Application of Different Acid Systems in Determination of Heavy Metal Content in Soil by ICP-MS

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Abstract

In this paper, microwave digestion was used as a pretreatment method for soil heavy metals to study the effect of different acid systems on the determination of heavy metal content in soil. Simultaneous determination of Cr, Ni, Cu, Zn, Cd and Pb in soil by inductively coupled plasma-mass spectrometry (ICP-MS) the content of 6 elements. The resu0000lts indicated that when the ratio of nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide was 4:1:1:1, the acid system was the optimum ratio of acid system for microwave digestion.

Keywords

Heavy metal elements, microwave digestion, ICP-MS.

1. Introduction

Soil is one of the important components of the natural environment. It is an irreplaceable natural resource and the basis for human survival. With the advancement of China's industrialization process and the rapid development of the economy, the problem of soil pollution has become increasingly prominent. Pesticides, organic waste, heavy metals and other pollutants have entered the soil, resulting in soil due to their own degradability and resilience. Physical and chemical properties are impaired. Among them, soil heavy metal pollution is one of the most concerned issues [1], because it is concealed, latent and difficult to recover, through sewage irrigation farmland, atmospheric deposition and other ways into the soil, and crops will be absorbed from the roots Heavy metals in soil pollutants, and long-term consumption of contaminated groundwater or consumption of contaminated food can cause great harm to people's health.

How to detect heavy metal content in soil with high efficiency, accuracy and environmental protection has become one of the most concerned issues in the process of environmental analysis. In the process of soil heavy metal determination, the pretreatment of soil samples is the most important link leading to the detection error. Different soil sample pretreatment methods and different acid system selections will have an important impact on the determination of heavy metals in soil. In recent years, the methods for determining heavy metals in soil have been mainly subjected to atmospheric pressure wet digestion and microwave digestion. The traditional soil digestion method is atmospheric pressure wet digestion. This pretreatment method is time-consuming and labor-intensive, and consumes a large amount of acid. The analyst is vulnerable to concentrated acid during the digestion operation, because the process is indirect and open heating. It causes the loss of volatilization of some heavy metal elements and the contamination of the sample, resulting in a large error in the measurement results. Microwave digestion has the characteristics of simple operation, high efficiency and rapidity, low reagent consumption, reduced labor intensity and pollution of analysts, safety, and less interference from matrix. It is widely used in sample pretreatment [2-6]. Although the microwave digestion

method has many advantages [7-12], in the actual soil sample analysis process, the sampling amount of the soil sample, the acid system to be digested, and the content of organic matter in the soil also affect the digestion result, which requires an analyst. Continuously explore in the actual work, and constantly improve to seek the best conditions for digestion. In this paper, the soil sample was subjected to microwave digestion using a nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide system, and the sample was digested by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [13-18]. The content of heavy metal elements in the determination of heavy metal elements was analyzed, and the effects of different acid systems on the determination of heavy metals such as Cu, Zn, Pb, Cd, Cr and Ni were analyzed, and a method for quickly and accurately determining heavy metals in soil was established.

2. Experimental part

2.1 Main instruments and reagents

Milli-Q ultra-pure water machine (Millet, USA); MARS 6 microwave digestion instrument (CEM); Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS); EHD-24 type acid absorbing instrument; Nitric acid (Luoyang Haotian Chemical Reagent Co., Ltd., excellent grade pure); hydrochloric acid (Luoyang Haotian Chemical Reagent Co., Ltd., excellent grade pure); hydrofluoric acid (Shanghai Sinopharm Reagent Group, excellent grade pure); hydrogen peroxide (Shanghai Sinopharm) Reagent Group, excellent grade pure); GBW07454 (GSS-25) soil composition analysis standard substance (National Standard Substance Center); Environmental Calibration standard (Agilent Technology 10ug/mL); experimental water is ultrapure water; used centrifuge tube, poly The tetrafluoroethylene digestion tube should be soaked overnight with 5% nitric acid, rinsed repeatedly with tap water, and finally rinsed with ultrapure water, dried and set aside.

2.2 Sample preparation

Accurately measure 0.1000±0.010 g GBW07454 (GSS-25) soil composition analysis standard materials, transfer them to the cleaned and dried polytetrafluoroethylene digestion tube, then add different acid systems according to Table 1, and shake them evenly. , placed in a microwave digestion instrument for digestion. The specific digestion procedure is set according to Table 2. After the digestion is completed, the sample is opened from the digestion apparatus, and the polytetrafluoroethylene digestion tube is placed in an acid-adjusting apparatus, and the acid is taken up at a high temperature of 160 ° C until the reaction liquid Drain or dry about 1mL or so, the process takes about 1.25h, and the Teflon digestion tube is taken out and cooled at room temperature. Transfer the reaction solution to a 50 mL centrifuge tube and dilute to 50 mL mark line with ultrapure water.

Table 1 9 groups of acid systems

编号	酸体系
1	1mLHNO_3+1mLHCl+1mLHF+1mLH_2O_2
2	2mLHNO_3+1mLHCl+1mLHF+1mLH_2O_2
3	3mLHNO_3+1mLHCl+1mLHF+1mLH_2O_2
4	4mLHNO_3+1mLHCl+1mLHF+1mLH_2O_2
5	5mLHNO_3+1mLHCl+1mLHF+1mLH_2O_2
6	4mLHNO_3+2mLHCl+1mLHF+1mLH_2O_2
7	4mLHNO_3+4mLHCl+1mLHF+1mLH_2O_2
8	4mLHNO_3+1mLHCl+1mLHF
9	4mLHNO_3+1mLHCl+1mLHF+2mLH_2O_2

Table 2 Microwave digestion procedure of sample

step	power（W,100%）	Heating time（min）	temperature（℃）	Hold time（min）
1	1200	10	120	10
2	1200	10	160	20
3	1600	10	180	20

3. Results and discussion

3.1 Standard curve drawing

Standard stock solution 10ug/mL (Environmental Calibration standard, 5% nitric acid medium): containing mixed elements such as Cr, Ni, Cu, Zn, Cd and Pb, and the standard solution is set to a concentration of 0, 0.1, 0.5, 2, 10 respectively. , 50, 200, 500 ug / L multi-element mixed standard solution, are all made up with 1% HNO3.

Table 3 Linearity parameters

element	Linear range ρ/(ug/L)	Linear regression equation	Linear correlation coefficient
Cr	0～500	y=0.0057X+8.6756×10-4	0.9996
Ni	0～500	y=0.0030X+3.2298×10-4	0.9998
Cu	0～500	y=0.0076X+0.0020	1.0000
Zn	0～500	y=0.0011X+0.0037	0.9996
Cd	0～500	y=0.0039X+1.4491×10-5	0.9996
Pb	0～500	y=0.0612X+0.0025	0.9998

3.2 Sample measurement result

According to the pretreatment of 9 different acid systems in Table 1, the contents of Cr, Ni, Cu, Zn, Cd and Pb in the GSS-25 soil composition analysis standard materials are shown in Table 4.

Table 4 Comparison of the results of 9 different acid systems for the determination of GSS-25 soil composition analysis standard materials

元素	标准值 ω(mg.kg-1)	不同酸体系的测定值ω(mg.kg-1)								
		1	2	3	4	5	6	7	8	9
Cr	66±4	51.6	60.0	50.4	63.3	66.0	63.6	64.8	48.9	70.0
Ni	30±1	26.6	31.7	24.8	30.4	30.3	29.4	31.4	35.0	38.9
Cu	23.6±1.0	20.3	23.2	19.0	24.1	23.7	28.4	24.0	24.4	29.0
Zn	66±2	66.4	66.4	52.4	64.2	65.2	66.9	67.6	75.4	82.7
Cd	0.175±0.01	0.12	0.15	0.12	0.17	0.17	0.17	0.16	0.16	0.19
Pb	22±1	17.8	19.2	16.4	21.3	22.0	21.0	19.9	21.7	22.2

It can be seen from the table that in the 1-3 group of nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide system, the amount of nitric acid added <4mL, the soil can not be chromium, nickel, copper, zinc in the soil during pretreatment microwave digestion. Six heavy metals, cadmium and lead, were completely released, resulting in the detection of the contents of six elements of chromium, nickel, copper, zinc, cadmium and lead by inductively coupled plasma mass spectrometry (ICP-MS) and the soil standard material GBW07454 (GSS-25). The standard value is too small; when the above conditions are the same, when the amount of nitric acid added is >4mL, when the volume of nitric acid is 4mL, the soil standard substance GBW07454 (GSS-25) contains 6 kinds of chromium, nickel, copper, zinc, cadmium and lead. The results of heavy metal determination are basically within the range of standard values. When the amount of hydrochloric acid added in the 7 groups of nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide system was 2 mL, the difference between the determination result and the amount of hydrochloric acid added after digestion was not significant; when the amount of hydrochloric acid added was 4 mL, the detection results of cadmium and lead were obtained. Both are smaller than the standard value. In the 8 experiments, when the acid system is nitric acid-hydrochloric acid-hydrofluoric acid, the value of the soil sample without the hydrogen peroxide digestion is smaller than the standard material value, because the organic content in the soil is too high, so it must be Hydrogen peroxide is added, otherwise the digestion is incomplete, resulting in a low measurement result. In the comparison experiments of 4 groups and 9 groups, it was found that the addition of 1 mL or 2 mL of the amount of hydrogen peroxide had little effect on the digestion results. In summary, the nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen

peroxide system is best when the heavy metal in the soil is digested by microwave digestion, and the most cost-saving is when the addition amount is 4:1:1:1. In addition, the environmental pollution is small.

4. Conclusion

In this paper, the standard analytical sample (GSS-25) with different digestion acid system was sampled and the content of six elements of chromium, nickel, copper, zinc, cadmium and lead was determined by inductively coupled plasma mass spectrometry (ICP-MS). The final measurement results show that the mixed acid system of nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide is an ideal digestic acid system for the determination of Cr, Ni, Cu, Zn, Cd and Pb in soil, among which nitric acid, hydrochloric acid, hydrofluoric acid and When the hydrogen peroxide is 4:1:1:1, it not only ensures that the heavy metal elements in the soil are completely released, but also reduces the consumption of reagents, reduces the labor intensity, pollution and safety of the analyst. An efficient and accurate detection method for determining the content of heavy metal elements in soil.

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