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Optimized microwave preparation procedure for the elemental analysis of aquatic sediment

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Abstract This paper summarizes several key points in applying the microwave preparation technique to the elemental analysis of aquatic sediments and reports systematic experiments in searching for an optimal microwave preparation procedure for element analysis in sediment samples. The determination of the elements Cu, Pb and Cd in a standard reference aquatic sediment sample (CRM 280, COMEUR) was achieved by first digesting the samples in a microwave oven equipped with PFA advanced composite vessels, followed by AAS measurement. The influence of microwave power, digestion time, various dissolution reagents and the HF removing conditions was studied. It has been shown that for a 0.1 g sediment sample the optimal microwave preparation conditions are: 4–5 ml $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}_2$ as solvent, digesting time 30 min with 100% microwave power and evaporating the residual acid within 8 min in an open vessel at 80 °C. The element recovery rates with AAS measurement can reach up to 92.4–100.6%.

Introduction

Dissolution is an important stage in the determination of elements in sediment. The microwave extraction technique has attracted much attentions in recent years. This technique takes the advantage of direct energy absorption by acid and water. Therefore, it can accelerate the digestion process. It can also avoid the spread of harmful gases with closed vessels and eliminate the uncontrolled loss of volatile molecular species. The technique has shown a promising future for the analytical community. It is predicted that this tech-

nique will eventually take the place of traditional digestion methods [1, 2].

Microwave digestion for sample preparation has been used for different materials such as biological materials, food, geological materials, soil, coal, oil sewage sludge, waste water, ores, etc. [3, 4]. There have also been reports on the application of microwave digestion for aquatic sediments [6–15]. They mainly focused on two categories: One was on the comparison between traditional digestion methods and the microwave preparation to prove the advantages of the new technique [4, 5]. The other one was on direct microwave digestion experiments with standard reference materials in searching for the optimal preparation procedure [6–15]. Several studies deal with the determination of some species of the elements. There are examples: The EPA 3051 method [4, 6] determines the environmentally available species of heavy metals by using 20 ml conc. HNO_3 as dissolution reagent and a microwave digestion time of 10 min under 100% microwave power on about 0.1 g sediment sample. Mahan et al. [7] performed a sequential extraction for several elements with microwave digestion. However, many research works focused on total element analysis [8–15]. In the process of microwave digestion the major factors that affect the measuring results include the dissolution reagents and their amount, digestion power and time, evaporation of the residual acid etc.

Reagent selection is one of the key steps for a successful microwave dissolution. For aquatic sediments, the common dissolution reagents used include HNO_3 , HCl , HClO_4 , HF and sometimes H_2O_2 . Until very recently, the selection of the dissolution reagent remained purely empirical [1].

HNO_3 is the only acid which can be used alone. It is already active at room temperature and decomposes organic materials, while at high temperature and high pressure almost complete mineralization can be achieved [8]. Because of these properties, there are some microwave digestion procedures with HNO_3 as

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dissolution reagent alone [6]. HClO_4 is also a very clean digestion reagent with high oxidative power. However for safety reason, it should be used along with other acids or solvents [8]. The reason is that in the microwave heating process the reaction of HClO_4 can cause considerable variation of pressures within closed vessels which is difficult to predict. If HClO_4 is used, the microwave power for sample digestion should be increased slowly and HClO_4 should be removed before the AAS or ICP determination of the elements [1, 8]. It has been suggested to avoid this acid in the microwave heating process [1]. HF is the only acid that can dissolve SiO_2 and silicates [9]. It is a prerequisite of a complete digestion of aquatic sediment samples [8–15]. However, HF is a highly dangerous acid. It can damage the following element analysis equipment and adulterate the analytical results. Therefore, it should be removed after the digestion process. It can be evaporated in open vessel within the microwave oven or by hot plate heating. These methods are time consuming. The evaporating temperature and step can somewhat affect the measuring results. There are also chemical methods for solving this problem, such as adding H_3BO_3 to react with the residual HF. It has been reported that are no effects when using the ICP measurement [14]. It has not been known very well whether it disturbs the AAS measurement. H_2O_2 is used as one of the dissolution reagents, too. It can produce highly active oxygen even at low temperatures and can be more effective in the dissolution process in combination with HNO_3 . The decomposition of H_2O_2 leads to only very simple products which do not interfere with the following measurement. The commonly used dissolution reagents include HNO_3/HF , $\text{HNO}_3/\text{HCl}/\text{HF}$, $\text{HNO}_3/\text{HCl}/\text{HF}/\text{HClO}_4$, $\text{HNO}_3/\text{HF}/\text{HClO}_4$, $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}_2$. Different researchers have their own selections [5, 8, 11–15]. There have been no general rules.

The choices of the microwave digestion procedure and time depend on the power of the microwave oven, the composition and quantity of the sample, the reagent and its amount. There are generally two kinds of digestion procedures. One is a heating-cooling-heating way [11–15] and the other one is a continuous heating, including heating only at one power or at a series of incremental powers [5, 13]. The heating time and procedures that have been used by researchers are different.

The sample amount is an important consideration. It is preferable to use as much sample as possible for some

trace element determinations, while the maximum pressure inside the closed vessel, which mainly results from the decomposition of organic material, should not increase above the limitation [13]. Therefore, if the organic content of a sample is high, the sample amount should be small. The generally used sample amount is from 0.1 g to 0.5 g [3, 6].

As mentioned above, the microwave preparation technique is still in its developing period and many aspects still need to be studied. This paper focuses on a systematic study of the crucial aspects of the sample digestion process and gives an optimal procedure for the analysis of Cu, Pb and Cd in aquatic sediments.

Experimental

Instrumentation

The sediment samples were decomposed in a microwave sample preparation system (MDS-2000, CEM) equipped with the microwave power from 0 to 100% (630 W), highest operating temperature 200 °C and highest operating pressure 1.38 MPa (14.08 kg/cm²). The microwave system has a rotary table on which a maximum of 12 100 ml vessels can be set. Advanced composite PFA vessels were used. The system allows energy and time to be programmed in a maximum of five steps.

The elements Cu, Pb and Cd in the digestion solutions were measured with a Perkin Elmer Model 3100 Atomic Absorption Spectrometer fitted with a deuterium arc background correction system, an HGA-600 graphite furnace and an AS-60 auto-sampler. Ar was used as the inert flow gas. Signal type was AA-BG and signal measurement was peak area. Slit width and height were 0.70 and low. The operation parameters of the AAS are given in Table 1. The range of the calibration line for Cu and Pb was 0–50 µg/L, for Cd 0–5 µg/L.

Reagents

The reagent used for sample decomposition were 11.7–12.0 mol/L HCl, 14.6–15.3 mol/L, HNO_3 , > 22.6 mol/L HF, 11.7–12.0 mol/L HClO_4 , 9.29 mol/L H_2O_2 , and 0.65 mol/L H_3BO_3 . All reagents were of analytical-reagent grade.

Standard solution of Cu, Pb and Cd were commercial products. The working standard solutions for AAS with acid concentration close to those of the samples were prepared daily.

Samples

A standard reference sediment sample (CRM280, COMEUR) which has certified concentration values of ten elements was used.

Table 1 Operation parameters of the AAS for element analysis

Element	Wavelength (nm)	Lamp current (mA)	Energy	Matrix modifier	Tube/site
Cu	324.8	17	63	No	Pyro/wall
Pb	283.3	10	60	No or $\text{NH}_4\text{H}_2\text{PO}_4$	Pyro/wall
Cd	228.8	10	60	$\text{NH}_4\text{H}_2\text{PO}_4$	Pyro/platform

Experimental steps

Three accurately weighed 0.1 g standard reference sediment samples were separately given into three advanced composite vessels. Care should be taken to avoid sample attaching to the wall of the vessel. Then the dissolution reagents were added to the samples within a hood. A blank containing only the digesting reagents was prepared. The vessels had to stand on the symmetrical position of the turntable. Then the microwave digesting program was set up and the microwave heating started. After digestion, the sample was washed into the measuring flask with distilled water or acid (for the residual of the evaporating process). When the reagents contain HF, an evaporating step was carried out before measuring the Cu, Pb and Cd concentrations with AAS. For a convenient comparison between the measured Cu, Pb and Cd values and the certified values, the units of the values measured by AAS were converted from $\mu\text{g/L}$ to mg/kg based on the amount of sample digested.

Experiments

The influence of the amount of reagents and microwave power on the consumed time to reach the pre-designed pressure inside the digesting vessels was tested. Aqua-regia was used as the digestion reagent. Two microwave powers were chosen for the reagent amounts of 4, 8 and 12 mL.

The determination of a proper time for a complete digestion was carried out. Experimental conditions were the following: pressure 0.5 MPa, digesting reagents $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}_2 = 2:1:1$, microwave power 100%, digesting time: 5, 10, 30 min.

Seven different kinds of reagent in different ratios were tested. These were aqua regia (3:1), aqua regia/HF (4:1), aqua regia/HF/ H_2O_2 (4:1:1), HNO_3/HF (3:1), $\text{HNO}_3/\text{HF}/\text{HClO}_4$ (2:1:1), $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}_2$ (2:1:1), $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}_2/\text{H}_3\text{BO}_3$ (2:1:1:1). Table 2 shows the microwave digestion procedures. For the test with reagents including HF, an evaporating step was fitted in.

Acid evaporation conditions were selected. When HF or HClO_4 were used, an additional step by evaporation was necessary before the AAS measurement could be made. The evaporation should guarantee that the residual becomes nearly but not totally dry [14]. Three evaporation times of 5, 10 and 30 min were taken and each was tested together with a temperature of 80, 100, 120 and 150 °C, respectively.

Results and discussion

The experimental results for the influence of the amount of reagents and microwave power on the time consumed to reach the pre-designed pressure inside the digesting vessels are listed in Table 3. The data in the table show that when the reagent amount is 8 ml or 12 ml and the microwave power is 80% or 100%, the consumed time for 0.55 MPa inside the digesting vessels does not show considerable difference. When

the reagent amount is 4 mL, the consumed time is longer. Less time is needed with 100% microwave power than with 80% power. From the point of shortening the consumed time, 8 mL or more reagent should be preferred. However, for a 0.1 g sample, less reagent is needed in consideration of the interference of reagent in the following AAS measurement. For shortening the consumed time, 100% microwave power should be chosen. We suggest using 4 mL reagent with 100% microwave power to digest 0.1 g sediment sample.

The digesting time controls the completeness of the digestion. A right selection of the digesting time is necessary not only for a complete sample digestion but also for time saving. The results of the digestion time experiments are shown in Table 4. When the heating time is 5 min or 10 min, the element recovery rates of Cu, Pb and Cd are all comparatively lower. The sample solutions after digestion were not clear and had some grayish settlements after a period of resting. This indicates an uncompleted digestion. In contrast to this, clear digestion solutions were obtained after 30 min microwave heating. The element recovery rates were increased to satisfaction. We know from this test that a longer digestion time is helpful to realize a complete sample digestion. 30 min microwave heating is a proper choice.

Reagents are key factors affecting digestion processes. The test results with 7 different compositions of reagents are shown in Table 5.

Digestion with aqua regia resulted in unclear solution containing a white precipitation. This means that the silicates are difficult to dissolve with aqua regia. Therefore, the element contained in silicates cannot be extracted, leading to lower recovery rates.

When employing aqua regia/HF, silicates were dissolved by HF and the precipitation decreased considerably. But some black particles, possibly carbon residuals of organic materials, appeared in the solution. The measuring results showed that the recovery rate for Pb was lower. An explanation for this is the formation of PbCl_2 which has a lower solubility. The recovery rates of Cu and Cd were higher than those with aqua regia alone, but were still not satisfactory.

The results of the digestion with HNO_3/HF were better than those with aqua regia/HF but there were still black particles. HNO_3 was not able to dissolve the black particles. The recovery rates for Cu and Cd were increased because these two elements were easier to be dissolved in HNO_3 . The recovery rate for Pb was good since there was no Cl^- ion in the digestion reagents.

Table 2 Working conditions of the microwave system

Steps	Power %	Pressure MPa	Time min	Temperature °C	Notes
1	100	0.55	7		
2	75	0.55	20		
3	100	0.55	3		
4	80		8	80	Evaporation

Table 3 Influence of microwave power and reagent amount on the digestion time

Pre-designed pressure (MPa)	Reagent aqua-regia amount (mL)	Power (%)	Time consumed (min)
0.55	4	80	12
		100	7
	8	80	2
		100	2
	12	80	2
		100	1.5

Table 4 Element measuring results under various digestion time^a

Element	Certified value mg/kg	Heating time min	Experimental value	
			Concentration (mg/kg)	Recovery rate (%)
Cu	70.5 ± 1.5	5	56.72 ± 3.21	80.45
		10	57.45 ± 1.55	81.49
		30	70.95 ± 4.42	100.46
Pb	80.2 ± 2.3	5	54.67 ± 4.29	68.17
		10	55.46 ± 1.15	69.15
		30	79.15 ± 2.72	98.69
Cd	1.6 ± 0.1	5	1.17 ± 0.02	73.13
		10	1.23 ± 0.10	76.87
		30	1.48 ± 0.06	92.50

^aDigestion reagent: HNO₃/HF/H₂O₂

The digestion with the remaining four reagent compositions led to clear solution without any settlement. However, according to the measuring results, only the digestion with the HNO₃/HF/H₂O₂ gave values close to the certified values for the three elements Cu, Pb and Cd. The other three reagent compositions did not provide high recovery rates for Cu and Cd. Removal of the residual HF with H₃BO₃ did not produce ideal results.

In other words, HNO₃/HF/H₂O₂ makes the most effective reagent in microwave digestion. The recovery rates were comparatively higher and the test values for Cu, Pb and Cd were close to the certified values. H₂O₂ took a good part in digesting the black organic particles and did not interfere with the evaporation of HF. This reagent composition did not disturb the AAS measurement.

From the selection experiments for dissolution reagents, we found that the recovery rates of Cd were lower under all conditions. Cd is relatively more volatile than Cu and Pb. Therefore, we supposed that the lower recovery rates for Cd were caused by loss in the evaporation step. Therefore, we assumed in this test that if Cd does not vaporize, Cu and Pb will not vaporize either. We selected HNO₃/HF/H₂O₂ as reagent which was proven to be the best one for microwave digestion in our experiments. The test results are shown in Table 6. They demonstrate that the recovery rate of Cd is lower

Table 5 Comparison of the recovery rate using various digestion reagents

Number	Digesting reagents ^a	Cu			Pb			Cd		
		Certified values mg/kg	AAS mg/kg	Recovery % rate	Certified values mg/kg	AAS mg/kg	Recovery rate %	Certified values mg/kg	AAS mg/kg	Recovery rate %
1	Aqua regia		57.33 ± 4.23	81.32		54.87 ± 4.17	68.42		0.63 ± 0.05	39.19
2	Aqua regia/HF		66.10 ± 2.00	93.76		41.33 ± 0.17	51.53		0.96 ± 0.02	60.56
3	Aqua regia/HF/H ₂ O ₂	70.5 ± 1.5	66.12 ± 2.09	94.46		54.87 ± 2.25	68.42	1.6 ± 0.1	0.71 ± 0.07	44.37
4	HNO ₃ /HF		66.01 ± 4.97	93.03		82.57 ± 4.24	102.96		1.34 ± 0.05	83.75
5	HNO ₃ /HF/HClO ₄		56.66 ± 1.62	80.37		78.54 ± 4.60	97.93		0.90 ± 0.06	56.25
6	HNO ₃ /HF/H ₂ O ₂		70.95 ± 4.42	100.60		79.15 ± 2.72	98.69		1.48 ± 0.06	92.50
7	HNO ₃ /HF/H ₂ O ₂ /H ₃ BO ₄		57.55 ± 4.23	81.63		83.78 ± 4.17	104.46		1.18 ± 0.02	73.75

^aThe concentrations and ratios of the reagents are given in the text.

Table 6 Results for Cd with various evaporating temperatures and times

Temperature °C	Evaporation time					
	12 min		10 min		8 min	
	Cd mg/kg	Recovery rate %	Cd mg/kg	Recovery rate %	Cd mg/kg	Recovery rate %
150	0.61 ± 0.05	38.44	0.71 ± 0.07	44.37	0.73 ± 0.10	45.62
120	0.63 ± 0.06	39.62	0.68 ± 0.07	42.37	0.92 ± 0.10	57.31
100	1.02 ± 0.07	63.75	0.90 ± 0.05	56.25	0.98 ± 0.03	61.25
80	1.02 ± 0.07	63.12	1.23 ± 0.10	76.87	1.51 ± 0.08	94.37

when the evaporation proceeded at 150 °C. In this case the reagent evaporated totally. The residual appeared to be dry pieces. The element was lost seriously. The Cd recovery rate increased more at evaporation temperatures of 120 °C or 100 °C than at 150 °C. But the Cd value is not close enough to the certified value. When the evaporation temperature was 80 °C, the recovery rate increased dramatically. At this temperature, when the evaporating lasted 8 min, the residual appeared to be a sticky liquid, but for 6 min it was still a solution, while for 12 min or 10 min it became dry pieces. This demonstrated that the optimum evaporation conditions are 8 min and 80 °C temperature.

Conclusions

Microwave preparation for the element analysis of aquatic sediments is highly efficient. However, much effort is required to make this technique a standard and widely spread application. We found that a longer heating time and lower evaporating temperature with a relatively shorter time can help to reach a good recovery. Not all the generally used reagents lead to good digestion results. High percentage of microwave power can save digestion time. We recommend an optimized microwave preparation procedure for the element analysis of Cu, Pb and Cd in about 0.1 g aquatic sediment. That is to use 4–5 ml HNO₃/HF/H₂O₂ as solvent, a digesting time of 30 min, with microwave power of 100%, and evaporating the resid-

ual acid within 8 min in an open vessel at 80 °C. The recovery rates with the AAS determination can thus reach 92.4–100.6%.

References

1. Kingston HM, Jassie LB (1988) Introduction to microwave sample preparation. American Chemical Society, Washington, DC
2. Han K (1994) Guowai fengxi yiqi 3:26–32
3. Kuss HM (1992) Fresenius J Anal Chem 343:788–793
4. Binstock DA, Grohse PM, Gaskill A Jr (1991) Assoc Off Anal Chem 7:160–166
5. Nieuwenhuize J, Poley-Vos CH, van den Akker AH, van Delft W (1991) Analyst 116:347–351
6. EPA Methoden (1990) EPA method 3051:11
7. Mahan KI, Foderaro TA, Garza TL, Martinez RM, Maroney GA, Trivisonno MR, Willging EM (1987) Anal Chem 59:938–945
8. Novozamsky I, van der Lee HJ, Houba VJG (1995) Mikrochim Acta 119:183–189
9. China Environmental Survey Center (1992) Modern element analysis method for soil. China Environmental Science Publication
10. Schnitzer G, Soubelet A, Testu C, Chafey C (1995) Mikrochim Acta 119:199–209
11. Krause P, Erbsloh B, Niedergesäß, Prange RA (1995) Fresenius J Anal Chem 353:3–11
12. Matusiewicz H, Sturgeon RE, Berman SS (1991) J Anal Atomic Spectrom 6:283–287
13. Nakashima S, Sturgeon RE, Willie SN, Berman SS (1988) Analyst 113:159–163
14. Nadkarni KA (1984) Anal Chem 56:2233–2237
15. Xu LQ, Shen WX, Zhu JF (1990) Fenxi huaxue 18:597–601