Research of Trace Elements Content in Tea Based on Flame Atomic Absorption Spectrometry

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Abstract—**The determination method for the content of trace element of Cu, Fe, Mn, Zn and Ni in tea by the wet digestion-flame atomic absorption spectrometry (FAAS) was established. The effect of digestive reagents, the volume of digestion and the digestion time were investigated in detail. The optimum condition for digesting samples was HNO_3-H_2O_2 system; the volume of H_2O_2, 4 mL; and digestion time, 60 min. The content of Fe in the analyzed samples was 115.62 μg/g, while the content of Cu was 42.54 μg/g, Mn 396.48 μg/g, Zn 50.69 μg/g, and Ni 14.88 μg/g. The recovery of the five elements was in the range of 96.37～103.92 %. Relative standard deviation (RSD) was less than 5 %. This method was simple, higher precision and accuracy. And experiment results were satisfactory.**

Keywords-flame atomic absorption spectrometry; tea; trace elements

I. Introduction

China is the hometown of tea, and drinking tea also has a long history. Analysis of the elements in food [1-4] is researched widely in the world. These researches can have two complementary goals: on the one hand, the interest can be focused on the metallic profile of the vegetal materials used for brewing. On the other hand, the research can be aimed at the determination of the metallic contents in the brewed samples [5].

The health benefits of tea are incomparable to other drinks. In addition to rich of polyphenols, caffeine and other organic ingredients in tea, it contains a variety of essential trace elements. These trace elements for human body are indispensable. But excessive consumption will be adverse effects on human body. Some human demanding very small elements intaking too much from food may be easy to produce toxic effects [6]. So it is necessary to determine the content of trace elements in tea.

In recent years, there were many the detection methods of the trace elements in tea. Pawel Pohl's research group detected Ca, Fe, K, Mg, Mn and Na by flame atomic absorption spectrometry (FAAS), and Al, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sr and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES) in black and green teas [7]. Koichi Chiba's team used inductively coupled plasma mass spectrometry (ICP-MS) determination of 19 elements [8]. Other papers reported electrothermal atomic absorption spectrometry (ETAAS) was also used to detection of trace

elements in tea. AAS is one of the most effective official techniques for food analysis and commonly used for the analysis of tea due to low operational costs and good analytical performance. Due to the constraints, we researched of trace elements content in tea by FAAS.

In this paper, we investigated the elemental concentrations in tea. The optimization of the experimental conditions on the extraction of Cu, Fe, Mn, Zn and Ni were also studied. We hoped that our research could help for food safety, environmental monitoring and other relevant studies.

II. Experimental

A. Materials and apparatus

A WYS2000 flame Atomic absorption spectrophotometer was purchased Wanyi instrument technology co., Ltd (Anhui, China). The oxidant flame was obtained with acetylene, purity 99.999%, from Yadong gas plant (Xuzhou, China). The air compressor was purchased Kemaihao Industry and trade co., Ltd (Tianjin, China).

HNO_3 (65%), HCl (36%), H_2O_2 (30%) solutions and other chemicals were used of analytical reagent grade (Fuchen reagent, Tianjin, China). HNO_3 (65%) for preparation of standard solution was guaranteed reagent. And it purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Standard stock solutions (1000 μg/mL) for Cu, Fe, Mn, Zn and Ni were obtained from state center for standard matter (Beijing, China). Deionized water was used for all dilutions, rinsing and dilutions.

All glass apparatus were washed and kept in 10% (v/v) HNO_3 solution for at least 24 h, and then rinsed with deionized water and dried in heat oven before use.

B. Experimental method

1) Sample pretreatment

The fresh tea washed with deionized water. The washing was carried out 3 times with deionized water, while sprigs were manually removed, and only the leaves were used as the raw material. After that, the tea leaves were dried in an oven at 80 ℃ for 4 h. The optimized digesting procedure was as follows. Approximately 2.0 g of the sample was precisely balanced and put into a small beaker, and then 10 mL of HNO_3 was added [8]. The small beaker was heated until most of the organic matter decomposition. In the heating

process, HNO_3 was constantly added. Then 4 mL of H_2O_2 was added in the beaker and continue heated. When the digestive solution appeared transparent and colorless, deionized water was added into. After that, the sample continued to boil for removing the rest of HNO_3. This process repeated twice. Finally, approximately 10 mL of the digested sample solution was obtained. The obtained digested solution diluted to 100mL volumetric flask by 2 % HNO_3 for measuring with the instruments.

2) Instrumental measurement conditions

Atomic absorption spectrometer for analyte elements were carried out in the air- C_2H_2 flame. For different elements, the air and C_2H_2 flow rate were slightly different. The single hollow cathode lamps of Cu, Fe, Mn Zn and Ni were used. The following resonance lines were selected: 422.7 nm (Cu), 248.3 nm (Fe), 279.5 nm (Mn), 213.9(Zn) and 232.2 (Ni). Slit width of the monochromator was set to 0.2 nm for all elements. The measurement time was 3.0 s, and the number of replicates was 3. Background corrected absorbance readings were taken using a timeaverage integration mode. Other operating conditions were used as recommended by the instrument manufacturer. The instrumental conditions were shown in Table I.

TABLE I.   INSTRUMENTAL MEASUREMENT CONDITIONS FOR THE DIFFERENT ELEMENTS

Element	Wave length (nm)	Lamp current (mA)	C_2H_2 (L/min)	Air (L/min)	Burner height (mm)	Slit width (nm)
Cu	324.8	3	2.0	8.0	10	0.2
Fe	248.3	3	2.2	9.0	9	0.2
Mn	279.5	3	2.4	9.5	9	0.2
Zn	213.9	4	2.0	8.0	9	0.2
Ni	232.2	4	2.2	9.0	9	0.2

3) The standard curve

The standard stock solutions (1000 μg/mL) for Cu, Fe, Mn, Zn and Ni were used to prepare single-element standard solutions for the calibration as well as 100 mL working standard solutions containing 50, 10, 100, 50 and 10 μg/mL of Fe, Cu, Mn, Zn and Ni, respectively.

With a pipette from 2.00, 4.00, 6.00, 8.00 and 10.00 mL working standard solution of Fe in 100 mL volumetric flask, added 2 % HNO_3 to constant volume. The concentration of Fe in the volumetric flasks was 1, 2, 3, 4 and 5 μg/mL, respectively.

With a pipette from 2.00, 4.00, 6.00, 8.00 and 10.00mL working standard solution of Cu in 100 mL volumetric flask, added 2 % HNO_3 to constant volume. The concentration of Cu in the volumetric flasks was 0.2, 0.4, 0.6, 0.8 and 1 μg/mL, respectively.

With a pipette from 2.00, 4.00, 6.00, 8.00 and 10.00mL working standard solution of Mn in 100 mL volumetric flask, added 2 % HNO_3 to constant volume. The

concentration of Mn in the volumetric flasks was 2, 4, 6, 8 and 10 μg/mL, respectively.

With a pipette from 1.00, 2.00, 3.00, 4.00 and 5.00mL working standard solution of Zn in 100 mL volumetric flask, added 2 % HNO_3 to constant volume. The concentration of Zn in the volumetric flasks was 0.5, 1, 1.5, 2 and 2.5 μg/mL, respectively.

With a pipette from 1.00, 2.00, 3.00, 4.00 and 5.00mL working standard solution of Ni in 100 mL volumetric flask, added 2 % HNO_3 to constant volume. The concentration of Ni in the volumetric flasks was 0.1, 0.2, 0.3, 0.4 and 0.5 μg/mL, respectively.

According to Table I, atomic absorption spectrometer was warmed up after 40 min, adjusted the instrument parameters to the best state, pumped in the air and acetylene gas, fired up, and setted zero with stabilization. We measured the absorbance, drawing the calibration curve. The regression equation and correlation coefficient were shown in Table II.

TABLE II.   THE LINEAR REGRESSION EQUATION AND CORRELATION COEFFICIENT

Element	Linear regression equation	Correlation coefficient(R^2)
Fe	y=0.0930x+0.0106	0.9984
Cu	y=0.1782x+0.0002	0.9998
Mn	y=0.2456x+0.0035	0.9998
Zn	y=0.0180x-0.0030	0.9987
Ni	y=0.0786x-0.0021	0.9992

III.   RESULTS AND DISCUSSION

A. Optimizing the sample processing

1) The choice of digestive reagents

The national standard method used HNO_3-$HClO_4$ to dissolve samples, but $HClO_4$ decomposed at room temperature and was heated easy to explode. Some papers used HNO_3- HF-H_2O_2 system [8], however, HF had corrosive strong. $HClO_4$ and HF had Strong ability of digestion, so they were widely used. Mastering skills badly might make the whole experiment failed even an explosion. We improved the sample digestion method without $HClO_4$ or HF in digestion system. HNO_3- H_2O_2 was used to dissolve samples. This method reduced the possibility of a failed experiments and explosion, improving the operability.

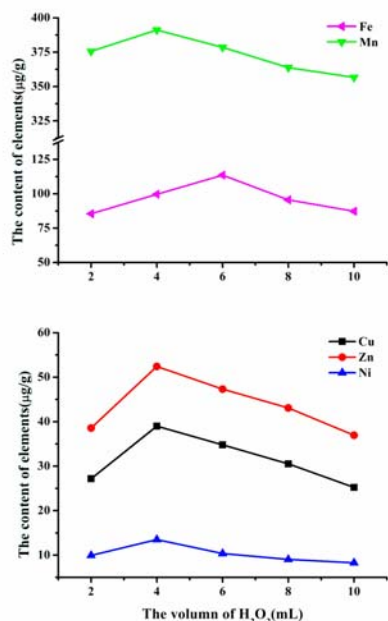*2) The effect of the volume of H_2O_2*

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Figure 1.   The effect of the volume of H_2O_2

Figure 1 illustrated that the content of extracted trace elements of Cu, Mn, Zn and Ni were best with 4 mL H_2O_2 [7]. However, the content of Fe was largest when the volume of H_2O_2 was 6mL. We considered that adding the volume of H_2O_2 was 4mL.
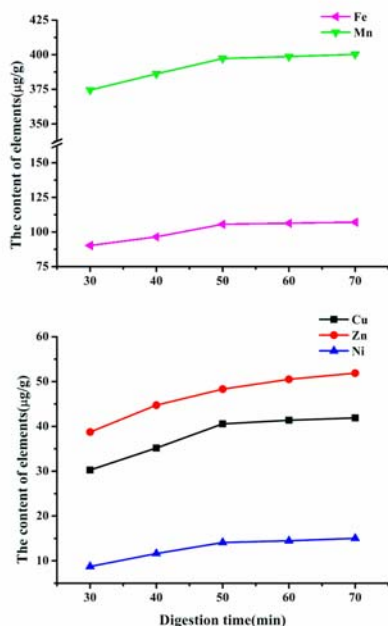
3)   The effect of digestion time

Figure 2.   The effect of digestion time

According to Figure 2, when the digestion time increased, the content of extracted trace elements also increased [9]. After 50 min, the elements content didn't

increase as much accordingly by improving the digestion time. The reason may lie in that longer heating time led to HNO_3 volatile. So we chose 60min as the digestion time finally.

B.   Sample analysis results

Weighing 2.0 g of tea samples, we used the above optimum method processing samples, determined of the content of each element in sample solution and repeated three times. The result was shown below.

TABLE III.   THE CONTENT OF EACH ELEMENT IN THE SAMPLE

Element	Sample 1 (μg/g)	Sample 2 (μg/g)	Sample 3 (μg/g)	The average (μg/g)
Fe	115.51	115.09	116.26	115.62
Cu	42.98	42.87	41.76	42.54
Mn	395.87	396.53	397.03	396.48
Zn	50.98	51.33	49.75	50.69
Ni	14.85	14.91	14.87	14.88

In the Table III, we knew that the content of the five elements in tea were not identical. The content of Mn was most and Ni was least. Mn was one of the trace elements closely related to human health. People who enjoyed a cup of tea could ingest 1/3 content of Mn and more every day.

C.   Recovery and precision experiment

TABLE IV.   THE RESULT OF RECOVERY AND PRECISION EXPERIMENT

Element	Back ground value (μg/g)	Adding quantity (μg/g)	Measured quantity (μg/g)	Average recovery rate/%	RSD/%
Fe	115.38	50.0	166.89		
	115.38	50.0	167.06	101.26	3.01
	115.38	50.0	164.08		
Cu	42.27	20.0	62.46		
	42.27	20.0	63.30	102.80	2.09
	42.27	20.0	62.73		
Mn	397.05	200.0	591.76		
	397.05	200.0	589.52	96.37	0.96
	397.05	200.0	588.10		
Zn	50.89	25.0	76.03		
	50.89	25.0	77.91	103.92	3.68
	50.89	25.0	76.67		
Ni	14.71	7.0	21.63		
	14.71	7.0	21.16	97.33	4.75
	14.71	7.0	21.78		

The correctness of results was verified by analyzing the concentration after addition of known amounts of trace element solutions into samples [5-7, 10]. As it is seen from Table IV, the results showed that the recovery of five elements was in the range of 96.37～103.92 %. RSD was less than 5 %. The method had better accuracy and precision.

IV. CONCLUSIONS

The proposed method for the determination of Fe, Cu, Mn, Zn and Ni in tea by FAAS with the wet digestion was established. The effect of digestive reagents, the volume of digestion and the digestion time were optimized. In comparison to official digestion methods that required $HClO_4$ for sample digestion, we used H_2O_2 instead of $HClO_4$ as digestive reagent. That improved the safety of the experiment. The contents of five trace elements in tea were detected 115.62 (Fe), 42.54 (Cu), 396.48 (Mn), 50.69 (Zn) and 14.88 μg/g (Ni). All the Cu content in the samples were below the maximum limit standards 60 μg/g. RSD for analytical elements were below 5 %. These results showed that Mn and Fe contents were rich in tea. This method was safe and convenient with higher accuracy and precision.

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