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Determination of Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Na, Se, and Zn in Foodstuffs by Atomic Spectrometry After Sample Preparation Using a Low-Cost Closed-Vessel Conductively Heated Digestion System

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Abstract Establishing fast, simple, low-cost, and efficient sample preparation procedures to determine elements in foodstuffs is a relevant aspect for nutritional and health purposes. For this reason, the recently proposed closed-vessel conductively heated digestion system (CHDS) was evaluated for the digestion of milk powder, chocolate powder, and soluble coffee samples aiming for Ca, Cu, Fe, K, Mg, Mn, Na, and Zn determinations by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) and Cd, Mo, and Se determinations by inductively coupled plasma mass spectrometry with tandem configuration (ICP-MS/MS). The accuracy was evaluated by analyzing two milk certified reference materials digested by the CHDS and a microwave oven for comparison. When using the CHDS, recoveries for the analytes varied from 91 to 104 %. For microwave digestions, recoveries within the 94–109 % intervals were obtained. The method was then applied to the samples. For comparative purposes, the analytes were also determined in the samples after microwave digestion, and the results between the two digestion systems showed no differences based on a paired t test at a 95 % confidence level. Similar analytical blanks were obtained because quartz digestion tubes were used in both digestion systems. The CHDS with quartz tubes is an interesting alternative for laboratories dedicated to large-scale routine

analysis because volatile elements usually found in very low concentrations in food samples such as Cd and Se can also be determined.

Introduction

Essential elements such as Ca, Cu, Fe, Mg, Mn, and Zn are frequently added in several industrialized food products to meet nutritional requirements (Inam and Somer 2000). Despite their great importance in human health, some of these elements can also present toxic effects when in high concentrations. Considering those aspects, the information about the metal content in industrialized food samples is a relevant aspect for nutritional and health purposes (Martino et al. 2000). Although the Codex Alimentarius Commission does not establish maximum concentration levels for essential elements in foodstuffs, determining the concentration of essential elements such as Fe, Cu, Mn, Zn, Ca, Mg, Na, K, Se, and Mo for nutritional purposes, as well as toxic elements such as Cd, is considered a recent trend in the literature (Bizzi et al. 2011a; Terol et al. 2010; Karadjova et al. 2000). Therefore, it is important to develop fast, simple, low-cost, and efficient sample preparation and analytical procedures for quality control.

Among the techniques used to determine metals in food samples, high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) can be considered an interesting alternative since it achieves limits of detection five times better in comparison to line-source flame atomic absorption spectrometry (LS FAAS) and allows multielemental analysis in fast sequential mode (Welz 2005). Comparing to

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conventional LS FAAS, possibilities of background correction and elimination of interferences are increased because the spectral environment of the analytical line can be completely explored. The greatest advantage of HR-CS FAAS in relation to LS FAAS is the need for only one single lamp for all elements instead of one lamp for each element (Welz et al. 2003, 2007; Becker-Ross et al. 2006; Villanueva-Alonso et al. 2009). In the recent years, it was demonstrated in literature a great interest in applying HR-CS FAAS to determine various analytes in food samples (Paz-Rodríguez et al. 2015; Ozbek and Baysal 2015; Li and Chen 2014; Brandao et al. 2010, 2011).

Inductively coupled plasma mass spectrometry (ICP-MS) is an important technique for trace element analysis due to its high sensitivity, multielement capability, and high sample throughput (Becker 2007). However, the main drawback to perform trace element analysis by ICP-MS is related to spectral interferences. In order to increase the potential to deal with spectral overlaps, an inductively coupled plasma tandem mass spectrometer (ICP-MS/MS) was recently proposed. It presents an octopole reaction system (ORS^3) located in-between two quadrupole analyzers and allows the operation of the ICP-MS instrument in MS/MS mode. This configuration improves the control of collision and reaction processes inside the ORS^3 due to the pre-selected mass/charge ratio, and it has been successfully applied in order to determine several elements in different types of sample (Balcaen et al. 2013; Amais et al. 2014, 2015; Amaral et al. 2015; Virgilio et al. 2015).

The sample preparation procedure must be reproducible and adequate to the sample introduction system. In addition, from a green chemistry perspective, sample decomposition with low consumption of reagents is also desirable (Bizzi et al. 2010, 2011a, b; Castro et al. 2009). The recently proposed closed-vessel conductively heated digestion system (CHDS) was applied for botanical samples and proved to be an efficient and cheaper alternative to closed-vessel microwave-assisted digestion (Miranda et al. 2014a, b). The CHDS can be considered an excellent option for sample preparation in atomic spectroscopy analysis due to the low costs

involved in acquisition and maintenance, efficient digestion using small volumes of reagents, and low analytical blanks.

The goal of this study was the evaluation of the CHDS with quartz tubes for the digestion of milk powder, chocolate powder, and soluble coffee samples aiming for Ca, Cu, Fe, K, Mg, Mn, Na, and Zn determinations by HR-CS FAAS and Cd, Mo, and Se determinations by ICP-MS/MS.

Experimental

Instrumentation

The CHDS is depicted in Fig. 1. The system comprises an aluminum heating block with 28 orifices (18.2 mm diameter, 50 mm deep) for quartz digestion tubes (15 mm internal diameter, 18 mm outside diameter, 200 mm height, and internal volume of 34 mL), a temperature control terminal, two cooling fans, and a digestion cabinet resistant to acid fumes (polypropylene coated inside). The equipment is operated via an industrial grade control terminal where the heating program is created and automatically followed by the system via a proportional-integral-derivative controller. The quartz digestion tube is maintained sealed during digestions by a Teflon cover containing a perfluorinated (FFKM) o-ring, which is pressed by the screw cap. The screw cap works as a safety seal and allows the integrity of the vessel in case of overpressure since it is more fragile than the tube. Samples and certified reference materials (CRMs) were digested using the CHDS. Further details about the CHDS can be found elsewhere (Miranda et al. 2014b).

A closed-vessel microwave (MW) oven (Multiwave, Anton Paar, Graz, Austria) equipped with a 6 position rotor for quartz vessels (internal volume of 50 mL, minimum filling volume of 6 mL) was employed as a comparative digestion system.

The micronutrients (Cu, Fe, Mn, and Zn) and the macronutrients (Ca, Mg, K, and Na) were determined when employing a ContrAA 300 high-resolution continuum source
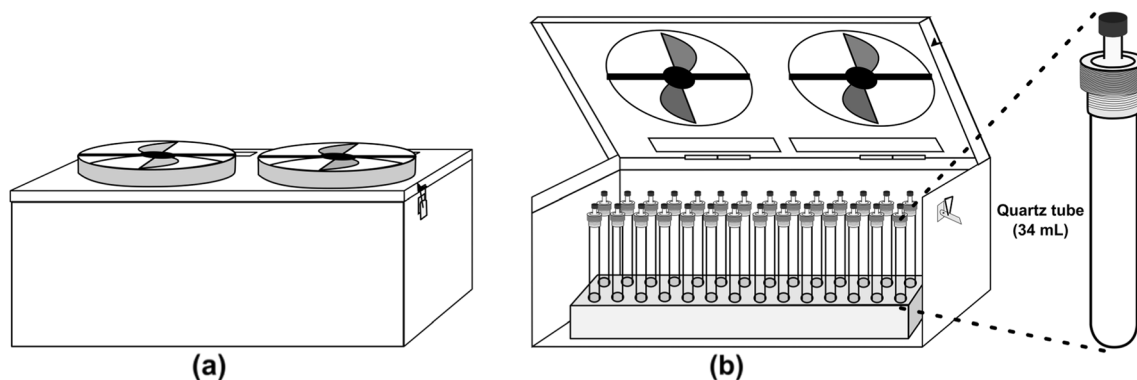
Fig. 1 Schematic setup details of the CHDS with quartz tubes

Quartz tube (34 mL)

Table 1 Instrumental operating conditions for HR-CS FAAS

Analyte	Wavelength (nm)	Air gas flow (L h^{-1})	C$_2$H$_2$ gas flow (L h^{-1})	Burner height (mm)
Ca	239.856	508	70	7
K	404.414	508	70	7
Mg	202.588	508	60	6
Na	330.237	508	80	6
Zn	213.857	508	60	6
Fe	248.327	508	65	7
Cu	324.754	508	40	6
Mn	279.482	508	80	6

flame atomic absorption spectrometer (Analytik Jena, Jena, Germany) equipped with a Xenon short-arc lamp (XBO 301, 300 W, GLE, Berlin, Germany) operating in a hot-spot mode as a continuum radiation source. High-purity acetylene (99.7 %, Air Liquid, São Paulo, Brazil) and air were used as fuel and oxidant gases, respectively. Micronutrients were determined at the main lines, macronutrients at alternative lines, and the aspiration rate was fixed at 5.0 mL min^{-1}. The instrumental operating conditions for analyte determination by HR-CS FAAS are described in Table 1.

Cadmium, Mo and Se determinations were carried out using an Agilent 8800 ICP-MS (Agilent Technologies, Japan) equipped with two quadrupole mass analyzers (Q1 and Q2), located in-between an octopole reaction system (ORS^3). Pure oxygen (≥99.999 %, Air Products, São Paulo, SP, Brazil) was used as a reaction gas to generate the oxide species of the analytes into ORS^3. The ICP-MS/MS operational parameters are shown in Table 2.

Reagents, Analytical Solutions, and Samples

Deionized water (18-ΩM-cm resistivity) obtained with a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q™ Academic® deionizer system (Millipore, Bedford, MA, USA) were used to prepare all solutions. All glassware and polypropylene flasks were washed with Extran® laboratory detergent (Merck, Darmstadt, Germany), soaked in 10 % (v/v) HNO$_3$ for 24 h, and rinsed with deionized water prior to use; 65 % m/m Suprapur® nitric acid (Merck, Darmstadt, Germany) and 30 % m/v H$_2$O$_2$ (Merck, Darmstadt, Germany) were used for sample digestion. Cd, Mo, and Se individual stock standards (SpecSol, São Paulo, Brazil) containing 1000 mg L^{-1} were used to prepare analytical standards by sequential dilution in 5 % (v/v) HNO$_3$, in the range of 0.025–10 μg L^{-1} for ICP-MS. Analytical calibration solutions of Ca, Cu, Fe, K, Mg, Mn, Na, and Zn were prepared by appropriate dilution of 10,000 mg L^{-1} individual stock standards (SpecSol, São Paulo, Brazil) in 1 % (m/v) La media for HR-CS FAAS. A 5 % (m/v) La stock solution was prepared by dissolving 58.6 g La$_2$O$_3$ (Merck, Darmstadt, Germany) in

250 mL of 37 % m/m hydrochloric acid (Spectrum, Gardena, USA) and making the final volume up to 1000 mL with deionized water. Two milk CRMs from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used to check the accuracy and precision: 1549 non-fat milk powder and 8435 whole milk powder. Milk powder, chocolate powder, and soluble coffee samples were purchased at a local market in Araraquara, São Paulo, Brazil.

CHDS Digestion Procedure

In order to avoid overpressure when using the CHDS, the sample mass is limited to 200 mg, a pre-digestion is performed to reduce the incidence of fast exothermic reactions and 1 mL of 30 % m/v H$_2$O$_2$ is added in the acid mixture to remove NO$_2$ from the gaseous phase during the digestion process. Hence, digestions can be performed at lower pressures, and quartz tubes with thinner walls (1.5 mm) can be used to improve heat exchange.

In comparison to open-vessel systems, costs for running sample digestion with the CHDS are lower because it requires small volumes of reagents (2 mL of HNO$_3$ and 1 mL of H$_2$O$_2$). The CHDS also provides faster digestions, minimizing

Table 2 Instrumental operating conditions for ICP-MS/MS

Instrument parameter	Operating condition
RF power (W)	1550
Sampling depth (mm)	8.0
Nebulizer	Concentric nebulizer—glass
Spray chamber	Scott type—double pass
Auxiliary gas flow rate (L min^{-1})	1.8
Carrier gas flow rate (L min^{-1})	1.09
Integration time (s)	3.0
Mass/charge ratios selected in Q1	^{80}Se, ^{98}Mo, ^{114}Cd
Operating mode	MS/MS
Cell gas	O$_2$
Oxygen flow rate (mL min^{-1})	0.50
Mass/charge ratios monitored in Q2	^{80}Se^{16}O, ^{98}Mo^{16}O$_2$, ^{114}Cd

Table 3 Results (mean±standard deviation, $n=3$) for Ca, K, Mg, Na, and Zn (mg kg^{-1}) in CRMs and samples by HR-CS FAAS after digestion with the CHDS and a closed-vessel microwave (MW) digestion system

		Element				
		Ca (mg kg^{-1})	K (mg kg^{-1})	Mg (mg kg^{-1})	Na (mg kg^{-1})	Zn (mg kg^{-1})
CRM						
Whole milk powder	Certified	9220±490	13,630±470	814±76	3560±400	28.0±3.1
	CHDS	9161±97 (99 %)	13,028±326 (96 %)	772±28 (95 %)	3229±229 (91 %)	28.4±0.5 (101 %)
	MW	8720±221 (95 %)	12,774±345 (94 %)	802±16 (99 %)	3372±245 (95 %)	30.4±0.9 (109 %)
Non-fat milk powder	Certified	13,000±500	16,900±300	1200±30	4970±100	46.1±2.2
	CHDS	12,734±295 (98 %)	15,864±426 (94 %)	1096±54 (91 %)	4632±175 (93 %)	45±2 (98 %)
	MW	12,790±305 (98 %)	16,103±354 (95 %)	1124±21 (94 %)	4689±125 (94 %)	45±1 (98 %)
Sample						
Non-fat milk powder	MW	5419±221	13,464±309	926±31	5992±44	63±1
	CHDS	5778±257	12,986±395	922±11	5896±112	64±3
Whole milk powder 1	MW	1785±161	8099±59	498 21	2247±40	89±6
	CHDS	1763±36	8198±182	486±9	2207±70	83±2
Whole milk powder 2	MW	2212±92	8300±216	513±20	2588±44	71±3
	CHDS	2173±154	8037±197	481±34	2604±42	73±1
Chocolate powder 1	MW	501±91	3850±188	390±2	1065±13	7.6±0.4
	CHDS	501±83	3820±106	405±16	1015±34	8.0±0.1
Chocolate powder 2	MW	270±14	3345±94	355±19	1550±49	6.0±0.9
	CHDS	276±14	3168±84	348±11	1660±67	6.1±0.5
Chocolate powder 3	MW	356±12	4251±166	389±16	1029±54	5.2±0.5
	CHDS	362±13	4098±177	367±22	1079±45	5.6±0.7
Soluble coffee 1	MW	1399±56	35,589±641	2879±100	96±4	<LOQ
	CHDS	1434±75	35,783±1768	2914±73	93±5	<LOQ
Soluble coffee 2	MW	1129±67	34,227±1118	2753±45	93±7	<LOQ
	CHDS	1147±84	33,996±839	2789±25	106±6	<LOQ
Soluble coffee 3	MW	1273±36	46,516±666	2971±27	154±6	<LOQ
	CHDS	1277±11	47,259±1146	3074±48	155±7	<LOQ

Values in parentheses are recoveries

electricity cost. In the context of contamination by reagents, for the same amount of sample, much less digestion reagent is needed with the CHDS. Another drawback in open-vessel digestion is that airborne contamination and/or losses by volatilization frequently occur.

Acid digestion using reflux system with cold finger is a simple way to mineralize several types of samples, and the loss of volatile elements is avoided due to the condensation of the volatile species. However, the main disadvantage is the relatively long time taken for digestion (from 2 to 4 h) and the low temperatures used. Decomposition effectiveness is limited by the boiling point of acids, and sulphuric acid is usually used to improve digestion efficiency, which is disadvantageous for many measurement techniques (Ferreira et al. 2013). On the other hand, there is no need to use sulphuric acid in the CHDS because the boiling point of the acid mixture (HNO_3/H_2O_2) is elevated when the pressure inside the vessel increases, leading to a faster and more efficient digestion.

Two CRMs, three milk powder, three chocolate powder, and three soluble coffee samples were digested in triplicate using the CHDS. Sample masses of 200 mg were accurately weighed directly in quartz digestion tubes followed by the addition of 2.0 mL of concentrated HNO_3 and 1.0 mL of 30 % m/v H_2O_2. According to the certificates, the concentrations of Cu, Fe, Mn, and Cd in the CRMs were below the typical LODs obtained for HR-CS FAAS (Cu, Fe, Mn) and ICP-MS/MS (Cd), so those elements were spiked before digestion in order to obtain final concentrations of 10 mg kg^{-1} Cu, 50 mg kg^{-1} Fe, 20 mg kg^{-1} Mn, and 1 mg kg^{-1} Cd. The quartz tubes were fully closed and placed in the heating block. The following heating program was applied: (1) 20 to 230 °C, 30 min ramp; (2) 230 °C, 15 min hold; and (3) 30-min ventilation until 60 °C. The digested samples were transferred to polypropylene flasks, and the volume was made up to 20 mL with deionized water.

Table 4 Results (mean±standard deviation, $n=3$) for Fe, Cu, and Mn in CRMs and samples by HR-CS FAAS after digestion with the CHDS and a closed-vessel microwave (MW) digestion system

		Element		
		Fe (mg kg^{-1})	Cu (mg kg^{-1})	Mn (mg kg^{-1})
CRM				
Whole milk powder	Certified (spiked)	1.8±1.1 [50.0]	0.46±0.08 [10.0]	0.17±0.05 [20.0]
	CHDS	48±1 (93 %)	10.9±0.2 (104 %)	20.7±0.3 (103 %)
	MW	50±1 (97 %)	10.3±0.2 (98 %)	20.8±0.3 (103 %)
Non-fat milk powder	Certified (spiked)	1.78±0.10 [50.0]	0.7±0.1 [10.0]	0.26±0.06 [20]
	CHDS	50±2 (97 %)	10.6±0.2 (99 %)	21.0±0.3 (104 %)
	MW	53±1 (102 %)	11.2±0.3 (105 %)	20.4±0.2 (101 %)
Sample				
Non-fat milk powder	MW	185±13	110±8	4.1±0.1
	CHDS	179±8	110±4	4.0±0.1
Whole milk powder 1	MW	100±3	65±2	1.26±0.02
	CHDS	106±4	67±1	1.22±0.03
Whole milk powder 2	MW	92±7	55±4	0.50±0.05
	CHDS	95±6	57±5	0.54±0.03
Chocolate powder 1	MW	42±1	3.5±0.1	4.6±0.1
	CHDS	40±1	3.3±0.2	4.9±0.2
Chocolate powder 2	MW	29±1	2.4±0.1	4.7±0.2
	CHDS	36±5	2.5±0.2	5.0±0.2
Chocolate powder 3	MW	32±1	3.7±0.2	4.8±0.1
	CHDS	31±3	3.2±0.4	5.0±0.6
Soluble coffee 1	MW	< LOQ	<LOQ	10.2±0.2
	CHDS	< LOQ	<LOQ	10.8±0.4
Soluble coffee 2	MW	15±3	<LOQ	10.3±0.2
	CHDS	16±2	<LOQ	10.3±0.2
Soluble coffee 3	MW	28±1	<LOQ	20.0±0.1
	CHDS	30±1	<LOQ	19.7±0.3

Values in parentheses are recoveries. Values in brackets are spiked concentrations in milligrams per kilogram

Microwave Digestion Procedure

In order to compare the results obtained with the CHDS, the same CRMs and samples were digested in triplicate using the microwave oven according to the following procedure: 200 mg of the material were accurately weighed in the microwave quartz vessels followed by the addition of 3.0 mL of concentrated HNO_3, 1.0 mL of 30 % m/v H_2O_2, and 2.0 mL of deionized water. Before the digestion, Cu, Fe, Mn, and Cd aliquots were spiked in the CRMs in order to obtain a final concentration of 10 mg kg^{-1} Cu, 50 mg kg^{-1} Fe, 20 mg kg^{-1} Mn, and 1 mg kg^{-1} Cd. Quartz tubes were fully closed and placed in the microwave oven. The following heating program was applied: (1) 100–600 W, 5 min ramp; (2) 600 W, 5 min hold; (3) 1000 W, 10 min hold; and (4) 0 W, 20-min ventilation. The maximum temperature was set to 230 °C. The digested samples were transferred to polypropylene flasks and diluted up to 30 mL with deionized water.

Results and Discussion

The HR-CS FAAS allowed fast sequential determination of Ca, Mg, K, Na, Cu, Fe, Mn, and Zn in only one run. This is interesting from the practical point of view because major and minor elements can be determined without further dilution of samples for measuring analytical lines of elements present at high concentrations (Ca, K, Mg, and Na). On the other hand, the determination of the same analytes by LS FAAS is more time consuming because the weak emission of hollow cathode lamps restricts the number of alternative lines available, requiring further dilutions of samples for the determination of Ca, K, Mg, and Na. The ICP-MS/MS allowed the determination of Cd, Mo, and Se in low concentrations, avoiding spectral interferences. The mass/charge ratios ^{80}Se, ^{98}Mo, and ^{114}Cd were selected in quadrupole 1, pure oxygen was used to generate the oxide species of the analytes in the ORS[3] and ^{80}Se^{16}O, and ^{98}Mo^{16}O$_2$ and ^{114}Cd were monitored in quadrupole 2.

Table 5 Results (mean±standard deviation, $n=3$) for Cd, Mo, and Se in CRMs and samples by ICP-MS/MS after digestion with the CHDS and a closed-vessel microwave (MW) digestion system

		Element		
		Cd (mg kg^{-1})	Mo (mg kg^{-1})	Se (mg kg^{-1})
CRM				
Whole milk powder	Certified (spiked)	0.0002 [1.0]	0.29±0.13	0.131±0.014
	CHDS	0.98±0.02 (98 %)	0.30±0.02 (103 %)	0.126±0.004 (96 %)
	MW	0.99±0.03 (99 %)	0.30±0.02 (103 %)	0.132±0.005 (101 %)
Non-fat milk powder	Certified (spiked)	0.0005±0.002 [1.0]	0.34	0.11±0.01
	CHDS	0.94±0.05 (94 %)	0.36±0.02 (104 %)	0.1093±0.0006 (99 %)
	MW	0.95±0.04 (95 %)	0.35±0.01 (103 %)	0.109±0.001 (99 %)
Sample				
Non-fat milk powder	MW	<LOQ	0.279±0.003	0.134±0.009
	CHDS	<LOQ	0.282±0.002	0.136±0.002
Whole milk powder 1	MW	<LOQ	0.220±0.008	0.087±0.002
	CHDS	<LOQ	0.216±0.003	0.090±0.003
Whole milk powder 2	MW	<LOQ	0.491±0.009	0.112±0.004
	CHDS	<LOQ	0.51±0.01	0.123±0.007
Chocolate powder 1	MW	0.0112±0.0003	0.059±0.002	0.043±0.0.002
	CHDS	0.0109±0.0002	0.057±0.001	0.042±0.04
Chocolate powder 2	MW	0.0162±0.0009	0.056±0.002	0.025±0.001
	CHDS	0.015±0.001	0.054±0.006	0.027±0.002
Chocolate powder 3	MW	0.024±0.009	0.073±0.001	0.041±0.007
	CHDS	0.027±0.003	0.074±0.002	0.041±0.003
Soluble coffee 1	MW	<LOQ	0.091±0.004	0.26±0.03
	CHDS	<LOQ	0.09±0.01	0.24±0.02
Soluble coffee 2	MW	<LOQ	0.094±0.002	0.215±0.007
	CHDS	<LOQ	0.093±0.002	0.210±0.004
Soluble coffee 3	MW	<LOQ	0.106±0.002	0.268±0.007
	CHDS	<LOQ	0.107±0.001	0.276±0.006

Values in parentheses are recoveries. Values in brackets are spiked concentrations in milligrams per kilogram

The CHDS has no specification for a minimum volume of reagents and allowed the digestion of food samples with only 2 mL of HNO$_3$ and 1 mL H$_2$O$_2$. Nevertheless, the microwave digestion system used in this work requires at least 6 mL of reagents. It was also possible to digest food samples with the CHDS without pressure/temperature monitoring by limiting the sample mass to 200 mg and using adequate amount of hydrogen peroxide (1 mL) in the acid mixture. During digestion, the main product NO$_2$ reacts with O$_2$ and H$_2$O to regenerate HNO$_3$. Nitric acid regeneration removes the excess of NO$_2$ from the gaseous phase and reduces the risks of overpressure (Miranda et al. 2014a). In the CHDS, an immersed temperature sensor is not mandatory because the heat transfer is limited by the temperature of the aluminum heating block. In microwave digestion systems, heating must be strictly controlled by an immersed temperature sensor. In closed-vessel digestion systems, a fast exothermic reaction can occur during the digestion of a new type of sample, but a temperature sensor cannot stop this sort of reaction anyway, and the rupture of the safety seal is unavoidable.

Table 6 Limits of quantification (LOQ) obtained with the CHDS and with the closed-vessel microwave digestion system

Technique	Element	LOQ (mg kg^{-1})	
		CHDS	MW digestion system
HR-CS FAAS	Ca	0.35	0.23
	K	0.03	0.04
	Mg	0.05	0.03
	Na	0.03	0.06
	Fe	14.5	14.6
	Cu	1.13	0.72
	Mn	1.76	1.03
	Zn	3.63	3.84
ICP-MS	Cd	0.0061	0.0048
	Mo	0.0100	0.0098
	Se	0.0073	0.0070

Table 7 Wet digestion sample preparation techniques

Sample preparation technique	Advantages	Drawbacks	Acquisition and maintenance cost	Green feature
CHDS	Fast digestions (~45 min), low sample contamination, low blank values, digests with low residual carbon content	Sample mass limited to approximately 200 mg (100 mg carbon content)	Low	Low acid consumption
Open-vessel wet digestion (digestion block/hot plate)	Higher sample masses can be digested	The efficiency of decomposition is limited to the boiling temperature of the reagents, sample contamination, and losses of volatile elements can occur, relatively long time taken for digestion (~4 h)	Low	
Wet digestion using reflux system with cold finger	Higher sample masses can be digested, loss of volatile elements is avoided due to the condensation of the volatile species	The efficiency of decomposition is limited to the boiling temperature of the reagents, relatively long time taken for digestion (~4 h), the experimental work is complicated when many samples have to be digested	Low	
Focused microwave-assisted wet digestion	Higher sample masses can be digested	The efficiency of decomposition is limited to the boiling temperature of the reagents, sample contamination, and losses of volatile elements can occur	Medium	
Microwave-assisted wet digestion	Fast digestions (~30 min), low sample contamination, low blank values, digests with low residual carbon content, possibility of using diluted acids	Sample mass limited to approximately 500 mg (250 mg carbon content)	High	Low acid consumption

The accuracy was evaluated by analyzing two CRMs digested by the CHDS and the microwave oven for comparison. The results obtained by HR-CS FAAS using both digestion systems are presented in Table 3 (Ca, K, Mg, Na, and Zn) and Table 4 (Cu, Mn, and Zn). The results obtained by ICP-MS/MS for Cd, Mo, and Se are shown in Table 5. When using the CHDS, recoveries for the analytes varied from 91 to 104 %. For microwave digestions, recoveries within the 94–109 % intervals were obtained. For all analytes determined by HR-CS FAAS and ICP-MS/MS, the precision as relative standard deviations (RSD) of three replicates were usually lower than 5 %. The method was then applied to milk powder, chocolate powder, and soluble coffee samples. For comparative purposes, the analytes were also determined in the samples after microwave digestion. The results between the two digestion systems depicted in Tables 3, 4, and 5 showed no differences based on a paired t test at a 95 % confidence level. The concentrations of Cu and Zn in all soluble coffee samples were below the limit of quantification (LOQ). The concentrations of Cd were above the LOQ only in chocolate powder samples.

For each analyte, the LOQ was calculated as the concentration corresponding to tenfold the standard deviation of 10 independent sample blank measurements divided by the slope of the analytical curve (Gustavo González and Ángeles Herrador 2007). According to the results presented in Table 6, LOQs were similar using both digestion systems. Similar analytical blanks were obtained because quartz digestion tubes were used in both digestion systems.

There are many systems with open or closed vessels for conductive heating digestion that have good performance and are still used by many laboratories for sample preparation for further determination of elements. The CHDS is also an alternative for wet digestion of food samples with high organic content

that presents many desirable features not found simultaneously in any conductively heated digestion system. The advantages, drawbacks and other characteristics of the CHDS, and other sample preparation techniques are presented in Table 7.

Safety Concerns

Operations with pressurized tubes containing a hot acid mixture must follow some precautions because a tube explosion is a hazard that must be cogitated. If the pressure inside the quartz digestion tube of the CHDS exceeds the limit during digestion, the screw cap ruptures and the pressure escapes. However, in case of destructive failure of the tube during digestion, the cabinet guards the analyst from personal injury.

Tubes were only handled after the block was cooled down from 230 to 60 °C. At 60 °C, internal temperatures and pressures are reduced to the point that the sealed quartz tubes can be safely opened. Using lab coat, goggles, and protective gloves, tubes were opened with the fume hood ventilation on and behind the protection shield.

Conclusion

The results obtained in this study extend the applications of the CHDS to food samples with higher contents of fat such as whole milk powder. This simple, low-cost, and high-throughput digestion system can be used to prepare samples for subsequent determination of a large number of elements by atomic spectrometry, including volatile species such as Cd and Se.

Compliance with Ethical Standards

Conflict of Interest Kelber Miranda declares that he has no conflict of interest. Alan Lima Vieira declares that he has no conflict of interest. Marcos André Bechlin declares that he has no conflict of interest. Felipe Manfroi Fortunato declares that he has no conflict of interest. Alex Virgilio declares that he has no conflict of interest. Edilene Cristina Ferreira declares that she has no conflict of interest. José Anchieta Gomes Neto declares that he has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

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