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The combination of infrared and microwave radiation to quantify trace elements in organic samples by ICP OES

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ABSTRACT

Sample-decomposition methods using microwave radiation in closed systems have been commonly used in the analysis of inorganic constituents; however, these methods are limited to small amounts of organic samples. This work proposes the combined use of infrared radiation and microwave radiation (IR-MW) to increase the amount of organic samples digested. The determination of Al, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn in human-feed samples was accomplished by ICP OES. The results were in agreement with those obtained from conventional decomposition by microwave radiation (closed system). The results obtained using the proposed IR-MW system for standard reference material (whole milk powder, NIST 8435) were also compared. Agreements of 85–100% were obtained for Al, Ca, Cu, Fe, K, Mg, Na, P and Zn in the standard reference material. The IR-MW system is simple to implement and cheap because it uses commercially available infrared lamps and allows the use of infrared radiation in the microwave-digestion vessel. Additionally, it is possible to reach better precision in the analysis of the human-feed samples using the IR-MW system. The proposed method also allows total digestion of large sample amounts or samples rich in organic compounds can also be performed in the IR-MW system using small volumes of nitric acid.

1. Introduction

In an analytical sequence, the steps of sampling and sample preparation are responsible for most of the inserted errors in the analysis results. According to the literature, the percentage of error generated by the sample preparation procedure can reach 100–300% [1]. Therefore, the development of sample preparation methods that provide reliable analytical results is necessary.

Sample decomposition methods using microwave radiation in closed systems have been commonly used in the analysis of inorganic constituents. This configuration has the advantages of increasing the boiling temperature of the reagents at increased pressure, which reduces the sample preparation time. Moreover, the technique requires smaller reagent volumes than traditional methods of sample digestion, prevents analyte loss by volatilization and reduces the risk of sample contamination [2]. However, one of the main drawbacks associated with closed systems is the limitation of the amount of sample that it can decompose [3]. Usually, the sample mass used in these methods is 250 mg or less when the sample contains high organic-matter content. Due to the high pressure produced in the decomposition process in closed systems, sample masses above this value can cause explosions. Thus, small amounts of sample would not be properly representative in cases whose samples have difficult homogenization. Moreover, the decomposition of small sample mass can hamper the detection of elements at low concentration. Some studies in the literature use preconcentration techniques with ion exchange resins to improve the detection of trace elements [4,5]. However, the use of these techniques increases the sample handling steps, and therefore, increases the probability of inclusion of systematic errors.

Despite modern models of cavity microwave oven allows to decompose up to 1 g of sample, maximum recommended temperature is 180 °C [6]. Since temperatures higher than 200 °C are required to a rapid and effective oxidation of organic matter, according to research of Wurfels et al. [7–10], samples with higher levels of organic matter would probably not be adequately decomposed when larger amounts of samples were employed in these new systems of decomposition.

Microwave ovens with focused radiation allow the decomposition of larger sample masses because they are open systems of decomposition. System decomposition assisted by focused microwave radiation operating in atmospheric pressure does not present the significant problems associated with increasing pressure found in closed systems. In addition to the ability to use up to 10 g of sample, adding reagents at any stage of the decomposition process is possible in this system [3]. However, these methods use high volumes of concentrated acids, which

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could generate digests with elevated acid concentrations. This generally requires extensive dilution before measurement when spectroanalytical techniques with conventional sample-introduction systems are used [11].

Another recently developed alternative method to the decomposition of larger masses of samples in the microwave is the use of microwave-induced combustion (MIC), which enables the digestion of masses up to 500 mg. In general, this method consists of sample combustion in sealed quartz vessels pressurized with oxygen using an ignition stage performed by microwave radiation. After combustion, the gases are absorbed in a suitable solution, and a reflux step may be applied to assure analyte recovery. This technique, which has been adapted to a commercial microwave oven, was originally developed for conventional closed-vessel wet digestion [12]. This method combines the advantages of traditional combustion technologies and the advantages of conventional microwave-assisted wet digestion [13].

One more procedure using combustion in microwave ovens was proposed. In this proposal, the decomposition is based on focused microwave-induced combustion (FMIC) [14]. A commercial focused microwave oven with a lab-made quartz sample holder and a modified glass vessel was used. The oxygen flow rate was controlled at 2.0 L min^{-1}, and it was verified that combustion did not occur using an initial oxygen flow rate higher than 5.0 L min^{-1}. The operational conditions were evaluated using the analysis of Al, Ba, Ca, Fe, Mg, Mn, Sr, and Zn in botanical samples. The combustion was completed in less than 2 min, and the temperature was higher than 950 °C. The results were compared with those obtained by focused microwave-assisted wet digestion and by high-pressure microwave-assisted wet digestion. An agreement of 95–103% was obtained for certified reference materials digested by FMIC. In the proposed procedure, complete sample decomposition (residual carbon content lower than 0.5%) was achieved with low reagent consumption, as evidenced by the fact that only 10 mL of diluted nitric acid was necessary. A low relative standard deviation (lower than 3.8%) was observed, and a large amount of sample (up to 1500 mg) could be digested, allowing lower limits of detection.

Infrared energy is rarely used in sample-preparation procedures [15]. One of the most common applications of infrared radiation in sample preparation is in the drying of samples or reagents using a tungsten lamp [16]. Another example is the sub-boiling distillation of acids using electrical resistance [17]. The infrared-assisted heat was used in a combustion system to decompose organic samples. The system is similar to a Schöniger flask and it consists of a combustion chamber with two sections. In the first section, the sample is placed in the focal point of two tungsten lamps in an oxygen atmosphere. Sample combustion occurs after 30 s of radiation. The produced vapors are absorbed by an acid solution in the second section of the chamber. This system was used to determine B, Cr, Fe, Mn and Zn by ICP OES; Cd and Pb by GFAAS; Hg by cold vapor AAS; As by hydrate generation; and Se by X-ray fluorescence in 7 certified samples with satisfactory results [18]. The same technique was used to determine iodine by ICP-MS in biological and food samples [19]. Another combustion system using three infrared lamps was used to directly determine Cd, Cu, Pb and Zn in solid samples by FAAS [20]. This combustion system consists of a T-shaped quartz tube adapted on the burner of the FAAS. The sample is placed in a quartz crucible and positioned in the center of the quartz tube. The infrared lamps (15 V and 150 W) focus in a unique point of the sample. The combustion of the sample occurs when a potential difference is applied to the set of lamps. The generated vapor is carried by airflow to the atomizer [21]. This arrangement of infrared lamps was also used in the direct determination of Hg in sediment samples by cold-vapor AAS [22].

In this work, another method to decompose larger sample quantities using microwave ovens is also reported. The method consists of a previous oxidation of the organic matter with nitric acid using infrared radiation prior to sample decomposition in a closed microwave oven. This device allows the digestion of larger sample quantities, making it suitable for samples that are difficult to homogenize and samples with high contents of organic substances. The new method was applied to human-feed samples, and the results are compared with conventional microwave-assisted wet digestion using a closed microwave oven. The determination of inorganic elements was accomplished by ICP OES.

2. Experimental

2.1. Samples, reagents and standards

The developed decomposition method was applied to commercial human-feed samples from a Brazilian market. The human-feed sample is a ration used as a complement for a healthy diet. This sample consists of a mixture of flaxseed, wheat bran, wheat germ, cashew nuts, soybeans, sesame seeds, brown sugar and oats.

Standard reference material whole milk powder NIST 8435 (National Institute of Standards and Technology, Gaithersburg, MD, USA) was analyzed in order to check the accuracy of the proposed method.

All solutions were prepared using ultrapure water (resistivity of 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). All glassware and polypropylene flasks were immersed in 10% w w^{-1} nitric acid (Merck, Darmstadt, Germany) for 24 h and rinsed with ultrapure water prior to use.

For sample digestion, 65% w w^{-1} concentrated nitric acid (Vetec, Rio de Janeiro, Brazil) and 30% w w^{-1} hydrogen peroxide (Vetec) were employed. Reference solutions were prepared after successive dilutions from 1000 mg L^{-1} Al, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn stock solutions (Acros Organics, Belgium). Stock solutions containing carbon (5.0% w v^{-1}) were prepared using urea (CH_4N_2O; Vetec). Standard solutions containing 0.05, 0.1, 0.2, 0.5, 1.0 and 2.5% carbon were prepared in 1.4 mol L^{-1} HNO_3 [23].

2.2. Instrumentation

For total sample digestion, a cavity microwave oven (Multiwave®, Anton Paar, Graz, Austria) equipped with 6 quartz closed vessels of 50 mL (maximum temperature and pressure: 300 °C and 75 bar) and a temperature sensor was used. In addition, an infrared lamp with 250 W of power, diameter of 127 mm and length 180 mm (E-27-5.000h, EMPALUX, Curitiba, PR, Brazil) was employed in the combined procedure of infrared heating and microwave (IR-MW) (Fig. 1).

The layout of the IR-MW system was idealized using a simple arrangement with a commercially available infrared lamp, normally used as a drier or to keep food warm in restaurants. The vessel used for heating in the infrared lamp is the same quartz vessel from the microwave oven. During the pre-digestion the lamp is attached to a support and a quartz vial containing the sample and the acid is positioned approximately 1 cm above the infrared lamp.

A dual-view Optima 4300 DV (Perkin Elmer) ICP OES was used for the Al, C, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn determinations. The ICP sample-introduction system was a Cross-Flow nebulizer with a double-pass spray chamber. The ICP operational parameters were the following: 40 MHz generator frequency; 1.1 kW radio-frequency power; 15 L min^{-1} argon plasma flow rate; 0.5 L min^{-1} auxiliary argon flow rate; 0.8 L min^{-1} nebulizer argon flow rate;

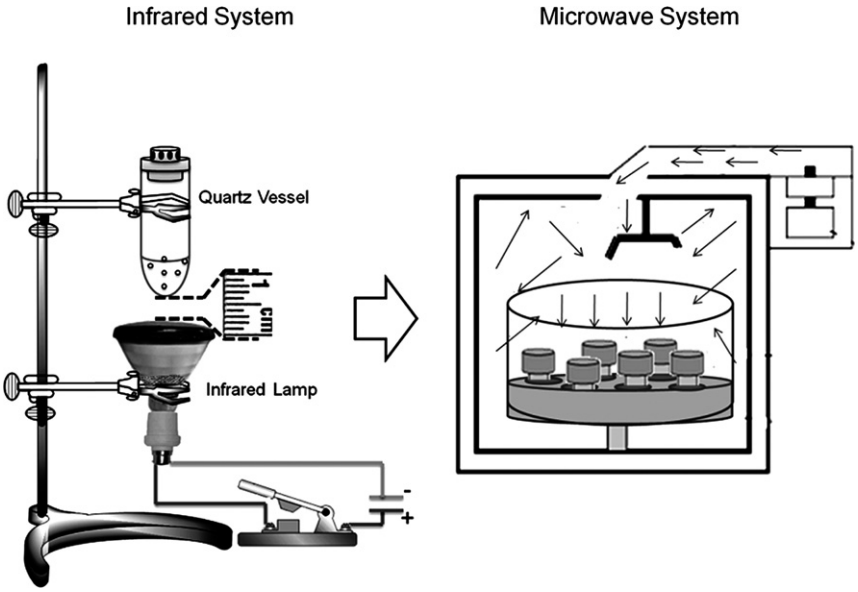

Fig. 1. Infrared-heating and microwave-digestion system (IR-MW).

and 1.4 mL min^{-1} sample flow rate. A 2.4 mm central tube internal-diameter torch was used. The wavelengths of the elements and the viewing position of the torch in the ICP OES are presented in Table 1.

2.3. Sample preparation in a conventional closed microwave oven

In the cavity microwave oven decomposition, a 200 mg sample was digested using 3 mL of 65% w w^{-1} HNO_3 and 2 mL of 30% w w^{-1} $\cdot H_2O_2$. After digestion, the solutions were diluted to 25 mL with ultrapure water. The microwave-oven heating program is shown in Table 2. The analytes were determined by ICP OES.

2.4. Sample preparation using infrared radiation combined with microwave-assisted digestion (IR-MW)

The reduction of the sample mass using the infrared radiation procedure was investigated. For this, 4 mL of 65% w w^{-1} $\cdot HNO_3$ were added to approximately 1.0 g of the sample. After 10 min of heating using the infrared lamp, the resulting mixture was filtered, washed with water and the solid material in the paper filter was dried in an oven at 60 °C for 24 h. The material was weighed, and the decrease of the mass was calculated.

In the proposed IR-MW procedure, 1.0 g of the sample was weighed into the quartz vessel of the microwave-oven system. After the addition of 4 mL of 65% w w^{-1} HNO_3, the covered quartz vessel was submitted to infrared radiation for 10 min. Next, the resulting solution was completely digested in a cavity microwave oven using the same heating program presented in Table 2. The analytes were determined by ICP OES. The exposure time to infrared radiation of the sample and the volume of nitric acid were evaluated using an experimental design.

Summary of the IR-MW system operation: (i) 1.0 g of the sample was weighed into the quartz vessel of the microwave oven; (ii) 4 mL of 65% w w^{-1} HNO_3 were added to the vessel; (iii) the mixture was heated with infrared lamp during 10 min; (iv) the quartz vessel with the solution was closed and placed in the cavity microwave oven; (v) the solution was digested in the microwave using the heating program presented in Table 2; and (vi) the digested solution was transferred and diluted to 25 mL with ultrapure water.

Table 1
Wavelengths of the monitored elements and the viewing position of the instrument.

Element	Wavelength (nm)	View position
Al	396.153	Axial
C	193.030	Axial
	193.030	Radial
Ca	317.933	Radial
Cu	324.752	Axial
Fe	259.939	Axial
K	766.490	Radial
Mg	285.213	Radial
Mn	257.610	Axial
Na	589.595	Radial
P	213.617, 214.914	Radial
Zn	213.857	Axial

Table 2
Heating program used for digestion in the microwave.

Step	Power (W)	Time (min)
1	100–600	5.0
2	600	5.0
3	1000	10.0
4	0	15.0

2.5. Experimental design

An experimental design was used in order to optimize the infrared pre-digestion step. Table 3 shows the experiments using the human-feed samples. The variables chosen for this study were heating time and volume of acid. The response was measured as residual carbon content (RCC) in the samples digested by IR-MW system.

All experiments were performed at two levels: normalized to −1 and +1. The values of volume of acid and exposure time to infrared radiation evaluated were, respectively: 4 mL (minimum, −1) and 8 mL (maximum level, +1), 10 min (minimum, −1) and 30 min (maximum level, +1).

Table 3
Results for the standard reference material (whole milk powder, NIST 8435).

Elements	IR-MW system	Certified Values
Al ($\mu g\,g^{-1}$)	1.19 ± 0.18*	(0.9)
Ca (wt%)	0.87 ± 0.03	0.92 ± 0.49
Cu ($\mu g\,g^{-1}$)	0.52 ± 0.18	0.46 ± 0.08
Fe ($\mu g\,g^{-1}$)	2.34 ± 0.41	1.80 ± 1.1
K (wt%)	1.289 ± 0.080	1.363 ± 0.470
Mg ($\mu g\,g^{-1}$)	849 ± 55	814 ± 76
Na (wt%)	0.351 ± 0.021	0.356 ± 0.400
P (wt%)	0.788 ± 0.06	0.780 ± 0.049
Zn ($\mu g\,g^{-1}$)	25.85 ± 0.54	28.0 ± 3.1

* Relative standard deviations for triplicate.

3. Results and discussion

3.1. Evaluation of the experimental parameters of the proposed digestion method

The layout of the IR-MW system was idealized using a simple arrangement with a commercially-available infrared lamp, normally used as a drier or to keep food warm in restaurants. The vessel used for heating in the infrared lamp is the same quartz vessel from the microwave oven. Therefore, the IR-MW system is simple to implement in analytical laboratories and it is a promising alternative to digest organic samples for trace analysis. The infrared predigestion procedure was optimized using a two-level full-factorial experimental design (FFD). This experimental design allows the evaluation of factors affecting digestion and all possible multifactor interactions. The following two factors were studied at two levels (maximum and minimum): heating time using the infrared lamp and HNO_3 volume. Residual Carbon Content (RCC) values were measured in the obtained digests to estimate the responses in every experiment. The axial viewer configuration was used to measure the RCC. RCC was chosen as the response to define the optimal exposure time and nitric acid volume for pre-digestion using the IR-MW system. According to the results obtained in full-factorial design, all experiments show RCC values lower than 3.1%. Therefore, the smallest volume of acid (4 mL) and the shortest pre-digestion time (10 min) were chosen.

In order to know whether the experimental conditions for pre-digestion under infrared radiation were adequate to obtain a mixture that could be safely decomposed in a cavity microwave oven, the reduction of sample mass after pre-digestion process was checked. With this study it was possible to know how much mass of sample remains after pre-digestion with infrared radiation, which would be conducted for the subsequent step, complete digestion in a microwave cavity. The reduction of mass achieved when 1.0 g of sample is predigested with 4 mL · HNO_3 during a 10 min pre-digestion is higher than 80%, i.e., after the procedure with the infrared radiation, the mass of the resulting sample is lower than 200 mg. Since, in general, approximately 250 mg are used depending on the organic matter of the sample, the mass of the resulting sample after pre-digestion in the infrared lamp is appropriate to be conducted to the microwave cavity to complete the digestion.

3.2. Precision and accuracy of the proposed digestion method

The accuracy of the proposed system (IR-MW) was tested using a standard reference material (whole milk powder, NIST 8435), and the results are summarized in Table 3.

No statistical differences existed between determined and certified values at the 95% confidence level (test t).

The results obtained for the SRM NIST 8435 for Al, Ca, Cu, Fe, K, Mg, Na, P and Zn are in agreement with the IR-MW procedure.

Relative standard deviations (R.S.D.) were found below 8% in almost all cases. Copper showed the worst repeatability (34.6%) and this was due to its lower concentration in the certified material, which leads in the final solutions to levels close to the limits of quantification of the method (10 $\mu g\,L^{-1}$). Although this problem can be avoided by using smaller dilution factors, it increases the matrix effects and therefore was considered impractical. Aluminum and iron presented 15.1 and 17.5% relative standard deviations, respectively. This is because they are also found in low amounts in milk samples. Therefore, it is impossible to accurately quantify these elements by ICP OES using smaller sample masses.

The novelty of this work is the ability to quantify trace elements by ICP OES with precision and accuracy. Therefore, digestion of larger amounts of samples is critical to the detection of elements such as Cu, Fe and Al by ICP OES in whole milk powder.

3.3. Application of developed method on samples

The human-feed has been widely used in treatments for weight loss due to its composition rich in fibers and proteins. Furthermore, the human-feed is a rich source of nutrients such as vitamins and minerals.

The human-feed samples were analyzed using the proposed IR-MW method. The elements were determined by ICP OES. The results were compared with conventional closed microwave-digestion procedure and the element amounts were not significantly different ($p > 0.05$) to those found with the digestion procedure using the proposed IR-MW method (Table 4).

The proposed procedure using the IR-MW system yielded better relative standard deviations (for five replicates) than the microwave-assisted digestion for all elements analyzed. This finding is due to the fact that higher masses were weighed, directly influencing the accuracy of the analysis, especially for heterogeneous samples, as the human-feed sample.

Aluminum and copper determinations presented higher relative standard deviations, 20.1 and 31.9%, respectively, in the microwave-assisted digestion (MW) because the determined values were near to the limit of quantification (LOQ) of the analysis for human-feed samples in the ICP OES. The same happened with Mg, Mn and Zn that showed relative standard deviations of 11.1, 16.9 and 11.8%, respectively.

The IR-MW system presented more precise amounts of Al, Cu, Mg, Mn and Zn in the human-feed samples due to their relative standard deviations bellow 10%.

Studies reported in the literature using microwave cavity (closed system) for digestion of complex matrices have employed 0.5 g of

Table 4
Results for the human-feed samples digested using the IR-MW system and the closed microwave (MW).

Elements	IR-MW system	MW
Al ($\mu g\,g^{-1}$)	131.66 ± 2.40*	135.04 ± 27.20
Ca (wt%)	0.22 ± 0.01	0.20 ± 0.02
Cu ($\mu g\,g^{-1}$)	13.09 ± 0.56	11.78 ± 3.76
Fe ($\mu g\,g^{-1}$)	276.55 ± 4.10	273.40 ± 19.35
K (wt%)	1.22 ± 0.04	1.18 ± 0.10
Mg (wt%)	0.26 ± 0.01	0.27 ± 0.03
Mn ($\mu g\,g^{-1}$)	59.43 ± 3.61	52.79 ± 8.90
Na ($\mu g\,g^{-1}$)	228.75 ± 6.18	230.21 ± 22.34
P (wt%)	0.69 ± 0.03	0.71 ± 0.04
Zn ($\mu g\,g^{-1}$)	65.28 ± 1.45	62.12 ± 7.35

* Relative standard deviations for five replicates.

sample mass [24–26]. Furthermore, the use of higher sample masses (up to 1.0 g) limits the maximum recommended temperature to 180 °C [3]. Complex matrices require temperatures above 200 °C in the digestion for availability of trace elements in solution. The proposed IR-MW system allows the reaching of temperatures above 200 °C in 1.0 g of sample during the process of digestion (microwave closed system). This is possible because there is a step of pre-digestion in the infrared lamp.

The results demonstrate the possibility of using the infrared lamp for the pre-digestion of organic samples. In this sense, it is possible to increase the mass in the digestion of the organic samples by using the infrared lamp combined with the closed microwave system.

4. Conclusions

This work presents an alternative procedure to digest organic samples combining infrared and microwave radiations (IR-MW). The main advantage of IR-MW is the possibility to decompose relatively large masses of organic samples (1000 mg), using cavity microwave oven, which contributes to lower LODs in comparison to conventional closed microwave oven method. In addition, digestion of higher sample masses provides more accurate results and it is important to heterogeneous sample analysis. The IR-MW system is simple and cheap because it uses commercially-available infrared lamps and allows the use of infrared radiation in the microwave-digestion quartz vessel. The proposed system (IR-MW) yielded suitable digestion of human-feed samples to the determination of Al, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn by ICP OES.

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