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COMPARISON OF HEATING TECHNIQUES USED IN WET ACID DIGESTION FOR THE DETERMINATION OF METALS FROM SOIL AND PLANTS

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ABSTRACT. Two wet acid digestion procedures using different heating techniques were tested on soil and plant certified reference materials for the determination of metals by inductively coupled plasma optical emission spectrometry (ICP-OES). The advantages and disadvantages of the two digestion methods were compared. The results obtained after conductive heating open vessel digestion were similar to those obtained by microwave assisted digestion both for soil and plant samples. The obtained recoveries (93–104%) showed that the procedures were precise and accurate for all elements, thus both digestion methods can be used for soil and plant sample dissolution prior to routine determination of metals by ICP-OES.

Keywords: *metal determination, sample digestion, soil, plants, certified reference materials, inductively coupled plasma optical emission spectrometry*

INTRODUCTION

Metal pollution has grown into one of the most important environmental problems all over the world [1]. Due to their high toxicity, persistence and bioaccumulation potential, metals can pose significant risks for water, soil, vegetation or fauna [2]. Thus, the measurement of metals concentrations in environmental matrices is the first step in the assessment of their potential health or ecological hazard. Moreover in case of water and soil the maximum allowable total contents for numerous metals have been legislated.

There are several methods that allow the metals determination directly from solid matrices, but most of the analytical methods require a sample preparation step in order to transform solid samples in solution [3, 4]. Sample preparation is the most time consuming step and represents an important source of errors and contamination. The hot plate, the block digester and the microwave oven are the most used heating devices in solid sample digestion [5]. Since the amounts of solubilized metals depend on the used digestion

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method and on the sample matrix, to achieve reproducible and accurate results, the selection of appropriate digestion method is mandatory. Moreover, problems such as incomplete dissolution, precipitation of insoluble analyte, sample contamination or loss of volatile elements can occur [6].

There are a wide range of digestion methods for solid samples that use different reagents and heating methods, but the most appropriate procedure is still under debate [7-10]. However, the majority of digestion procedures heat the sample with strong acid solutions in conventional conductive heating or microwave-heating systems [11-14]. The most commonly used digestion reagents are nitric acid, hydrochloric acid, sulfuric acid, hydrofluoric acid, perchloric acid and hydrogen peroxide. The advantages of digestion in closed systems consist in the higher working temperatures. While in open systems the operating temperatures are limited by the boiling point of the acid mixtures, in closed systems higher temperatures can be reached. Microwave-assisted acid digestion techniques have become popular and are widely used, due to their suitability for the digestion of complex matrices, low reagent and sample usage, short digestion times, good recoveries and enhanced operator safety [15]. Moreover, microwaves heat the sample to high temperatures very rapidly while the closed vessel helps in preventing losses due to volatilization of elements [16].

Aqua regia is a mixture of conc. HCl and conc. HNO_3 in 3/1 (v/v) ratio, and is one of the most used wet digestion methods for the estimation of maximum element availability for plants [17]. By its strong oxidizing effect completely solubilize the soil organic components and partially the elements bound to the siliceous matrix. Its dissolution efficiency depends on the sample grain size, type of matrix, energy input and reaction time. For the digestion of plant samples, generally HNO_3 or a mixture of HNO_3 and H_2O_2 are used. The addition of H_2O_2 in oxidizing mixtures increases the oxidation efficiency without to dissolve the siliceous matrix [18, 19].

The objective of the study was to compare the main analytical parameters of metals routine determination by inductively coupled plasma optical emission spectrometry (ICP-OES) after wet acid digestions by classical conductive and microwave heating. For the study two soil and two plant certified reference materials (CRMs) were used.

RESULTS AND DISCUSSION

The digestion efficiency of the two heating procedures using a mixture of HCl/HNO_3 for soils and HNO_3/H_2O_2 for plants was evaluated using two soil and two plant CRMs. The obtained results are presented in Table 1-4. The comparison using the T-test showed no significant differences between the two digestion methods.

Table 1. Certified (median value) and determined (average± SD) metal concentrations in CRM SRM 2709 San Joaquin Soil after aqua regia digestion

Element	**Certified value (mg kg^{-1})**	**Obtained value**			
		Conductive heating (mg kg^{-1})	**Recovery (%)**	**Microwave heating (mg kg^{-1})**	**Recovery (%)**
Al	26000	26800±2100	103	25800±3000	99
Ca	15000	15600±330	104	15400±780	103
Co	12	11.6±1	97	12.2±0.8	102
Cr	79	76±3	96	81±5	103
Cu	32	33±2	103	31±2	97
Fe	30000	31000±1600	103	29500±3300	98
K	3200	3050±710	95	3300±850	103
Mg	14000	13400±600	96	14100±740	101
Mn	470	457±40	97	477±38	101
Na	680	710±26	104	650±46	96
Ni	78	75±5	96	80±4	103
Pb	13	12.4±1	95	13.2±0.8	102
Zn	100	96±4	96	101±3	101

Table 2. Certified (average± U) and determined (average± SD) metal concentrations in CRM LGC 6135 Hackney Brick Works Soil after aqua regia digestion

Element	**Certified value (mg kg^{-1})**	**Obtained value**			
		Conductive heating (mg kg^{-1})	**Recovery (%)**	**Microwave heating (mg kg^{-1})**	**Recovery (%)**
Al	22700±4600	23400±3100	103	22800±2900	100
Ca	21900±520	22200±490	101	21600±610	99
Co	20±4	19±3	95	20±2	100
Cr	336±28	327±50	97	346±22	103
Cu	105±5	103±6	98	108±9	103
Fe	40900±2700	42400±1970	104	42200±2400	103
K	5100±920	5250±850	103	5140±690	101
Mg	7000±580	6750±430	96	7200±730	103
Mn	348±18	359±12	103	351±21	101
Na	362±44	376±27	104	361±32	100
Ni	277±13	282±24	102	271±18	98
Pb	391±16	382±30	98	380±28	97
Zn	316±41	305±36	97	329±27	104

In the selection of the sample digestion method, besides the method precision, accuracy and dissolution efficiency, the sample homogeneity, reagent consumption and equipment cost should be also considered. The microwave assisted procedure is preferred, in case of small to medium sample number due to reduction of operating time, accurate results and good recoveries. In case of large number of samples, due to the fact that microwaves have 8-20 posts, the saved time decreases and the classical conductive heating digestion method can be used with good results.

Table 3. Certified (average) and determined (average±SD) metal concentrations in CRM IAEA 359 Cabbage after HNO_3/H_2O_2 digestion

Element	Certified value (mg kg^{-1})	Obtained value			
		Conductive heating (mg kg^{-1})	**Recovery (%)**	**Microwave heating (mg kg^{-1})**	**Recovery (%)**
Ca*	18500	17800±160	96	18900±120	102
Cr*	1.3	1.21±0.3	93	1.26±0.2	97
Cu	5.67	5.5±0.5	97	5.7±0.4	101
Fe	148	140±11	95	150±12	101
K	32500	33000±2800	102	32000±2400	98
Mg	2160	2250±210	104	2100±180	97
Mn	31.9	31.5±3.0	99	31.4±2.6	98
Na*	580	592±46	102	572±48	99
Zn	38.6	39.6±3.2	103	39.2±2.6	102

*Information values

Table 4. Certified (average± U) and determined (average± SD) metal concentrations in CRM NCS ZC 85006 Tomato after HNO_3/H_2O_2 digestion

Element	Certified value (mg kg^{-1})	Obtained value			
		Conductive heating (mg kg^{-1})	**Recovery (%)**	**Microwave heating (mg kg^{-1})**	**Recovery (%)**
Al	2950±430	2800±320	95	3000±340	102
Ca	53100±1900	49800±1730	94	53000±1800	100
Cu	21.1±2.5	19.8±1.8	94	20.8±2.2	99
Fe	1380±150	1300±90	94	1400±120	101
K	5790±520	5840±480	101	5900±500	102
Mg	7360±570	6766±740	92	7200±640	98
Mn	87.1±5.6	87.7±4.2	101	86.8±6.2	100
Pb	4.97±0.54	4.78±0.31	96	4.80±0.62	97
Zn	36.2±3.1	34.9±2.8	96	35.4±3.0	98

Our results are in agreement with those of Chen [17] who found that the precision and accuracy of soil metal determination by ICP-OES using microwave aqua regia and hotplate aqua regia digestion methods were comparable, except for the silicate-binding metals, such as Al, Ba, K, whose dissolution was slightly greater using microwave digestion. Senila et al. [20] found no significant differences between metal contents in perennial plants determined by ICP-OES after hot plate and microwave digestion using a mixture of HNO_3/H_2O_2, while Demirel et al. [21], reported better recoveries and more accurate results after microwave digestion than after dry and wet digestion, for trace element determination in food materials by atomic absorption spectrometry.

CONCLUSIONS

Both the conductive heating open vessel digestion and microwave assisted digestion can be used for soil and plant sample dissolution prior to metals determination by ICP-OES. In case of a small sample number the microwave assisted digestion is faster, but in case of large number of samples, the saved time decreases.

EXPERIMENTAL SECTION

Reagents and materials

Analytical grade reagents (65% HNO_3, 37% HCl, 30% H_2O_2) and 1000 mg/l multi-element stock solutions were purchased from Merck (Darmstadt, Germany). High purity deionized water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used. To compare the digestion procedures the following CRMs were used: SRM 2709 San Joaquin Soil (National Institute of Standards and Technology, USA), 6135 Hackney Brick Works Soil (LGC, UK), IAEA 359 Cabbage (International Atomic Energy Agency, Austria), and NCS ZC 85006 Tomato (National Analysis Center for Iron and Steel, China). All the PTFE and glass vessels were cleaned by soaking in 10% HNO_3 and rinsed with ultrapure water before use.

Digestion procedure

Three replicates of approximately 1 g CRM were subjected to open vessels digestion on sand bath. The soil CRMs, were treated with 15 ml conc. HCl and 5 ml conc. HNO_3, while the plant CRMs with 10 ml conc. HNO_3 and 2.5 ml H_2O_2.The digestion was conducted for 16 h at room temperature for slow oxidation of the organic matter then the temperature of the reaction mixture was slowly raised until reflux conditions and maintained for 2h. After cooling to room temperature, the slurry was diluted to 100 ml with distilled water and then filtered through a 0.45 μm cellulose acetate membrane filter.

Three replicates of 0.5 g CRMs were digested with 7.5 ml conc. HCl and 2.5 ml conc. HNO_3 (soils) and 6 ml conc. HNO_3 and 2 ml H_2O_2 (plants). Sampled were left overnight at room temperature for pre-digestion. The microwave assisted digestion program is presented in Table 5. After cooling to room temperature, the slurry was diluted to 50 ml with distilled water and then filtered through a 0.45 μm cellulose acetate membrane filter. For each procedure blank samples were prepared.

Instruments

The determinations were carried out using the 2100 Optima DV ICP-OES (Perkin Elmer Optima). Details about operating conditions are summarized in Table 6, while the wavelengths and detection limits (DL), calculated according to 3s criterion, are given in Table 7. A Berghoff MWS-3+ closed vessel microwave system (Eningen, Germany) and a SD8 Sand Bath (Gestigkeit, Germany) were used for the sample heating.

Table 5. Operating conditions for the microwave digestion system

	Stage				
	1	**2**	**3**	**4**	**5**
Temperature (^{o}C)	145	170	190	100	100
Pressure (bar)	30	30	30	0	0
Ramp time (min)	5	1	1	1	1
Hold time (min)	25	10	15	10	10
Power (%*)	80	80	80	0	0

*100 % power corresponds to 1400 W

Table 6. Instrumental parameters and operation conditions for ICP-OES

Generator	**Free-running, 40.68 MHz, operated at 1300 W**
Plasma torch	Inductively coupled plasma, dual viewing Outer flow 15 L min^{-1}, Intermediate flow 0.5 L min^{-1} Nebulizer flow 0.8 L min^{-1}
Sample introduction	3 channel peristaltic pump, concentric nebulizer, Scott type spray chamber, sample uptake rate:2 mL min^{-1}, flushing time:20s, delay time:40s
Optics	multichannel spectrometer with Echelle grating 165 – 780 nm, chamber filled with Ar
Detector	CCD detector
Data processing	WinLab 32 Software two points linear background correction, integration time 10 s, 3 successive measurements for each sample

Table 7. Wavelengths and detection limits for metals determination by ICP-OES

Metal	**λ (nm)**	**DL (mg kg^{-1})**	**Metal**	**λ (nm)**	**DL (mg kg^{-1})**
Al	396.153	1.6	K	766.497	2.5
Ca	317.935	0.8	Mg	285.215	0.4
Cd	228.805	0.5	Mn	257.611	0.5
Co	228.618	1.0	Na	589.593	4.3
Cr	267.713	0.9	Ni	231.606	1.5
Cu	327.398	1.1	Pb	220.355	3.0
Fe	238.205	0.9	Zn	213.859	0.4

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