.015	0.55 ± 0.0048	0.65 ± 0.016	0.14 ± 0.0007	0.62 ± 0.011	0.14 ± 0.0062	0.043 ± 0.0012	0.16 ± 0.0007	0.023 ± 0.0007	0.14 ± 0.0055	0.027 ± 0.0005	0.086 ± 0.0002	0.013 ± 0.0002	0.093 ± 0.0002	0.013 ± 0.0002
FYCC	0.15 ± 0.0012	0.21 ± 0.0035	0.20 ± 0.0016	0.037 ± 0.0009	0.15 ± 0.0002	0.028 ± 0.0012	0.012 ± 0.0007	0.034 ± 0.0007	0.004 ± 0.0002	0.023 ± 0.0014	0.005 ± 0.0002	0.016 ± 0.0005	0.002 ± 0.0002	0.017 ± 0.0002	ND
YCC	0.053 ± 0.0007	0.23 ± 0.0018	0.25 ± 0.0050	0.020 ± 0.0002	0.075 ± 0.0036	0.012 ± 0.0010	0.015 ± 0.0002	0.019 ± 0.0002	ND	0.007 ± 0.0002	ND	0.004 ± 0.0002	ND	0.003 ± 0.0002	ND
BLCC	0.056 ± 0.0025	0.12 ± 0.0065	0.18 ± 0.0036	0.021 ± 0.0007	0.085 ± 0.0061	0.014 ± 0.0025	0.010 ± 0.0004	0.019 ± 0.0009	ND	0.009 ± 0.0007	ND	0.005 ± 0.0002	ND	0.004 ± 0.0002	ND
BSHCC	0.15 ± 0.0064	0.15 ± 0.010	0.21 ± 0.0080	0.037 ± 0.0007	0.16 ± 0.0007	0.031 ± 0.0025	0.010 ± 0.0001	0.037 ± 0.0002	0.005 ± 0.0002	0.026 ± 0.0005	0.005 ± 0.0002	0.017 ± 0.0002	0.002 ± 0.0002	0.018 ± 0.0002	ND
XDSFC	0.046 ± 0.0025	0.20 ± 0.0089	0.28 ± 0.0022	0.026 ± 0.0005	0.098 ± 0.0007	0.015 ± 0.0012	0.020 ± 0.0012	0.022 ± 0.0005	ND	0.007 ± 0.0003	ND	ND	ND	ND	ND
XC1C	0.079 ± 0.0014	0.20 ± 0.0014	0.31 ± 0.0020	0.032 ± 0.0004	0.12 ± 0.0009	0.020 ± 0.0011	.0079± 0.0004	0.027 ± 0.0023	0.002 ± 0.0002	0.011 ± 0.0002	ND	0.007 ± 0.0009	ND	0.006 ± 0.0002	ND
XC2C	0.080 ± 0.0012	0.31 ± 0.0085	0.35 ± 0.0031	0.034 ± 0.0024	0.13 ± 0.0050	0.019 ± 0.0002	.0095 ± 0.0005	0.029 ± 0.0002	0.002 ± 0.0002	0.010 ± 0.0002	ND	0.005 ± 0.0005	ND	0.003 ± 0.0002	ND
XC3C	0.095 ± 0.0033	0.13 ± 0.0038	0.24 ± 0.0069	0.029 ± 0.0021	0.12 ± 0.0010	0.024 ± 0.0029	.0092 ± 0.0012	0.028 ± 0.0007	0.003 ± 0.0002	0.016 ± 0.0005	0.003 ± 0.0002	0.010 ± 0.0010	ND	0.010 ± 0.0002	ND
BLCC	0.11 ± 0.0018	0.30 ± 0.0044	0.36 ± 0.0004	0.046 ± 0.0007	0.18 ± 0.0015	0.031 ± 0.0007	0.010 ± 0.0004	0.039 ± 0.0011	0.003 ± 0.0002	0.016 ± 0.0013	0.003 ± 0.0002	0.010 ± 0.0011	ND	0.009 ± 0.0002	ND
Detection limit	0.0042	0.0028	0.0021	0.0021	0.0014	0.0038	0.0014	0.0010	0.0020	0.0014	0.0024	0.0031	0.0020	0.0024	0.0035

[a]Results are based on the "dry weight" material, mean ± SD (n = 3); [b]ND: not detected (below detection limit)

Contents of rare earth elements in the infusion of green tea samples: Consumers in China always drink the infusion of green teas as daily beverage, so determination of the concentration of contaminants in the tea infusion do more than that in the tea leaves. The infusions of 6 green tea samples, which concentration of total rare earth elements oxide exceed the national standard were tested. The results were showed in Fig. 2; it shows that the LREE were dominant in the infusion, whereas the number concentrations were less than 0.6 μg L^{-1}. Different element of rare earth elements has variable toxicity to human being, the permission contents of rare earth elements in drinking water are listed in Table-5[10] and the minimum permission content is 2 μg L^{-1}. So people drinks the infusions of green teas are safe even though the contents of total rare earth elements oxide of tea leaves are exceeding the national standards.

The extraction efficiency was estimated as the ratio of its concentration in tea infusions to total content in tea leaves. Fig. 3 shows the extraction efficiency of 6 green tea samples, the average extraction efficiency is 3.4 %, the maximum is 6.4 %. The low extraction efficiency of rare earth elements in tea leaves can protect people health from expose to high concentration of rare earth elements in tea infusion.

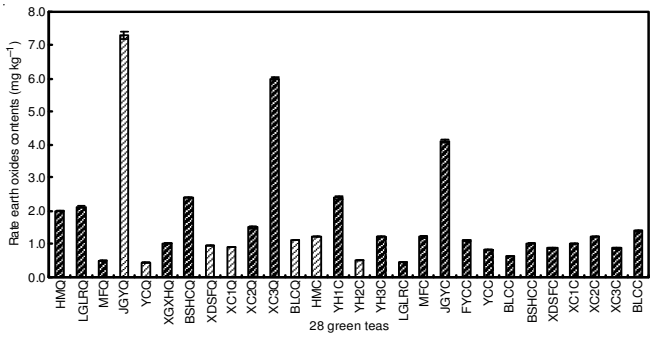

Fig. 1. Contents of total rare earth elements oxide in 28 green teas (total rare earth elements oxide: contents of total rare earth elements oxides of 15 rare earth elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)

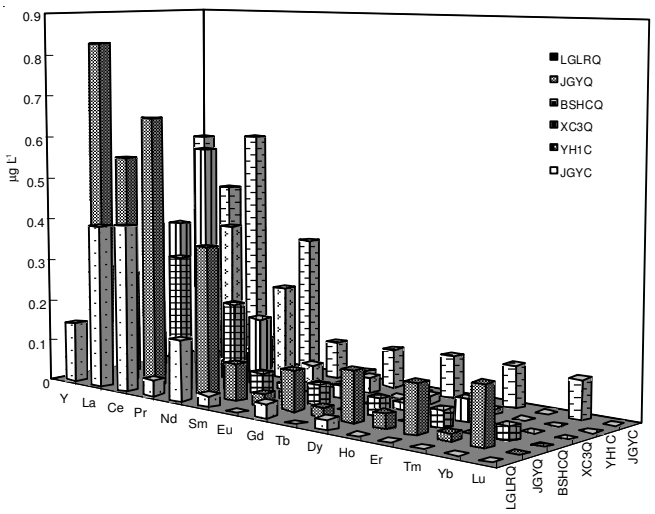

Fig. 2. Fifteen rare earth elements concentration in 6 green teas infusion

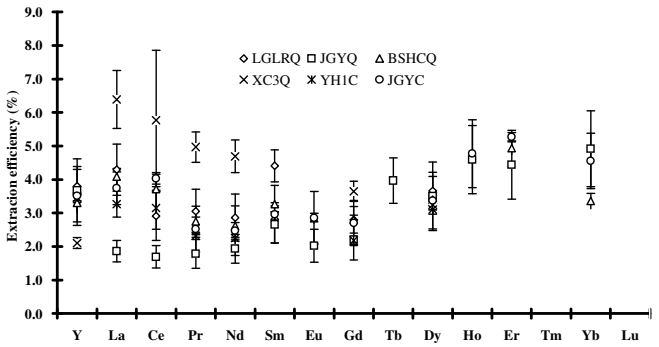

Fig. 3. Extraction efficiency of fifteen rare earth elements in the infusion of 6 green teas (the error bars are SD of means)

TABLE-5
PERMISSION CONCENTRATIONS OF RARE EARTH ELEMENTS IN DRINKING WATER

Rare earth elements	μg L^{-1}
Pr, Nd, Sm, Eu, Dy, Ho, Er, Lu	1050
Gd, Tm	10.5
Sc, Y, La, Ce, Tb, Yb	2.0

Conclusion

Light rare earth elements are relatively enriched in green tea samples. La, Ce and Nd are the dominant elements, ranging from 0.061-1.3, 0.097-2.0 and 0.056-0.94 μg g^{-1}, accounting for 23.7, 31.8 and 15.8 %, respectively. The total rare earth elements oxide contents in the studied 28 green teas are significant difference, ranging from 0.4 μg g^{-1} to 7.3 μg g^{-1} and 6 samples exceed the Chinese safety standards. Otherwise, make a detail study in the infusion of the 6 green teas the rare earth elements concentrations in the infusion are far more lower than the permission concentrations of drink water. The extraction efficiency of rare earth elements is less than 6.4 % during consumer drink the green teas. Thus it needs the academician carrying out more studies in the MLs of green tea.

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REFERENCES

1. S.-M. Ding, T. Liang, C.-S. Zhang, L.-J. Wang and Q. Sun, *Pedosphere*, **16**, 82 (2006).
2. F.-S. Wei, Y.-L. Liu and E.J. Teng, *Chin. J. Environ. Sci.*, **12**, 78 (1991).
3. J.-X. Yin, *J. Tea*, **18**, 24 (1992).
4. D.-F. Wang and C.-H. Wang, *Chin. Rare Earths*, **17**, 46 (1996).
5. G.-L. Zhou, *Stud. Trace Elem. Health*, **20**, 6 (2003).
6. R.-X. Lin, L. Chen and C.C. Xie, *China Tea*, **11**, 10 (2010).
7. J. Zhang, S. Luo and H.J. Liu, *China Pharmaceut.*, **20**, 39 (2011).
8. G.L. Long and J.D. Winefordner, *Anal. Chem.*, **55**, 713A (1983).
9. R.E.S. Khadijeh, S.B. Elias, A.K. Wood and A.M. Reza, *J. Rare Earths*, **27**, 1066 (2009).
10. J.-F. Qin, X.-Y. Chen and Z.-X. Li, *Guangdong Trace Elem. Sci.*, **9**, 1 (2002).