Microwave digestion method in environmental analysis

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Abstract——This paper introduced the history, equipment and mechanism of the microwave diges-
tion method. This paper studied the optimization parameter of digestion conditions, such as acid
and acid combination, digestion time and applied microwave power, particle size, and other factors.
The analytical performance in environmental research and the modification of the microwave diges-
tion method were also discussed.
Keywords: microwave digestion; environmental analysis; optimization parameter.

1 Introduction

1.1 History

Microwave energy was first introduced by Abu-Samra in 1975 as heat source to promote
the acidic digestion of biological samples. In 1985, closed-vessel microwave digestion was
first employed by Matthes. The quantitative studies concerning relationship between dissolu-
tion acid and microwave energy, conducted by Kingston in 1986, made possible wide applica-
tion of microwave digestion method in sample preparation. In 1988, the first book on the
technique, introduction to microwave sample preparation: theory and practice, summarized
systematically the theoretical basis and predictive microwave-assisted acid dissolution
method. Today, microwave digestion was employed for elemental analysis of almost all ma-
trices, including geological (Kingston, 1992; Kokot, 1992; Carbinell, 1992; Guardia,
1993; Gulmini, 1994; Saraswati, 1995; Bettinelli, 1995), biological (Mincey, 1992; Koji-
ma, 1992; Navarro, 1992; Bitsch, 1992; Welz, 1992; Burguera, 1992; 1993; Krushevska,
1993; Williams, 1993; Baldwin, 1994; Ducros, 1994; Pitts, 1994; 1995; Heltai, 1994;
Lan, 1994a, 1994b, 1994c; Arruda, 1995; Lippo, 1995) botanical (Guo, 1993; Burguera,
1993; 1995), medical (Lajunen, 1992; Chakraborty, 1995), metallurgical (Reid, 1993;
Tamba, 1994; Platteau, 1994; Borszeki, 1994; Zehr, 1994; Ali, 1995) and food (Reid,
1993; Greenway, 1994; Stewart, 1994; Sheppard, 1994; Fuente, 1995; Bratter, 1995)

samples. Moreover, the techniques saw recent application in environmental analysis.

1. 2   Equipment

The equipment used for microwaves digestion consists four major components; the magnetron (microwave generator), the microwave cavity, the microwave guide and pressure/temperature indicator and so far has been of two basic types: open atmospheric pressure digestion vessel and closed overpressure digestion vessel.

1. 3   Mechanism

Microwave digestion is based on the interaction between electromagnetic field and dielectric material. There are two main mechanism (Kingston, 1992; Zotorzynski, 1995), ionic conductance and dipole rotation, so far relating to the microwave heating process. When exposed to an applied electromagnetic field, ions in solution receive two opposite direction forces. One is from the electromagnetic field which keeps ions migrating in the solution. The other is from the solution which prevent ions from moving in the solution. The net result of two forces leads to an absorption of energy and Joule heating. This phenomenon is referred to ionic conductance. Dipole rotation results from the reorientation of permanent dipoles with an applied electromagnetic field. With the increase of electromagnetic field strength, the dipole alignment becomes more in order. After the disappearance of applied electromagnetic field, the dipole takes a certain time to return to its original disorder and during the same period, release thermal energy. As to solid sample, the mechanism is a little complicated (Platteau, 1994). It takes two more steps, vaporization of solvent and trap in the pores of the particles, which lead to a fragmentation of solid particles under the same solvent heating mechanism as discussed above.

2   Optimization of digestion conditions

The microwave digestion of a sample is governed by many complicated relationship that must be taken into consideration at least to some extent. Such parameters as acids or acid combination, applied microwave power, digestion time, particle size (for solid sample), sample mass, length and diameter of coiled tubing inside the oven, flow rate, injection volume (last four for flow injection system) influence the efficiency in digestion of the sample matrix.

2. 1   Acid or acid combination

Appropriate acid or combination of acids can be chosen on the knowledge of the sample matrix and its major elements and compounds as well as the understanding of interaction between the acid and the component of the sample matrix. It is usually desirable for the acid or acid combination to form a soluble salt with the metal ion of interest. In addition, the acid or acid combination must ensure sufficient decomposition of the sample matrix. Due to these reasons, nitric, hydrochloric, sulfuric and perchloric acid are widely used in sample preparation. Among them, sulfuric acid and perchloric acid are less preferred because the former attacks Teflon material at high temperature and the latter is potentially explosive in contact

with organic material(Burguera, 1993). Hydrofluoric acid is needed for botanical samples because they contain siliceous materials(Kojima, 1992). H_2O_2 was added occasionally to increase the oxidizing power of HNO_3(Guardia, 1993). Nitric acid should be used very carefully in the digestion process where preliminary reduction is necessary(Saraswati, 1995). The acid concentration is of great importance for sufficient digestion. In principle, microwave energy can be absorbed by dilute acid more strongly than by concentrated acid due to the large fraction of water present in dilute acid (Burguera, 1993; Stewart, 1994). On the other hand, concentrated acid favors rapid decomposition of organic matrices for microwave digestion. In general, the lowest possible acid concentration is preferred as long the sample digestion is completed. Some examples are listed in Table 1.

Table 1   Optimization conditions of microwave digestion

Element	Matrix	Acid/Acid combination	Power/time program	Reference
Ca, Cu, Fe, Mg, Mn, Zn	Biological sample	HNO_3-$HClO_4$-HCl-HF	200W/5min 500W/4min	Kojima, 1992
Al, Ca, Cu, Cr, Fe, K, Mg, Mn, Si, Ti, Zn	Plant tissue sample	HNO_3-HF-H_2O_2	Three-stage	Lajunen, 1992
As, Ba, Ca, Cd, Cu, Fe, Zn, K, Mg, Mn, Na, P, Pb, Sr	Biological sample	HNO_3-H_2SO_4-H_2O_2	10% power/4min 40% power/4min	Krushevska, 1993
Pb	Biological sample	HCl-HNO_3	Single-stage	Burguera, 1993
Cu, Mn	Solid sample	HNO_3-H_2O_2	Single-stage	Guardia, 1993
Al	Steel, iron ores	H_2SO_4-H_3PO_4-HF	Single-stage	Tambs, 1994
Cu, Zn, Cd	Biological tissue	HNO_3	600W/2min 0W/2min 450W/45min	Baldwin, 1994
Mo, NI, Co, Al, Si, Fe, Ti, V,	Catalyst	HNO_3-HF	90% power/5min 0% power/5min 90% power/5min	Platteau, 1994
As, Se	Sludge	HNO_3-H_2SO_4	70% power/20min 100% power/35min	Saraswati, 1995
As, Cd, Pb	Seafood	HNO_3	537W/14min 567W/30min 0 W/15min	Sheppard, 1994
Ti, Cr, Ni, Mn, V, Cu	Copper alloys	HCl-HNO_3-H_2SO_4-H_3PO_4	300W/2min 600W/5min 750W/2min	Borszeki, 1994

2. 2 Digestion time and applied microwave power

It is evident that complete digestion of sample matrix and reasonable result will be obtained with an increase in the digestion time and/or applied microwave power. Large amounts of studies showed that a multi-stage microwave digestion program with respect to digestion time and power was superior to single-stage one. Under certain circumstance, gradual stepping of power was essential to avoid evaporation of the acids and insufficient decomposition of the sample matrix in open digestion system(Ali, 1995). The criteria for the selection of multi-stage program included: minimized power and time requirement, best overall recovery and lowest standard deviation between replicates (Baldwin, 1994). Some power/time cycle example are listed in Table 1.

2. 3 Particle size

The efficiency of microwave energy in decomposition of solid samples depends strongly on the size of the particle in the solution. It is generally known that the bigger the particle size of solid sample is, the less it absorbs microwave energy. Platteau *et al.* (Platteau, 1994) concluded that the solid particles should pass through a 325 screen under their experimental conditions.

2. 4 Others

The effect of sample mass on the recovery of trace metals from marine biological tissue was investigated by Baldwin's group (Baldwin, 1994) and they found that the maximum amount of sample that can be digested is determined by gas pressure from the decomposition of organic material. In their lab, dry sample mass ranging from 20mg to 0. 1g yielded acceptable results. For the flow injection(FI) microwave digestion, reaction coil length, flow rate and injection volume influence digestion efficiency very much. Guardia *et al.* (Guardia, 1993) found that the use of high length reaction coil did not provide any enhancement of sample digestion, especially with a certain carrier flow of 8. 8 ml/min. Williams *et al.* (Williams, 1993) indicated that the optimum carrier flow rate exists. It is time consuming at low flow rate and on the other hand decomposition is insufficient at higher flow rate. In general, the signal increase when the sample injection volume increases. However, according to Guardia *et al.* , the volumes greater than 100 μl did not improve the accuracy of the procedure but could cause damage in the nebulizer due to the introduction of high amount of sample.

3 Analytical performance

From the analytical performance's point of view, microwave digestion method shows same if not better limit of detection(LOD), precision, accuracy , and recovery compared with its conventional counterpart(Table 2).

Ducros *et al.* (Ducros, 1994) compared two digestion methods, microwave and acid-ashing method, for the determination of selenium in biological samples. LODs for microwave and wet acid-ashing method were 1. 8μg/L and 2. 8μg/L and RSD 8. 3% and 12. 3%, respectively. There was a good relationship between two digestion method with the same accuracy.

Tamba *et al.* (Tamba, 1994) drew the conclusion in the determination of aluminum in steels and iron ores that due to less handling , minimum acid requirements and complete elimination of fluxes which combined to reduce the blank values, microwave digestion method had a lower LOD and higher precision than conventional dissolution procedures.

Saraswati *et al.* (Saraswati, 1995) found that LOD, precision and accuracy were similar for the reflux and microwave digestion for the determination of arsenic and selenium in sludge using flow injection hydride generation and atomic adsorption spectrometry.

Maw *et al.* (Maw, 1994) compared traditional water-bath digestion used in US EPA method 7471 with microwave digestion method 3051 and concluded that no statistical difference in data precision or accuracy existed between the two methods. The same conclusion was also obtained by Tahan *et al.* (Tahan, 1993) while comparing convection heating and microwave heating for the determination of total mercury by cold atomic absorption spectrometry.

Table 2   Analytical performance of microwave digestion method

Elements	Matrix	LOD	RSD, %	Recovery, %	References
Hg	Fish	0. 195ng/ml	4. 73	>98	Navarro, 1992
Hg	Biological	53ng/L	3. 7	>98	Tahan, 1993
Al	Steel, iron, ores	10ng/L	1. 5	96. 8±3. 3	Tamba, 1994
Se	Biological	1. 8ng/L	8. 3	-	Ducros, 1994
As, Se	Sludge	0. 15,0. 17ng/L	2. 4,1. 6	-	Saraswati,1995
Ca, Mg, K,Na	Milk	63,15,72,18μg/ml	1—2	99—100	Fuente, 1995
Cr	Sediment, botanical	0. 14—0. 84ng/ml	2. 8—5. 5	98—103	Chakraborty,1995
Al	Shellfish	10μg/L	4. 3	90	Arruda,1995
Se(IV),Se(VI)	Aqueous sample	0. 2,0. 3μg/L	1. 5,2. 0	-	Pitts, 1995

4   Modification

Large amounts of work have been performed for the last three years to make microwave digestion method more efficient. Some interesting work are included:

Mincey *et al.* (Mincey, 1992) developed a temperature controlled microwave oven digestion system using an inexpensive non-invasive infrared probe assembly to monitor the temperature of each digestion vessel. Temperature is the most important factor because it governs the reaction rate, equilibrium and solvent interactions during the digestion.

A new type of polytetrafluorethylene (PTFE) bomb was constructed by Heltai *et al.* (Heltai, 1994) in which vapor pressure can be maintained on moderated level (150 — 300 kPa) by means of water cooling inserted into the close space through the cover.

Burguera *et al.* (Burguera, 1992) introduced ground glass ball joint connection between the tubes enabling sample to rotate and therefore ensuring uniform heating of sample for the

dissolution of biological samples.

The fumes generated from acid decomposition of organic material reduced the precision of the measurement and endangered the analyst. Burguera *et al.* (Burguera, 1993) employed the fume-removal method which included a gas diffusion cell connected to a vacuum pump.

An open-vessel predigestion technique under reflux was designed by Reid *et al.* (Reid, 1993) to enable the escape of oxidation products, such as CO_2, without incurring evaporation of acid or analyte in order to prevent excessive pressure rises in closed microwave acid digestion of fairly large (1g) samples of high organic products.

Liquid nitrogen cooling subsequent to or between heating cycles was found by Reid *et al.* (Reid, 1993) to be very effective in reducing sample preparation time due to delay in opening Teflon pressure vessel after digestion.

Kojima *et al.* (Kojima, 1992) drew a conclusion that the presence of an alkaline solution between the PTFE vessel was very effective in aiding the digestion and absorption of evolved acid gases.

In order to control Pb blank contamination problem, an extensive wash, including several DDI water, methanol, and nitric acid wash cycles, of Teflon lines was performed by Sheppard *et al.* (Sheppard, 1994) and this cleaning procedure worked well.

Baldwin *et al.* (Baldwin, 1994) described the use of low-volume microwave digestion for the determination of copper, zinc and cadmium in marine biological tissues to avoid the relatively high dilution of the digest.

The use of bases in the microwave digestion of inorganics which contain barium, cobalt oxide, molybdenum oxides, thorium oxide and tungsten oxides should be considered as an alternative to typical acid microwave digestion(Zehr, 1994).

A new sample pretreatment procedure, Oxisolv plus microwave (Bitsch, 1992), was successfully used in trace analysis of heavy metals in presence of the complexing agents like NTA and EDTA.

5 Summarry

Although effective, sample pretreatment based on traditional water-bath or hot-plate digestion method is labor-intensive and time-consuming (about 70%—90% of the time devoted to the overall analytical process). In addition, manual digestion are prone to contamination and difficult to automate. They consume large amounts of sample as well as reagent and may incur loss of volatile materials. Moreover, they are subject to potential health hazards and occasionally expensive (particularly when ultrapure acids are needed). In contrast, microwave digest produce equal if not better results in an efficient, fast, economical, safe and automated way. No wonder after first application of this technique in 1975, the field has grown by leaps and bounds(Burguera, 1993; Tamba, 1994; Arruda, 1995).

Due to the direct coupling of microwave energy into the solution(Kingston, 1992) as well as increased oxidizing power of the acid resulting from elevated temperature and pres-

sure in the microwave oven (Baldwin, 1994), the acid digestion time reduced from several hours to a few minutes. On the other hand, the ability to accurately transfer precise amount of energy to the acid (Kingston, 1992) along with the strict control over the heating power and time during digestion produce reproducible digestion conditions. These two factors, rapid heating and reproducibility, make microwave digestion method well suit for intelligent automation (Kingston, 1992). The microwave equipment automatically monitors and controls key parameters such as time, temperature, and pressure, so it can run unattended and enhance the sample preparation efficiency.

Moreover, on-line microwave digestion method is particularly suitable for batch system (Burguera, 1992). Since microwave oven should not be operated empty or nearly empty for extended period due to the risk of damage to the magnetron.

In a word, microwave digestion, as a heat source, is an effective alternative to conventional procedures with increased digestion speed, less possibility of element loss due to volatilization, low reagent consumption and metal blank level by the use of small volume of acid for digestion.

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