TECHNICAL NOTE

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A convective heated digestion system with closed vessels: a new digestor for elemental inorganic analysis†

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This work presents a new, robust, and reliable conductively heated digestion system with closed vessels (CHDS) for the preparation of plant materials for elemental determination by inductively coupled plasma optical emission spectrometry (ICP OES). The proposed system combines the simplicity of a 24-slot resistively heated aluminum block with the key advantages inherent to closed vessels. Fundamental studies on temperature and pressure were also performed and the difference between the liquid phase temperature (190 °C) and the aluminum block temperature (240 °C) was assigned to the dynamic condensation of the gaseous phase during digestion. The optimized digestion procedure was achieved for 250 mg test portions, 2.0 mL of HNO_3 (65% v v^{-1}), 1.5 mL of H_2O_2 (30% v v^{-1}), and a temperature of 240 °C, with a heating rate of 10 °C min^{-1} and dwell time of 20 min. Under these conditions, the residual carbon contents in digests were generally below 700 mg L^{-1}. The performance of the CHDS was checked by analyzing plant certified reference materials and the determined concentrations of B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn presented no significant differences when compared to the certified values at the 95% confidence level. Recoveries in the 75–108% range and relative standard deviations ≤3% (n = 3) were typically obtained. Also, the system was applied to the analysis of sixteen samples from an interlaboratory trial, and a comparison with alternative single reaction chamber microwave-assisted digestion (SRC MWAD) and open vessel nitro-perchloric decomposition (NP) digestion methods also showed equivalence at a 95% confidence level in most cases. The CHDS system based on thermally convective heating allowed digestion of up to 24 different plant materials in *ca.* 50 min, but it is not limited to samples and analytes chosen in this work: the CHDS is designed for typical use in elemental inorganic analysis techniques that require liquid-based sample introduction.

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Introduction

Most modern spectrometric methods such as inductively coupled plasma optical emission spectrometry (ICP OES) or inductively coupled plasma mass spectrometry (ICP-MS) rely on sample introduction systems based on liquid solutions, whether using discrete sample volumes or pneumatic nebulization.[1] Despite the high energy and temperature of ICPs, which make this source inherently robust and tolerant to a wide variety of samples, a deficient sample preparation or unsuitable configuration of the sample introduction system can deteriorate the analytical signal, increase the background noise, increase the detection limits and cause unexpected interference.[2] Thus, the analysis of solid samples must be preceded by a sample preparation step, in order to produce clear aqueous solutions, suitable for introduction into the measurement instrument. Regardless of the sample preparation method chosen, this step is crucial for the quality of the results, being also the most subject to errors, time consuming and costly in the analysis process. For organic samples, the digestion procedures are among the most employed, due to the capacity to efficiently eliminate the matrix while promoting the analyte to the liquid phase.[3]

Digestion using open vessels in heating blocks or hotplates is a simpler and cost-effective approach for sample preparation. Despite the advantages, the temperatures reached in these systems at atmospheric pressure are limited to the boiling point of the acids or mixtures employed as reactants, which may

impair proper matrix decomposition and increase the susceptibility to interference. Furthermore, open systems are more time-consuming and prone to contamination and risks of analyte loss, which may impact the accuracy and limits of detection for key elements. Nevertheless, acid digestion in open systems is still widely used, in the agricultural industry. In this sense, the digestion efficiency and sample throughput may be further improved when closed vessels are employed.[3]

Microwave-assisted digestion or microwave-induced combustion in closed vessels is the most modern method for the decomposition of organic samples, although the former method is still the most commonly used for trace element analysis.[4] Relying on the system pressurization provided by closed vessels, microwave-assisted digestion (MWAD) may reach higher temperatures and therefore provide better decomposition efficiency in a shorter time. Higher operational safety, minimization of contamination and analyte loss risks, lower reagent consumption and cleaner analytical blanks may also be pointed as advantages for MWAD.[5] On the other hand, instrumentation and maintenance are relatively expensive and, in most systems, the simultaneous digestion of different matrices is not allowed. Thus, the proposition of simple, efficient, and affordable methods for sample digestion in closed systems is still relevant for both research and routine analysis.

The conductively heated digestion system with closed vessels (CHDS) was proposed in 2014 for plant analysis[6] and it has been successfully applied to different matrices such as agriculture materials (biomass, biochar, oyster shell flour, bone meal and swine manure),[10] plant tissues (sugarcane, lettuce, kale, white cabbage, arugula, spinach, wild chicory and senna),[6,7] foods (raw meats, milk, chocolate, and coffee)[8,9] and others.[11] Recently, that system was redesigned, underwent significant technological changes, and became commercially available in 2023 by the release of the new Simplify Digestor (Vert Technologies). This benchtop digestor is attractive because it combines simplicity, user-friendly operation and the low cost of the resistively heated aluminum block with the advantages of closed-vessel digestion.

The instrument is mounted in a digestion cabinet resistant to acid fumes with venting systems and comprises an aluminum block with 24 slots equipped with a temperature control terminal. Digestion is performed in quartz tubes with a capacity of 45 mL that are sealed with PTFE lids equipped with built-in breakable safety disks designed for 28 bar maximum pressure. So far, the digestor has been proven as a versatile and affordable option for sample preparation aiming at elemental determination, due to its high digestion efficiency, lower reagent consumption, analytical blanks adequate for trace analysis and the capacity to perform simultaneous digestion of different matrices in the same run.[9–11]

In this work, the performance of the Simplify Digestor was further investigated by analyzing plant certified reference materials with emphasis on the determination of B, C, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn by ICP OES. The volumes of reactants (HNO_3 and H_2O_2) as well as the temperature were optimized. The pressure and temperature of the liquid phase were measured during the digestion to provide further information

for better understanding the fundamentals of chemical reactions in this system. Residual carbon content (RCC) was monitored to check the digestion efficiency. The proposed method was applied to sixteen plant materials (leaves and grains of a wide variety of plants) from an interlaboratory trial and the results were compared to those obtained either by microwave-assisted wet digestion using a nitric-peroxide mixture or nitric-perchloric acid in the open digestion method.

Experimental

Instrumentation

Sample and Standard Reference Material (SRM) digestion was conducted in a conductively heated digestion system (CHDS), model Simplify Digestor (Vert Technologies, São Paulo, Brazil). The equipment is provided with a 1600 W powered aluminum block used for heating, equipped with a cooling system for enhancing the cooling step after the heating procedure, with the maximum digestion temperature at 350 °C. The block was positioned inside a thermally insulated heating chamber, preventing the heating of the other system parts. The maximum temperature reached on the upper plate (*i.e.*, digestion chamber floor) is ~50 °C during the heating cycle, providing operator safety when opening the flasks. The benchtop Simplify Digestor is equipped with a Programmable Logic Controller to manage the heating program and provide communication with the automatic raising system of the vessels, which is lowered at the beginning of heating and raised to the initial position after the end of heating. The fans below the aluminum block are activated automatically during the cooling step. The digestion chamber features a venting system connected to an output hose, which is able to exhaust acid fumes and also create an air flux that refrigerates the upper part of the digestion vessels. An overview picture of the digestion system is shown in Fig. 1.

The digestion vessels comprise a polytetrafluorethylene (PTFE) lid, 45 mL quartz tubes (SiO_2 with 99.9% purity), and a polyvinyl chloride (PVC) fixture that connects the lid to the tube. The PTFE lid features a top screw to relieve the residual pressure after digestion. Additionally, a rupture seal with a maximum pressure of 28 bar is located on the side of the PTFE lid.

For temperature and pressure studies a special quartz flask (Fig. 2a) was developed to record the temperature directly in the liquid phase using a digital thermometer with a thermocouple probe TH-1600 (Instrutherm, São Paulo, Brazil) with a maximum temperature of 220 °C. That flask has a side access for inserting a thermocouple probe directly into the liquid phase (Fig. 2b), which is filled with 0.5 mL of mineral oil (100% purity) for the stability of the temperature record (Fig. 2c). An analog manometer with an indicator manifold (Pressage, São Paulo, Brazil) with a maximum pressure of 60 bar was used to record the internal pressure of the flask. The manometer and the flask were properly connected by means of a high-pressure hose with a PTFE interior, which was filled with deionized water to reduce the oxidation of the metallic components of the manometer and the dead volume of the apparatus (Fig. 2d).

The manometer connected to the upper part of the flask does not compromise either the functioning of the rupture seal or
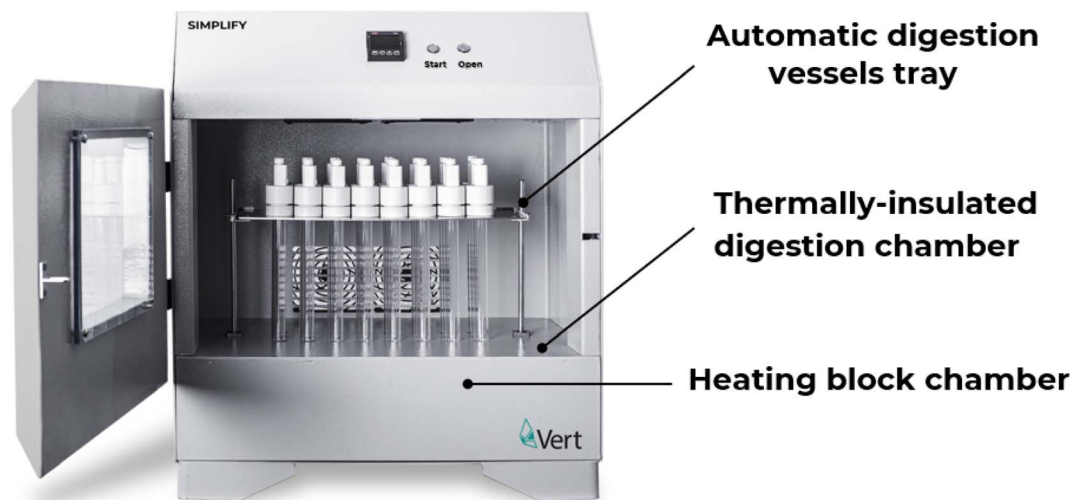
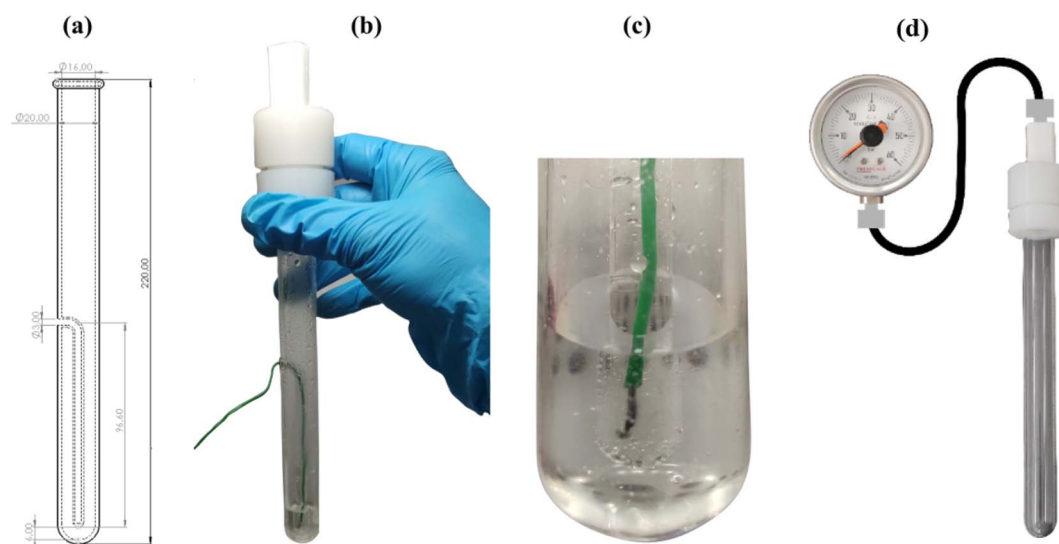Fig. 1 Overview of the inside part of the Simplify Digestor.

Fig. 2 Quartz vessel and instrumental apparatus developed for the monitoring of liquid phase temperature and system pressure: (a) schematics of the vessel with dimensions in millimeters, (b) real vessel picture, (c) details of the interface of the thermometer and the liquid phase, and (d) analog manometer coupled for pressure monitoring.

the pressure relief in the flask at the end of digestion. The temperature and internal pressure data of the flask were collected manually from the manometer and digital thermometer readings, respectively, in the footage taken with a smartphone during the heating program.

The determination of B, C, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn in CRM and plant digests employed a Thermo Scientific iCAP 6500 Duo inductively coupled plasma optical emission spectrometer (Waltham, USA) equipped with axially and radially viewed plasma, a charge injection device (CID), an Echelle polychromator (166.25 to 847.00 nm) and a 27.12 MHz radiofrequency source. Argon with a purity of 99.998% (White Martins, Sertãozinho, Brazil) was used to generate and maintain the plasma and to introduce the sample aerosol. The operating parameters are shown in Table 1.

Reagents, reference solutions and samples

Analytical solutions were prepared using distilled-deionized water (resistivity $\geq$ 18.2 MΩ.cm) obtained using a reverse osmosis system (Gehaka, São Paulo, Brazil). Trace-metal-grade $HClO_4$ 70% v v^{-1} (Merck, Darmstadt, Germany), HNO_3 65% v v^{-1} (Synth, Diadema, Brazil) purified in a sub boiling system and H_2O_2 30% w w^{-1} (Merck, Darmstadt, Germany) were employed for sample digestion. Single-element 1000 $\pm$ 1 mg L^{-1} stock solutions of B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn (Specsol, Jacareí, Brazil) were used to obtain the calibration curves. Carbon stock solution was prepared by direct dissolution of oxalic acid (Merck, Darmstadt, Germany), used as the primary standard for the determination of residual carbon content.

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Table 1 Instrumental operating parameters used for ICP OES data acquisition

Instrumental parameters	Operating conditions
Power supply	1150 W
Plasma gas-flow	12 L min^{-1}
Auxiliary gas-flow	0.5 L min^{-1}
Nebulizer gas-flow	0.7 L min^{-1}
Spray chamber	Cyclonic
Nebulizer	Concentric
Operation mode	Axial
Wavelengths monitored[a]	B(I) 249.773 nm, Cu(I) 324.754 nm, Fe(II) 238.204 nm, Mn(II) 259.373 nm, Zn(I) 213.857 nm, Ca(I) 422.673 nm, K(I) 766.490 nm, Mg(II) 279.553 nm, P(I) 213.618 nm, S(I) 180.731 nm and C(I) 193.026 nm

[a] (I) Atomic and (II) ionic lines.

Three plant standard reference materials (1547 Peach Leaves, 1515 Apple Leaves, and 1570a Spinach Leaves) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used for method validation. Dried plant tissue samples were obtained from the 2022 trail of the Interlaboratory Analysis Program for Plant Tissues – PIATV (Piracicaba, Brazil). This PIATV program was based on 160 participating laboratories dedicated to promoting good laboratory practices and quality in the analysis of leaves. The PIATV samples were composed of 16 laboratory samples of several crops presenting a wide range of macro- and micro-nutrients concentrations: four samples of maize (*Zea mays*) grains and 1 sample each of soy (*Glycine max*), sorghum (*Sorghum bicolor*), eucalyptus (*Eucalyptus* sp), figueira (*Ficus* sp), acerola (*Malpighia emarginata*), persimmon (*Diospyros kaki*), macadamia (*Macadamia* sp), teak (*Tectona grandis*), grass (Poaceae sp), palm tree (Arecaceae sp), pau rei (*Pterygota brasiliensis*) and caja mirin (*Spondias mombin*) leaves.

Sample preparation procedures

The optimization of the volume of reagents (HNO$_3$ and H$_2$O$_2$) and temperature for the digestion in the CHDS was univariately studied using 250 mg of sugarcane leaves. Volumes of 1.0, 1.5, 2.0 and 2.5 mL of HNO$_3$ 65% v v^{-1} were initially evaluated. During the HNO$_3$ optimization, 1.0 mL of H$_2$O$_2$ and a temperature of 220 °C were kept constant. After the optimization of acid concentration, volumes of 1.0, 1.5 and 2.0 mL of H$_2$O$_2$ were also evaluated at the same temperature. Finally, the optimal mixture of HNO$_3$ and H$_2$O$_2$ was employed in digestion at 220, 230 and 240 °C. All experiments were conducted using a heating rate of 10 °C min^{-1}, from room temperature to the maximum temperature evaluated (*ca.* 20 min), and remained at this plateau for 20 min. The final volumes were made to 25 mL with ultrapure water. The optimization was performed considering the internal pressure of the vessel and the yellow color intensity in the final solution, as it may be an indicative of low digestion efficiency. The coloring intensity was monitored by the inverse of the reflectance signal for the blue channel (1/B), obtained from a smartphone image analyzed with Inkscape software using the RGB color system. This channel was selected as the blue color is complementary to yellow, and thus maximum reflectance is expected.

Comparative single reaction chamber microwave-assisted digestion (SRC MWAD) was performed using 250 mg test portions and a mixture of 6.0 mL of HNO$_3$ 20% v v^{-1} and 1.0 mL of H$_2$O$_2$ 30% v v^{-1}. The samples were digested under the following heating program: (i) 5 min ramp to 100 °C, (ii) 15 min ramp to 180 °C, (iii) 15 min ramp to 240 °C and (iv) 10 min hold at 240 °C. After cooling down, the final volumes were made up to 25 mL with ultrapure water. The other comparative method based on nitro-perchloric digestion (NP) in a heating block with open vessels was performed using sample masses of 500 mg and 5 mL of HNO$_3$ 65% v v^{-1}. The samples were digested as follows: (i) 60 min ramp to 180 °C, (ii) 60 min plateau at 180 °C, (iii) 60 min cooling down followed by the addition of 2 mL HClO$_4$, (iv) 60 min ramp to 210 °C and (v) 60 min hold at 210 °C. After cooling to room temperature, the final volumes were made to 50 mL with ultrapure water.

Results and discussion

Optimization and fundamental studies of temperature and pressure

A special quartz flask (Fig. 2) and other conventional quartz flasks were used for digestion of SRMs and PIATV samples. In the first experiment, different volumes (1.0, 1.5, 2.0 and 2.5 mL) of concentrated HNO$_3$ with a fixed sample mass, volume of 1.0 mL of H$_2$O$_2$ and temperature of 220 °C were evaluated. Under these conditions, a decrease in the intensity of the yellowish color in the final digestates was observed as the volume of nitric acid increased. In this case, a clean solution was obtained when 2.0 mL of HNO$_3$ was used. The use of 2.0 mL of HNO$_3$ and 2.0 mL of H$_2$O$_2$ caused a sudden increase in pressure to 17 bar, due to decomposition of H$_2$O$_2$ into H$_2$O and O$_2$. Therefore, considering the increase in H$_2$O$_2$ volumes (1.0 and 1.5 mL), keeping constant 2.0 mL of HNO$_3$ and temperature (220 °C) it was possible to observe a decreased in the pressure inside the quartz vessel (12 to 10 bars), as shown in Fig. 3a (conditions I and II, respectively). The pressure reduction is possible due to the greater amount of O$_2$ generated during the peroxide decomposition, which reacts with NO and produces NO$_2$. The regeneration reaction of HNO$_3$ depends on the reaction of NO$_2$ with H$_2$O and further condensation of the product (HNO$_3$) to a liquid phase, increasing the efficiency of

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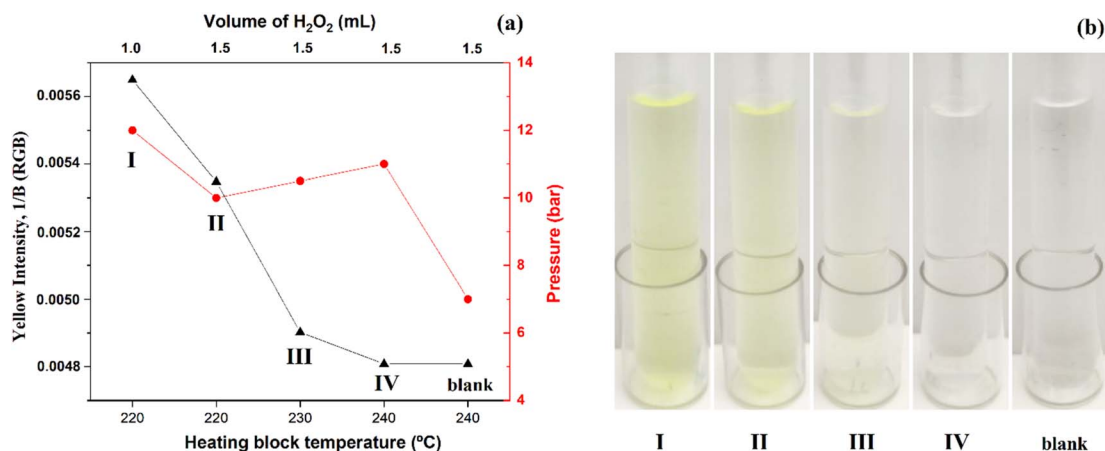*J. Anal. At. Spectrom.*, 2024, **39**, 356–363 | **359**

Fig. 3 Effect of temperature and H₂O₂ volume on the maximum pressure and yellow color intensity (a) and visual aspect of the final solutions for digestion of 250 mg of sugar cane leaves using 2.0 mL of concentrated HNO_3 (b). Conditions I–IV correspond to samples and 1/B means the inverse of the reflectance intensity measured for the blue channel in the RGB system.

digestion.[12] A volume of 1.5 mL of H_2O_2 30% v v^{-1} was selected for the next step. Therefore, a test portion of 250 mg, 1.5 mL of H_2O_2 and using 2.0 mL of HNO_3 were fixed for the optimization of the block temperature at 220, 230 and 240 °C, as depicted in Fig. 3a (conditions III, IV and blank, respectively). It was observed that higher temperatures resulted in a slight increase in the internal pressure of the flask (from 10 to 11 bar). However, digestion efficiency was further improved as the color obtained for the digestate (condition IV) was close to that of the analytical blank, at 240 °C. It was possible to notice an increase in digestion efficiency by comparing the disappearance of the yellowish color of the solution (Fig. 3b). Thus, the best conditions for sample digestion were obtained using 250 mg test portion, 2.0 mL HNO_3, 1.5 mL H_2O_2 and block temperature at 240 °C.

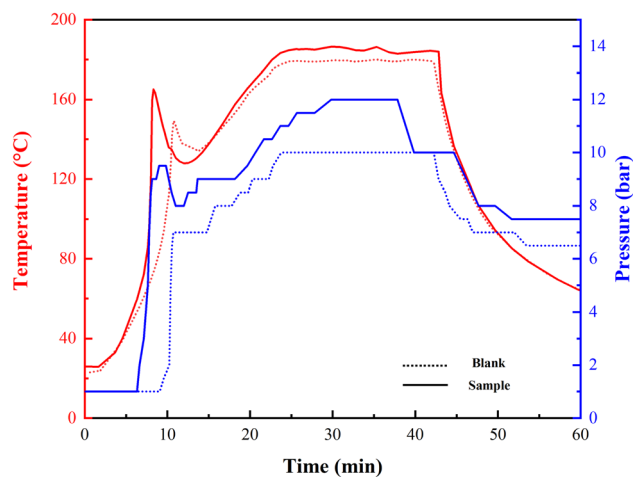Under these conditions, the internal pressure and temperature of the special quartz flask were monitored for sample and analytical blank digestion procedures (Fig. 4). The maximum pressure and temperature of the reaction medium were respectively 10 bar and 180 °C for the blank, and 12 bar and 190 °C for the sample. It was observed that the temperature of the reaction medium, in both cases, was lower than the temperature of the aluminum block (*i.e.*, 240 °C). This is mainly due to the presence of O_2 from H_2O_2 decomposition and temperature gradient over the tube length,[9] which promotes the regeneration of HNO_3 and condensation back to the liquid phase during the digestion process.[13–15] Despite the difference, the temperatures reached are high enough to decompose complex biomolecules such as carbohydrates (>140 °C), proteins (>160 °C) and fat (>180 °C), generally present in organic matrices.[3] Thus, efficient digestion and colorless final solutions are typically obtained under these conditions. In addition, Fig. 4 shows typical temperature and pressure peaks at the beginning of the heating program (around 5–10 min), which are caused by the exothermic decomposition of H_2O_2. In the case of sample digestion, the temperature of the reaction medium exceeds 160 °C, initiating the decomposition process of carbohydrates and proteins that results in brown fumes of $NO_{(g)}$ and $NO_{2(g)}$, which further contribute to increase the pressure, but they can react with O_2 or H_2O for regeneration of HNO_3.

The residual carbon content (RCC) in the digestate is a widely used parameter to measure digestion efficiency.[16] Thus, the RCC results for plant CRMs, and sample digestion obtained by the proposed closed vessel procedure using the conductively heated digestion system (CHDS) and by using single reaction chamber microwave-assisted digestion (SRC MWAD)[17] were compared as shown in Fig. 5. RCC data for NP digestion were very low (*ca.* 10 mg L^{-1} C^{-1}) and were not included in the manuscript.

The presence of high residual carbon content in the digested samples may be an issue for the determination of key elements such as As and Se by ICP-based techniques, due to signal enhancement from charge transfer reactions from carbon in the
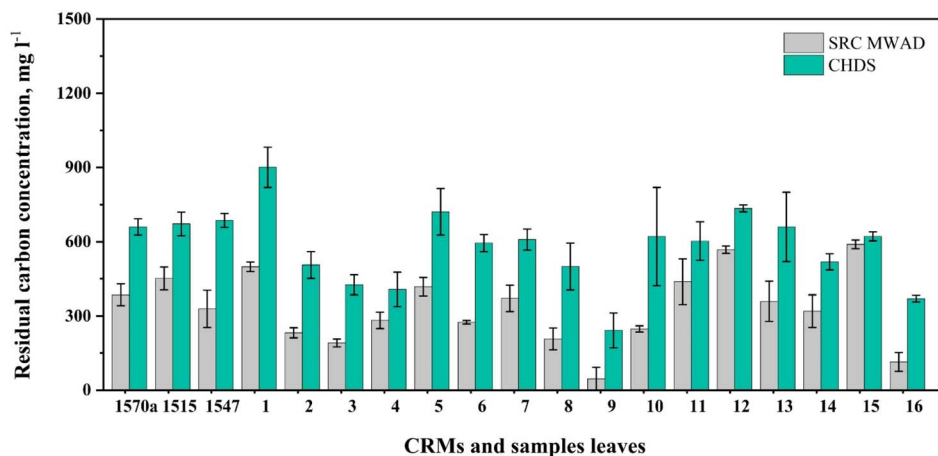

Fig. 4 Temperature and internal pressure monitoring in the vessels during the digestion of 250 mg of sugar cane leaves under the optimized experimental conditions: 2.0 mL of HNO_3, 1.5 mL of H_2O_2 and 240 °C.

Fig. 5 Residual carbon contents (RCC, mg L^{-1}) for CRMs (1570a, 1515, and 1547) and leaf samples obtained by the proposed closed vessel conductively heated digestion system (CHDS) and single reaction chamber microwave-assisted digestion (SRC MWAD).

plasma.[18,19] However the RCC obtained in this work was up to 13-fold lower than those reported in the literature, and thus the carbon effects may not be significant. It should be emphasized that carbon concentrations up to 2000 mg L^{-1} are considered compatible with most determination experiments by ICP techniques.[20] The oxidant mixture of nitric acid and perchloric acid is a classic method and is still widely used in the agricultural industry due to the exceptional oxidative power of organic matter and, consequently, low residual carbon concentrations, and inexpensive instrumentation costs (*i.e.* <US$2000). However, the HClO$_4$ used in this procedure reacts violently with organic matter and may be prone to high explosion risk. Thus, these digestates were not used for RCC comparison. In general, the concentrations of carbon in the final solutions of SRMs and plant samples were slightly higher than those obtained for microwave-assisted digestion. These results are expected

considering that liquid phase temperatures up to 240 °C were achieved in the SRC MWAD, while the CHDS reaches around 190 °C during the digestion procedure. Nevertheless, RCC data obtained by the CHDS are fit for the intended purpose, since digests with carbon concentrations lower than 2000 mg L^{-1} are considered adequate for the majority of elements determined by ICP OES and ICP-MS,[18] which demonstrates that both systems are suitable for determination of macro- and micro-nutrients.

Analysis of reference materials and laboratory samples

The performance of the CHDS was checked for the determination of macro- (P, K, Ca, Mg, and S) and micro-nutrients (B, Cu, Fe, Mn and Zn) in three plant standard certified materials (1547 peach leaves, 1515 apple leaves, and 1570a spinach leaves). For comparison purposes, those SRMs were also digested by using

Table 2 Limits of quantification (LOQ), and results for macronutrients (g kg^{-1}) and micronutrients (mg kg^{-1}) in SRMs determined ($n = 3$) by ICP OES employing digestion by CHDS, MWAD and NP methods

CRM	Method	Macronutrient concentration (g kg^{-1})					Micronutrient concentration (mg kg^{-1})				
		P	K	Ca	Mg	S	B	Cu	Fe	Mn	Zn
1570a	Certified	5.19 ± 0.07	29 ± 0.26	15.26 ± 0.66	9[a]	5[a]	37.7 ± 1.2	12.22 ± 0.86	230[a]	76 ± 1.2	82.3 ± 3.9
	CHDS	4.8 ± 0.2	27.3 ± 1.0	13.1 ± 0.8	8.4 ± 0.2	4.0 ± 0.4	35 ± 1	11.9 ± 0.3	233 ± 6	73 ± 2	68 ± 2[b]
	MWAD	4.9 ± 0.2	24.5 ± 1.2[b]	12 ± 1	7.9 ± 0.4	4.4 ± 0.9	35.4 ± 0.8	11.8 ± 0.3	242 ± 7	73 ± 2	68 ± 3[b]
	NP	4.9 ± 0.1	25.0 ± 0.5[b]	12.5 ± 0.9	7.8 ± 0.4	4.0 ± 0.5	—	13.8 ± 0.6	240 ± 3	73 ± 1	67 ± 3[b]
1515	Certified	1.59 ± 0.07	16.08 ± 0.21	15.25 ± 0.01	2.71 ± 0.12	1.8[a]	27.6 ± 2.8	5.69 ± 0.13	82.7 ± 2.6	54.1 ± 1.1	12.45 ± 0.43
	CHDS	1.5 ± 0.1	17.5 ± 0.7	14.4 ± 0.8	2.5 ± 0.1	1.6 ± 0.1	24.8 ± 0.9	5.1 ± 0.3	64 ± 2[b]	50 ± 2	11.4 ± 0.4
	MWAD	1.52 ± 0.05	17 ± 1	14 ± 1	2.6 ± 0.1	1.65 ± 0.05	26.0 ± 0.2	5.2 ± 0.2	66.3 ± 0.9[b]	51 ± 1	12.4 ± 0.9
	NP	1.59 ± 0.02	17.0 ± 0.8	16.7 ± 0.8	2.9 ± 0.1	1.77 ± 0.03	—	6.4 ± 0.5	66.2 ± 0.5[b]	53 ± 1	9.3 ± 0.5[b]
1547	Certified	1.37 ± 0.08	24.33 ± 0.38	15.59 ± 0.16	4.32 ± 0.15	2[a]	28.37 ± 0.81	3.75 ± 0.37	220 ± 7	97.8 ± 1.8	17.97 ± 0.53
	CHDS	1.38 ± 0.09	24 ± 2	18 ± 1	4.6 ± 0.4	1.6 ± 0.2	26.0 ± 0.8	3.5 ± 0.1	197 ± 7	101 ± 4	17.3 ± 0.6
	MWAD	1.32 ± 0.09	24 ± 4	16 ± 3	4.3 ± 0.6	1.7 ± 0.4	25.8 ± 0.9	3.16 ± 0.2	196 ± 8	96.2 ± 0.9	17.0 ± 0.4
	NP	1.35 ± 0.04	23 ± 1	16 ± 1	4.1 ± 0.2	1.5 ± 0.3	—	3.6 ± 0.1	187 ± 11	96.5 ± 0.5	14 ± 1[b]
LOQ	CHDS	0.001	0.002	0.06	0.002	0.008	0.3	0.6	6	0.1	0.9
	MWAD	0.0009	0.002	0.04	0.001	0.01	0.4	0.6	13	0.2	1
	NP	0.001	0.007	0.03	0.008	0.02	—	0.1	17	0.2	2

[a] Uncertified values. [b] Non-concordant values at the 95% confidence level (*t*-test).

the SRC MWAD and nitric-perchloric acid (NP) procedures. The results of the analyte concentrations and limits of quantification (LOQs) obtained for each digestion procedures are shown in Table 2. The concentrations obtained by each method were compared with the corresponding certified values using the unpaired t-test at the 95% confidence level. In general, no significant differences were observed between the certified and determined values, except for K in SRM 1570a (SR MWAD and NP), Fe in SRM 1515 (all procedures), and Zn in SRM 1570a (all procedures) and NP digestates of SRMs 1547 and 1515. For Fe, the low recovery rates may be related to the presence of silicates and possible formation of less soluble complexes with iron, as no complexing acids were employed during the digestion. Despite the absence of certified values for S in all materials, all values were close to the informative value and concordant among themselves. It is important to consider that external calibration was performed in all cases, which indicated that the matrix was properly decomposed and matrix effects based on carbon were negligible for the elements evaluated in this work.

The limits of quantification were in the 0.0009–0.06 g kg^{-1} range for macronutrients (P, K, Ca, Mg and S) and in the 0.1–17 mg kg^{-1} range for micronutrients (B, Cu, Fe, Mn and Zn), which may be considered suitable for their determination in plant tissues. The comparison of the different methods shows equivalent values for SR MWAD and CHDS, and generally higher values for NP. For boron, the determination was not conducted due to the incompatibility with the NP method, which is related to the volatilization of B species under elevated temperatures and acidic conditions in the reaction medium.

The performance of the Simplify Digestor was also evaluated by digesting sixteen plant samples using an interlaboratory program, and all materials were also digested by the SR MWAD and nitric-perchloric acid (NP) procedures (ESI 1 and 2†). The determined concentrations were in the 0.54–4.6 g kg^{-1} range for P, 2.96–34 g kg^{-1} for K, 0.14–46 g kg^{-1} for Ca, 0.61–10.9 g kg^{-1} for Mg, 0.69–3.78 g kg^{-1} for S, 5.8–76 mg kg^{-1} for B, 1.5–14.8 mg kg^{-1} for Cu, 132–572 mg kg^{-1} for Fe, 4.2–1475 mg kg^{-1} for Mn and 7.2–36 mg kg^{-1} for Zn, and the results showed no
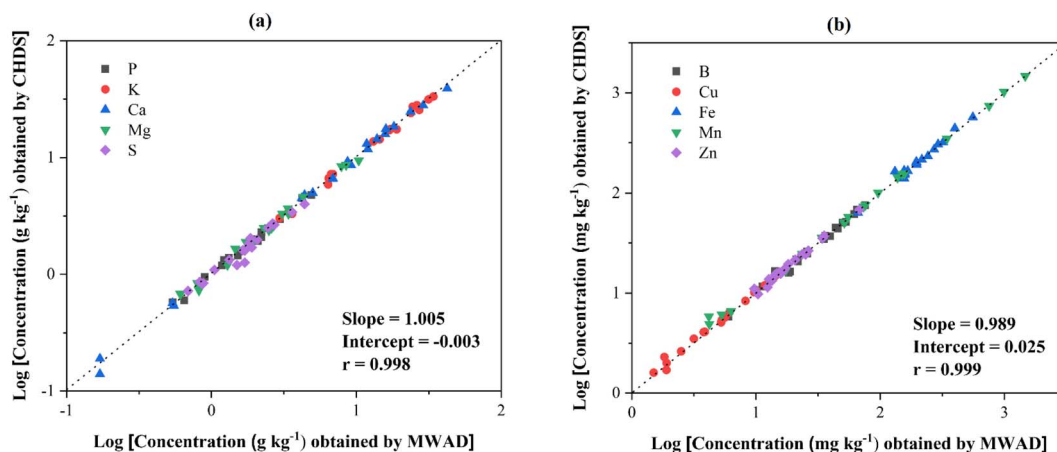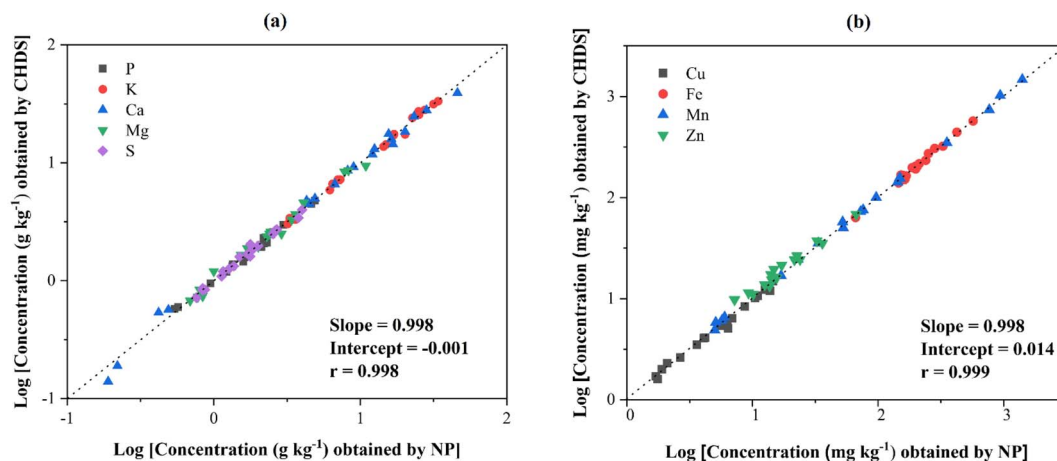

Fig. 6 Correlation plot for the log of concentrations of macronutrients (a) and micronutrients (b) determined by ICP OES after CHDS digestion (y-axis) and SRC MWAD digestion (x-axis). Dashed lines are the identity function $y = x$.

Fig. 7 Correlation plot for the log of concentrations of macronutrients (a) and micronutrients (b) determined by ICP OES after CHDS digestion (y-axis) and NP digestion (x-axis). Dashed lines are the identity function $y = x$.

significative difference among digestion methods at a 95% confidence level (unpaired *t*-test). Relative standard deviations were ≤10%.

Correlation plots between analyte concentrations found by CHDS (*y*-axis) and analyte concentrations found by SRC MWAD (*x*-axis) (Fig. 6), and analyte concentrations found by CHDS (*y*-axis), and analyte concentrations found by NP (*x*-axis) (Fig. 7) showed that correlation coefficients (*r*) were better than 0.997 (CHDS *vs.* MWAD) and 0.995 (CHDS *vs.* NP). For the CHDS *vs.* MWAD plots, slopes were close to 0.991 (macronutrients) and 1.01 (micronutrients); for the CHDS *vs.* NP plots, slopes were close to 0.96 and 1.04 for macro- and micro-nutrients, respectively.

Conclusions

The proposed digestion system based on conductively heated wet digestion in closed vessels is a reliable alternative for organic sample preparation aiming elemental determination by plasma-based techniques. Optimal conditions for plant materials involved a sample mass of 250 mg, 2.0 mL of HNO_3, 1.5 mL of H_2O_2 and block temperature set at 240 °C. Under these conditions up to 190 °C was achieved for liquid phase temperatures and 700 mg L^{-1} was obtained for residual carbon contents. Concerning the digestion efficiency, the CHDS was comparable with SRC MWAD and the RCC values were considered adequate for ICP analysis of plants for most elements. The limits of quantification were also comparable in both cases as cleaner blanks were typically obtained when quartz closed vessels are employed for the CHDS. The method has proved to be accurate as no significant differences between certified and determined values were found. Comparative results between CHDS, SRC MWAD and NP digestion showed equivalence between then for the determination of macro- and micro-nutrients in plant materials. The CHDS may be considered simple and presents very affordable acquisition, operation and maintenance costs and high sample throughput due to its capacity to simultaneously digest 24 different samples in 50 min, including the cooling step. In comparison with NP digestion, which is often found in routine labs running official methodologies for plant analysis, the CHDS has proven to be a highly effective, faster, and safer alternative.

Conflicts of interest

Alan Lima Vieira and Gabriel Gustinelli Arantes de Carvalho are associated with Vert Chemicals.

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