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A new closed-vessel conductively-heated digestion system: Fostering plant analysis by inductively coupled plasma optical emission spectroscopy

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Abstract

Open-vessel acid digestion is a low cost and easily automated sample decomposition method commonly used in laboratories involved in routine plant analysis. However, large amounts of reagents are required, decomposition efficiency is limited by the boiling point of the digestion mixture and sample contamination and losses of volatile elements can frequently occur. In addition, the venting of large amounts of acid fume is undesirable due to its impact to the analyst and environment. For this reason, a simple, rugged and low cost closed-vessel conductively-heated digestion system was developed and evaluated. The system accommodates 38 reaction vessels and enables the digestion of 200 mg of plant samples for subsequent elemental determination. The digestion procedure was optimized with the help of video images. Accuracy was confirmed by analyzing five certified reference materials digested by the proposed system. Digestion efficiency was evaluated by determining residual carbon content and residual acidity. When plant samples were digested using the proposed system, results for Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S and Zn by inductively coupled plasma optical emission spectroscopy were in agreement with those obtained after closed-vessel microwave-assisted digestion.

Keywords: closed-vessel, digestion, plant, conductive heating, ICP OES.

1. Introduction

Routine analysis of plants by inductively coupled plasma optical emission spectroscopy (ICP OES) usually requires a previous conversion of solid samples into solutions because the residual carbon content or suspended particles may cause analytical biases or even block the sample introduction system.[1,2] Regarding plant digestion for inorganic analysis, microwave-assisted sample preparation has become a standard,[3] providing several methods such as microwave-assisted wet digestion,[4] oxygen pressurized microwave-assisted digestion with diluted nitric acid,[5] focused microwave-assisted wet digestion,[6,7] microwave-induced combustion[8,9] and focused microwave-induced combustion.[10]

In spite of the high efficiency of microwave-assisted digestion systems, this technology has not been implemented to any considerable extent in large scale routine analyses of plants due to high costs involved in acquisition and maintenance.[11] As a result, most small to medium-size laboratories worldwide involved in plant analysis commonly employ methods based on dry ashing or wet digestion in open vessels for plant decomposition.

Wet digestion of plant samples in open vessels is usually performed using nitric acid as oxidant alone, in combination with other acids or with hydrogen peroxide.[11] Hot plates and digestion blocks are among the heating devices commercially available.[12,13] In open-vessel digestions, decomposition effectiveness is limited by the boiling point of acids, consumption of reagents is relatively high, and airborne contamination and/or losses by volatilization frequently occur. In addition, the venting of large amounts of acid fume is

undesirable due to its impact to the analyst and environment.[14] These shortcomings may be circumvented by using closed vessels.[15-17]

With regard to closed-vessel digestion under high temperature and pressure, the boiling point of the acid is elevated when the pressure inside the vessel increases, leading to a faster and more efficient digestion.[12] In addition, the low amount of reagents required leads to lower blank values.[16,17] Although closed-vessel digestion systems may employ microwave-assisted or conductive heating,[5] most recent research and development in the sample preparation field is concentrated on the former.[4,5,8,9,10,18] Considering that digestion blocks are commonly used in most small to medium-size laboratories worldwide involved in plant analysis, the development of a simple, rugged, low cost and efficient device for sample preparation based on conductive heating and closed-vessels may be considered attractive.

In this study, a closed-vessel conductively-heated system employing sealed borosilicate glass tubes was developed and applied to plant digestion. The performance of the system was evaluated by determining macro- and micronutrients most frequently required in foliar analysis (Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn) in five plant certified reference materials and seven plant samples by ICP OES. Residual carbon content and residual acidity were also determined.

2. Experimental

2.1. Instrumentation

The proposed conductively-heated digestion system (CHDS) is depicted in Figure 1. The system comprises an aluminum heating block (380 mm length,

80 mm width, 54 mm height) that provides uniform heating with 38 orifices (17 mm diameter, 50 mm deep) for borosilicate glass digestion tubes (14.5 mm internal diameter, 16.5 mm outside diameter and 200 mm height), a temperature control terminal, two cooling fans, a digestion cabinet resistant to acid fumes (polypropylene coated inside) and a transparent acrylic safety shield (12 mm thick). The equipment is operated via an industrial grade control terminal where the heating program is created by setting up target temperatures, ramp and hold time. The system automatically follows the heating program via a proportional-integral-derivative controller. A video camera positioned inside the cabinet allows following or recording the digestion process in real time.

The digestion tube (internal volume of 32 mL) depicted in Figure 2 was developed with a rounded base and an external screw thread round the neck to take a Bakelite (plastic) screw cap. These tubes fit auto-samplers directly. In order to keep the glass tube sealed during digestions, a Teflon cover containing a perfluorinated (FFKM) o´ring is pressed by the screw cap. Since the screw cap is more fragile than the tube, it also works as a safety seal, allowing the integrity of the vessel in case of overpressure. Teflon covers, FFKM o´rings and caps are all re-usable.

In order to avoid excessive heating of the upper part of tubes, they were developed without casings (jackets) and all 38 cavities were designed on the edge of the heating block. Also, an orifice (60 mm diameter) on the bottom of the digestion cabinet (positioned under the heating block) allowed external air to flow through it with the help of the fume hood ventilation. With this arrangement, the temperature of the vapor phase remained much lower than that reached in

the liquid phase, allowing to perform digestions at low pressure. Hence, digestion tubes with thinner walls (1 mm) improved heat exchange and reduced the waiting time for heating and cooling.

A closed vessel microwave (MW) digestion system (Multiwave 3000, Anton Paar, Graz, Austria) equipped with a rotor for 48 reaction PFA vessels (internal volume of 50 mL, minimum filling volume of 6 mL, maximum temperature and pressure of 200 °C and 20 bar, respectively) equipped with an immersing pressure/temperature sensor in one reference vessel was employed for comparison of digestion efficiency.

Macronutrients and micronutrients were determined in digests by ICP OES (iCAP 6500 Duo, Thermo Scientific, Waltham, MA, USA). Operating conditions are described in Table 1. Three emission lines were tested for each element and the selected line was based on sensitivity and selectivity. Data processing was performed both with the ICP OES software and using Microsoft Excel 2007 in order to confirm the results obtained.

Residual carbon content (RCC, mg C/100 mg of sample) was determined in digested solutions by ICP OES according to conditions described elsewhere.[19]

An infrared thermometer with laser pointer (model 9200-008, Allafrance, Chemillé, France) was used to check the temperature profile of the borosilicate glass tubes during digestion.

Plant samples were powdered using a Wiley type cutting mill (TE-648, Tecnal, Piracicaba, SP, Brazil).

2.2. Reagents, analytical solutions and samples

All reagents were analytical grade and deionized water (18.2 MΩ cm resistivity) obtained with a Milli-Q® water purification system (Millipore, Bedford, MA, USA) was used to prepare all solutions. Nitric acid (69%, J.T. Baker, Deventer, Holland) and H_2O_2 (30%, Merck, Darmstadt, Germany) were used for sample digestion.

Multi-element analytical solutions in the 0.1-10 mg L^{-1} Al, 0.02-2 mg L^{-1} B, 0.5-50 mg L^{-1} Ca, 0.005-0.5 mg L^{-1} Cu, 0.1-10 mg L^{-1} Fe, 0.3-30 mg L^{-1} K, 0.2-20 mg L^{-1} Mg, 0.1-10 mg L^{-1} Mn, 0.05-5 mg L^{-1} P, 0.1-10 mg L^{-1} S, 0.05-5 mg L^{-1} Zn concentration ranges were prepared by appropriate dilution of individual 1000 mg L^{-1} Spex plasma standards.

Standardized sodium hydroxide solution (0.1078 mol L^{-1}) was employed for determining residual acidity in digests by titration. Carbon reference solutions used to external calibration for RCC determination (250 - 3000 mg L^{-1}) were prepared by dissolution of appropriate amounts of citric acid (Merck, Darmstadt, Germany) in water.

Accuracy was evaluated by analyzing five certified reference materials from National Institute of Standards and Technology (1515 Apple Leaves, 1547 Peach Leaves, 1573a Tomato Leaves, 1575a Trace Elements in Pine Needles, and 1570a Trace Elements in Spinach Leaves).

The samples spinach (*Spinacia oleracea L.*), lettuce (*Lactuca sativa L.*), white cabbage (*Brassica oleracea L. var. capitata*), wild chicory (*Cichorium intybus L.*), arugula (*Eruca sativa L.*), kale (*Brassica oleracea L. var. acephala D.C.*) and senna *(Cassia angustifolia)* were purchased at a local market in

Araraquara, São Paulo, Brazil. Samples were powdered in a Wiley type cutting mill fitted with a 30-mesh screen at the bottom of the cutting chamber.

All glassware and polypropylene flasks were washed with soap and soaked in 10% (v/v) HNO_3 for 24 h, rinsed with deionized water and dried in a dust free environment before use.

2.3. Sample preparation

All samples were dried at 65°C for 48 h in a forced air oven, ground and digested using the CHDS and MW digestion system.

Digestion by CHDS: a sample mass of 200 mg was accurately weighted in digestion tubes followed by addition of 1.5 mL of concentrated (69%) HNO_3. Pre-digestion was performed at room temperature for 15 min and then 1.5 mL of (30%) H_2O_2 was added. Tubes were fully closed using Teflon covers and screw caps, respectively, and placed in the heating block. The cabinet cover was closed and the optimized heating program described in Table 2 was run. The cabinet has a sliding door which is opened when the heating program is completed, followed by turning on the fans that cool the heating block for further opening of the digestion tubes. The resulting solutions were then transferred to polypropylene flasks and diluted up to 20 mL with water.

Digestion by MW system: 200 mg of sample and 3.0 mL of concentrated (69%) HNO_3 were added into PFA vessels. Pre-digestion was performed at room temperature for 15 min. Then, 1.5 mL of (30%) H_2O_2 and 1.5 mL of water were added. The following heating program was applied: (1) 20 ºC (room) to 195 ºC with a ramp of 20 min; (2) 15 min at 195 ºC; (3) 40 min cooling (from 195

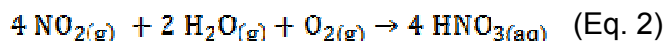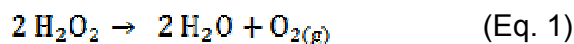ºC to 60 ºC). The final solutions were transferred to polypropylene flasks and diluted up to 25 mL with water.

3. Results and discussion

In spite of the fact that digestions with closed vessels are usually more efficient than opened-vessel digestions due to boiling point elevation of reagents, great care should be taken because the oxidation of organic matter may increase pressure beyond the safety limits of the vessels. Therefore, preliminary experiments were performed using spinach leaves in order to establish the maximum sample size to be digested by the CHDS without developing excessive pressure.

In order to study the combined effect of HNO_3 and H_2O_2 on pressure, 200 mg of spinach leaves were digested using 1.5 mL of concentrated (69%) HNO_3 with and without the addition of 1.5 mL of (30%) H_2O_2. The heating program described in Table 2 was employed. It can be observed in Video 1 that when the block reached 110 ºC, an exothermic reaction took place inside the vessel containing H_2O_2. The liberation of oxygen and energy from the decomposing hydrogen peroxide provided a fast decomposition of the organic matter. This exothermic reaction did not happen in the vessel without H_2O_2.

During the second step of the heating program (10 min at 120 ºC), it can be seen in Video 1 that the brown color of NO_2 fumes in the gaseous phase gradually became lighter in the vessel with H_2O_2 probably due to the regeneration of HNO_3. When concentrated HNO_3 is used for oxidation of organic matter, the main product NO_2[20] reacts with O_2 and H_2O regenerating HNO_3 according to the following reactions:[21]

$$2\,H_2O_2 \rightarrow\ 2\,H_2O + O_{2(g)} \qquad \text{(Eq. 1)}$$

$$4\,NO_{2(g)} + 2\,H_2O_{(g)} + O_{2(g)} \rightarrow 4\,HNO_{3(aq)} \quad \text{(Eq. 2)}$$

These reactions are dependent on the amount of NO_2, O_2 and H_2O in gaseous phase and also on the temperature gradient in the digestion vessel.

During the second step of digestion at 120 ºC, the temperature of closed vessels inside the CHDS was checked by using a laser pointer infrared thermometer. The temperature was 120 ºC and 25 ºC at the bottom and top, respectively. This gradient enhanced the absorption of gaseous products by the liquid phase and clearly played a role in the process of nitric acid regeneration.[22]

It can be observed in Video 1 that when the temperature reached 220 ºC, the vessel without H_2O_2 presented a dark brown color in the gaseous phase due to the accumulation of NO_2 that broke the screw cap by overpressure. The screw cap was not broken in the vessel containing H_2O_2 because the consumption of NO_2 from the gaseous phase to produce HNO_3 reduced the pressure inside the vessel.

Considering that nitric acid regeneration leads to a reduction in pressure, the possibility of increasing the sample mass was evaluated. This hypothesis was tested by digesting 200, 300 and 400 mg of spinach leaves using 2.0 mL of (69%) HNO_3, 2.0 mL of (30%) H_2O_2, and the optimized heating program described in Table 2. This experiment can be seen in video 2. Masses up to 400 mg were efficiently converted into clear solutions without breaking any screw cap. The addition of H_2O_2 combined with a step at 120 ºC with hold time of 10 minutes led to the regeneration of nitric acid, reducing molecules from the

gaseous phase and avoiding overpressure before the final temperature of 220 ºC was reached. This aspect was visually confirmed by observing that the dark brown color of the gaseous phase gradually became lighter during the 10 min hold time at 120 ºC. The mass selected for further investigations was 200 mg. This mass is adequate to guarantee the homogeneity of plant samples powdered in a Wiley type cutting mill and certified reference materials.

The video images presented in this study can be better understood in combination with the results obtained by Veschetti et al.[23] The authors studied the behavior of H_2O_2 in the presence of a sewage-sludge sample acidified with nitric acid and concluded that the addition of H_2O_2 produced a pressure peak between 65 and 105 ºC with its height proportional to the volume of H_2O_2.

Five certified reference materials were digested with the CHDS using the optimized conditions (200 mg sample, 1.5 mL concentrated (69%) HNO_3, 1.5 mL (30%) H_2O_2, heating program in Table 2) and analyzed by ICP OES. Results obtained for Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S and Zn are presented in Table 3. For all 11 elements selected and determined by ICP OES, the relative standard deviation (RSD) of three replicates was typically below 5%. Residual acidity was determined in final digests and varied from 92 to 95%.

Seven botanical samples (senna, lettuce, kale, white cabbage, arugula, spinach and wild chicory) were also digested with the proposed CHDS using the optimized conditions and MW system as comparative procedure. Results for Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S and Zn determinations (Table 4) were in fair agreement between two systems. The limit of detection (LOD) was calculated for both digestion systems as the concentration corresponding to 3-fold the standard deviation of 10 independent sample blanks divided by the slope of the

analytical curve[24] and the results can be seen in Table 5. The LOD was similar for Cu, Fe, K, Mg, Mn, P and S for both digestion systems. However, when using the CHDS, the LODs for Al, B, Ca and Zn were respectively 3.5, 3, 6, and 5 times higher than the LODs obtained with the MW digestion system. A possible explanation for this fact is that boron and many other contaminants can be released from borosilicate glass tubes during digestion, resulting in higher blank values for this elements and consequently in LODs.

Results for RCC are presented in Table 6. The CHDS allowed efficient decomposition of plant materials, eliminating most of the organic matter as indicated by the adequate RCC in digests (from 5.3 to 7.0% m/m). These values were similar to those obtained by the low pressure (< 20 bar) MW digestion system used in this study (from 6.6 to 8% m/m). The heating block of the CHDS was heated up to 220 ºC during digestion. The temperature of the liquid phase inside the glass tubes was not measured because an immersing temperature sensor was not used. Considering that the results obtained for RCC using the two digestion systems was similar, the temperature of the liquid phase inside the glass tubes of the CHDS might have reached 180-200 ºC.

The CHDS is in between open-vessel digestion and closed-vessel microwave digestion. Costs for running plant sample digestion with the CHDS are lower because it requires small volumes of reagents (1.5 mL of HNO_3 and 1.5 mL of H_2O_2). In comparison to open-vessel digestion, CHDS provides faster digestions, minimizing electricity cost. Also, expensive perchloric acid is not used and a high-grade fume hood is not required. In relation to microwave systems, maintenance and consumable parts such as FFKM o´rings and Bakelite screw caps are less expensive.

Macro- and micro nutrients frequently required in plant analysis were contemplated in this study. Volatile elements usually found in very low concentrations in plants such as Cd, Pb, As, Hg and Se could not be determined by ICP OES.

4. Safety concerns

Explosion of a sealed glass tube containing a hot acid mixture under pressure is a hazard that must be considered. Likewise, operations with pressurized tubes must follow some precautions in order to guard against personal injury.

Each glass tube of the CHDS has a screw cap that works as a safety seal. If the pressure exceeds the limit during digestion (due to overloading or spontaneous chemical reactions), the screw cap ruptures and the pressure can escape. This usually prevents the tube from rupturing. However, in case of unforeseen destructive failure of the tube during digestion, the cabinet gives adequate protection to the analyst.

At the end of every heating process, the heating block containing the sealed tubes with the processed samples was cooled down from 220 °C to 40 °C. This was done primarily to reduce internal temperatures and pressures to the point where the tubes could be safely handled and opened. After that, using goggles, protective gloves and lab coat, each tube was vented by opening the screw cap very slowly behind the cabinet safety shield, with only the analyst hands inside the open cabinet. With a short turn of the screw cap using only finger force, vapors were easily released. Tubes were opened with the fume hood ventilation on and behind the protection shield in order to contain and

convey reaction vapors. It must be emphasized that tubes should never be opened before they have been sufficiently cooled. These precautions were mandatory for these operations.

5. Conclusion

The proposed closed-vessel conductively-heated digestion system is a simple and effective alternative for wet digestion of plants. The developed equipment presents the following desirable features[25]: (a) ease of use; (b) compatibility with multi-element analysis; (c) safety; (d) high sample throughput; (e) ability to provide a representative sample; (f) completeness and reproducibility of recovery; (g) stable digests with low RCC, low residual acidity and low concentration of dissolved solids. In addition, the proposed system operates in agreement with the recommendations of the green chemistry[26] since low amounts of reagents are required and the generation of laboratory residues is minimum.

The feasibility of increasing the sample mass in digestions of plant materials using the CHDS was proved by taking advantage of the reduction in pressure promoted by the regeneration of nitric acid. It is very clear that the regeneration process can be used to diminish the pressure inside the vessel by creating hold times in the temperature program and by establishing a quantitative relationship between the sample mass and the volume of hydrogen peroxide. The former is related to the amount of NO_2 produced during digestion and the latter with necessary quantities of O_2 and H_2O in the gaseous phase to regenerate HNO_3.

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Figure Captions

Figure 1. Schematic set-up Details of the CHDS designed and proposed for plant digestion.

Figure 2. Borosilicate glass tubes designed for low pressure digestion with the CHDS.

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Table 1. Operational conditions for ICP OES measurements.

Parameter	Setting
RF generator frequency (MHz)	40
RF applied power (kW)	1.15
Observation view	axial
Purge gas	Argon
Plasma gas flow rate (L min^{-1})	12 L min^{-1}
Auxiliary gas flow rate (L min^{-1})	0.5 L min^{-1}
Nebulizer gas flow (L min^{-1})	0.7 L min^{-1}
Analytes	Emission line (nm)
Al (I)	396.152
B (I)	249.773
C (I)	193.027
Ca (I)	422.673
Cu (I)	324.754
Fe (II)	238.204
K (I)	766.485
Mg (I)	285.211
Mn (II)	257.610
P (I)	213.618
S (I)	181.972
Zn (I)	213.857

(I) = atomic line ; (II) = ionic line.

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Table 2. Optimized heating program of the CHDS.

Step	Time (min)	Temperature
1	10	20 ºC (room) to 120 ºC
2	10	120 ºC
3	10	120 ºC to 220 ºC
4	10	220 ºC
Cooling	40	220 ºC to 40 ºC

Table 3. Results (mean ± standard deviation) for Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S and Zn (mg kg^{-1}) in CRMs digested (n = 3) by the CHDS.

Element		CRM				
		Apple Leaves	Tomato Leaves	Pine Needles	Spinach Leaves	Peach Leaves
Al	Certified	286 ± 9	598 ± 12	580 ± 30	310 ± 11	248 ± 8
	Found	275 ± 3	465 ± 12	572 ± 17	232 ± 11	226 ± 5
	Recovery (%)	96	78	99	75	91
B	Certified	27 ± 2	33.3 ± 0.7	9.6 ± 0.2	37.6 ± 1.0	29 ± 2
	Found	22 ± 2	32.0 ± 0.9	9.7 ± 0.4	43 ± 2	25 ± 2
	Recovery (%)	81	96	101	114	86
Ca	Certified	15260 ± 150	50500 ± 900	2500 ± 100	15270 ± 410	15600 ± 200
	Found	15560 ± 30	47000 ± 300	2500 ± 200	15100 ± 100	15910 ± 60
	Recovery (%)	102	93	100	99	102
Cu	Certified	5.64 ± 0.24	4.70 ± 0.14	2.8 ± 0.2	12.2 ± 0.6	3.7 ± 0.4
	Found	5.3 ± 0.2	4.51 ± 0.01	2.74 ± 0.04	11.27 ± 0.06	3.7 ± 0.6
	Recovery (%)	94	96	98	92	100
Fe	Certified	83 ± 5	368 ± 7	46 ± 2	NC	218 ± 14
	Found	71 ± 3	298 ± 10	48 ± 2	230.8 ± 0.7	176 ± 7
	Recovery (%)	86	81	104	-	81
K	Certified	16100 ± 200	27000 ± 500	4170 ± 70	29030 ± 520	24300 ± 300
	Found	14870 ± 70	26300 ± 400	3920 ± 20	28600 ± 300	23200 ± 200
	Recovery (%)	92	97	94	99	95
Mg	Certified	2710 ± 80	(12000)	(1060 ± 170)	(8900)	4320 ± 80
	Found	2650 ± 20	10770 ± 20	970 ± 1	8320 ± 80	4260 ± 20
	Recovery (%)	98	90	92	93	99
Mn	Certified	54 ± 3	246 ± 8	(488 ± 12)	75.9 ± 1.9	98 ± 3
	Found	47.85 ± 0.07	212 ± 3	451 ± 6	65.7 ± 0.2	84 ± 1
	Recovery (%)	89	86	92	87	86
P	Certified	1590 ± 110	2160 ± 40	1070 ± 80	5200 ± 100	1370 ± 70
	Found	1550 ± 40	2110 ± 50	1030 ± 20	4970 ± 50	1270 ± 20
	Recovery (%)	98	98	97	96	93
S	Certified	(1800)	(9600)	NC	(4600)	(2000)
	Found	1690 ± 30	8970 ± 30	850 ± 20	4500 ± 100	1860 ± 30
	Recovery (%)	94	93	-	98	93
Zn	Certified	12.5 ± 0.3	30.9 ± 0.7	38 ± 2	82 ± 3	17.9 ± 0.4
	Found	11.9 ± 0.7	29 ± 1	41 ± 3	77.2 ± 0.2	18 ± 1
	Recovery (%)	95	94	108	94	101

Values in brackets are not certified.

Table 4. Results (mean ± standard deviation) for Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S and Zn (mg kg^{-1}) in plant samples digested (n = 3) by the CHDS and by closed-vessel microwave digestion system (MW).

Element		Sample						
		Senna	Lettuce	Kale	White cabbage	Arugula	Spinach	Wild chicory
Al	MW	340 ± 17	72 ± 2	40 ± 2	12.6 ± 0.3	51 ± 2	240 ± 5	139 ± 2
	CHDS	321 ± 4	76 ± 3	42 ± 2	12.0 ± 0.4	49 ± 3	231 ± 6	135 ± 3
B	MW	32 ± 1	30 ± 1	28.1 ± 0.9	29 ± 2	70 ± 2	22.7 ± 0.7	25 ± 2
	CHDS	30 ± 2	29 ± 2	30 ± 1	31 ± 2	73 ± 2	23 ± 1	23 ± 1
Ca	MW	27666 ± 464	9952 ± 120	27621 ± 306	6977 ± 64	31851 ± 391	17186 ± 412	13268 ± 118
	CHDS	27409 ± 447	10343 ± 37	27678 ± 375	6825 ± 85	31629 ± 424	17049 ± 160	13555 ± 331
Cu	MW	4.0 ± 0.1	6.3 ± 0.3	2.2 ± 0.1	2.85 ± 0.06	2.11 ± 0.04	7.71 ± 0.08	11.26 ± 0.09
	CHDS	4.4 ± 0.1	6.1 ± 0.1	2.2 ± 0.1	3.00 ± 0.05	2.13 ± 0.6	7.5 ± 0.1	11.2 ± 0.3
Fe	MW	222 ± 19	104 ± 10	52 ± 1	24.0 ± 0.9	69 ± 2	144 ± 1	122 ± 2
	CHDS	201 ± 3	100 ± 8	53 ± 1	26 ± 1	67 ± 2	136 ± 2	120 ± 2
K	MW	11359 ± 184	48808 ± 172	46362 ± 1171	23100 ± 200	64074 ± 496	75571 ± 1565	58480 ± 815
	CHDS	11941 ± 489	51395 ± 540	47426 ± 1624	22754 ± 807	64163 ± 2183	74224 ± 662	60338 ± 1075
Mg	MW	3329 ± 51	2555 ± 20	3762 ± 42	1642 ± 12	3366 ± 31	10738 ± 185	3203 ± 8
	CHDS	3357 ± 184	2663 ± 11	3839 ± 57	1650 ± 63	3576 ± 162	10406 ± 15	3273 ± 133
Mn	MW	25.1 ± 0.4	33.8 ± 0.3	43.9 ± 0.4	< LOQ	96 ± 2	324.5 ± 0.4	152 ± 1
	CHDS	26.0 ± 0.3	35.1 ± 0.4	46 ± 1	< LOQ	94 ± 3	311 ± 1	150 ± 1
P	MW	4308 ± 95	20478 ± 181	7527 ± 288	12163 ± 135	20457 ± 125	10817 ± 216	11545 ± 172
	CHDS	4427 ± 259	21441 ± 275	7463 ± 44	11697 ± 300	19630 ± 295	10553 ± 107	11493 ± 347
S	MW	1719 ± 156	2927 ± 174	8628 ± 263	5823 ± 60	11449 ± 184	4301 ± 126	2791 ± 104
	CHDS	1706 ± 71	3115 ± 106	8948 ± 293	5682 ± 202	10995 ± 163	4277 ± 62	2849 ± 133
Zn	MW	11 ± 1	58 ± 3	32.5 ± 0.2	20.7 ± 0.4	49.4 ± 0.5	53.7 ± 0.3	60.4 ± 0.7
	CHDS	9.7 ± 0.3	61 ± 2	30 ± 1	19 ± 1	51 ± 3	49.6 ± 0.3	59 ± 2

Table 5. Limits of detection (LOD) obtained with the CHDS and with a closed-vessel microwave digestion system.

Element	LOD (mg kg^{-1})	
	MW digestion system	CHDS
Al	0.66	2.30
B	0.70	2.16
Ca	0.72	4.19
Cu	0.21	0.19
Fe	0.44	0.40
K	0.33	0.45
Mg	0.14	0.20
Mn	0.08	0.07
P	2.54	3.44
S	0.35	0.44
Zn	0.14	0.71

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Table 6. Residual carbon content (mean ± standard deviation) obtained from digestions (n = 3) performed with the CHDS and MW digestion system.

CRM	System	RCC (% m/m)
Apple leaves	CHDS	7.0 ± 0.7
Tomato leaves	CHDS	5.5 ± 0.3
Pine needles	CHDS	6.2 ± 0.4
Spinach leaves	CHDS	5.6 ± 0.8
Peach leaves	CHDS	5.3 ± 0.3
Sample		
Senna	MW	8 ± 1
	CHDS	7.0 ± 0.3
Lettuce	MW	7.1 ± 0.8
	CHDS	6.8 ± 0.4
Kale	MW	6.8 ± 0.6
	CHDS	6.5 ± 0.3
White cabbage	MW	7.2 ± 0.4
	CHDS	7.0 ± 0.4
Arugula	MW	7.1 ± 0.6
	CHDS	7.0 ± 0.3
Spinach	MW	6.6 ± 0.8
	CHDS	6.6 ± 0.5
Wild chicory	MW	7.6 ± 0.3
	CHDS	6.8 ± 0.7

Figure 1

Removale acrylic safety shield

Cooling fan

Air exit

Cabinet cover

Removable sliding door

Temperature control terminal

Aluminum heating block
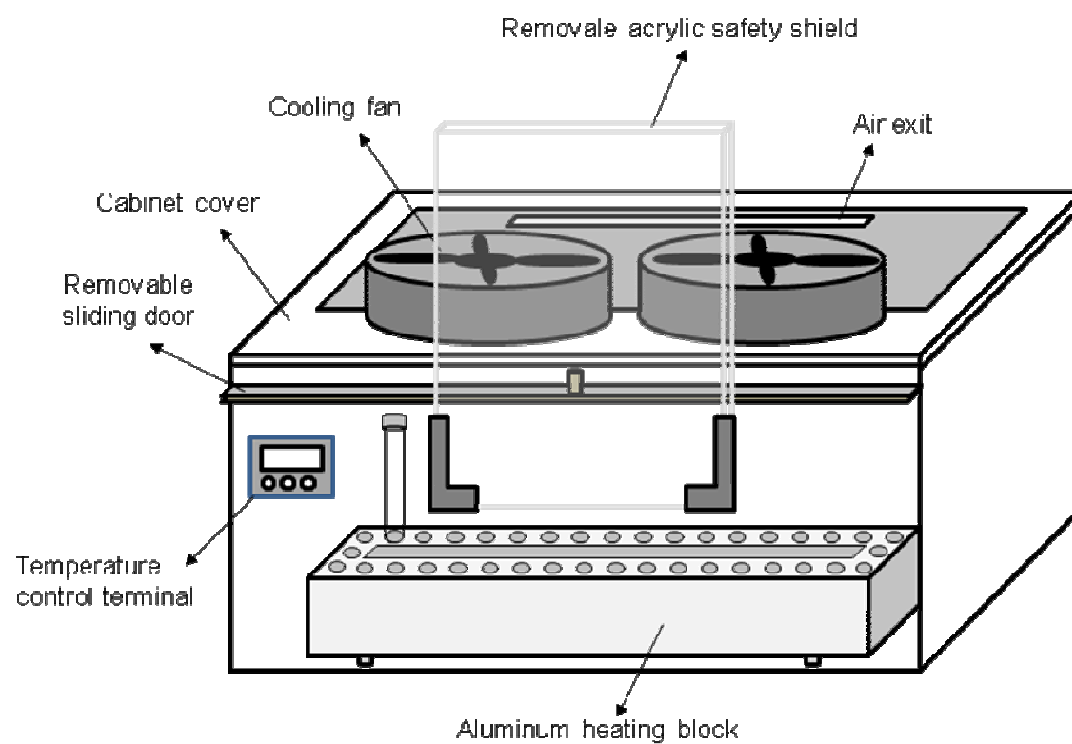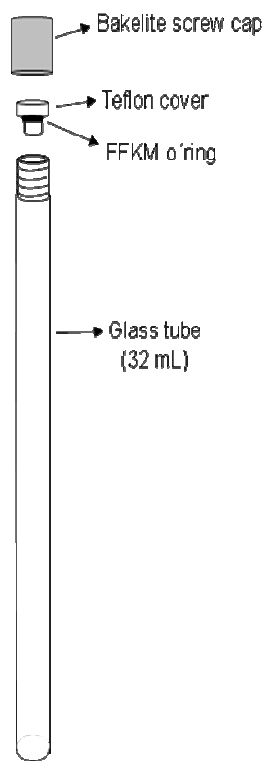
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Figure 2

Bakelite screw cap

Teflon cover

FFKM o'ring

Glass tube
(32 mL)