

Effects of Microwave Digestion with Different Acid System Proportions on the Determination of Heavy Metal Content in Soil by ICP-MS

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Abstract

In this paper, microwave digestion is used as a pretreatment method for soil heavy metals. Different ratios of HNO₃, HCl, HF, and H₂O₂ are selected. The effect of different acid systems on the determination of soil heavy metals Cr, Ni, Cu, Zn, Cd, and Pb is studied. The measured values of Cr, Ni, Cu, Zn, Cd and Pb by ICP-MS were compared with the standard values of national standard material certificate. The results showed that the soil heavy metals were digested with 4 mL HNO₃ + 1 mL HCl + 1 mL HF + 1 mL H₂O₂. The laboratory measurements of Cr, Ni, Cu, Zn, Cd, and Pb were 63.3 mg/kg, 30.4 mg/kg, 24.1 mg/kg, 64.2 mg/kg, 0.17 mg/kg, and 21.3 mg/kg. Therefore, the values are all within the standard value of the national standard material certificate, which is the optimal proportion of the acid system for microwave digestion. It not only ensures that the heavy metal elements in the soil are completely released, but also has the advantages of less reagent consumption and reduced analysis pollution. Provide an efficient and accurate pretreatment method for determining the content of heavy metal elements in soil.

Keywords

Soil; Heavy metal; Acid system proportions; Microwave digestion; ICP-MS.

1. Introduction

Soil is one of the important components of the natural environment, an irreplaceable natural resource, and the foundation for human survival. With the rapid development of my country's industrialization, the resulting soil pollution problems have become increasingly prominent. Pollutants such as pesticides, organic wastes, and heavy metals enter the soil. Due to their limited degradation and recovery capabilities, the physical and chemical properties of the soil are damaged. Among them, soil heavy metal pollution is one of the most concerned issues, because of its concealment, latent and difficult to recover [1]. How to detect the content of heavy metals in soil efficiently, accurately, and environmentally has become one of the most concerned issues in the process of environmental analysis. In the process of soil heavy metal determination, sample pretreatment is an important link that leads to detection errors. Different soil sample pretreatment methods and the choice of different acid systems will all have an important impact on the determination of heavy metals. In recent years, soil heavy

metal digestion methods mainly include atmospheric wet digestion and microwave digestion. The traditional soil digestion method is atmospheric wet digestion. The digestion process of this pretreatment method is time-consuming and laborious, and consumes a large amount of acid. The analysts are vulnerable to concentrated acid during the digestion process, because the process is indirect and easy to open heating. Causes the volatilization loss of some heavy metal elements and sample contamination, which makes the measurement results produce large errors. The microwave digestion method has the characteristics of simple operation, high efficiency and fast speed, low reagent consumption, reduced analysis pollution, safety, and less interference from the matrix. It is currently widely used in the sample pretreatment process [2-6]. Although the microwave digestion method has many advantages, in the actual soil sample analysis process, the sampling amount of the soil sample, the digested acid system, and the content of organic matter in the soil will also affect the digestion results [7-12]. This requires analysts to constantly explore and improve in actual work to find the best conditions for digestion. In this paper, a nitric acid-hydrochloric acid-hydrofluoric acid-hydroperoxy acid system was used to digest soil samples by microwave, and inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the heavy metals in the samples after digestion and analyze different acids. The influence of the system on the determination results of six heavy metals of Cu, Zn, Pb, Cd, Cr, and Ni, to establish a fast and accurate method for pretreatment and digestion of soil heavy metals [13-18].

2. Experimental Design

2.1. Instruments and Reagents

Agilent 7700e inductively coupled plasma mass spectrometer ICP-MS (Agilent, USA); Milli-Q ultrapure water machine (Millipore, USA); MARS 6 microwave digestion instrument (CEM, USA); BSA224S-CW one ten-thousandth electronic balance (Mettler-Toledo, USA); EHD-24 type acid analyzer; nitric acid: $\rho(\text{HNO}_3)=1.42\text{g/ml}$, excellent grade pure; hydrochloric acid: $\rho(\text{HCl})=1.19\text{g/ml}$, excellent Grade pure; Hydrofluoric acid: $\rho(\text{HF})=1.49\text{g/ml}$, excellent grade pure; Hydrogen peroxide: $\omega(\text{H}_2\text{O}_2)=30\%$, excellent grade pure; GBW07454 (GSS-25) soil composition analysis standard material (national Standard Material Center); Multi-element mixed standard solution for environmental analysis (Part#8500-6944) and internal standard solution (Part#5183-6525) (Agilent, USA); The experiment water is ultrapure water. The centrifuge tubes and PTFE digestion tubes used need to be soaked in 5% nitric acid overnight, rinsed repeatedly with tap water, and finally rinsed with ultrapure water, and then dried for later use.

2.2. Sample Processing

The choice of acid system in soil digestion plays a key role in the determination of heavy metal elements, and the amount of acid has an important influence on the measured value. If the amount of acid is too much, although the digestion is complete, the time to catch up with the acid will increase, causing waste of acid and environmental pollution; too little amount of acid will lead to incomplete digestion and inaccurate analysis. Therefore, in this study, the soil samples were digested by microwave by changing the ratio of different acid systems under the same weighing volume.

Because the soil contains silicate and some heavy metal elements are in the crystal lattice of soil minerals, hydrofluoric acid is the only inorganic acid that can react quickly with it. The final product at room temperature is strong acid HSiF_6 . When heated, H_2SiF_6 decomposes into gaseous SiF_4 , so a silicon-free solution is obtained. Therefore, the digestion acid system without hydrofluoric acid cannot remove silicon, and a large amount of solid residues after digestion affect the measurement results. Considering the effect factors of the initial digestion system,

adding 1 mL of hydrofluoric acid in all steps can decompose the refractory lattice system in the soil minerals, such as silicate-bound metals.

Weigh 0.1000 ± 0.010 g GBW07454 (GSS-25) soil composition analysis standard substance, transfer it to a clean and dry PTFE digestion tube, and then add different acid systems according to Table 1, shake well, and cover. Place it in a microwave digestion apparatus for digestion. The specific digestion procedure is set according to Table 2 below. After the digestion is completed, cool to room temperature, take the sample out of the digestion apparatus, open the lid, and place the Teflon digestion tube in the acid removal apparatus. Acid, until the reaction solution is completely dry or about 1mL of the remaining acid is completed, this process takes about 1.5 hours, take out the polytetrafluoroethylene digestion tube and cool it at room temperature. Use deionized water to clean the inner wall of the lid of the PTFE digestion tank, the inner wall of the tank and the filter residue at least 3 times. The washing liquid is filtered and collected in a volumetric flask, and the volume is made up to 50mL with deionized water. Take the supernatant and measure it by inductively coupled plasma mass spectrometer (ICP-MS).

Table 1. 9 groups of acid systems

Serial number	Acid system
1	1mLHNO ₃ +1mLHCl+1mLHF+1mLH ₂ O ₂
2	2mLHNO ₃ +1mLHCl+1mLHF+1mLH ₂ O ₂
3	3mLHNO ₃ +1mLHCl+1mLHF+1mLH ₂ O ₂
4	4mLHNO ₃ +1mLHCl+1mLHF+1mLH ₂ O ₂
5	5mLHNO ₃ +1mLHCl+1mLHF+1mLH ₂ O ₂
6	4mLHNO ₃ +2mLHCl+1mLHF+1mLH ₂ O ₂
7	4mLHNO ₃ +4mLHCl+1mLHF+1mLH ₂ O ₂
8	4mLHNO ₃ +1mLHCl+1mLHF
9	4mLHNO ₃ +1mLHCl+1mLHF+2mLH ₂ O ₂

2.3. Standard Curve Configuration

Use 2% nitric acid to prepare a multi-element mixed standard solution with a concentration of 0, 0.1, 0.5, 1, 5, 10, 20, 50, 100, 200, 500 $\mu\text{g}\cdot\text{L}^{-1}$, and use 2% nitric acid to prepare 500 $\mu\text{g}\cdot\text{L}^{-1}$ Multi-element (including Rh, In, Re, Lu, Li) internal standard solution.

Table 2. Linearity parameters

element	Linear range $\rho/(\mu\text{g}/\text{L})$	Linear regression equation	Linear correlation coefficient
Cr	0~500	$y=0.0057X+8.6756 \times 10^{-4}$	0.9996
Ni	0~500	$y=0.0030X+3.2298 \times 10^{-4}$	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	$y=0.0039X+1.4491 \times 10^{-5}$	0.9996
Pb	0~500	$y=0.0612X+0.0025$	0.9998

2.4. Sample Quantitative Analysis

2.4.1 Working conditions of ICP-MS

Plasma gas flow rate 15 L/min, auxiliary gas flow rate 0.8 L/min, carrier gas flow rate 0.8 L/min, compensation/dilution gas flow rate 0.8 L/min, spray chamber temperature 2°C, sampling depth 8 mm, RF coil power 1550W, pump speed 2 r/min.

2.4.2 Microwave Digestion Apparatus Program

Table 3. Microwave digestion procedure of sample

step	Power (W,100%)	Heating time (min)	Temperature (°C)	Hold time (min)
1	1200	10	120	10
2	1200	10	160	20
3	1600	10	180	20

2.5. Sample Quantitative Analysis

Set up the full quantitative analysis method in the Agilent ICP-MS software, including the selection of the elements to be determined, the number of repeated determinations, the signal integration time of each element, the internal standard elements, the interference equation, the determination method and the calibration curve table, etc. After the plasma ignition of the instrument is stable for 30 minutes, the internal standard tube is put into the internal standard solution prepared by the nitric acid solution after the instrument is tuned, and the prepared heavy metal mixed standard solution is measured respectively to obtain the curve, and the sample and processing data are measured.

3. Results and Discussion

3.1. Sample Measurement Result

The most important factor influencing the results of soil samples is the choice of digestion method and acid. In the past, the commonly used method of soil sample digestion in geological and mineral laboratories was the electric heating plate method. The acid used for digestion was HNO_3 , HCl , HF , HClO_4 , H_2O_2 , etc., but this method takes a long time to digest, consumes a large amount of acid, and has a great impact on reagents. It has high requirements and large environmental pollution. In addition, when the digestion content is low and unstable elements such as As and Hg, there is instability. The new microwave digestion method has significant advantages such as reliable performance, easy operation, high automation, and low reagent consumption. Therefore, on the basis of the current soil heavy metal pretreatment, this article carried out a microwave digestion inductively coupled plasma mass spectrometer under different acid system ratios to determine soil heavy metals to determine a set of rapid and accurate soil heavy metal microwave digestion pretreatment methods.

According to the nine different acid systems in Table 1, the pre-treatment of microwave digestion was carried out, and the content of Cr, Ni, Cu, Zn, Cd and Pb in the GSS-25 soil composition analysis standard material was measured 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

element	standard value ω (mg.kg ⁻¹)	Measured values of different acid systems 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

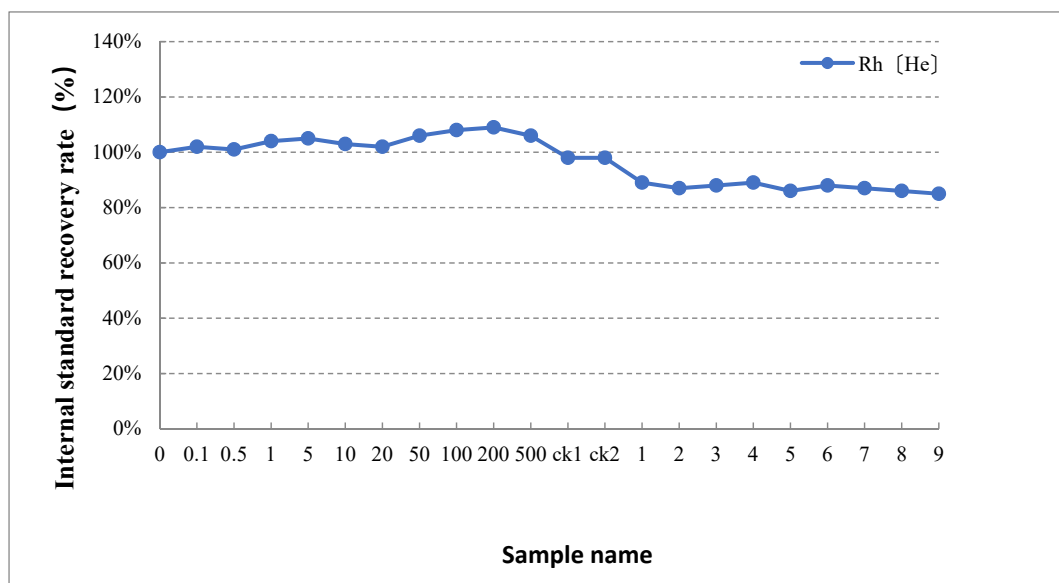


Figure 1. Recovery curve of internal standard for sample determination

It can be seen from the sample recovery curve of the internal standard in Figure 1 that the curve is smooth and the fluctuation is small, indicating that the influence of the instrument fluctuation and the matrix is small, indicating that the instrument detection has a small influence on the comparison error of the sample results in this experiment, and it is more significant for comparison. The influence of acid digestion system on the results of heavy metals.

3.2. The Influence of the Amount of Acid on the Measured Value of Heavy Metals

From the measurement results of the standard sample GSS-25 in Table 4, it can be seen that the results of different acid digestion systems are different. In the 1-3 groups of nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide systems, when the amount of nitric acid added is less than 4mL, the soil is The six heavy metals of chromium, nickel, copper, zinc, cadmium and lead in the soil cannot be completely released during pre-treatment microwave digestion, resulting in the detection of Cr, Ni, Cu, Zn, Cd by inductively coupled plasma mass spectrometer (ICP-MS) The content of the 6 elements of Pb and Pb is smaller than the standard value of the soil standard material GBW07454 (GSS-25). When the above conditions are the same, when the amount of nitric acid added is more than 4mL, and when the volume of nitric acid added is 4mL, the determination results of the six heavy metals of Cr, Ni, Cu, Zn, Cd and Pb in the soil standard GBW07454 (GSS-25) are basically in Within the standard value range. When the amount of hydrochloric acid added in the 7th group of nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide system is 2mL, the measurement result after digestion is not much different from the added amount of 1mL hydrochloric acid; when the amount of hydrochloric acid added is 4mL, the detection of cadmium and lead the results are all less than the standard value. In the eighth group of experiments, when the acid system is nitric acid-hydrochloric acid-hydrofluoric acid, the measured values of the soil samples without hydrogen peroxide digestion are lower than the values of the standard substances, because the organic matter content in the soil is too high, so Hydrogen peroxide must be added, otherwise the digestion is not complete, resulting in low test results. In the comparative experiments between the 4th group and the 9th group, it was found that the addition of 1mL or 2mL of hydrogen peroxide had little effect on the digestion results. In summary, the nitric acid-hydrochloric acid-hydrofluoric acid-hydrogen peroxide system is the best when microwave digestion method is used to digest heavy metals in the soil, and the addition amount is 4:1:1:1, that is, 4 mL HNO₃+1mL HCl + 1 mL HF + 1 mL H₂O₂ digestion, the laboratory measured values of Cr, Ni, Cu,

Zn, Cd and Pb are 63.3mg/kg, 30.4 mg/kg, 24.1 mg/kg, 64.2 mg/kg, 0.17 Both mg/kg and 21.3 mg/kg are within the standard value range of the national standard material certificate, and are the most cost-effective and have the least environmental pollution.

4. Conclusion

In this paper, microwave digestion is used as the pretreatment method of soil heavy metals. Different ratios of HNO₃, HCl, HF, and H₂O₂ are selected, and the standard analysis sample (GSS-25) is subjected to sample pretreatment. The Cr is determined by inductively coupled plasma mass spectrometry (ICP-MS), Ni, Cu, Zn, Cd and Pb 6 elements experimentally measured values and the national standard material certificate standard values are compared. The final measurement results show that the mixed acid system of HNO₃, HCl, HF, H₂O₂ is an ideal digestion acid system for the determination of Cr, Ni, Cu, Zn, Cd and Pb in the soil, using 4 mL HNO₃+1 mL HCl +1 mL HF+1 mL H₂O₂. After H₂O₂ digestion, the laboratory measured values of Cr, Ni, Cu, Zn, Cd and Pb are 63.3 mg/kg, 30.4 mg/kg, 24.1 mg/kg, 64.2 mg/kg, 0.17 mg/kg, 21.3 mg/kg, respectively. They are all within the standard value range of the national standard material certificate, which is the best acid system ratio for microwave digestion. It not only ensures that the heavy metal elements in the soil are completely released, but also has the advantages of low reagent consumption and reduced analysis pollution. It provides an efficient and accurate pretreatment method for determining the content of heavy metal elements in the soil.

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