



Focused microwave-induced combustion for digestion of botanical samples and metals determination by ICP OES and ICP-MS

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ABSTRACT

The advantages and shortcomings of focused microwave-induced combustion (FMIC) for digestion of plant samples were studied. The effects of sample mass, absorbing solution, oxygen gas flow-rate, and time of reflux step on recoveries of major, minor and trace metals were systematically evaluated. Afterwards, Al, Ba, Ca, Co, Cr, Cu, Mg, Mn, Ni, Sr, V, and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP OES) and by inductively coupled plasma mass spectrometry (ICP-MS). The main advantages of FMIC when compared to microwave-assisted wet digestion (MAWD) and focused-microwave-assisted wet digestion (FMAWD) are the possibility to digest larger masses of samples (up to 3 g) using shorter heating times and diluted nitric acid solution for absorbing all analytes. Using the selected experimental conditions for FMIC, residual carbon content was lower than 0.7% for all samples and relative standard deviation (RSD) varied from 1.5 to 14.1%. Certified reference materials (NIST 1515 apple leaves and NIST 1547 peach leaves) were used for checking accuracy and determined values for all metals were in agreement with certified values at a 95% confidence level. No statistical difference (ANOVA, 95% of confidence level) was observed for results obtained by FMIC, FMAWD, and MAWD. Limits of detection were lower when using FMIC in the range of 0.02–0.15 $\mu\text{g g}^{-1}$ for ICP OES and 0.001–0.01 $\mu\text{g g}^{-1}$ for ICP-MS, which were about 3 and 6 times lower than the values obtained by FMAWD and MAWD, respectively. It is important to point out that FMIC was a suitable sample preparation method for major, minor and trace metals by both determination techniques (ICP OES and ICP-MS). Additionally, since it allows lower LODs (because up to 3 g of sample can be digested) and diluted acid solutions are used (without any further dilution), the use of ICP-MS is not mandatory.

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1. Introduction

Focused microwave radiation ovens have full capacity for working with relatively high sample masses for sample digestion using concentrated acids. However, main limitations are related to the amount of concentrated acids required, including sulfuric acid, and the relatively poor efficiency of digestion [1]. The use of a microwave oven with multiple reaction vessels and only one magnetron also implies that could occur a heterogeneous distribution of microwave radiation for each vessel and consequently the efficiency of digestion can be affected [1,2]. However, it was demonstrated that focused microwave radiation oven can be successfully

used when adopting tailored procedures [1] and its performance can be improved by minor changes in the experimental procedure, such as the gradual addition of sample to pre-heated concentrated acids [1,3].

Other alternative for sample digestion, the microwave-induced combustion (MIC) is well established as an efficient method for decomposition of many matrices and despite its all advantages there is a limitation related to the sample mass that can be digested based on the maximum pressure that a closed vessel typically can support in comparison to the usual sample masses digested in open systems [4–7]. It was recently demonstrated that the shortcomings of both MIC and focused-microwave ovens can be overcome by combining both systems, the so called focused microwave-induced combustion (FMIC) [8]. It was shown that by using FMIC, higher sample masses can be digested without using concentrated reagents and leading to low residual carbon contents, i.e. lower than 1%.

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As previously described for MIC methods, combustion may be induced by microwave radiation using ammonium nitrate for ignition, but the critical point for performing FMIC was related to the supply of oxygen to start and to keep the combustion process. It was demonstrated that a too low flow-rate would not be enough for starting ignition, but the use of a too high flow-rate may dry the solution containing the igniter and consequently the combustion could not start [8]. In order to allow sample combustion, a special device was built for supporting the sample, the flask was modified to allow a continuous oxygen flow-rate and a water condenser was adapted to the upper part of the reaction vessel for avoiding losses by volatilization [8].

Despite the proof of the concept [8], the application of FMIC would be improved by further investigations taking into account critical experimental variables, such as type and mass of sample, concentration of absorbing solution, flow-rate of oxygen gas, and losses of volatile analytes. These experimental parameters and their effects on digestion efficiency were evaluated in the present work for different plant samples in order to allow the digestion of higher sample mass and to improve the limits of detection (LODs). Metals which are commonly determined in botanical matrices, such as Al, Ba, Ca, Co, Cr, Cu, Mg, Mn, Ni, Sr, V, and Zn [9–11] were determined in plants by ICP OES and ICP-MS.

2. Experimental

2.1. Instrumentation

A commercial microwave oven with focused microwave radiation (with two cavities, Star System 2, 800 W, CEM, Matthews, USA) was used for FMIC studies and also for focused microwave assisted wet digestion (FMAWD). The focused microwave oven was equipped with a vapor collection and automatic reagent addition modules (CEM, model reagent addition EX4, model number 560980). The equipment works at atmospheric pressure and allows independent temperature control in each cavity. Borosilicate glass vessels of 180 mL of capacity were used equipped with lab-made condensers. The maximum temperature was set at 430 °C and also maximum microwave power (800 W) was applied for ignition (for FMIC procedure).

The original glass vessels were modified according to a previous work [8] to allow oxygen flow entrance for ignition and also the introduction of a sample quartz holder inside the vessel. A laboratory made water-cooled condenser was used instead of the conventional air-cooled system provided by the manufacturer. The height of sample quartz holder inside the vessel was optimized to maintain it in a position of maximum microwave radiation incidence. The region of maximum incidence of microwave radiation was previously shown [1,2] as well as the main characteristics of the built device [8]. Samples were also digested by conventional focused-microwave assisted wet digestion (CEM system) and by high-pressure microwave-assisted wet digestion for results comparison. A microwave-assisted sample preparation system (Multiwave 3000 microwave sample preparation system, Anton Paar, Graz, Austria) equipped with eight high pressure vessels (80 mL of internal volume and maximum pressure and temperature of 8 MPa and 280 °C, respectively) was used for high pressure microwave-assisted wet digestion (MAWD).

Metals were determined by ICP OES and ICP-MS and general instrumental parameters were used as recommended by the instrument manufacturer [12,13]. An inductively coupled plasma optical emission spectrometer (Spectro CIROS CCD, Spectro Analytical Instruments, Kleve, Germany) with axial view configuration was used for metals and residual carbon content (RCC) determination. A cross-flow type nebulizer (Glass Expansion, Melbourne,

Australia), a double pass Scott type spray chamber (Glass Expansion, Melbourne, Australia) and a quartz torch (2.5 mm i.d. injector tube, Glass Expansion) were used. Residual carbon content (RCC) in digests obtained by FMIC was determined according previous work [14]. The radio frequency applied power was set at 1500 W and plasma gas flow-rates were 15.0, 1.0 and 1.0 L min⁻¹ for principal, auxiliary and nebulization gas, respectively. The selected wavelengths were 167.078 nm (Al), 233.527 nm (Ba), 317.933 nm (Ca), 228.616 nm (Co), 267.316 nm (Cr), 327.393 nm (Cu), 766.490 nm (K), 285.213 nm (Mg), 257.610 nm (Mn), 589.592 nm (Na), 231.604 nm (Ni), 407.771 nm (Sr), 290.880 nm (V) and 213.857 nm (Zn). Carbon was determined at 193.091 nm emission line [14].

Determination of trace levels of Co, Ni, and V after sample digestion was also performed using an inductively coupled plasma mass spectrometer (PerkinElmer-SCIEX, Model Elan DRC II, Thornhill, Canada) equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion) and a quartz torch with a quartz injector tube (2 mm i.d.). Radio frequency applied power was 1400 W, plasma, auxiliary and nebulizer gas flow-rate were 15.0, 1.2 and 1.15 L min⁻¹, respectively. Measurements were performed using ⁵⁹Co, ⁵¹V, and ⁶⁰Ni isotopes. Platinum sampler and skimmer cones were used, and ions lens and dwell time were 7.2 V and 50 ms, respectively. Argon 99.996% (White Martins-Praxair, São Paulo, Brazil) was used for all plasma measurements.

2.2. Samples, reagents and standards

Oregano (*Origanum majorana* sp.), parsley (*Petroselinum crispum*), basil (*Ocimum basilicum*), cilantro (*Coriandrum sativum*), and chives (*Allium schoenoprasum*) samples obtained from a local market was used to optimize the operational conditions for FMIC. Samples were heated at 60 °C in an oven (model 400/2ND, Nova Ética, São Paulo, Brazil) and ground using a cryogenic mill (Spex Certiprep, Model 6750, Metuchen, USA) with a pre-cooling time of 5 min followed by 2 min of grinding. This procedure was repeated using 1 min of re-cooling between grinding steps. Certified reference materials (CRMs) provided by National Institute of Standards and Technology (NIST, Gaithersburg, USA), apple leaves (NIST 1515) and peach leaves (NIST 1547) were used to evaluate the accuracy. For digestions by FMIC, samples and CRMs were pressed as pellets (diameter of 13 mm) using a hydraulic press set at 3 ton by 1 min (Specac, Orpington, UK).

Analytical-grade reagents (Merck, Darmstadt, Germany) were used to prepare all solutions and standards. Water was purified using a Milli-Q system (18.2 M cm, Millipore, Bedford, USA). Concentrated nitric acid was distilled in a sub-boiling apparatus (model DuoPur, Milestone, Sorisole, Italy) and it was used for FMAWD, MAWD and as absorbing solution for FMIC. Sulfuric acid and hydrogen peroxide (30% (m/m), Synth, Diadema, Brazil) were also used for FMAWD. Ammonium nitrate solution (6 mol L⁻¹, salt from Merck) and a small disc of filter paper (15 mm of diameter, 12 mg) with low ash content (Black Ribbon Ashless, Schleicher & Schuell GmbH, Dassel, Germany) were used as igniter for the combustion process. Filter paper was previously cleaned with 10% (v/v) HNO₃ for 20 min in an ultrasonic bath, rinsed with water and dried in a Class 100 laminar flow bench (CFLH-12, Veco, Campinas, Brazil). Washing procedure for glass and quartz materials were performed in 10% (v/v) HNO₃ for 48 h and they were thoroughly washed with water before use. Quartz vessels used for MAWD were cleaned with 6 mL of concentrated HNO₃, for 10 min at 1400 W. Vessels used for FMIC (with quartz holders) and for FMAWD were cleaned with 15 mL of concentrated HNO₃, for 10 min at 130 °C. Reference standard solutions were prepared before use by dilution of a stock reference solution containing 10 mg L⁻¹ of analytes (PlasmaCal calibration solution SCP33MS, SCP Science, Quebec, Canada) in 5%

(v/v) HNO_3 . A stock reference solution for RCC determination was prepared by dissolution of citric acid in water.

2.3. Digestion methods

2.3.1. Focused microwave-assisted wet digestion in open vessels

Samples were previously decomposed by FMAWD as recommended in CEM Application Number SS08 (ID-2) for citrus sample [15]. The recommended procedure uses the commercial air-cooled condenser, 1 g of sample, 2.5 mL of concentrated H_2SO_4 , 24 mL of concentrated HNO_3 and 20 mL of H_2O_2 (30%) [15]. Heating program was as follows: (i) ramp of 3 min up to 130°C ; (ii) 1 min at 200°C (ramp of 1 min); (iii) 5 min at 250°C (ramp of 1 min) and (iv) 10 min at 200°C (H_2O_2 is added only for this step). After digestion, samples were diluted with water to 50 mL in polypropylene vessels prior to analysis.

2.3.2. High pressure microwave-assisted wet digestion

In order to compare the results obtained by FMIC and by wet digestion in open system, samples were also digested in closed vessels. Microwave heating program was performed as described by instrument manufacturer for plant digestion, using 6 mL of concentrated HNO_3 and 500 mg of sample [16]. After digestion, the resulting solution was transferred to 30 mL polypropylene vials and diluted with water for subsequent metals determination by ICP OES and ICP-MS.

2.3.3. Focused microwave-induced combustion

Sample pellets (0.1–3 g) were placed together with filter paper on the quartz holder device specially designed for FMIC procedure. Then, 50 μL of 6 mol L^{-1} NH_4NO_3 solution was added to the filter paper and the quartz holder was introduced inside the digestion

vessel. The vessel was placed inside the focused microwave oven and the condenser was connected to the upper part. A continuous flow-rate of oxygen (2 L min^{-1}) was introduced through the vessels by the side entrance. The microwave heating program was immediately started: (i) 5 s at maximum power for sample ignition and (ii) microwave radiation was interrupted (after sample ignition) and oxygen flow-rate was increased ($5\text{--}15\text{ L min}^{-1}$) to maintain the combustion process up to the complete sample digestion. After 10 min (cooling step), a volume of 10 mL of absorbing solution ($1\text{--}14\text{ mol L}^{-1}$ HNO_3) was automatically added using the reagent addition module and a reflux step was performed under focused microwave radiation, at 125°C for 5 min. Digests were diluted to 30 mL with water in polypropylene vessels for metals determination by ICP OES and ICP-MS.

These three procedures are summarized in Fig. 1 for a better overview.

3. Results and discussion

3.1. Evaluation of oxygen gas flow-rate and maximum sample mass for FMIC procedure

In order to optimize the proposed FMIC system initial tests were performed for evaluating the oxygen gas flow-rate necessary to maintain the combustion process. In previous work [8] this parameter was not investigated and combustion was performed using 2 L min^{-1} in the first step (for ignition) and after the ignition oxygen flow-rate was increased to 15 L min^{-1} (for sample burning). In the present work, the sample mass that could be combusted in the FMIC system was increased and consequently optimization of oxygen gas flow-rate was necessary.

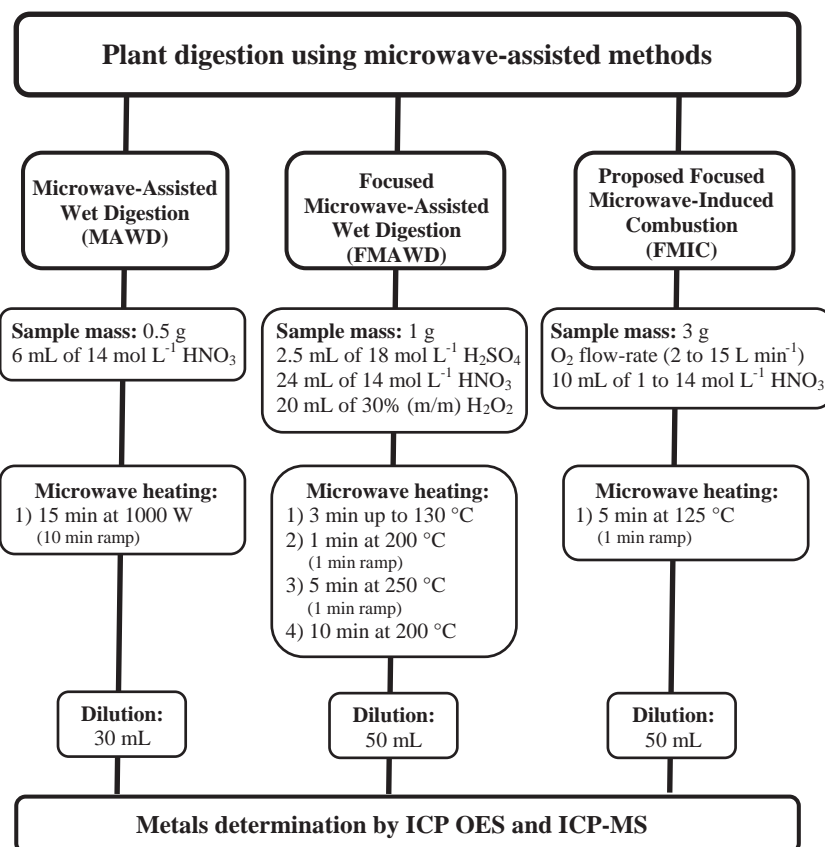


Fig. 1. Experimental digestion procedures studied in this work.

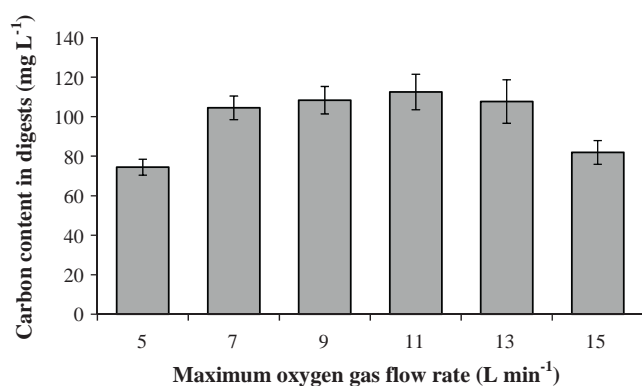


Fig. 2. Results of carbon contents in digests using different oxygen flow-rates.

The effect of oxygen flow-rate was investigated from 5 to 15 L min⁻¹ for combustion of 1 g of sample. After combustion, the carbon content was determined in the digests by ICP OES. Results are shown in Fig. 2.

It was observed that when the oxygen gas flow-rate was lower than 11 L min⁻¹, solid residues remained in digests after combustion process and the digestion was not complete. Concerning the results obtained for carbon content in digests, it was verified that the values increased when higher oxygen gas flow-rates were used from 5 to 11 L min⁻¹. These results could be expected since with the use of higher oxygen gas flow-rates, the system was cooled down and the efficiency of digestion decreased. On the other hand, using oxygen gas flow-rate set at 13 or 15 L min⁻¹, the combustion was practically complete and no residues were observed. Using the oxygen gas flow rate set at 15 L min⁻¹ the carbon content was lower (82 mg L⁻¹) and this flow rate was also suitable for digestion of sample masses up to 3 g. Therefore, 15 L min⁻¹ of oxygen was used as maximum gas flow-rate for further studies. Using this condition, values of carbon content in digests were lower than 120 mg L⁻¹ when using 3 g of sample, diluted to 30 mL (0.24 mg C/100 mg of sample which represents less than 0.7% of RCC considering the original C content in sample matrix).

For all samples the particle size obtained was lower than 80 μm and no difficulties regarding to sample pressing and pellet formation occurred. The combustion showed similar behavior even for different plants and the time for complete combustion was related to the amount of sample (ranging from 60 to 300 s for 500 and 3000 mg of sample mass, respectively).

3.2. Optimization of absorbing solution for FMIC procedure

It is well discussed in the literature concerning sample digestion by combustion methods, that the absorbing solution is a crucial parameter for analytes recoveries [4,17]. In general, for further metals determination by different techniques (e.g. ICP OES and ICP-MS), diluted nitric acid in the range of 2–4 mol L⁻¹ have been recommended for analytes retention [4,17–20]. On the other hand, depending on the analytes, sometimes it may be necessary to add HCl to achieve quantitative recoveries [21,22]. In previous work using FMIC [8], absorbing solution for metals retention was set at 4 mol L⁻¹ HNO₃ without previous optimization. In this sense, in the present work, a systematic study was performed using different concentrations of HNO₃ as absorbing solution (1, 4, 7 and 14 mol L⁻¹) for further Al, Ba, Ca, Co, Cr, Cu, Mg, Mn, Ni, Sr, V and Zn determinations by ICP OES and ICP-MS in order to obtain a suitable solution for retention of all analytes. In this study, 10 mL of the absorbing solution was used and results are shown in Fig. 3.

According to Fig. 3, even using HNO₃ solution as diluted as 1 mol L⁻¹, it was possible to achieve quantitative recoveries for

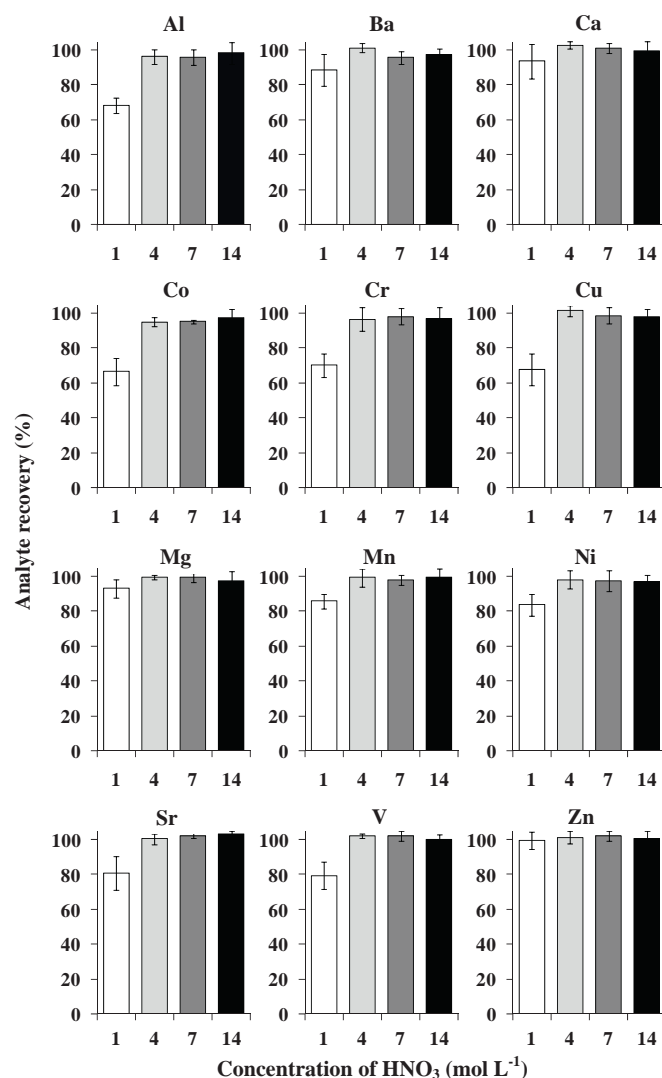


Fig. 3. Agreement to values obtained by MAWD for different concentrations of absorbing solutions using ICP OES or ICP-MS (Co, Cr, Ni and V, $n=3$).

Zn. Recoveries around 93% were obtained for Ca and Mg. On the other hand, recoveries lower than 88% were obtained for Al, Ba, Co, Cr, Cu, Mn, Ni, Sr, and V. In addition, using 1 mol L⁻¹ HNO₃ higher relative standard deviations (RSD), in the range of 6–20%, were observed. Using 4 mol L⁻¹ HNO₃ as absorbing solution, quantitative recoveries (higher than 95%) were obtained for all metals investigated and RSD values were always lower than 5%. Increasing the nitric acid concentration for 7 and 14 mol L⁻¹, the same behavior was observed and recoveries higher than 95% were achieved for Al, Ba, Ca, Co, Cr, Cu, Mg, Mn, Ni, Sr, V and Zn. Taking into account that the use of diluted acids is advantageous concerning lower blank values and green chemistry recommendations, 4 mol L⁻¹ HNO₃ was chosen as absorbing solution for further studies.

The lifetime of quartz sample holder was studied using high amounts of sample and consequently long times of combustion. On this aspect, it is important to point out that during the experiments of optimization of absorbing solution, retention of Na and K was studied. It was verified that for these elements, recoveries lower than 60–75% were achieved for investigated samples and also for the CRMs investigated. This fact could be related to Na and K adsorption in the quartz surface of the sample holder during the combustion process, since the quartz holder becomes porous after

Table 1
Determination of metals in CRMs (mean \pm standard deviation, $n = 3$) using FMIC (4 mol L⁻¹ HNO₃ as absorbing solution).

Element	Concentration ($\mu\text{g g}^{-1}$)			
	NIST 1515 – apple leaves		NIST 1547 – peach leaves	
	FMIC	Certified value	FMIC	Certified value
Al ^b	289 \pm 7	286 \pm 9	248 \pm 18	249 \pm 8
Ba ^b	47 \pm 1	49 \pm 2	123 \pm 9	124 \pm 4
Ca (%) ^b	1.56 \pm 0.04	1.53 \pm 0.02	1.52 \pm 0.02	1.56 \pm 0.02
Co ^c	0.09 \pm 0.01	0.09 ^a	0.07 \pm 0.01	0.07
Cr ^c	0.30 \pm 0.01	0.3 ^a	0.94 \pm 0.09	1 ^a
Cu ^b	5.50 \pm 0.25	5.64 \pm 0.24	3.8 \pm 0.4	3.7 \pm 0.4
Mg (%) ^b	0.26 \pm 0.01	0.27 \pm 0.01	0.42 \pm 0.01	0.43 \pm 0.01
Mn ^b	55 \pm 1	54 \pm 3	96 \pm 4	98 \pm 3
Ni ^c	0.88 \pm 0.12	0.91 \pm 0.12	0.67 \pm 0.09	0.69 \pm 0.09
Sr ^b	24 \pm 3	25 \pm 2	55 \pm 2	53 \pm 4
V ^c	0.27 \pm 0.01	0.26 \pm 0.03	0.36 \pm 0.02	0.37 \pm 0.03
Zn ^b	12.3 \pm 0.2	12.5 \pm 0.3	17.4 \pm 0.9	17.9 \pm 0.4

^a Informed value.^b Determinations by ICP OES^c Determinations by ICP-MS.**Table 2**
Determination of metals by ICP OES in plant samples (mean \pm standard deviation, $n = 3$) using FMIC and comparison with microwave-assisted digestion in high pressure system (MAWD) and open system (FMAWD).

Sample	Element	Digestion procedure		
		MAWD	FMAWD	FMIC
Basil	Al ($\mu\text{g g}^{-1}$)	622 \pm 47	678 \pm 62	648 \pm 52
	Ba ($\mu\text{g g}^{-1}$)	27.1 \pm 0.3	26.3 \pm 1.5	27.4 \pm 0.4
	Ca (%)	2.26 \pm 0.05	2.48 \pm 0.22	2.37 \pm 0.18
	Cu ($\mu\text{g g}^{-1}$)	15.8 \pm 0.9	16.6 \pm 0.9	15.2 \pm 0.9
	Cr ($\mu\text{g g}^{-1}$)	1.05 \pm 0.04	1.12 \pm 0.08	1.08 \pm 0.06
	Mg (%)	0.615 \pm 0.022	0.681 \pm 0.069	0.660 \pm 0.049
	Mn ($\mu\text{g g}^{-1}$)	74.9 \pm 1.2	69.5 \pm 5.8	73.3 \pm 1.9
	Sr ($\mu\text{g g}^{-1}$)	181 \pm 2	187 \pm 12	185 \pm 4
	Zn ($\mu\text{g g}^{-1}$)	38.2 \pm 1.9	43.7 \pm 4.6	42.0 \pm 2.3
Cilantro	Al ($\mu\text{g g}^{-1}$)	860 \pm 59	878 \pm 84	900 \pm 70
	Ba ($\mu\text{g g}^{-1}$)	13.9 \pm 0.3	13.6 \pm 0.6	13.4 \pm 0.4
	Ca (%)	1.22 \pm 0.04	1.21 \pm 0.10	1.22 \pm 0.07
	Cu ($\mu\text{g g}^{-1}$)	9.36 \pm 0.30	9.25 \pm 0.43	9.01 \pm 0.45
	Cr ($\mu\text{g g}^{-1}$)	1.62 \pm 0.06	1.74 \pm 0.09	1.69 \pm 0.06
	Mg (%)	0.294 \pm 0.036	0.327 \pm 0.042	0.321 \pm 0.037
	Mn ($\mu\text{g g}^{-1}$)	44.5 \pm 1.2	43.9 \pm 2.7	45.3 \pm 1.1
	Sr ($\mu\text{g g}^{-1}$)	92.5 \pm 1.9	91.4 \pm 7.8	90.8 \pm 1.3
	Zn ($\mu\text{g g}^{-1}$)	23.4 \pm 1.2	22.1 \pm 2.2	23.0 \pm 1.8
Chives	Al ($\mu\text{g g}^{-1}$)	116 \pm 9	127 \pm 9	108 \pm 10
	Ba ($\mu\text{g g}^{-1}$)	21.8 \pm 0.9	25.0 \pm 2.2	24.6 \pm 1.4
	Ca (%)	0.945 \pm 0.036	0.926 \pm 0.061	0.949 \pm 0.047
	Cu ($\mu\text{g g}^{-1}$)	8.48 \pm 0.49	8.99 \pm 0.93	7.96 \pm 0.56
	Cr ($\mu\text{g g}^{-1}$)	0.181 \pm 0.010 ^a	0.202 \pm 0.19 ^a	0.199 \pm 0.014
	Mg (%)	0.315 \pm 0.012	0.296 \pm 0.028	0.326 \pm 0.018
	Mn ($\mu\text{g g}^{-1}$)	67.9 \pm 2.6	67.1 \pm 4.4	66.2 \pm 3.4
	Sr ($\mu\text{g g}^{-1}$)	38.9 \pm 3.1	38.4 \pm 3.3	36.9 \pm 1.0
	Zn ($\mu\text{g g}^{-1}$)	20.6 \pm 1.2	21.2 \pm 1.8	19.6 \pm 1.5
Oregano	Al ($\mu\text{g g}^{-1}$)	456 \pm 17	412 \pm 31	440 \pm 26
	Ba ($\mu\text{g g}^{-1}$)	11.4 \pm 0.5	10.9 \pm 0.5	11.5 \pm 0.5
	Ca (%)	1.06 \pm 0.03	1.09 \pm 0.06	1.12 \pm 0.04
	Cr ($\mu\text{g g}^{-1}$)	0.961 \pm 0.083	1.02 \pm 0.09	0.976 \pm 0.095
	Cu ($\mu\text{g g}^{-1}$)	10.3 \pm 0.3	9.5 \pm 0.6	10.2 \pm 0.3
	Mg (%)	0.192 \pm 0.005	0.215 \pm 0.020	0.191 \pm 0.009
	Mn ($\mu\text{g g}^{-1}$)	50.3 \pm 0.8	51.0 \pm 3.9	50.1 \pm 1.6
	Sr ($\mu\text{g g}^{-1}$)	35.6 \pm 1.7	33.9 \pm 3.0	35.1 \pm 1.8
	Zn ($\mu\text{g g}^{-1}$)	24.5 \pm 1.9	23.2 \pm 0.6	24.8 \pm 2.1
Parsley	Al ($\mu\text{g g}^{-1}$)	1040 \pm 80	1120 \pm 120	1060 \pm 50
	Ba ($\mu\text{g g}^{-1}$)	80.0 \pm 2.2	82.6 \pm 4.1	79.0 \pm 3.5
	Ca (%)	0.849 \pm 0.057	0.886 \pm 0.070	0.887 \pm 0.038
	Cu ($\mu\text{g g}^{-1}$)	10.4 \pm 0.5	11.7 \pm 0.7	10.8 \pm 0.5
	Cr ($\mu\text{g g}^{-1}$)	1.77 \pm 0.11	1.79 \pm 0.21	1.89 \pm 0.09
	Mg (%)	0.345 \pm 0.025	0.358 \pm 0.024	0.347 \pm 0.011
	Mn ($\mu\text{g g}^{-1}$)	63.0 \pm 1.9	65.7 \pm 3.5	63.8 \pm 2.9
	Sr ($\mu\text{g g}^{-1}$)	82.9 \pm 3.2	85.2 \pm 4.1	84.8 \pm 3.6
	Zn ($\mu\text{g g}^{-1}$)	34.1 \pm 1.8	38.2 \pm 3.1	37.6 \pm 2.4

^a Results obtained by ICP-MS.

Table 3

Determination of metals by ICP-MS in plant samples ($n=3$, mean \pm standard deviation) using FMIC and comparison with microwave-assisted digestion in high pressure system (MAWD) and in open system (FMAWD).

Sample	Element	Digestion procedure		
		MAWD	FMAWD	FMIC
Oregano	Co ($\mu\text{g g}^{-1}$)	0.116 \pm 0.006	0.114 \pm 0.009	0.117 \pm 0.007
	Ni ($\mu\text{g g}^{-1}$)	1.02 \pm 0.02	1.05 \pm 0.03	1.04 \pm 0.04
	V ($\mu\text{g g}^{-1}$)	0.530 \pm 0.017	0.527 \pm 0.017	0.527 \pm 0.017
Parsley	Co ($\mu\text{g g}^{-1}$)	0.225 \pm 0.010	0.230 \pm 0.020	0.222 \pm 0.014
	Ni ($\mu\text{g g}^{-1}$)	2.20 \pm 0.06	1.99 \pm 0.18	2.26 \pm 0.04
	V ($\mu\text{g g}^{-1}$)	1.03 \pm 0.02	1.10 \pm 0.05	1.08 \pm 0.04
Basil	Co ($\mu\text{g g}^{-1}$)	0.372 \pm 0.049	0.380 \pm 0.056	0.391 \pm 0.045
	Ni ($\mu\text{g g}^{-1}$)	1.71 \pm 0.11	1.69 \pm 0.15	1.65 \pm 0.13
	V ($\mu\text{g g}^{-1}$)	1.01 \pm 0.06	1.08 \pm 0.09	1.06 \pm 0.09
Cilantro	Co ($\mu\text{g g}^{-1}$)	0.072 \pm 0.006	0.075 \pm 0.012	0.071 \pm 0.010
	Ni ($\mu\text{g g}^{-1}$)	0.674 \pm 0.040	0.687 \pm 0.055	0.657 \pm 0.045
	V ($\mu\text{g g}^{-1}$)	0.415 \pm 0.030	0.440 \pm 0.053	0.433 \pm 0.042
Chives	Co ($\mu\text{g g}^{-1}$)	0.030 \pm 0.004	0.035 \pm 0.005	0.032 \pm 0.004
	Ni ($\mu\text{g g}^{-1}$)	0.898 \pm 0.084	0.741 \pm 0.166	0.797 \pm 0.063
	V ($\mu\text{g g}^{-1}$)	0.662 \pm 0.072	0.741 \pm 0.166	0.554 \pm 0.078

20 cycles of combustion due to high temperature achieved and long time of sample combustion (about 5 min for 3 g of sample). Therefore, determination of Na and K in digests obtained by FMIC was not possible and, for these elements, further investigation will be necessary. The quartz sample holder lifetime was about 60 cycles of combustion for 1 g of sample.

After optimization of FMIC system, accuracy was evaluated using CRMs of apple and peach leaves (NIST 1515 and NIST 1547,

respectively), using 4 mol L⁻¹ HNO₃ as absorbing solution and determination was performed by ICP OES and ICP-MS. Results are shown in Table 1.

It was observed that for all investigated metals, results obtained by FMIC were in agreement in the range of 96–104% with certified values (except for Cr which was 94%). In addition, RSD values were lower than 5% except for Ni which is present in relatively low concentrations.

Table 4

Limits of detection obtained by ICP OES and ICP-MS for digestion of plant samples using FMIC, microwave-assisted digestion in high pressure system (MAWD) and in open system (FMAWD).

Element	Determination technique	Digestion method		
		MAWD ^a	FMAWD ^b	FMIC ^c
Al ($\mu\text{g g}^{-1}$)	ICP OES	0.32	0.75	0.12
	ICP-MS	ND	ND	ND
Ba ($\mu\text{g g}^{-1}$)	ICP OES	0.28	0.25	0.06
	ICP-MS	0.04	0.03	0.01
Ca ($\mu\text{g g}^{-1}$)	ICP OES	0.55	1	0.15
	ICP-MS	ND	ND	ND
Co ($\mu\text{g g}^{-1}$)	ICP OES	0.25	0.22	0.05
	ICP-MS	0.012	0.010	0.002
Cr ($\mu\text{g g}^{-1}$)	ICP OES	0.27	0.25	0.06
	ICP-MS	0.026	0.022	0.007
Cu ($\mu\text{g g}^{-1}$)	ICP OES	0.14	0.24	0.05
	ICP-MS	0.032	0.030	0.006
Mg ($\mu\text{g g}^{-1}$)	ICP OES	0.26	0.41	0.08
	ICP-MS	ND	ND	ND
Mn ($\mu\text{g g}^{-1}$)	ICP OES	0.05	0.10	0.02
	ICP-MS	0.003	0.002	0.001
Ni ($\mu\text{g g}^{-1}$)	ICP OES	0.15	0.24	0.05
	ICP-MS	0.017	0.014	0.003
Sr ($\mu\text{g g}^{-1}$)	ICP OES	0.05	0.12	0.02
	ICP-MS	0.006	0.005	0.001
V ($\mu\text{g g}^{-1}$)	ICP OES	0.06	0.05	0.03
	ICP-MS	0.006	0.005	0.001
Zn ($\mu\text{g g}^{-1}$)	ICP OES	0.12	0.45	0.06
	ICP-MS	0.09	0.55	0.05

ND: not determined.

^a Sample mass: 0.5 g; dilution up to 30 mL.

^b Sample mass: 1 g; dilution up to 50 mL.

^c Sample mass: 3 g; dilution up to 30 mL.

3.3. Comparison of FMAWD, MAWD, and FMIC for sample digestion and metals determination in plant samples by ICP OES and ICP-MS

The determination of Al, Ba, Ca, Co, Cr, Cu, Mg, Mn, Ni, Sr, V, and Zn was performed in digests by ICP OES and also by ICP-MS after MAWD, FMAWD, and FMIC. For all elements, no significant difference was observed between the results obtained by ICP OES and ICP-MS (except for Al, Ca, and Mg which were determined only by ICP OES due to isobaric interferences in ICP-MS). On the other hand, Co, Ni, and V determinations were carried out preferentially by ICP-MS due to the low concentrations of these elements especially when samples were digested by MAWD (0.5 g of maximum sample mass). A comparison of results obtained after different digestion procedures is shown in Tables 2 and 3 (determinations by ICP OES and ICP-MS, respectively).

No statistical difference (ANOVA, 95% of confidence level) was observed between the results obtained by MAWD, FMAWD and FMIC for elements in all plant samples (results obtained by ICP OES and ICP-MS). Analysis of plant samples for analytes in ng g^{-1} level was possible when digestion methods were combined to ICP-MS determination. In particular, for chives samples only FMIC was feasible as digestion method for determination of Cr (using ICP OES) due to the relatively high sample mass that was possible to digest (3 g). When digestion was performed by MAWD and FMAWD the final concentration was lower than the respective LOD for Cr by ICP OES. In this case, results presented for Cr in Table 2 were obtained by ICP-MS. Thus, it is important to point out that FMIC contributes to analyte determination in relatively low levels even using ICP OES without dependence of using ICP-MS. Furthermore, results presented in Tables 2 and 3 show that FMIC is a feasible digestion method for determinations by both analytical techniques.

Table 4 shows the LODs obtained using ICP OES and ICP-MS for MAWD, FMAWD, and FMIC. It was expected that FMIC procedure would allow lower values for LODs in comparison to MAWD and FMAWD once it uses a high sample mass (3 g). This aspect is particularly important for some analytes typically present at low concentrations, such as Co, Cr, Ni, and V in plant samples. In addition, the blank values obtained by FMAWD were higher for almost all analytes probably due to contamination by reagents (sulfuric acid and hydrogen peroxide). Another advantage to the FMIC method in comparison to FMAWD and MAWD is the use of diluted acid solutions as absorbing medium contributing to lower acid concentrations in final digests and reducing reagents consumption and residues generation. Residual carbon contents were about 4–6% for digests obtained by MAWD and FMAWD in comparison to the RCC lower than 0.7% obtained by FMIC.

4. Conclusions

Results obtained in this study shows that FMIC is a feasible method for digestion of plants for metals determination using ICP OES and ICP-MS. As one of the main advantages, FMIC allows the digestion of relatively higher sample masses, up to 3 g, which contributes to lower LODs in comparison to MAWD and FMAWD. In addition, a 4 mol L^{-1} HNO_3 solution was used in FMIC method as

absorbing medium for analytes released during combustion which minimizes the use of concentrated acids and decreases the generation of residues that is in agreement with green chemistry recommendations. Using both FMIC and a diluted acid solution as absorbing medium it was possible to determine 12 major, minor and trace elements in plant samples resulting in digests suitable for analysis by ICP OES and ICP-MS.

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