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Application of closed–vessel microwave digestion method for the determination of multi–elements in environmental samples by sequential ICP–AES

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Abstract—A closed–vessel microwave digestion method is described for the rapid dissolution of environmental samples such as foods, soils and sediments. Depending on the sample type, 0.1–0.2 g sample was decomposed with HNO_3/H_2O_2 or HNO_3 / H_2O_2/HF acid mixture in a PTFE digestion vessel by using microwave heating for 2–3 min at 500W of microwave power. The solution, or to which 0.5 g of boric acid was added, was diluted to 25–50 ml and directly determined by sequential ICP–AES. The accuracy of the procedure was validated by the analysis of six standard reference materials for 10 elements. All results were in a good agreements with the certified values.

Keywords: microwave digestion; environmental sampl; sequential ICP–AES; elemental analysis.

In many research programmes such as public health monitoring, environmental monitoring, survey of total diet and food composition table a great number of biomedical or environmental samples should be analysed in order to obtain the results with the statistical significance. The sample analysis throughput is of crucial importance. The modern analytical instruments such as atomic absorption spectrometer and ICP spectrometer are widely used in the routine analysis of environmental samples. But the sample decomposition step is frequently the slowest and most lobour–intensive step in the procedure, especially in the elemental analysis of soils, sludges and sediments which contain silicate matrix. A review of decomposition methods used for the elemental determinations in environmental samples revealed that all these methods have limitations. The dry ashing method is not widely used in the trace element determinations due to the loss of volatile elements and serious contamination. The wet ashing methods using various strong mixed acids require constant attention of operators and are tedious which lead possible loss and contamination of analytes. The low temperature ashing method using excited oxygen is also time–consuming and needs costly equipment. The sample type which can be decomposed by this method is rather limited. The Teflon–lined pressurised bomb digestion method is the most convenient one for the determinations of trace elements in biological samples, especially for volatile elements. But it typical takes 4–6 hrs. In recent years , some authors used the microwave energy as the heat source to accelerate the decomposition process. In this study, a PTFE closed–vessel microwave digestion method was applied to decompose the environmental samples such as foods, soil and sediments. The accuracy of the analytical procedure was tested by analysis of six standard reference materials.

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EXPERIMENTAL

Instrumentation

A domestic microwave oven, Feiyue WL 5001 (Shanghai No. 18 Radio Factory) was used, which has a variable time cycle from 15 s to 35 min and two power settings of 255 W and 500 W, respectively. The glass turntable in the microwave oven was replaced by a PTFE one with the same dimension, on which total six digestion vessels can be spaced symmetrically to minimize the influence of the different locations in the oven.

Thick-wall PTFE vessel as shown in Fig.1 was made in Shanghai Institute of Metallurgy. The inner volume is 44 ml.

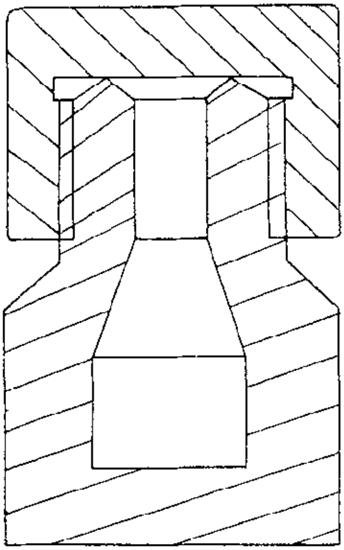

Fig. 1 PTFE digestion vessel

A sequential spectrometer JY 38 (Instruments S.A.) was employed to the determination of Ca, Mg, Mn, Zn, Fe, Ba, Cr and P. Details of operating parameters were described previously (Xu, 1986).

Reagents and standards

HF (40%), H_2O_2 (30%) and H_3BO_3 were of analytical reagent grade. HNO_3 (70%) was of ultrapure grade. Deionized water was used to dilute the solution. The stock solutions were obtained by dissolving the pure metal or their compounds (Johnson Mathy Chemicals Ltd. UK) in HNO_3, HCl or their mixture and used to prepare the calibration standards. In the analysis of biological samples, the acidity of calibration standards was 5% HNO_3. In the analysis of soils and sediments , two blanks containing the same amounts of chemical reagents prepared throughout the analytical procedure and used as the matrix of two-points multi-element calibration standards.

Analytical procedure

The decomposition process is illustrated in Fig. 2 and Fig.3.

RESULTS AND DISCUSSION

Digestion vessel

The use of closed vessel can speed up the decomposition process by allowing a higher temperature. The amount of reagents needed and the air-borne contamination are less than those in the open vessel, thus leading to a low blank. Being transparent to the microwave and due to its low surface contamination and non-wetting characteristics PTFE is a suitable material to make the closed–vessel used in the microwave oven. Fischer (1986) and Aysola (1987) used a Teflon digestion vessel manufactured by Sivillex Corp (Minnesota, USA). Lamothe (1986) used a polycarbonate bottle double wrapped with a Teflon tape to ensure a tight seal. We designed a thick–wall PTFE vessel. For the reason of safety, the sample weight, heating time, power setting and the amounts of acid mixture in the analytical procedure should be optimized.

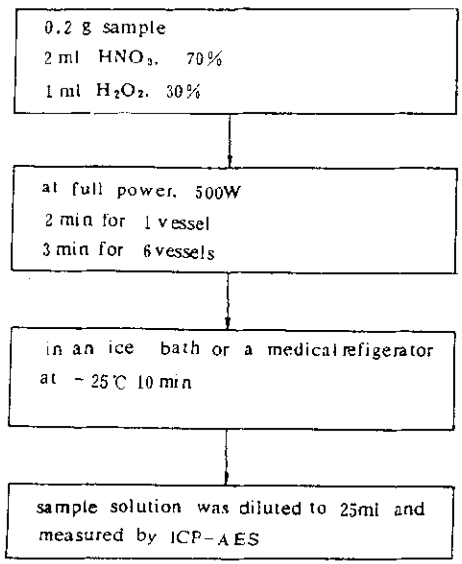

Fig. 2 Analytical procedure for biological samples

Chemical reagents

In the literature, aqua regia, aqua regia/HF, $HNO_3/HClO_4/HF$ were used to decompose a variety of samples. By our experiments it was found that there was a thin layer of gray substance adhering to the inner wall of the digestion vessel when using aqua regia/HF to decompose soil. It was thought that certain amount of organic matrices were not decomposed by this acid mixture. Due to the oxygen species with high reaction activity generated in the decomposition of H_2O_2 a mixture of H_2O_2/HNO_3 can greatly increase the reaction rate and consequently accelerate the digestion process of the organic matrices. In addition, the reaction products are similer than other acid combination. Large amount of H_2O_2 will cause a sudden short burst of gas out of the vessel while opening the cap even if the vessel is cooled. The residual acidity in the final 25 ml of volume was about 5.6% (v/v) HNO_3, which was determined by acid–base titration method. In the analysis of soils and sediments HF was added to decompose silicate and boric acid was added after decomposition to complex the residual HF. The solution was directly analysed by ICP–AES. Sometimes it could be found that small amount of undissolved material remained after the degestion of some type of samples. The reasons for this are due to the acid resistant minerals present, such as Al_2O_3, quartz, rutile and zircon. In this case the solution was filtered and the filtrate was analysed by ICP–AES.

The efficiency of sample decomposition depends on the particular acid, the total amounts of acid present, the sample weight, the power setting and the heating time. The effects of different heating time and numbers of digestion vessels on the recoveries of Ca, Mg, Fe, Mn, Zn, Cr and Sr were investigated. The results are shown in Table 1. The amount of chemical reagents used was the same as in the analytical procedure. It can be seen that the recoveries of most elements are satisfactory even if 1 min of heating time was used for 0.1 g sample in single

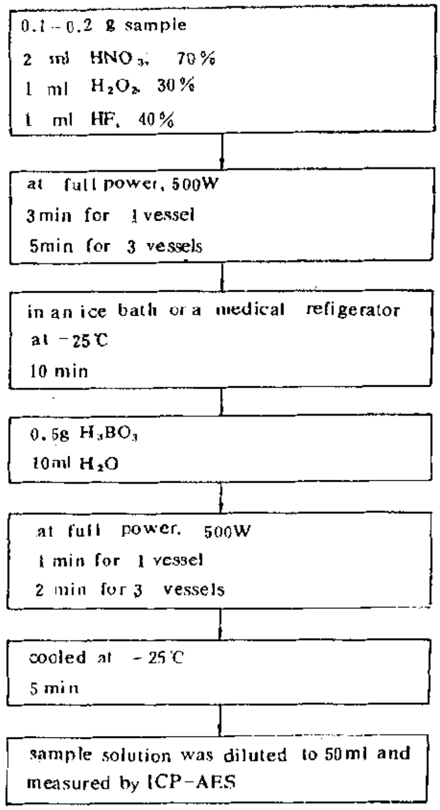

Fig. 3 Analytical procedure for soils and sediments

digestion vessel. In order to recover the elements in soil sample completely 2–3 min of heating time for single vessel and 4–5 min for three vessels were recommended. It is relative easy to decompose the biological samples. Three min of heating time was enough for six digestion vessels.

Okamoto (1984) reported low recovery for Cr in pond sediment due to the insoluble chromite. Huang (1984) reported that Sr and Ba were in the insoluble residue after pressurized bomb decomposition of soil with $HNO_3/HClO_4/HF$ leading to low recoveries. However, we did not observe low recoveries for Cr, Sr and Ba in soil an sediment samples, which indicated that the closed–vessel microwave digestion method was more effective. As an explanation for the mechanism it is supposed that the surface of solid samples is agitated and ruptured continuously under the microwave action leading to exposition of fresh sample surface to the acid.

Method accuracy

The accuracy of this analytical procedure for elemental determination was validated by analysing six standard reference materials. The results are shown in Table 2 and 3. They all were in a good agreement with the certified values. The relative standard deviations ranged from 1–5%.

Conclusion

Compared with other traditional decomposition methods, the proposed method is more suitable to decompose environmental samples for elemental determination due to the distinct improvements in sample analysis throughout, operating convenience, good repeatability, negligible element contamination or loss, low blank and cost. All these characters lead to the high laboratory efficiency.

Table 1 Effects of heating time and sample weight on recoveries of elements in soil-1 (Beijing Monitoring Center of Environmental Protection)

Element	Certified, μg/g	Weight, g	Time, min	Measured, μg/g 1 vessel	Recovery, %	3 vessels	Recovery, %
Ca	4.79±0.34	0.1	1	4.86	102		
			2	4.78	100		
			3	5.01	105	4.52	94
			4			4.6	96
			5			4.83	101
		0.2	3	4.75	99		
			4	4.89	102		
			5	4.96	104		
Mg	1.30±0.16	0.1	1	1.28	102		
			2	1.26	100		
			3	1.29	105	1.17	90
			4			1.20	92
			5			1.31	101
		0.2	3	1.32	99		
			4	1.37	102		
			5	1.38	104		
Fe	2.97±0.18	0.1	1	2.82	102		
			2	2.95	100		
			3	2.84	105	2.57	87
			4			2.67	90
			5			2.85	96
		0.2	3	2.85	99		
			4	2.92	102		
			5	2.89	104		
Mn	519±36	0.1	1	505	102		
			2	520	100		
			3	537	105	475	92
			4			496	96
			5			513	99
		0.2	3	521	99		
			4	522	102		
			5	537	104		
Zn	256±25	0.1	1	221	102		
			2	235	100		
			3	235	105	241	94
			4			252	98
			5			246	96
		0.2	3	266	99		
			4	271	102		
			5	276	104		

Table 1 continued

Cr	111±9	0.1	1	103	102		
			2	107	100		
			3	103	105	92	83
			4			102	92
			5			107	96
		0.2	3	103	99		
			4	103	102		
			5	110	104		
Sr	406 ±30	0.1	1	368	102		
			2	405	100		
			3	402	105	369	91
			4			391	96
			5			400	99

Table 2 Analytical results of 3 food SRMs (mean ± S.D. μg/g)

Element	Pig liver		Wheat flour		Mixed diet RM 8431	
	Certified	This work (n=6)	Certified	This work (n=6)	Certified	This work (n=6)
Ca	197±14	190±1	441±22	434±9	1940±140	1880±40
Mg	747±52	732±16	551±21	561±4	650±40	673±14
Cu	17.2±1.0	17.5±0.8	4.40±0.31	4.32±0.10	3.36±0.33	3.41±0.37
Zn	172±8	174±4	22.7±2.0	21.1±0.36	17.0±0.6	16.7±1.6
Mn	8.32±0.38	8.51±0.14	19.6±1.0	18.4±0.39	8.12±0.31	7.60±0.36
Fe	1050±80	1120±20	39.8±2.6	38.4±1.4	37.0±2.6	36.5±0.6
P			1500	1420±40		

Pig liver (The Ministry of Commerence, China)
Wheat flour (The Ministry of Commerence, China)
Mixed diet RM 8431 (NBS, USA)

Table 3 Analytical results of 3 soil and sediment SRMs (mean ± S.D. μg/g)

Element	Soil 83401		Soil-1		Pond Sediment No.2	
	Certified	This work (n=6)	Certified	This work (n=6)	Certified	This work (n=6)
Ca(%)	2.59±0.04	2.61±0.02	4.79±0.34	4.74±0.04	0.81±0.06	0.83±0.04
Mg (%)	1.53±0.04	1.55±0.02	1.30±0.16	1.25±0.03	—	0.69±0.04
Fe (%)	3.34±0.11	3.34±0.03	2.97±0.18	2.89±0.03	6.53±0.35	6.46±0.03
Mn	667 ±23	696 ±2	519 ±36	511 ±6	770	790 ±28
Cu	24.6±2.8	25.0±2.0	121 ±12	123 ±1	210 ±12	206 ±6
Zn	58.0±6.6	57.9±4.4	256 ±25	272 ±8	343 ±17	329 ±14
Sr	163 ±29	175 ±2	110	96 ±6	406 ±30	409 ±5
Ba	509	500 ±11	724 ±34	713 ±20	—	309 ±12
Cr	60.8±3.6	62.8±1.1	111 ±9	109 ±2.0	75 ±5	71 ±4

a-reference value

Soil 83401 (Institute of Environmental Protection, China)
Soil-1 (Beijing Monitoring Center of Environmental Protection, China)
Pond Sediment No.2 (The National Institute for Environmental Studies, Japan)

REFERENCES

Aysola,P., Anal. Chem., 1987, 59 : 1592
Fischer, L. B., Anal. Chem., 1986, 58 : 1582
Huang, B.L., Fenxi Huaxue(in Chinese), 1984, 12 : 585
Lamothe, P.J., Anal. Chem., 1986, 58 : 1881
Okamoto, K., Bunseki., 1984, 113: 321
Xu, L.Q., Li Hua Jian Yan(in Chinese), 1986, 22 : 78