

Determination of trace bismuth in soil and sediment by ultrasonic water bath digestion-Atomic Fluorescence Spectrometry

ZHOU Zi-Kai^{1,*}, LI Luan¹, ZHANG Chao²

1. School of Resources Environmental & Chemical Engineering, Nanchang University, Nanchang city, 330031, China

2. School of Materials Science and Engineering, Nanchang University, Nanchang city, 330031

**Corresponding author*

Keywords: Bismuth, Digestion methods, Soil, Sediment, Environmental monitoring, Atomic fluorescence spectrometry

Abstract: The Chinese national environmental standard detection method HJ 680-2013 was improved. The sample was pretreated and digested by acid mixtures and ultrasonic water bath digestion method. The trace bismuth in soil and sediment were determined by atomic fluorescence spectrometry. GBW07430, GBW07446 and GBW07452 were selected as the national first-class standard materials for soil composition analysis. The effects of 12 kinds of acid mixtures digestion systems on the determination results of trace bismuth in soil and sediment were discussed, and the best experimental conditions were selected. The hydrochloric acid, nitric acid, sulfuric acid and hydrofluoric acid (volume ratio: 0.5:1.5:0.5:0.5) was used as the digestion solution in the acid mixtures system, and the samples were digested by ultrasonic water bath method. The digestion time was 0.5 h. That trace bismuth mass concentration were in the range of 0.10 to 10.0 $\mu\text{g/L}$ and that had a good linear relationship, the linear correlation coefficient was more than 0.9998, the limit of detection (LOD) was 0.005 mg/kg, the limit of quantitation (LOQ) was 0.015 mg/kg, the relative standard deviations (RSD) were 0.39 to 6.65%, and the recoveries were 103 to 112%. The method has been verified by the national first-class standard material for soil composition analysis and the types of agricultural, construction soil and pipeline sludge sediment samples collected from Taizhou environment. It is proved that the method can effectively digest different types of samples, meet the current environmental analysis of soil and sediment detection work, and effectively improve the accurate and rapid determination work, the requirement of high-throughput sample determination of trace bismuth was solved.

With the development of human scientific and technological civilization and the continuous test of man-made elements, heavy metal elements have accumulated in the living environment for a long time, which can not only change the soil ecosystem, but also endanger health through the

enrichment of food chain. Bismuth is a rare element, which exists in the form of free metals and minerals. It is widely used in semiconductor industry, coating industry, medical treatment and other fields [1]. The current Chinese national standards GB 15618-2018 soil environmental quality risk control standard for soil contamination of agricultural land (Trial)[2] and GB 36600-2018 soil environmental quality risk control standard for soil contamination of development land (Trial)[3] do not specify the limit of bismuth. Bismuth is not an essential element for human body. It has cytotoxicity and weak radioactivity. It can accumulate in human kidney and cause chronic poisoning. Bismuth in environmental soil is easy to enter human body through food chain or other activities, and then affect human health. Therefore, it is of great significance to accurately determine the content of bismuth in soil.

The main Chinese national standard detection methods for bismuth are as follows: electric heating plate digestion inductively coupled plasma mass spectrometry [4] and microwave digestion atomic fluorescence spectrometry [5], which provide technical support for soil monitoring data and work of various departments in the country. However, there are still deficiencies in the existing standard methods: The digestion time of DB 32/T 4032-2021 electric heating plate is long, and the digestion end point is not easy to interpret. The subsequent silicon flying and acid driving links increase the workload and acid reagent consumption. The manual operation of multiple links also brings inconvenience. The consumption of acid reagent in the digestion solution is large, and it is inconvenient to observe many times in the middle; HJ 680-2013 microwave digestion is not easy to interpret the digestion end point. The sample transfer step of additional heating and acid removal increases the risk of contamination error, time consumption and instrument limitations, and it is unable to effectively prepare samples at high throughput. Bismuth is a volatile element, which is easy to cause volatilization loss under high temperature environment. Therefore, the operation process needs to be strictly controlled in sample pretreatment and analysis, otherwise it will have a certain impact on the determination results. It is easy to find that the relative standard deviation of the determination results of the same sample is quite different, the precision is not high, and it is difficult to meet the determination requirements. The above problems directly and indirectly lead to the reproducibility and stability of adverse results, and virtually improve the personnel and technical threshold.

In this study, the samples were digested by water bath method, the energy required for digestion was increased by ultrasonic assisted enhancement, the digestion time was effectively shortened, and the use of acid reagent was reduced. Combined with atomic fluorescence spectrometry, the method has the advantages of convenience, low cost, high universality, good safety and high sensitivity, good results have been obtained by testing the national first-class soil composition analysis standard materials and the environmental samples.

1. Experiments

1.1 Instruments and reagents

Atomic fluorescence photometer: Beijing Purkinje general instrument, PF31 model; Electric heating plate heater: Beijing LabTech instrument, S36 model; Industrial ultrasonic electrothermal constant temperature cleaning machine: Zhejiang Jiugong environmental protection equipment, JG-24L model(1440W); Multi flux microwave digestion instrument: Shanghai Sineo microwave chemistry technology, Jupiter-B model; Electric blast drying oven: Tianjing taisite instrument WGLL-230BE model; Analytical balance: Sartorius CPA225D model; Bismuth single element standard stock solution: 1000 mg/L, Tan-Mo quality of science and technology; Hydrochloric acid, nitric acid and sulfuric acid used in the experiment are superior pure grade reagents and perchloric

acid, hydrogen peroxide and hydrofluoric acid are analytical pure grade reagents; Environmental Soil and sediment samples: Soil and pipeline sludge sediments for agriculture and construction in Taizhou City, Zhejiang Province; The experimental water is ultrapure water, Sartorius pro-UV model, the resistance value 18.2 MΩ·cm; National standard material for soil composition analysis: GBW07430[GSS-16, Zhujiang delta], GBW07446[GSS-17, Sandy soil in ulatehou banner, Inner Mongolia], GBW07452[GSS-23, Beach sediments in Xiangshan, Zhejiang Province], Institute of geophysical and geochemical exploration, Chinese Academy of Geological Sciences; Before use, glassware and digestion tube shall be heated and boiled with aqua regia solution (1+1) for 2.0h, and then washed with ultrapure water. This cleaning step shall be recycled twice to complete the cleaning [6]; all reagents are prepared for immediate use.

1.2 Instrument conditions

Preheat and start the atomic fluorescence photometer for 0.5-1.0h to stabilize the system and lamp source. See the table 1 for instrument parameter settings. Optimization principle of instrument condition parameters: 0.50 μg/L bismuth standard solution can produce strong fluorescence intensity; when measuring analytes with low concentration, properly adjust the lamp current, negative high voltage value and atomizer height to ensure the sensitivity of the instrument, and use the standard curve in the low concentration range.

Table 1 Instrument conditions

Element	Lamp current (mA)	Negative high voltage (V)	Atomization temperature (°C)	Carrier gas flow (mL·min ⁻¹)	Shielding gas flow (mL·min ⁻¹)	Analysis time/Integral mode
Bismuth	80	280	200	300	600	25s/peak area

1.3 Sample collection and preparation

The samples were collected, transported, prepared and stored in Taizhou City, Zhejiang Province according to relevant standards of GB 17378.3-2007[7], HJ/T 166-2004[8] and NY/T 395-2012[9]. After the samples are picked, the sundries are removed, flattened and dried in the shade, then they are manually crushed, grinded and screened (2.0mm) by the quartering method, collected and sealed for testing. The dry matter is determined according to HJ 613-2011[10], the moisture content is determined according to GB 17378.5-2007[11], and the bismuth content of soil and sediment samples is calculated according to HJ 680-2013.

1.4 Sample processing and determination

Prepared samples and standards materials, Each accurate scale takes 0.1000g(± 0.50%) is placed in a 25.0mL glass tube. First add 0.2-0.5ml water for wetting, then add the digestion solution of hydrochloric acid nitric acid hydrofluoric acid perchloric acid hydrogen peroxide digestion system, finally add nitrogen to replace the air in the tube, cover it, heat it in a water bath for ultrasonic digestion for 0.5-2.0h, cover it all the way to complete the digestion, and after the digestion is completed, directly volume it to the marking line for testing. In order to ensure quality control, each batch of samples It is necessary to prepare more than 2 blank samples of the whole procedure (without samples or standards), and ensure that the concentration of the blank samples of the preservation procedure is lower than the lower limit of the method.

2. Results and discussion

2.1 Selection of digestion system and digestion solution

According to the previous work [12] and references [13, 14], hydrochloric acid, nitric acid, sulfuric acid, hydrofluoric acid, perchloric acid and hydrogen peroxide were combined to form 12 digestion systems. Three different types of national soil composition analysis standard materials were selected and measured under the working conditions of 1.4 instrument under the digestion time of 2.0h. The effects of different digestion systems on the determination results were investigated. The results are shown in Table 2.

Table 2 Effects of different digestion systems on soil standard test results($n=6$)

No	Digestion systems	Average of recovery/%(RSD/%), $n=6$			Consistency of results ¹⁾
		GBW07	GBW0	GBW07	
	hydrochloric acid+nitric acid+sulfuric acid+perchloric acid+hydrofluoric acid+hydrogen peroxide	430 (± 7.64 %)	7446 (± 13.3 %)	452 (± 6.82 %)	
1 [#]	1+3+0+0+0+0	65.2 (4.78)	70.5 (4.55)	68.6 (4.46)	Unqualified
2 [#]	1+3+1+0+0+0	110 (3.84)	108 (3.65)	112 (3.88)	Partially qualified
3 [#]	1+3+0+1+0+0	72.1 (4.62)	69.6 (4.80)	75.8 (4.56)	Unqualified
4 [#]	1+3+0+0+1+0	121 (3.78)	126 (3.66)	125 (3.81)	Unqualified
5 [#]	1+3+0+0+0+1	138 (4.75)	132 (4.61)	127 (4.82)	Unqualified
6 [#]	1+3+1+1+0+0	85.4 (3.28)	93.7 (3.46)	84.8 (3.51)	Partially qualified
7 [#]	1+3+1+0+1+0	126 (3.58)	129 (3.82)	128 (3.63)	Unqualified
8 [#]	1+3+1+0+0+1	128 (3.74)	135 (3.68)	131 (3.77)	Unqualified
9 [#]	1+3+1+1+1+0	133 (4.21)	142 (4.08)	136 (4.40)	Unqualified
10 [#]	1+3+1+1+1+1	132 (4.28)	138 (4.19)	135 (4.34)	Unqualified
11 [#]	1+3+0.5+1+0+0	91.2 (3.31)	94.5 (3.26)	90.6 (3.67)	Partially qualified
12	0.5+1.5+0.5+0.5+0+0	95.8	94.2	96.1	Qualified

#	(3.22)	(3.02)	(3.41)	d
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Note: 1) The conformity of the results is determined according to the standard value and uncertainty presented by the standard certificate.

It can be seen from table 2 that the results of only 2[#] digestion systems in 1[#]-5[#] are partially qualified, which is more consistent with previous work. As the results were still poor, the digestive system was further optimized according 1[#]-5[#] to the results. 6[#]-10[#]. According to previous experimental experience, increasing the concentration of chloride ion can increase the dosage of hydrochloric acid and effectively reduce the interference to the measured matrix. Through a series of experiments, it is found that the precision of the digestion system (2[#], 6[#]) with sulfuric acid and hydrofluoric acid is stable and the results are good. After 11[#] reducing the amount of sulfuric acid in the digestion solution, better results can be obtained. Further tests 12[#] confirm that reducing the amount of overall acid in the digestion solution can still show good results and obtain better precision. Comprehensively, hydrochloric acid, nitric acid, sulfuric acid and hydrofluoric acid (volume ratio: 0.5:1.5:0.5:0.5) digestion system is adopted as the digestion solution.

2.2 Selection of digestion methods

Hydrochloric acid, nitric acid, sulfuric acid and hydrofluoric acid (volume ratio: 0.5:1.5:0.5:0.5) were used as digestion solution. GBW07430 is pretreated by three different pretreatment methods respectively. Measured under the instrument conditions in 1.2, the results are shown in Table 3. It can be seen from table 3 that the recovery rate of ultrasonic water bath method can meet the requirements and the precision is good under the condition of 2.0h at 100 °C. Ultrasonic water bath method can increase water shear and cavitation of liquid samples by using ultrasound. The stirring and shaking of the sample form a rapid movement penetration between the substance and the solvent, which can effectively accelerate the dissolution effect of the solute, increase energy and shorten the extraction time. Due to its strong force, it is not necessary to manually observe and shake the sample during the experiment, and effectively reduce the labor demand. The results show that the recovery and precision can meet the requirements at 90°C for 2.0h and 100°C for 0.5, 1.0, 2.0h. The results of electric heating plate and microwave method are unqualified and the precision is poor. Based on the data in Table 3, the digestion solution of this digestion system can obtain good results in ultrasonic water bath method. It is recommended to use ultrasonic water bath method for digestion at 100°C for 0.5h, which can effectively improve the working efficiency, improve the precision of sample digestion and obtain better digestion results.

Table 3 Comparison of effects of different digestion methods on sample(n=6)

Digestion methods	Digestion temperature/°C	Digestion time/h	Average of recovery/%(RSD/%), n=6 GBW07430 (±7.64%)	Consistency of results ¹⁾
Ultrasonic water bath	80	2	80.2 (3.65)	Unqualified
	90	2	95.8 (3.22)	Qualified
	90	1	92.0 (3.87)	Unqualified
	90	0.5	87.5 (4.45)	Unqualified

	100	2	103 (2.28)	Qualified
	100	1	101 (1.76)	Qualified
	100	0.5	98.5 (1.55)	Qualified
Electric heating plate	160	4	66.8 (8.75)	Unqualified
	160	6	79.5 (8.84)	Unqualified
	160	8	82.3 (8.62)	Unqualified
Microwave	100(2)+150(3)+180(25)	0.5	88.4 (7.25)	Unqualified
	120(3)+150(3)+180(3)+200(25)	0.6	91.6 (7.79)	Unqualified
	150(2)+180(3)+200(25)	0.5	80.2 (7.60)	Unqualified

Note: 1) The conformity of the results is determined according to the standard value and uncertainty presented by the standard certificate.

It can be seen from table 4 that the results of different digestion methods are different. The total consumption time and precision of electric heating plate and microwave method are poor, and the result consistency is unqualified. Considering comprehensively, the ultrasonic water bath method was selected to digest the sample at 100°C for 0.5h.

Table 4 Comparison of results of different digestion methods($n=6$)

Digestion methods	Pretreatment and instrument preparation time/h	Digestion time/h	Heating acid removal time/h	Total consumption time/h	Recovery/%	RSD/%	Conformity of results ¹⁾
Ultrasonic water bath		0.5	0	2.0	98.5	1.55	Qualified
Electric heating plate	1.5	8.0	0	9.5	82.3	8.62	Unqualified
Microwave		0.6	5	7.1	91.6	7.79	Unqualified

Note: 1) The conformity of the results is determined according to the standard value and uncertainty presented by the standard certificate.

2.3 Linear equation and LOD

Under the 1.2 instrument conditions, the instrument will automatically dilute the bismuth concentration to 0.00, 0.10, 0.50, 1.00, 2.00, 5.00 and 10.0 µg/L. Linear regression was carried out

with the mass concentration of the solution (x , $\mu\text{g/L}$) as the abscissa and the absorbance intensity (y) of the instrument response as the ordinate. According to the sample processing method 1.2, first prepare 11 blank samples of the whole procedure in parallel, determine them under the instrument conditions 1.4, calculate the standard deviation of the 11 determination results, take the concentration corresponding to 3 times of standard deviation as the LOD of the method, and define 10 times of standard deviation as the limit of quantitative (LOQ), and then calculate the LOD and LOQ of element, as shown in Table 5. It can be seen from table 5 that the linear range, equation, correlation coefficient, LOD and LOQ can meet the standard requirements of analysis and determination.

Table 5 Linear range, equation, correlation coefficient and detection limit of elements ($n=6$)

Concentration range/ $\mu\text{g}\cdot\text{L}^{-1}$	Linear equation	Correlation coefficient	LOD/ $\text{mg}\cdot\text{kg}^{-1}$	LOQ/ $\text{mg}\cdot\text{kg}^{-1}$	limit / $\text{mg}\cdot\text{kg}^{-1}$
0.1~10.0	$y=132.25x-0.4262$	0.9998	0.005	0.015	0.010

2.4 Precision

Weigh 12 parts of GBW07430, GBW07446 and GBW07452 in parallel, process the samples according to the method in 1.4, and determine them under the instrument conditions in 1.2. See Table 6 for the results. It can be seen from table 6 that the precision of this method is good, and the RSD range of the element determination results is 0.39-6.65% ($n=12$), which can meet the standard requirements of analysis and determination.

Table 6 Results of precision ($n=12$)

Standard value/ ($\text{mg}\cdot\text{kg}^{-1}$)	Measured of value/ ($\text{mg}\cdot\text{kg}^{-1}$)	Average of value/ ($\text{mg}\cdot\text{kg}^{-1}$)	RSD/%
GBW07430 1.44 \pm 0.11	1.4246, 1.4321, 1.4395, 1.4147, 1.4047, 1.4122, 1.3948, 1.4308, 1.4495, 1.3985, 1.3936, 1.4346	1.4191	0.39
GBW07446 0.15 \pm 0.02	0.0149, 0.0137, 0.0162, 0.0149, 0.0137, 0.0149, 0.0137, 0.0162, 0.0137, 0.0149, 0.0149, 0.0162	0.0148	6.65
GBW07452 0.44 \pm 0.03	0.4164, 0.4252, 0.4202, 0.4152, 0.4326, 0.4177, 0.4239, 0.4140, 0.4326, 0.4289, 0.4127, 0.4202	0.4216	1.66

2.5 Accuracy

2.5.1 Determination of standard samples

Weigh 6 parts of GBW07430, GBW07446 and GBW07452 in parallel, process the samples according to the method in 1.4, and determine them under the working conditions of the instrument in 1.2. See Table 7 for the results. It can be seen from table 7 that the measured values of bismuth in the three national standard materials for soil composition analysis are within the range of standard values and uncertainty, indicating that the accuracy of this method can meet the standard requirements for analysis and determination.

Table 7 Results of standard samples($n=6$)

Samples	Standard value of Bismuth content/ ($\text{mg}\cdot\text{kg}^{-1}$)	Average of measured value/ ($\text{mg}\cdot\text{kg}^{-1}$)
GBW07430	1.44±0.11	1.419
GBW07446	0.15±0.02	0.147
GBW07452	0.44±0.03	0.422

2.5.2 Standard addition recovery

After different kinds of samples are added with different concentrations of standard solutions of 0.02, 0.10 and 1.00 mg/kg, the samples are processed according to the method of 1.4, and the results are determined under the instrument conditions of 1.2. The results are shown in table 8. It can be seen from table 8 that the recovery rate of sample standard addition is 103~112%, which is within the allowable range and can meet the standard requirements of analysis and determination.

Table 8 Recovery of standard addition

Samples	Background value/ ($\text{mg}\cdot\text{kg}^{-1}$)	Detection value/ ($\text{mg}\cdot\text{kg}^{-1}$)	Recovery/%
Construction soil	0.065	0.092~1.099	105~108
Agricultural soil	0.022	0.047~1.073	105~112
Pipeline sludge sediment	0.058	0.081~1.085	103~108

2.6 Method comparison

The comparison between this method and the literature results is shown in Table 9. It can be seen that this method is superior to the methods reported in the literature and meets the standard requirements of analysis and determination. The optimized water bath method can digest more than 84 samples at the same time, greatly improve the accurate and rapid determination efficiency, and solve the needs of trace bismuth in high-throughput samples.

Table 9 The results compared with references

Digestion / determination method	Digestion time/h	LOD ($\text{mg}\cdot\text{kg}^{-1}$)	Recovery/%	RSD/%	Conformity of results ¹⁾
Water bath / Atomic Fluorescence Spectrometry[6]	2.0	0.005	102~107	1.30~5.50	Qualified
Water bath / Atomic Fluorescence Spectrometry[12]	0.5	0.008	101-109	2.53~4.06	Qualified
Water bath / Atomic Fluorescence Spectrometry[13]	2.0	0.01	97.6~104	2.5~12.4	Qualified
Water bath / Atomic Fluorescence Spectrometry[14]	2.0	0.001	93.0~98.2	2.0~2.6	Qualified

Ultrasonic water bath / Atomic Fluorescence Spectrometry (This report)	0.5	0.005	103~112	0.39~6.65	Qualified
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Note: 1) The conformity of the results is determined according to the standard value and uncertainty presented by the standard certificate.

3. Conclusion

The pretreatment method of ultrasonic water bath was tested by national first-class soil composition analysis reference materials GBW07430, GBW07446 and GBW07452. The effects of digestion solutions of 12 digestion systems on the determination results of trace bismuth in soil and sediment were discussed, and the best experimental conditions for the determination of Trace bismuth by atomic fluorescence spectrometry were selected. This method can reduce the use of acid reagent, and can use the same digestion tube to complete all the operation steps of digestion, constant volume and computer analysis, so as to avoid the error opportunities caused by other transfer steps and operations. This method has the advantages of short digestion time, low cost, high popularity, high accuracy and precision, and good safety, It can complete a batch of high-throughput digestion of more than 84 samples, which has strong practicability and solves the needs of the current detection and analysis industry.

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