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STUDY ON HEAVY METAL ELEMENT DETECTION OF CHINA TEA BASED ON ICP-MS METHOD

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ABSTRACT

In order to improve the heavy metal detection of China tea effectively, the ICP-MS method is applied in it. Firstly, the basic characteristics of ICP-MS method are summarized. Secondly, the experimental device, experimental material, experimental method, and the test solution preparation of heavy metal in China tea based on ICP-MS method are set, and the linear fitting is carried out based on weighted linear programming method. Finally, the experimental results are obtained, results show that the China tea sample has heavy metal excessive phenomenon, and therefore the heavy metal problem should be concerned sufficiently.

Keywords: China tea, ICP-MS method, heavy metal.

1. INTRODUCTION

China is the birthplaceof tea, not only the cultivated area and tea type are the world leader, but also the resources of tea are rich, which offer material basis for Chinese tea industry development. In recent years, part of trading nation adjust the quality standard of tea, because the entirehygienic quality of tea in China is not high, the tea export in China is affected. The excessive heavy metal problems have restricted the economical benefit of tea industry in China. Tea concludes a many kinds of heavy metal, such as plumbum, copper, mercury, chromium, arsenic, cadmium, and these heavy metals can enter into the tea leaf through tea tree. A lot of heavy metals are not the necessary for human body, if the intake of tea is more, the human body will be damaged. Therefore it is necessary to find out an effective inspection method to inspect the heavy metal content of tea.

The sample pretreatment and detection technology of Chinese traditional medicinal materials are relatively backward. The traditional pretreatment method that is used to measure the heavy metal in Chinese traditional medicinal materials has long time consumption, complex steps, low efficiency, and big labor strength. In addition, the heating and digesting process of open system has poor safety. The microwave digestion technology has been concerned by people at present, which is the optimal processing method of measuring the heavy metal in Chinese traditional medicinal materials, the mercury, arsenic in heavy metal applying other digesting methods can lead to loss of digestion, and the microwave digesting technology can make up the disadvantage of other methods, the microwave digesting technology has become a kind of normal sample processing method. So far the detection methods of measuring the heavy metal in Chinese traditional medicinal materials conclude spectrophotometric method, atomic absorption spectrometry, atomic emission spectrometry, fluorescence analysis and soon, however these methods only measures the single element, and the operation is complex, and the requirement for the light source is high, some trace elements can not be measured. While the inductively coupled plasma mass spectroscopy (ICP-MS) can measure all components with big difference in content, and the detection limit is extreme low, the detection limit amends 2-3 order of magnitude comparing with ICP-AES method, and reaches the level of $pg \cdot mL^{-1}$, this kind of method has become a strength tool of analyzing trace element of Chinese traditional medicinal materials (Huang*et al*., 2010).

The heavy metal detection of the China tea can be carried out based on ICP-MS method, then the effect of heavy metal on the China tea can be analyzed in depth, and measuring results can offer technical support for producing and cultivating the China tea with high quality.

1.1 Basic characteristics of ICP-MS method

The ICP-MS method occupies the important situation in field of analyzing microelement, which can detect many kinds of microelements in one time detection. The ICP-MS method has many kinds of preprocessing methods. Comparing with traditional wet digestion method, the microwave digestion method can use less reagent quantity and is be hermetic, then the sample pollution leading by spreading particles in the air can be reduced. Under high temperature and pressure environment, the sample processing time can be shortened greatly, and has relative low blank value (Zhang *et al*., 2011).

The ICP-MS method has two kinds of interferences, which are spectral interference and matrix interference. The spectral interferences conclude isobaric interference, Polyatomic Ion interference, refractory oxide ion interference, double charge ion interference.

Because ICP-MS method can measure many kinds of elements, however the matrix effect in whole quality range is different, the multiple element mixed internal standard is used to correct the matrix effect, and the detection sensitivity of ICP-MS method is high, therefore the effect of heavy metal introduced into the laboratory and reagent should be avoided. The ICP-MS method has correcting curve with wide range and has better ability of resisting disturbance. The ICP-MS method has some advantages, which shows the superiority of measuring the heavy metal in China tea. During the

procession of heavy metal detection, the analysis conditions should be controlled strictly, and the pollution and loss should be avoided. Because the device of ICP-MS method has high cost, and the reagent used in the test is the Import reagent with high pureness and super clean, therefore the ICP-MS method is limited by economics (Liang*et al.*, 2012).

1.2 Experimental analysis of heavy metal in China tea based on ICP-MS method

The ICP-MS method is applied in measuring the content of heavy metal in China tea, and the harmful elements detection method are confirmed, and results offer scientific basis for safe use of China tea.

a) Device and material

Device concludes the Agilent 7700X ICP-MS made by American Agilent, the atomizer applies Aglient 100 $\mu L \cdot \min^{-1}$ PFA Micro Flow Nebulizer, the atomizer chamber applies quartz dual channel, the temperatue of Pilitier semiconductor ranges from 1.9℃ to 2.1℃. The torch tube is quartz integration which 2.5mm central channel; the sampling cone material is nickel. Millipore Mill Q super pure water machine manufactured by America Millipore Company is used, and the CEM MARS5 microwave digestion instrument is also used (Habte*et al.*, 2015).

The standard solution of heavy metal element is bought from national standard material centre, and the concentration of the heavy metal solution is 100 $\mu L \cdot \min^{-1}$, the tuning solution uses In, Co, U standard solution, the concentration is 100 $\mu L \cdot \min^{-1}$, the concentrated nitric acid and 30% H_2O_2 used in the measuring experiment, and the standard reference material is tea leaves standard substance GBW08513 (Zhang et al., 2014).

b) Experimental method

The ICP-MS measuring conditions are listed as follows:

RF power is 1200W, the cooling gas flow rate is 15 $L \cdot \min^{-1}$, and the auxiliary gas velocity is 0.75 $L \cdot \min^{-1}$, the atomizing gas velocity is 0.89 $L \cdot \min^{-1}$, and the sampling depth is 8.0mm, the intercept cone aperture is 0.7 mm, and the sampling and lifting speed is 0.4 $mL \cdot \min^{-1}$, and the fog chamber temperature is 2℃ (Dai*et al*., 2012).

The microwave digestion conditions are listed in Table-1.

Table-1. Microwave digestion conditions.

Step	**Power**/W	**Temperature**/℃	Time/min
1	550	20-140	0-6
2	650	130-190	6-12
3	650	210	12-18
4	550	120	18-22

c) Draw the standard curve and prepare the internal standard solution

Every standard reserve solution is absorbed critically, and 10% hydrogen nitrate is used to deliquate it for making the mixing series solution of corresponding element mass concentration. The corresponding results are listed in Table-2.

Table-2. Mixed series solution of every heavy metal element.

Heavy metal	**Concentration/** $\mu g \cdot \mathrm{m}L^{-1}$					
	1	**2**	**3**	**4**	**5**	**6**
Plumbum	0	0.2	0.5	2	8	15
Copper	0	0.2	0.5	2	8	15
Mercury	0	0.5	1	10	15	25
Arsenic	0	0.5	1	10	15	25
Chromium	0	1	2	6	10	15
Cadmium	0	2	5	15	25	30

In addition, the proper internal standard solution is taken, and the water is used to deliquate it as the mixed solution with the concentration of 1 $\mu g \cdot \mathrm{m}L^{-1}$, that is internal standard solution.

d) Prepare the test solution

The 0.2g China tea dried about 4 hour under temperature of 60℃ is taken, and is weighed precisely, then is put into the microwave digestion tank with high temperature and pressure resistance, and the 5mL hydrogen nitrate, 2mL hydrogen peroxide and 5mL water are put into the tank respectively, then the teflon tank cap is covered well, and the protect cap is screwed (Stadlbauer *et al*., 2005). At same time, the pressure-temperature digestion tank is sealed, and the digestion tank is put in the wheel of digest instrument, then the pressure-temperature sensor is connected well, and the solution after digestion is transferred to the 100mL teflon measuring bottle quantificationally, and the digestion tank is washed three

times by a small quantity of water, and is merged into the measuring bottle, and is diluted to scale by water, and is homogeneousl mixed, then the solution need to be measured can be obtained. The chemical reagent works and standard reference material solution are made at same time. The blank, standard, pending sample solution and internal standard solution are introduced based on double tube peristaltic sampling system, then the corresponding measurement is carried out according to ICP-MS measuring working conditions.

The linear fitting is carried out based on weighted linear programming method; the experimental data can be fitted as the following linear function (Wang *et al*., 2013):

$$y = b_1 + b_2 x \quad (1)$$

where $b_1 > 0$, $b_2 > 0$.

There are n pairs data obtained from ICP-MS experiment, which are defined as $\{[h_j, r^*(h_j)]_{j=1,2,\cdots,n}\}$, these data can be transferred to the following forms $\{[y_j, x_j]_{j=1,2,\cdots,n}\}$, and define the following expression:

$$t_j = | y_j - b_0 - b_{1x} | \quad (2)$$

The optimal fitting should satisfy the following expression:

$$\min S = \sum_{j=1}^{n} t_j \quad (3)$$

The different t_j can correspond to different weight ω_j, then the expression (3) can be amended as the following expression:

$$\min S = \sum_{j=1}^{n} \omega_j t_j \quad (4)$$

And the theory models of weighted linear programming method are listed as follows:

The weight can be calculated by the following expression:

$$\omega_j = \sqrt{\frac{1}{h_j} \cdot \frac{N(h_j)}{\sum_{j=1}^{n} N(h_j)}} \quad (5)$$

where h_j denotes thedelay distance, $N(h_j)$ denotes the number of data pairs of calculating $r^*(h_j)$ when the delay distance is h_j. According to the principle of least square, the fitting of ICP-MS experimental data can be expressed as follows:

$$\omega_j = \sqrt{\frac{1}{h_j} \cdot \frac{N(h_j)}{\sum_{j=1}^{n} N(h_j)}}$$

$$\begin{cases} \min \ S = \sum_{j=1}^{n} \omega_j t_j \\ t_j + b_0 + b_{1x} \geq y_j \\ -t_j + b_0 + b_{1x} \leq y_j \\ b_i \geq 0, i = 0,1 \\ t_i \geq 0, \ j = 1,2,\cdots,n \end{cases} \quad (6)$$

Based on the expressions (1) to (6), the standard curve of every heavy metal element can be obtained.

The standard curve of every heavy metal element drawn has good linear relationship, which is listed in Table-3.

Table-3. Linear relationship of every heavy metal element.

Heavy metal element	Regression equation	r	Linear range/ $\mu g \cdot mL^{-1}$
Plumbum	$y = 5962x + 1893$	0.993	0-15
Copper	$y = 28654x + 905$	0.995	0-25
Mercury	$y = 643x + 764$	0.997	0-25
Arsenic	$y = 5083x + 743$	0.995	0-15
Chromium	$y = 4027x + 804$	0.994	0-15
Cadmium	$y = 7462x + 993$	0.998	0-30

e) Sample recovery test

0.2g testing sample is taken for carrying out test, and the six shares are measured parallel. The content of every heavy metal element in the experiment is measured, 1/2 of 100%, 80%, and 120% for these values are considered as the additive amount of comparing sample, every kind of additive amount is prepared two copies, and the corresponding comparing solution are added critically,

and the sampling recovery situation are confirmed, and the recovery rate ranges from 98% to 106%, and RSD<12%.

2.1 Experimental results and discussion

The verification of correctness of experiment, the tea leaves standard substance GB208513 can be used as the reference value, and the correctness of evaluation method can be confirmed, and the corresponding analysis results are listed in Table-4. As seen from Table-4, the standard reference value is agreed with measured value, results show that the ICP-MS method has good correctness.

Table-4. Measuring results of tea leaves standard substance.

Heavy metal element	Standard reference value/ $\mu g \cdot g^{-1}$	Measured value/ $\mu g \cdot g^{-1}$	RSD/%
Plumbum	0.018-0.028	0.026	6.8
Copper	(0.018)	0.019	7.4
Mercury	0.90-1.10	1.08	0.8
Arsenic	0.14-0.22	0.21	6.0
Chromium	0.12-0.25	0.20	4.6
Cadmium	0.18-0.29	0.25	6.8

The content of heavy metal in China tea is measured based on ICP-MS method, which is listed in Table-5.

Table-5. Content of heavy metal in China tea.

Number	Producing area	Plumbum	Copper	Mercury	Arsenic	Chromium	Cadmium
1	Shifeng moutain	0.584	0.435	0.168	10.58	6.54	3.27
2	Meijiawu	0.418	0.235	0.248	0.635	3.20	3.45
3	Wengjia mountain	0.053	0.064	0.495	2.07	5.17	3.80
4	Yunxi	1.06	0.995	0.293	5.97	4.52	5.03
5	Hutiao	0.532	0.662	0.392	4.06	2.99	3.72
6	Jinzai	0.582	0.794	0.184	0.885	0.63	5.36
7	Qiyang	0.559	0.683	0.205	2.91	2.95	5.85

According to the limited index of relating standard, the total amount of heavy metal should be less than 20 $mg \cdot kg^{-1}$.

According to the experimental results, the China tea sample has heavy metal excessive phenomenon, therefore the heavy metal problem should be concerned sufficiently, and the corresponding control should be strengthened. The content of heavy metal in the China tea coming from different producing area has big difference, and results show that Chinese soil and water quality environment and other factors have big difference.

2. CONCLUSIONS

The ICP-MS method is applied in the detection of heavy metal in the China tea, the microwave digestion system can cope with the sample quickly, and the operation is simple, and the digestion of sample are more mean, the safety of experiment can be improved, and the digestion temperature programmer can be set smoothly, and results show that the ICP-MS method can measure the content of heavy metal in China tea. And inspection results can offer effective basis for establishing the measurement of preventing the excessive heavy metal in China tea.

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