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An Experimental Method for Effectively Digesting Geological Samples

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Abstract

The material composition of geological samples is very complicated. Generally, the method for accurately determining trace elements in geological samples needs to digest the solid samples into liquid state, which is convenient for inductively coupled plasma mass spectrometry. The previous digestion method takes a long time and the operation process is complicated. The Ultra CLAVE microwave digestion instrument was used to digest the geological samples. The types and dosages of the acid used for digestion and the optimal conditions for instrumental testing were published. The results show that this method has short processing time, small data error, safer operation and good digestion effect. This method is suitable for geological sample analysis.

Keywords

Microwave Digestion, Geological Sample, Acid Ratio, Time

1. Introduction

The analysis of the sample digestion is elemental analysis of an important part of the development of digestion technology which is crucial for the development of chemical analysis (Liu & Tang, 2012). The traditional digestion technology (dry digestion and wet digestion) plays an important role in chemical analysis, which has good universality, but it needs relatively longer pretreatment time, complex procedure which has some impact on the results. To solve these problems, a new way of Digestion-microwave Digestion has been developed fast in recent years. The microwave digestion is a fast, accurate, reproducible digestion method. Compared with conventional digestion methods, microwave digestion is mainly

carried out in a closed container with a small amount of acid, for the determination of volatile elements with high precision. After Years of research and application, microwave digestion technology has evolved into a powerful, technologically advanced sample pretreatment method (Zeng, 2012). Most digestion aims to remove organic impurities in the sample to obtain the desired trace amounts of elements. But the major inorganic component is not easy digestion in geological samples. Accurate determination of elements in geological samples, for recycling, minerals and other elements of the assessment is important. Therefore, quickly and efficiently digested sample is a question of Geology Geological workers that have been concerned.

Geological samples are the most common minerals, soils, and stream sediments, and its composition is a mixture of various minerals, commonly used method of acid-soluble and alkali fusion decomposition. This experiment uses UltraCLAVE microwave digester to digest geological samples, and then discuss on experimental procedure, and parameters and matters need attention.

2. The Instrument and Reagent

The instrument: UltraCLAVE IV Microwave digestion instrument, Milestone of Italy; Milli-Q Ultrapure water system (18.7 MΩ·cm); Acid purification system, Milestone of Italy; Acid cleaning system, Milestone of Italy; Electric heating plate.

The reagent: Hydrogen peroxide, Perchlorate, Sulfuric acid, Nitric acid, Hydrofluoric acid.

3. Microwave Digestion Process

1) Experimental preparation

The experiment required container (PTFE and PFA digestion vessel flask) should soaked in 5% HNO_3 (superior grade pure) in more than 24 h. then use acid cleaning system for cleaning (260°C, 3 - 4 h). After acid cleaning, remove the container and promptly washed 3 - 5 times with ultrapure water (resistance rate 18.7 MΩ·cm) placed in a fume cupboard t to dry for next experiment.

2) Weigh the sample

The samples were crushed to 200 meshes, and then grinded 20 min in a mortar. Accurately weigh about 50 mg of sample in accuracy of 0.1 mg. The sample was carefully transferred to a digestion tube to avoid sample attaching to tube inner surface.

3) Add acid

Join 0.5 mL MOS level H_2O_2 in weighed sample digestion tube which has loaded sample, soaked 4 - 5 h or stand overnight, then add 0.5 mL H_2O_2 (MOS level). Then digestion tube was added into 5 mL HNO_3 and 2 mL HF (the acid ratio is applicable to the ash yield < 50%, when the ash yield is too large, increase the amount of HF and decrease the amount of HNO_3), give HNO_3 priority of joining. In adding acid process should try to wash the sample to the bottom of the

tube digestion which adheres to the wall, after the addition of acid, covered the tube with a lid, ready for digestion. Digestion tube according to the above-described method for simultaneous processing of two rock reference material and two full blank, as a quality control and a control sample. After the sample with acid, if the reaction is severe, you need to put some time and then be reacted by microwave heating. For the initial violent reaction of the sample with acid, the acid may be added for several times, in order to avoid acid spill out.

Experimental study focused on acid system and digestion temperature, beside the use of HF, conventional acid digestion method to destroy the mineral lattice, and to break down completely, add HNO_3, H_2SO_4, $HClO_4$ in mixed acid (Yang & Li, 2011). However, H_2SO_4 is tending to form char residue that hard to destroy. alkaline metals in earth and lead the formation of insolubility of the compound; difference $HClO_4$ purity easily into impurity, prone to violent reaction with organic explosion, do not recommend using hydroelectric acid is the only decomposed to silicon. Inorganic acid matrix sample digestion is suitable for all types of geological samples, when heated, H_2SiF_6 decompose into gaseous SiF_4, silicon-free solution obtained, and without HF acid digestion system was unable to remove the silicon (Liu, 2001).

4) Microwave digestion

Add about 330 mL of ultra-pure water, 30 mL of H_2O_2 and 1mL of H_2SO_4 to the reaction tank. After putting the reaction tank into the microwave digestion reaction chamber, carefully fix digestion tube to rack, start the microwave digestion procedure (Table 1). The program runs about two hours. Digestion could separate in two stages, organic matter easily oxidized at 1000 W, difficult to break down organic matter when 1200 W, digestion experiments show good results.

Microwave digestion conditions directly determine the final results of the analysis. After digestion large amount of solid residues will affect the subsequent determination. The energy required to break down the sample depends on the composition and amount of sample, the type of container, reagent type and proportion and so on. Seal pressure generated inside the container lead the boiling point of the reagent increased. Thus digestion requires higher temperatures. Temperature and pressure can significantly shorten the time of sample decomposition, and lead some of the more insoluble compounds to be digested. Volatile elements, such as, Cr, Hg, Sb, Se, Sn will be retained within the container,

Table 1. Program parameter of microwave digestion

Step	Time (min)	Temperature (°C)	Pressure (bar)	Power (W)
1	12	60	100	1000
2	20	125	100	1000
3	8	160	130	1000
4	15	240	160	1200
5	60	240	160	1000

can be well preserved in solution, reduce evaporation losses. In order to ensure and thus safe sample dissolution, Microwave digestion instrument used in this experiment using dual monitoring and control of temperature and pressure. Microwave program uses pre-digestion heating system and the power increases by stepwise, avoid leaving violent reaction and pressure soared.

Since HNO_3 and HF in different roles in the digestion process, the ratio of the two has great impacts for the digestion effect. To solve this problem, experiment take different acid ratio on the same geological samples (50 mg) digestion, and digestion effect is obvious difference (Table 2). Experiments show that when HNO_3 and HF are respectively 2 mL and 5 mL, complete digestion is better.

5) Transfer and dilute

Transfer sample digested with ultrapure water to a 100 mL PFA volumetric flask, seal, shake and let stand, test.

4. Catch Acid and Extract

Catch the acid and extraction process: When the program execution is completed, and the tank pressure has eliminated, Transfer sample digested with ultrapure water to a 100 mL PFA volumetric flask, control liquid volume stand about 60 mL. Add 2 - 3 drops of $HClO_4$ into beaker, the beaker was placed on a hot plate heated (150°C), heated the beaker (including cup wall) until it out of any liquid, add HNO_3 With the volume of water in one to one into beaker. When the 5 mL HNO_3 in beaker evaporate completely, Then add 5 mL HNO_3 (1:1) and extract for 15 min. Transfer the liquid in beaker with ultra-pure water to a 100 mL PFA volumetric flask, seal, shake and let stand, test.

Element exist in complex form in the Geological sample, in a certain extent; limit the dissolution of rare earth elements. Adding hydrofluoric acid, samples can be effectively open when HNO_3-HF-H_2O_2 mixed in acid, and dissolve the sample efficiently. As a result, get higher dissolution rate of the rare earth element (Chen et al., 2011). HF, H_2O_2 can enhance the dissolution rate of rare earth elements, HF can effectively silicate becomes volatile SiF_4, use a small amount of HF in combination with other acid, prevents the formation of analyte in the sample silicate (Zhang et al., 2010). Because HF can form insoluble fluoride complex precipitation and rare earth elements (especially light rare earth element), thereby enabling the measurement result is low (Wang et al., 2000; Liu, Yun, & Wang, 2005). Therefore, accurate determination of rare earth elements needed

Table 2. Method of microwave digestion and evaluation.

Method	Acid system			The solution color	Residue color	Dispelling effect
	HNO_3	HF	H_2O_2			
1	5 mL	2 mL	1 mL	Light yellow	Light gray	Completely
2	3 mL	3 mL	1 mL	Light yellow	Gray	Incompletely
3	2 mL	5 mL	1 mL	Colorless	Gray and black	Incompletely

to catch the acid extraction, acid extraction experiments show catch Process for the determination of volatile elements unstable element or influential.

5. ICP-MS Test

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a new technology developed in the 1980s, plasma is source of mass spectrometry, sample in the ion source produce a variety of positively charged ions after ionization. And under the influence of the acceleration electric field, form a particle beam incident on the analyzer. Since the electromagnetic field, according to mass the various ions charge ratio of the size separated, and then the mass spectrum obtained by the recording system, the position of each line of the spectrum in accordance with and the number of charges corresponding qualitative analysis of ions, and pressing the appropriate ionic strength were quantitatively analyzed the ionic based on ionic strength.

5.1. The Prototype and the Internal Standard

ICP-MS linear range is relatively wide, linear dynamic range up to 9 orders of magnitude (Liu et al., 2005). What standard that experiment. Followed is the Standard Series 1 ppb, 10 ppb, 50 ppb, 100 ppb, control 2% HNO_3 system; ultra-pure water preparation 2% HNO_3 (via sub-boiling purification) do standard blank, and regularly updated internal standard. Test procedure adopts Rh^{103} correction method; through online add internal standard solution to monitor changes in the signal. Using internal standard calibration analyte results can be effectively overcome the impact generated by the instrument drift, improve the accuracy of analysis (Ai et al., 2002; Luo et al., 2009).

5.2. The Main Working Parameters of ICP-MS

Radio frequency power, sampling depth, nebulizer gas, auxiliary gas, and cooling gas flow rates are the main operating parameters of ICP-MS analysis (Table 3). The instrument will meet thermal drift in the beginning of 1 - 2 hours; we should pay attention to control the time in stable.

Table 3. Work parameter of ICP-MS.

Project	Parameter	Project	Parameter
Forward power	1400 W	Nebulizer	Meinhard
Sampling depth	150 step	Nebulizer temp	3˚C
Nebulizer gas	0.85 L/min	Pump speed	30 r/min
Auxiliary gas	0.80 L/min	Survey	Peak jump
Cooling gas	13.0 L/min	Channels	3
Oxide	<0.5%	Dwell time	10 ms
ICP&MS connector	Xt	Main runs	2
Internal standard	^{103}Rh-10 ppb	Sweeping times	>100/run

Table 4. The result of rock sample (10^{-6}).

The elements	Li	Be	V	Ni	Cu	Zn	Ga	Rb	Y
Standard values	32.9	17.2	179	1.75	11.8	112	35.8	130	24.7
The standard deviation	3.4	2.0	11	12.5	1.7	7	4.9	8	2.10
The measured values	31.6	19.1	171	1.53	12.4	119	37.1	132	22.8
The elements	Nb	Mo	Ba	La	Ce	Dy	Hf	Th	U
Standard values	66.9	0.26	251	149	242	4.70	34	79.3	14.6
The standard deviation	6.9	0.09	19	16	19	0.72	6.4	6.4	1.9
The measured values	68.3	0.19	264	157	255	4.09	30	77	15.3

5.3. The Determination Results of ICP-MS

The result of ICP-MS measurement not only has detected low detection limit, and its work curve is good at linear correlation, can effectively guarantee the accuracy of the measured data. It determines each concentration point of calibration curve to calculate the linear regression equation and the correlation coefficient R, and all measured elements linear correlation coefficient are greater than 0.9995.

In order to evaluate the accuracy of the method, the experiment choose GBW07109 rock composition as standard analysis material, this material was calibrated with a variety of methods as X-ray fluorescence, colorimetry and weighing method, by the China Institute of Metrology sciences and other 18 test experimental determination units. The measurement results consistent well with standard values, within the accepted error range (Table 4).

6. Conclusion

Use microwave digestion, which inductively coupled plasma mass spectrometer and atomic absorption spectroscopy as a unit; make the test period short, loss and low, and precision high; speed up the pace of geology and mineral resources research. This approach optimizes the experimental conditions of microwave digestion, shortens the period, reduces pollution, ensures safe performance, and simplifies the operation. Because those common geological samples mainly formed by silicate mineral partly made of organic matter have better digestion and could meet the demand of simple, rapid, geological samples which are in simple, rapid and batch analysis.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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