



A critical evaluation of digestion procedures for coffee samples using diluted nitric acid in closed vessels for inductively coupled plasma optical emission spectrometry

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ABSTRACT

The efficiency of diluted nitric acid solutions for digesting regular coffee samples was evaluated employing two closed vessel procedures: one was based on microwave-assisted heating and the other was based on conductive heating using pressurized Parr bomb. The efficiency of digestion was evaluated by determining residual carbon content (RCC) and residual acidity. The digestion was effective using both procedures, i.e. there were no solid residues after the decomposition reactions when using up to 3.5 mol L^{-1} nitric acid solutions. It was demonstrated that the digestion procedures are critically dependent on reactions occurring in liquid and gas phase and that the formation of NO and its conversion to NO_2 by O_2 exerts a major effect in the oxidation of organic matter. These processes are more effective in closed vessels heated by microwave radiation due to the greater volume of these flasks and the temperature gradient that exists during the first step of the digestion process. The proposed model for the digestion processes in diluted nitric acid solution is corroborated by data about consumption of acid during the digestion and by measuring the pressure during the whole process.

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1. Introduction

Sample pretreatment is frequently the most time consuming step of an analytical procedure and the bottleneck of the whole analytical process when elements are determined in solid samples [1]. Occasionally solid sample preparation for trace element determination can be performed by simple dilution [2,3], however, usually, chemicals and different energy sources are associated for total or partial sample decomposition [2–12]. Two procedures are generally employed for sample preparation: dry and wet decomposition. For wet decomposition, pressurized closed vessels are usually employed to avoid contamination and losses of volatile elements during acid digestion [2,3,8]. Digestion in closed systems at elevated temperatures begin to be successfully used only after the introduction of polytetrafluoroethylene (PTFE, Teflon®) as material for the reaction vessels due to the high degree of chemical

and thermal resistance [10]. Digestions at elevated temperature and pressure in closed systems present advantages, such as the decrease of both decomposition time and reagent volumes required for sample digestion [11].

Most digestion procedures for biological samples employ nitric acid because it is a strong oxidizing agent at high temperatures and concentrations. Additionally, nitric acid is easily purified and diluted solutions can be used for sample preparation step in order to increase the safety and to decrease reagent volumes and residues. Diluted nitric acid solutions were successfully used for microwave-assisted plant digestion [13–18], leading to low blank values. The effect of nitric acid and hydrogen peroxide concentrations on closed vessel microwave-assisted digestion of plant materials was previously described [14] and the residual carbon did not exceed 13%. In another work, a closed vessel microwave-assisted procedure was combined with diluted nitric acid solution for digesting bovine liver and spinach leaves standard reference materials and accurate results were obtained for Al, Ca, Cu, Fe, K, Mg, Mn, P, and Zn [15]. Recently, an experimental design approach was applied to optimize the extraction of trace elements from raft mussel samples with

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Table 1

Instrumental parameters for elements determination using axial ICP OES.

Instrumental parameter	
RF generator (MHz)	40
Applied power (kW)	1.3
Plasma gas flow-rate (L min ⁻¹)	15.0
Auxiliary gas flow-rate (L min ⁻¹)	1.5
Nebulizer gas flow-rate (L min ⁻¹)	0.7
Integration time (s)	1.0
Stabilization time (s)	15
Reading time (s)	1
Replicates	3
Spray chamber	Cyclonic
Nebulizer	Concentric
Analytical wavelengths (nm)	
C I	193.025
Ba II	455.396
Cu II	327.395
P I	177.432

I: Atomic line, II: Ionic line.

diluted acids associated to hydrogen peroxide by exploring closed vessel short microwave irradiation cycle [16]. Major improvements in the extraction techniques have been introduced not only aiming the preparation time but also to simplify sample preparation handling for trace elements determination [18–21]. However, the behavior of closed vessel using diluted acid digestion procedures to extract trace elements from diverse matrices has not been fully explained.

Therefore, the aim of the present work was to perform a systematic investigation about the efficiency of closed vessels digestion using nitric acid solutions in different concentrations associated with hydrogen peroxide to digest organic matrices (regular powdered coffee samples) by employing heating either by microwave radiation or by conduction. Finally, a general mechanism for organic matter decomposition in both closed vessel digestion procedures were proposed based on the comparison of diverse parameters such as final acidity, residual carbon contents (RCC) as well as element concentrations.

2. Experimental

2.1. Equipments

A closed vessel microwave digestion system with control sensor pressure and temperature (ETHOS EZ, Milestone, Sorisole, Italy), and a pressurized bomb Parr (Model 4746, Parr Instrument Company, Moline, IL, USA) were used for sample digestion.

An inductively coupled plasma optical emission spectrometer with axial viewing - ICP OES (Vista Pro, Varian, Mulgrave, Australia) equipped with solid state detector, cyclonic spray chamber, and concentric nebulizer was employed for analytes and residual carbon content determinations. The operational parameters adopted are listed in Table 1. All measurements were carried out using argon as plasma gas. Total carbon concentration in powdered coffee samples was determined by elemental analyzer (ThermoQuest® Finnigan Flash EA 1112).

2.2. Reagents, solutions and samples

All solutions were prepared with analytical grade reagents (Merck, Darmstadt, Germany), and deionized water from Millipore water purification system (Milli-Q, Millipore, Bedford, MA, USA), was used for the preparation of the samples and standards. Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution. Glasses were rinsed with freshly deionised water and dried in a dust free environment before use.

Table 2

Microwave heating program for digestion of powered coffee samples.

Step	Time (min)	Temperature (°C)
1	5	120
2	3	120
3	10	210
4	15	210

Reference solutions containing from 50 to 1500 mg L⁻¹ C were prepared using 5.0% (w/v) C stock solution prepared from urea (Reagen, Rio de Janeiro, Brazil) as earlier reported [22].

One regular powder coffee sample purchased in a local market was manually ground and sieved to a 100–500 µm particle size range.

2.3. Digestion procedures

2.3.1. Microwave-assisted acid digestion

Masses of 250 mg of coffee samples were directly inserted into microwave closed vessels made with perfluoroalcoxi polymer (PFA) with a volume of 100 mL. Volumes of 7.0 mL of nitric acid solution were added in the following concentrations: 14.0, 10.5, 7.0, 3.5, 1.7 and 1.0 mol L⁻¹. Then, volumes of 1.0 mL of 30% (w/w) H₂O₂ were also added to each vessel. The heating program described in Table 2 was applied to six reagent vessels. The power and maximum pressure were set in 750 W and 35 bar, respectively. After sample digestion, digests were transferred to glass volumetric flasks and the volumes were made up to 20.0 mL with distilled-deionized water.

2.3.2. Pressurized bomb acid digestion

Masses of 200 mg of coffee samples were directly introduced into PTFE closed vessels with volumes of 23 mL. A volume of 2.0 mL of the previously described nitric acid solutions was added to each vessel. Then, a volume of 1.0 mL of 30% (w/w) H₂O₂ was also added to each reaction vessel. Parr bombs were sealed and put in a muffle furnace set at 120 ± 10 °C and remained at this temperature during 12 h. After cooling down at room temperature, solutions were transferred to glass volumetric flasks and volumes were made up to 15.0 mL with water.

3. Results and discussion

The use of nitric acid for organic matrices digestion is the most usual approach for wet sample pretreatment to facilitate trace elements determination. Ideally, the best digestion should led to a complete decomposition of organic material using minimal amounts of nitric acid which should be as diluted as possible to decrease residual carbon and the acid concentration in the resulting digest solution with the aim to avoid critical effects on instrument parts, such as nebulizer, nebulization chamber and torch in ICP OES [11]. The minimization of nitric acid amount for promoting decomposition processes can be performed by two different approaches: (i) by adding aliquot volumes as low as possible of concentrated nitric acid, or (ii) by using a diluted nitric acid solution. In fact it is required a minimum volume of acid solution to merge with the solid sample particles throughout the material decomposition because it may be supposed that the solid sample digestion occurs in the solid–liquid interface. In addition, a significant volume of acid solution is transferred to the gas phase when the sample digestion is carried out in pressurized closed vessels independently on the heating strategy. Therefore, the use of greater volumes of diluted nitric acid for sample decomposition have been more exploited than the minimization of the volume of concentrated solutions, in special for microwave-assisted digestion of biological samples [13–21]. Addi-

Table 3
Mean values and standard deviations ($N=4$) for efficiency of organic matter decomposition (EOMD), residual acidity of the digests and Ba, Cu and P determinations in coffee samples applying both closed vessel digestion procedures.

Closed vessel system	HNO ₃		Efficiency of organic matter decomposition (%)		Elemental concentration		
	Initial (mol L ⁻¹)	Final (mol L ⁻¹)	Consumed (%)		Ba (μg g ⁻¹)	Cu (μg g ⁻¹)	P (mg g ⁻¹)
Parr Bomb	14	1.58 ± 0.07	88.8 ± 0.5	98.9 ± 0.2	3.4 ± 0.2	12.6 ± 0.1	1.84 ± 0.04
	10.5	1.011 ± 0.003	90.37 ± 0.03	98.60 ± 0.04	3.7 ± 0.1	12.7 ± 0.1	1.88 ± 0.02
	7	0.69 ± 0.02	90.1 ± 0.3	98.42 ± 0.05	3.8 ± 0.2	12.9 ± 0.2	1.83 ± 0.03
	3.5	0.31 ± 0.02	91.2 ± 0.6	98.16 ± 0.08	3.9 ± 0.2	12.9 ± 0.3	1.82 ± 0.04
Microwave	10.5	3.82 ± 0.01	63.6 ± 0.1	98.0 ± 0.2	3.7 ± 0.1	12.1 ± 0.2	1.66 ± 0.04
	7	2.50 ± 0.03	64.2 ± 0.5	97.7 ± 0.2	3.7 ± 0.1	12.0 ± 0.2	1.64 ± 0.03
	3.5	1.22 ± 0.04	65 ± 1	97.8 ± 0.5	3.6 ± 0.2	12.0 ± 0.3	1.73 ± 0.04

tionally, the use of diluted nitric acid solutions in routine analysis increases the safety of the procedure. A further advantage of the digestion using diluted nitric acid solutions is highlighted once blank values can be diminished resulting in lower limits of quantification. Despite the proper precision and accuracy when comparing diverse analytical results obtained from different digestion strategies as it can be observed in Table 3, the digestion procedure carried out with diluted nitric acid in closed vessels still needs a better understanding about the chemical processes behind organic matter decomposition. A hypothesis to explain the efficiency of closed vessel microwave-assisted organic matter digestion was recently presented and it was based on the oxygen amount and the gradient of temperature inside the digestion vessel during the beginning of the process [11].

The digestion procedures for coffee samples applied in the present work were based on the use of diluted HNO₃ solution and H₂O₂ as auxiliary reagent to take advantage of the high microwave energy absorption by water, as earlier discussed by Kingston and Haswell [23]. As a statement, the conversion of microwave energy in heat is maximized by using diluted acidic solutions.

Two different digestion alternatives for coffee sample preparation procedures with diluted nitric acid solutions were investigated for metal contents determination: microwave-assisted and pressurized bomb digestion (Table 3). A set of blanks was prepared together with each batch of samples. It is important to point out that it was not possible to perform the experiments exactly in the same experimental conditions due to safety aspects. The microwave vessel has a volume of 100 mL and it allows working safely with 250 mg of sample without any sudden increase of pressure. Taking into account vessel characteristics, the digestion was carried out using 7.0 mL nitric acid and 1.0 mL hydrogen peroxide. On the other hand, using the pressurized bombs with volumes of 23 mL it was feasible to digest only 200 mg of sample with 2.0 mL nitric acid and 1.0 mL hydrogen peroxide solutions. Solutions containing different nitric acid concentrations were employed to test their efficiency and to get a better understanding of the conductive-assisted and microwave-assisted digestion processes.

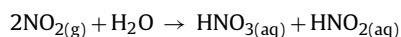
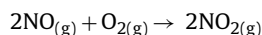
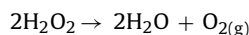
All digestion procedures were evaluated by comparing diverse parameters: residual RCC, residual acidity of the digests and the major, minor and trace element recoveries (Table 3) and no significant differences were observed for 95% confidence level by applying one-way ANOVA followed by the application of multiple comparisons Bonferroni test [24,25] for acid concentrations greater than 3.5 mol L⁻¹. As previously mentioned, it is well known that the acid concentration of digests affect pneumatic nebulization and aerosol formation whereas RCC affects plasma excitation conditions and causes spectral interferences mainly at low wavelengths. Notwithstanding, partial solid sample decomposition were obtained for experiments carried out with HNO₃ concentrations lower than 2 mol L⁻¹, some results obtained for digestion procedures using 1.75 and 1.0 mol L⁻¹ nitric acid solutions in microwave and pressurized

bomb systems were used to explain the processes behavior. The residual acidity of the solutions obtained after the digestion procedures performed with closed vessel microwave and in pressurized bomb systems varied from 0.31 ± 0.03 to 4.66 ± 0.02 and from 0.16 ± 0.03 to 1.58 ± 0.07 mol L⁻¹, respectively. The calculated residual acid concentrations were evidently lower starting from more diluted HNO₃ solution and the dispersions of these results (RSD, in %) were increased for microwave-assisted and conductive heating by decreasing the initial nitric acid concentration. The relative standard deviations associated to the parameter residual acid concentration for mutually independent digestions ($N=4$) of the same regular coffee sample carried out with 1 mol L⁻¹ and concentrated HNO₃ solutions by exploring conductive and microwave heating were 18 and 9.6% and 4.4 and 0.4%, respectively. The increases of RSD values for digestions carried out with 1 mol L⁻¹ HNO₃ solution were related to the fact that only a fraction of organic matter was decomposed when using this solution.

The evaluation of the chemical mechanisms involved with microwave and pressurized digestion processes is better accomplished considering the percentage of nitric acid consumed (Table 3). Using closed vessels heated by microwave radiation, the nitric acid consumption varied in the 63.6 to 66.7% range and with pressurized bomb vessels varied in the 88.8 to 91.2% range. The greater consumption of nitric acid in pressurized bomb was a hint for understanding the processes behind the digestion. The model proposed involves conversion processes in liquid and gas phases.

The effectiveness of the digestion processes was also evaluated by the efficiency of organic matter decomposition (EOMD, expressed in %) which value is calculated by the ratio between the difference of total carbon contents (TCC) and the residual RCC determined in the digests and TCC, i.e. $(TCC - RCC/TCC) \times 100$. This proposed parameter only can be considered when a homogeneous liquid phase or only silicate solid phase residues are obtained after the digestion. The EOMD was always higher than 98% for the evaluated closed vessel digestion processes (Table 3).

It is known that the main product when employing concentrated nitric acid is NO₂ [11]. On the other hand, in diluted nitric acid solutions there is a preferential production of NO. In this case, during the oxidation of organic matter by nitric acid, NO is produced and it reacts with O₂ in gas phase generating NO₂. After, the formed NO₂ can be reabsorbed in the liquid phase leading to NO₃⁻ and HNO₂ production. This reaction cycle proceeds till complete consumption of the O₂ in the gas phase. These chemical processes are represented by the following equations:



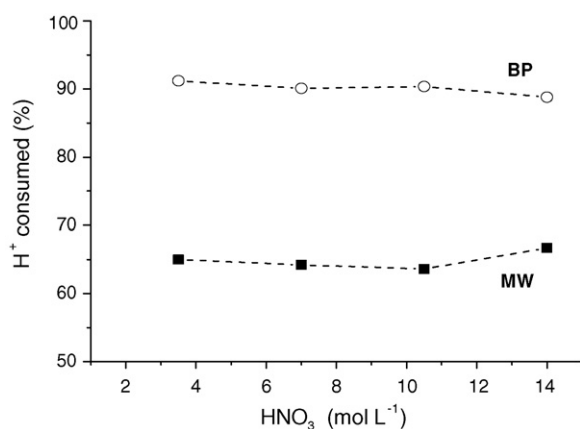
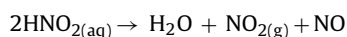


Fig. 1. Evaluation of HNO₃ consumption for digestions of coffee sample in Parr bomb (BP) and microwave oven (MW).



It is clear that these processes are critically dependent on the volume of O₂ in the closed vessel. As already pointed out, the microwave vessel has a 100 mL volume and the pressurized bomb

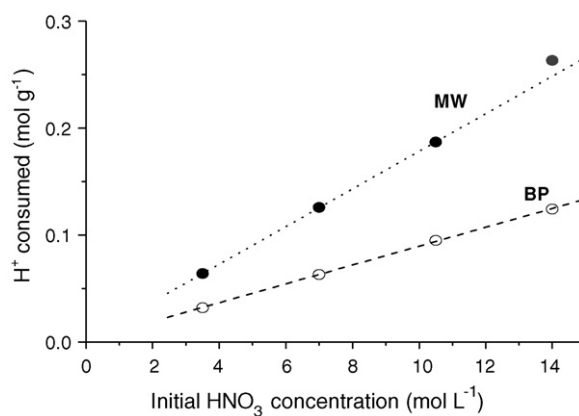


Fig. 3. Consumption of H⁺ (mol) necessary to decompose 1 g of coffee sample by employing Parr bomb (BP) and microwave oven (MW) procedures.

has a 23 mL volume. The greater volume of the former vessel implies that there is more O₂ available to promote oxidation processes in the gas phase despite aliquots of the same volume of H₂O₂ were added in digestion vessels.

In addition to the difference in volume, it is important to emphasize that closed vessels heated by microwave radiation present an intense temperature gradient during the first step of digestion. This

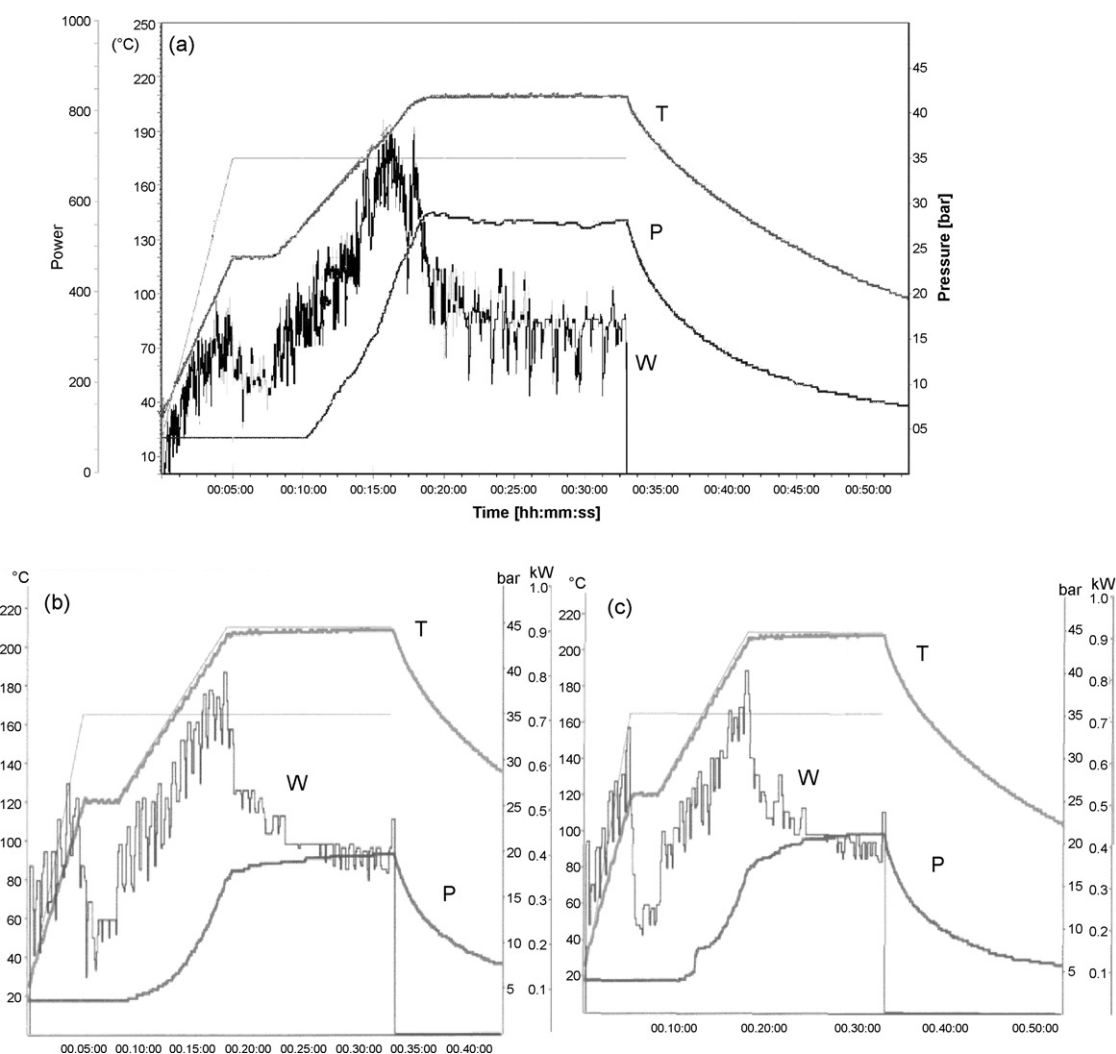


Fig. 2. Profiles of temperature and pressure during the digestion in closed vessel microwave system. T: Temperature; P: Pressure; W: variation of applied power to reach the set temperature. (a) HNO₃ 14 mol L⁻¹; (b) HNO₃ 7.0 mol L⁻¹; (c) HNO₃ 3.5 mol L⁻¹.

aspect can be explained due to the transparency of the vessel to the microwave radiation and the intense absorption of it by the liquid phase but not by the gas phase. Consequently, in the first step of digestion the soluble gases as well those formed by evaporation and chemical processes are transferred to the gas phase, which remains at low temperature, and suffers condensation. This temperature gradient also acts to improve the reaction between NO, produced by the oxidation of organic matter during the digestion, and O₂ leading to NO₂ production. The formed NO₂ is reabsorbed in the acid solution and regenerates HNO₃, as discussed. The more intense occurrence of these processes in microwave-heated vessels was experimentally proved by the lowest consumption of HNO₃ during the digestion process (Fig. 1). Another evidence of the occurrence of these processes was the less intense increase of pressure observed when microwave digestion process was carried out with diluted nitric acid solution. Fig. 2 shows the variations of temperature and pressure during the digestion in closed vessel microwave system and it corroborates the proposed mechanism once the increase of pressure is slow and less pronounced only for the digestion processes with diluted nitric acid solutions (Fig. 2b and c). The pressure variation during the digestion carried out with concentrated nitric acid solution can be seen in Fig. 2a.

In other approach the quantity of matter of nitric acid consumed to decompose 1 g of coffee sample can be easily calculated for both digestion systems evaluated using diverse initial concentrations of nitric acid solutions. The aliquot volume of nitric acid solution used for digestions in Parr bomb (2 mL) was lower than that used for microwave-assisted digestions (7 mL) and thus the quantity of matter of H⁺ from nitric acid consumed was higher for digestions in microwave system (Fig. 3). As it can be seen in Fig. 3, the amount consumed of H⁺ per gram of sample has a linear dependence with the initial concentration of nitric acid solution and it may be supposed that the same decomposition mechanism was followed independent on the nitric acid concentration. A consistent linear relation ($r=0.9999$) was obtained for microwave-assisted digestions carried out with diluted nitric acid solutions (Fig. 3). In theory, the quantity of matter of H⁺ consumed for the decomposition of 1.0 g of coffee sample with concentrated nitric acid (14 mol L⁻¹) by closed vessel microwave digestion process would be 0.249 ± 0.001 mol, i.e. 5% lower than that determined (0.262 mol), sustaining the hypothesis of HNO₃ regeneration.

Finally, the results obtained when these analytical methods were applied to Ba, Cu and P determination in coffee samples were summarized in Table 3 and the calculated element concentrations were similar to those obtained in other studies with Brazilian coffee samples [8,26,27]. Notwithstanding excellent agreements were obtained for Cu and Ba concentrations by comparing coffee sample digestions in pressurized Parr bomb and microwave system independent on the concentration of nitric acid. However a bias (ca. +9%) was observed by comparing phosphorous concentration after the digestion in Parr bomb and microwave system for all range of evaluated nitric acid concentrations (from 3.5 to 14 mol L⁻¹), however no significant differences were verified for 95% confidence level independently on the initial nitric acid concentration used for coffee sample decomposition with the same digestion system. Thus, the systematic error observed for phosphorous concentration determined from digests obtained by employing closed vessels conductive and microwave heated was explained by kinetic aspect.

So, taking into account important parameters such as the safety of the sample preparation procedure, operator comfort and atom economy, the use of diluted nitric acid solutions is advantageous compared to the classical microwave-assisted-acid digestion.

4. Conclusions

The use of diluted nitric acid solutions in closed vessels is a good strategy for digestion of regular coffee samples and the digestion process is critically dependent on the vessels size, availability of O₂ and temperature. Experimental data proved that the formation of NO, its conversion to NO₂ by O₂ action, and the regeneration of HNO₃ may explain the chemical processes involved with the digestion. The use of diluted nitric acid solutions for promoting digestions is promising and certainly it will open new routes for performing clean digestions compatible with trace analysis requirements.

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