

Effects of water bath digestion and DEENA pretreatment on mercury content detection in soil

Yabo Zhang ^{1, 2, 3, 4, *}

¹Shaanxi Land Engineering Construction Group Co., Ltd., Xi'an 710075, Shaanxi, China

²Shaanxi Institute of Land Engineering Technology Co., Ltd., Xi'an, 710075, Shaanxi, China

³Key Laboratory of Degraded and Unused Land Remediation Engineering, Ministry of Land and Resources, Xi'an, Shaanxi, 710075, China

⁴Shaanxi Land Consolidation Engineering Technology Research Center, Xi'an 710075, Shaanxi, China

Abstract. There are many sample preparation methods for heavy metal detection of soil samples, but each has its advantages and disadvantages. Based on the above two pretreatment methods, the detection limit, precision, accuracy and actual soil sample measurement value of mercury detection in soil by atomic fluorescence were compared with atomic fluorescence, and the results showed that the automatic digestion and pretreatment system (DEENA) could digest soil samples to meet the requirements of GB/T 22105.1-2008 standard. Moreover, there was no significant difference between the two digestion methods on the detection results of mercury in soil, and the automatic digestion and preparation system (DEENA) was convenient, operable and highly automated, which was more advantageous for sample digestion.

1. Introduction

In recent years, with the continuous attention to soil quality issues, the detection of heavy metal pollution in soil has become one of the key contents of environmental monitoring and agricultural environmental protection. Mercury is a highly toxic element that is biotoxic and reserved, and measuring mercury levels in soil is an integral part of soil quality assessment.

At present, the detection methods of mercury in soil mainly include graphite furnace atomic absorption method, atomic fluorescence method and inductively coupled plasma mass spectrometry [1], among which atomic fluorescence method has the advantages of simple spectral line, high sensitivity, low detection limit and wide linear range, and this method is widely used in the detection of trace mercury. Soil samples need to be digested before monitoring, and the digestion methods mainly include water bath digestion, graphite digestion, electric hot plate digestion and microwave digestion[2-5]. In this study, the soil samples were pretreated by water bath digestion method and graphite digestion method, and the mercury content in soil samples was determined by hydride generation atomic fluorescence method, and the advantages and disadvantages of the two digestion methods were compared and analyzed, which provided reference for subsequent soil heavy metal detection.

2. Experimental part

2.1 Main instruments and reagents

2.1.1 Instrument

AFS-9760 atomic fluorescence photometer; DEENA 60 sample automatic graphite digester; Milli-Q Integral 15 Ultrapure Water Meter; BSA224S-CW electronic balance; DZKW-S-8 type water bath.

* Corresponding author: 987474549@qq.com

2.1.2 Test

Nitric acid (excellent pure), hydrochloric acid (excellent pure), potassium hydroxide, potassium hydrogen boride, mercury standard stock solution (1000 mg/L), ultrapure water (conductivity 1 $\mu\text{S}/\text{cm}$, resistivity 0.1 $\text{M}\Omega\cdot\text{cm}$). Add 300 mL of hydrochloric acid, 400 mL of distilled water and 100 mL of nitric acid to the beaker to prepare aqua regia; Weigh 5 g of sodium hydroxide in a beaker, add a small amount of water to dissolve, and then weigh 5 g of potassium borohydride in sodium hydroxide solution, dilute it with water to 1 L to obtain sodium hydroxide-potassium borohydride mixed solution; The cleaning solution is a 5% (volume fraction) nitric acid solution.

2.1.3 Samples

After the soil dries, it is ground through a 0.149 mm sieve and stored in a brown jar. Prepare soil reference materials GBW07454 (GSS-25) and GBW07454 (GSS-32) simultaneously.

2.2 Resolution

(1) Water bath digestion

Weigh 0.500 0~0.509 9 g of the sample to be measured in a 50.0 mL plug colorimetric tube, wet the sample with a little water, add 10 mL of aqua regia, add stopper and shake well, boiling water bath for 2 h, shake once during the period, take out and cool, use deionized water to set the volume to the scale line, mix well, stand for clarification, and make blank samples in the same batch.

(2) Graphite digestion method

Weigh 0.500 0~0.509 9 g of the sample to be measured in a 50.0 mL digestion tube, put the digestion tube into the graphite digester, and the digestion steps are: add 1mL of ultrapure water, add 10mL of aqua regia, and vibrate for 30 s at 50% intensity and 30% height; Heat at 100 °C for 135 min; Shake for 30 s at 50% strength and 30% height, cool for 20 min, set the volume to 50 mL with pure water, and make blank samples in the same batch.

3. Results and discussion

The samples treated by two different pretreatment methods were determined using the same atomic fluorescence spectrometer and setting the same working parameters, and the specific working parameters of the instrument are shown in Table 1.

Table 1 Working parameters of atomic fluorescence photometer

Parameter	data
Negative high voltage /V	290
Total current /mA	30
Auxiliary cathode current /mA	0
Carrier gas flow /(mL·min ⁻¹)	500
Shielding gas flow /(mL·min ⁻¹)	900
Atomic gasifier height /mm	10
Reading time /s	16
Delay time /s	4
Measure the number of repetitions	2

3.1 Atomic fluorescence assay results

3.1.1 Drawing of standard curves.

The mercury standard solution was diluted three times to obtain 20 $\mu\text{g}/\text{L}$ mercury standard solution, and 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 6.0 mL of mercury standard solution were piped into a 50 mL volumetric flask, and the volume was fixed to the scale line, so as to obtain a gradient solution with mercury mass concentration of 0, 0.2, 0.4, 0.6, 0.8, 1.2 $\mu\text{g}/\text{L}$, and the first curve of fluorescence intensity and mercury mass concentration was obtained by atomic fluorescence determination, and the curve correlation coefficient was 0.999 2. It can be seen that mercury has a good linear relationship within 0.0~1.2 $\mu\text{g}/\text{L}$.

3.1.2 Determination results of detection limits

The blank sample was measured 15 times consecutively, and the ratio of the standard deviation to the slope of the standard curvature was calculated 3 times the 11 measured values, that is, the detection limit was obtained [6]. The results show that the detection limit of the atomic fluorescence method is below 0.002 µg/L, which meets the standard requirements.

3.1.3 Determination results of precision and accuracy

Six replicates were performed on GSS-25 (mercury identification value of 0.043±0.003 mg/kg) and GSS-32 (mercury identification value of 0.026±0.003 mg/kg), and the mean values of mercury in GSS-25 and GSS-32 were 0.044 and 0.026 mg/kg, respectively, the relative standard deviation was 3.74% and 3.44%, and the absolute values of relative error were 0~4.65% and 0~3.85%, respectively. Explain that the detection method meets the precision and accuracy requirements.

3.2 Actual soil sample measurement results

Thirteen actual soil samples (numbered SJ-1~SJ-13) were subjected to water bath digestion and graphite digestion, and detected with atomic fluorescence photometer, and the results are shown in Table 2.

Table 2 Actual sample measurement results

Sample number	Measured value /(mg·kg ⁻¹)		Relative error /%
	Graphite digestion	Water bath digestion	
SJ-1	0.086	0.084	1.19
SJ-2	0.080	0.085	3.26
SJ-3	0.155	0.169	4.40
SJ-4	0.061	0.057	3.22
SJ-5	0.146	0.132	4.98
SJ-6	0.065	0.071	4.18
SJ-7	0.054	0.051	2.82
SJ-8	0.030	0.031	1.64
SJ-9	0.107	0.098	4.56
SJ-10	0.123	0.134	4.28
SJ-11	0.188	0.208	5.00
SJ-12	0.080	0.082	1.23
SJ-13	0.166	0.171	1.35

3.3 Comparison of two pretreatment methods

3.3.1 Comparison of digestion procedures

The graphite digestion method uses a fully automatic digestion and pretreatment system for digestion, the main advantage is its rapid temperature rise, and it can complete the digestion of 60 samples at a time, which is suitable for batch testing samples. The method is simple to operate, high degree of automation, the instrument can automatically add reagents, temperature regulation, quasi-determination volume, and three-dimensional graphite heating module by establishing simple commands, uniform heating. The water bath digestion method uses a water bath for heat digestion, and its advantage is that it is cheaper than fully automatic graphite digestion, and the number of samples can be digested up to 120 at a time. The disadvantage is that the heating is uneven, and the addition of reagents and volume fixing need to be completed manually in turn, which is time-consuming and laborious, and the efficiency is low. Therefore, from the perspective of instruments, the automatic graphite digester is more convenient, operable and highly automated, which is more advantageous for sample digestion.

3.3.2 Comparison of test results

Two certified standard samples were detected by two methods, and their precision and accuracy met the standard requirements. After digestion of 13 actual soil samples, the relative deviation of the measured values of the two groups was within 5.0%, indicating that there was no significant difference in the influence of the two digestion methods on the detection results.

4. Conclusion

Atomic fluorescence method was used to determine mercury in standard solution, and the linear relationship between mercury within 0~1.2 µg/L was good, and the detection limit of the method was below 0.002 µg/L, which met the requirements. Water bath digestion and graphite digestion were used to digest soil reference materials and actual soil samples, and there was no significant difference in the impact of the two digestion methods on the detection results of mercury in soil, among which the automatic graphite digester was more convenient, operable and highly automated, and had more advantages for sample digestion.

Acknowledgements

Relying on the project: "Construction of Shaanxi soil mass quality detection and evaluation sharing platform (2021PT-053) "

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