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Short communication

Microwave-assisted digestion of organic samples: How simple can it become?

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ABSTRACT

Advancements in sample preparation for performing trace analysis of inorganic analytes are coming from the dissemination of microwave-assisted procedures, but there is still room for improvements by looking for simple and easily applied procedures. Recently it was proposed a new approach called single reaction chamber with capability for digestions at high pressures and temperatures using simple vials and racks. This was a limitation of former cavity microwave ovens with closed vessels. It was demonstrated here that the use of single reaction chamber approach allows the implementation of efficient digestions using diluted solutions of nitric acid and also allows addressing a critical need of sample preparation for inorganic analysis by running mixed batches of samples. The feasibility of this procedure was demonstrated for organic samples and accuracy was proved by using certified reference materials of apple leaves, bovine liver and whole milk powder. Digestions performed of whole milk powder and bovine liver using 2.0 mol L^{-1} nitric acid solution plus concentrated hydrogen peroxide at 240 °C led to residual carbon contents of 0.825 and 1.50% and residual acidities of 1.04 and 0.618 mol L^{-1}, respectively. These parameters are fully compatible with further measurements using ICP OES or ICP-MS. Al, Cu, Fe, Mn, Mo, Rb, Se, Sr, and Zn were accurately determined by ICP OES or ICP-MS depending on their concentrations in digests.

1. Introduction

Microwave-assisted sample preparation has become a standard for sample digestion in inorganic and organic analysis [1,2]. This is an important advancement in analytical chemistry tools for routine analysis because the fast evolution of instrumentation must be parallel to the development of straightforward and simple strategies for sample preparation or this initial step will remain as a bottleneck in the whole analytical procedure. However, despite these advancements the predominant use of concentrated acid solutions must be rethought and it should be remembered that this aspect is even more critical when working with focused-microwave oven [3,4]. No doubts these conditions led to efficient digestion with low residual carbon contents for organic samples, but due to the high residual acidities frequently the resulting digests must be highly diluted before introducing it by pneumatic nebulization in inductively coupled plasmas for avoiding transport interference effects. Based on modern principles of green chemistry it seems important to evolve from procedures that convert solid samples to solutions using too strong reaction conditions to tailored procedures that carefully led to the desired solutions without using more reagents, energy, temperature, and generation of residues than needed.

Recently Nóbrega and Donati [5] have stated that an ideal sample preparation procedure for analysis of organic samples should present the following attributes:

- Capability of digesting large amounts of samples;
- Compatibility with multi-element analysis;
- Safety;
- Compatibility with green chemistry principles;
- High sample throughput; and
- Ease of use.

Additionally, the obtained digests should be stable and characterized by low residual acidity, low residual carbon content (RCC), and low concentration of dissolved solids.

We may state that most microwave-assisted sample preparation procedures for inorganic analysis of organic samples have reached almost all of these attributes, but certainly there is room

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for improvements in labor requirement, analyst training, and green chemistry strategies [6]. So, new designs of microwave ovens have to overcome these limitations.

Based on this consideration it was tested here a new instrument recently launched with simple reaction vessels rack positioned inside a single reaction chamber (SRC). The so called UltraWAVE™ microwave oven is easily operated and allows reaching temperatures of up to 300 °C and pressures of 199 bar. A sample rack accommodates simple borosilicate, quartz or TFM tubes and all analytical procedure can be implemented as a single vessel procedure [7–9]. Pressure and temperature can be directly controlled for each and for all samples.

Taking into account the characteristics of this instrument, experiments were designed for evaluating the effects of temperature and reagent composition on digestion efficiency of samples containing high amounts of organic compounds. The oxidant reagent tested was composed by nitric acid solutions at various concentrations and mixtures of nitric acid solutions and hydrogen peroxide. The use of diluted acid solutions as low as 2 mol L^{-1} HNO_3 was tested because we target the development of a simple procedure compatible with green chemistry requirements [10–14]. In all experiments, the digestion efficiency was established by measuring residual carbon content (RCC) and residual acidity. It was demonstrated that olive leaves, apple leaves, peach leaves, and pine needles can be digested using 3 mol L^{-1} HNO_3 in a vessel pressurized with 5 bar of oxygen and the residual acidity was as low as 1.3 mol L^{-1} HNO_3 and RCCs were lower than 5% [11]. Similar conditions for digesting whole and non-fat milk powders led to RCCs around 0.17% [10]. It must be mentioned that these microwave-assisted digestions were performed in vessels pressurized with oxygen and it was clearly demonstrated the effect of this gas on the digestion conditions [12].

The goal here was to develop an analytical procedure that could be easily applied for promoting an efficient digestion of organic samples without any major risks either for the analyst or for the environment. Minor and trace elements were determined in the digests using inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS).

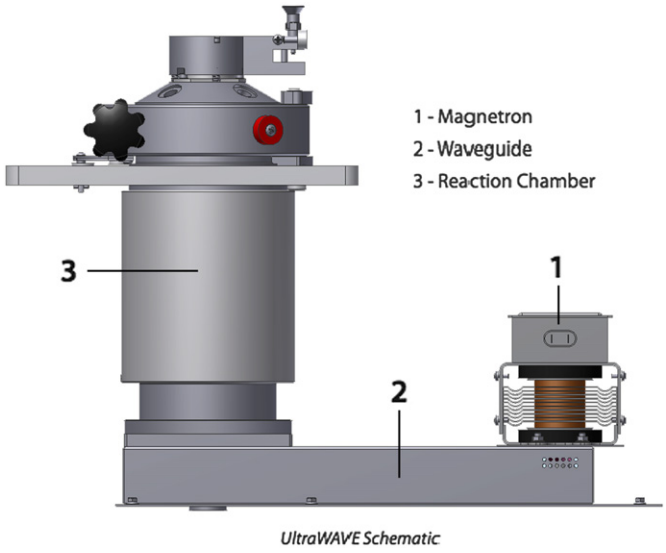

Fig. 1. Schematic representation of UltraWAVE™ SRC.

2. Experimental

2.1. Instrumentation

All digestions were developed using an UltraWAVE™ microwave oven based on the SRC design (Fig. 1, Milestone, Sorisole, BG, Italy). The UltraWAVE™ has a 1500 W microwave power source that delivers microwave energy to a 1 L chamber that can hold racks with 5, 15 or 22 vessels depending on vessels volume. Direct pressure and temperature control of the chamber gives direct control of every sample. A flow diagram of SRC operation is shown in Fig. 2. All experiments were carried out using two set of vessels. The first one was a rack with 15 TFM vessels with 15 mL each vessel. The second one was a rack with 5 quartz vessels with 40 mL volume each vessel.

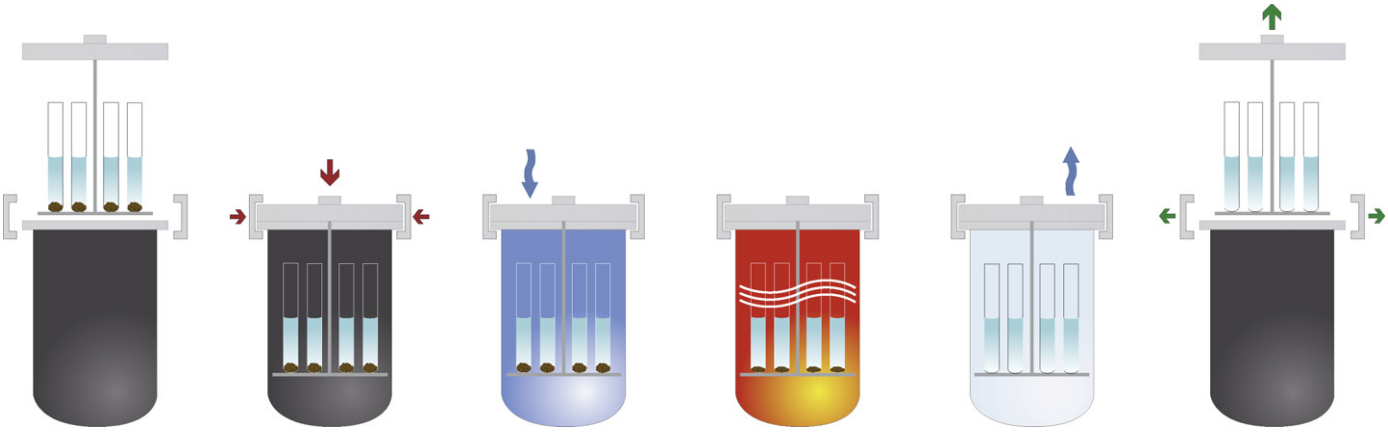

Fig. 2. Flow diagram of SRC operation.

Table 1
Operational conditions for ICP OES and ICP-MS measurements.

Parameter	ICP OES	ICP-MS
RF generator frequency (MHz)	40	27
RF applied power (kW)	1.0	1.4
Plasma gas flow rate (L min^{-1})	15.0	18.0
Auxiliary gas flow rate (L min^{-1})	1.5	1.8
Nebulizer gas flow rate (L min^{-1})	0.75	1.02
Stabilization delay (s)	15.0	10.0
Observation view	axial	–
Analytes	Emission line (nm)	Isotope (m/z)
Al	396.152	27
C	193.027	–
Cu	324.754	65
Fe	328.204	–
Mn	259.372	55
Mo	–	96
Rb	780.026	–
Se	–	82
Sr	407.771	–
Zn	213.857	–
Internal Standard	–	Y and Rh

Determinations of metals and Se were performed by ICP OES with axial viewing (ICP OES AX, Varian, Melbourne, Australia) and ICP-MS (ICP-MS model 820-MS, Varian). Carbon determination for RCC was measured by ICP OES. Both instruments were operated in conventional conditions as shown in Table 1.

2.2. Reagents, samples and solutions

All reagents were analytical grade and all solutions were prepared using a Milli-Q water system that produced pure water with resistivity higher than 18.2 MΩ cm (Millipore, Billerica, MA, USA). Solutions of nitric acid (Merck, Darmstadt, Germany) containing 7.0; 4.0; 2.0 and 1.0 mol L^{-1} were prepared from dilution of subdistilled concentrated pure acid using a sub boiling apparatus (Milestone). Concentrated hydrogen peroxide (30% (m/m), Merck) was also used.

Most experiments were performed using samples of biological materials, one reference material of whole milk powder (NIST RM 8435, Gaithersburg, MD, USA), and two standard reference materials of bovine liver (NIST SRM 1577b) and apple leaves (NIST SRM 1515) as representative of animal and botanical tissues. Tested samples were grass, bovine semen, bovine kidney, polymer, biodiesel, and lubricant oil. Solid samples were ground before digestion using conventional grinding equipment. Bovine semen and bovine kidney were lyophilized before grinding.

Standardized sodium hydroxide solution (0.1486 mol L^{-1}) was prepared for determining residual acidity in digests by acid–base titration.

2.3. Microwave-assisted sample preparation

2.3.1. Effect of temperature on whole milk powder and bovine liver digestion

All digestions were tested with masses around 0.5000 g exactly weighed and with 5 mL nitric acid solution at different concentrations (14.0, 7.0, 4.0, 2.0 and 1.0 mol L^{-1}). A volume of 3.0 mL of concentrated hydrogen peroxide was added when needed. Microwave-assisted heating program was implemented using 20 min for ramp time and 10 min for hold time at 1500 W applied power. Temperatures were set at 150, 180, 210, 240, and 270 °C. These experiments allowed establishing reagent and temperature conditions for biological samples, such as bovine liver, bovine kidney, apple leaves, and whole milk powder. All digestions were performed using TFM or quartz vials. Volumes of 120 mL of water and 5 mL of concentrated hydrogen peroxide were inserted into the SRC and the chamber was pressurized to 100 bar. After cooling down to 65 °C, the chamber was depressurized and digests were diluted with distilled–deionized water without transferring the solution to any other vessel. It should be pointed out that all sample preparation steps were carried out using single vessel strategy without any need of vessel assembly and disassembly or solutions transference.

2.3.2. Simultaneous digestion of mixed batch of samples

The goal here was to establish a heating program that could simultaneously run a mixed batch of samples. Masses of 0.5000 g of grass, bovine semen, bovine kidney, bovine liver, milk powder, and apple leaves were transferred to 15 mL TFM vials in a rack with capacity for 15 vessels. A volume of 5 mL concentrated nitric acid was added to each vessel and the following heating program was applied: 1st step—14 min to 120 °C, 2nd step—11 min to 250 °C, and 3rd step—hold at 250 °C for 8 min. All steps were performed at 1500 W of applied power. Maximum pressure was set at 120 bar.

In a second experiment with samples containing even higher amounts of organics, masses of 0.5000 g of polymer, biodiesel, lubricant oil, and a 4:1 m/m mixture of biodiesel and lubricant oil were transferred to 40 mL quartz vials in a rack with capacity for 5 vessels. A volume of 5 mL concentrated nitric acid was added to each vessel and the adopted heating program was the same described above.

All digests were diluted to 50 mL for determining RCC and residual acidity.

3. Results and discussion

The digestion of samples containing mainly organic compounds is essentially the establishment of reaction conditions to promote oxidative processes. Consequently, two parameters are critical for adjusting proper experimental conditions: the acid mixture used for digestion and the applied temperature for promoting reactions. Of course, time is also an important parameter, but we cannot promote oxidative processes unless we have the minimum temperature to go through activation energies of chemical reactions [15]. Based on these premises and on previous experiences with microwave-assisted digestion we decided to focus this study in the use of solutions containing different concentrations of nitric acid with or without adding hydrogen peroxide. It is well known that the use of high pressures systems led to elevated boiling points for nitric acid solutions which speed up chemical reactions and increase the oxidant power of this reagent [1]. This chemical behavior of nitric acid at high pressures completely avoids the use of perchloric acid in microwave-assisted digestion in closed vessels which is an important path towards safer procedures.

The first experiment dealt with the use of 7.0 mol L^{-1} HNO_3 solution for digestion of 0.500 g of whole milk powder and bovine liver. As discussed in Section 2 temperature was increased till the set point in 20 min and the maximum temperature was kept during 10 min. Results for RCC and residual acidity are shown in Table 2. As expected, lower RCCs were obtained when the digestion temperature was increased. The RCCs were 0.0500 and 0.200% for whole milk powder and bovine liver digests, respectively, when the digestion was carried out at 270 °C. On the other hand, digests obtained at maximum temperature of 150 °C contained remained solid particles and digests obtained at 180 °C were yellowish indicating a partial digestion process. It should be mentioned that digestions at these temperatures were also performed using concentrated nitric acid and the same behavior was

observed indicating that both parameters should be correlated to reach proper digestion, in other words high nitric acid concentrations at relatively low temperature cannot promote efficient digestions. Residual acidities decreased at higher digestion temperatures owing to the consumption of the nitric acid by oxidative processes and also due to its decomposition under heating. Residual acidities varied from 5.22 to 1.62 mol L^{-1} for samples of whole milk powder digested at 150 and 270 °C, respectively. Similar behavior was observed for bovine liver digests. Based on the literature [16] we may consider that lower nitric acid concentrations at high temperatures would be efficient and this condition can be easily implemented using modern microwave ovens and certainly it is attractive when searching for green chemistry sample preparation procedures. Thus, it was investigated here the use of solutions containing 2.0 and 4.0 mol L^{-1} nitric acid. In both cases digestions were not successful and solid residues were observed in the yellowish resulting digests.

Table 2
Effects of temperature on residual carbon contents (%) and residual acidities (mol L^{-1}) for digestions of whole milk powder and bovine liver.

Temperature (°C)	Whole milk powder		Bovine liver	
	RCC	Residual acidity	RCC	Residual acidity
150	2.86*	5.22	2.69*	5.15
180	1.91	4.35	2.17	4.58
210	0.380	3.10	0.430	3.06
240	0.100	2.15	0.290	2.14
270	0.0500	1.62	0.200	2.18

* These values of RCC are estimated because the digestions were not complete and digests containing solid residues. All RCC are mean values of 3 determinations and relative standard deviations were lower than 20% except for digests obtained at 150 °C. All residual acidities are mean values of 3 acid-base titrations.

Table 3
Residual carbon contents (%) and residual acidities (mol L^{-1}) for digestions of whole milk powder and bovine liver with diluted nitric acid plus hydrogen peroxide (mean ± standard deviation, $n=3$).

Sample	RCC	Residual acidity
Whole milk powder	0.82 ± 0.04	1.00 ± 0.14
Bovine liver	1.50 ± 0.02	0.61 ± 0.06

Notwithstanding, it is well established in the literature the feasibility of using diluted nitric acid solutions for promoting efficient digestions of organic samples [16] and it was clearly demonstrated the effects of the temperature gradient inside the reaction vessel [17] and the benefits coming from the addition of oxygen to the reaction vessel atmosphere [10–14]. The profile of the temperature inside reaction vessels is not known but we may suppose that despite the homogeneous distribution of microwave radiation inside the SRC, temperature will be higher in the vessel bottom in contact with the reagent solution. On the other hand, it is not recommended to pressurize the SRC with oxygen for avoiding critical safety conditions. Consequently, the easiest and most practical way to supply oxygen to the reaction vessel is by adding hydrogen peroxide to the reagent solution. So, we investigated the digestion efficiency using 5 mL 2.0 mol L^{-1} nitric acid solution plus 3 mL 30% (m/m) hydrogen peroxide and clear solutions were obtained when working at 240 °C. Residual acidities and RCCs are shown in Table 3.

Al, Cu, Fe, Mn, Mo, Rb, Se, Sr, and Zn were determined in digests of apple leaves and bovine liver, both certified reference materials, and a reference material of whole milk powder (Table 4). Inductively CP OES or ICP-MS were used depending on both the final concentrations of analytes in the digests and the occurrence of spectral interferences. The feasibility of the developed procedure was demonstrated by the proper accuracy reached for most measurements. All measurements were performed by applying the standard additions method and internal standard. There was no need of further dilution of the digests and the only dilution of the digest occurred by the addition of each analyte for calibration purposes.

It may be concluded that this is a simple procedure easily applicable to routine analysis of large batches of biological materials samples. There is no shortcomings for vessel assembly and all analytical operations, i.e. sample weighing, addition of reagents, sample digestion, and digest dilution, are carried out at each single vessel without any need of transference of samples and solutions. This approach together with the external pressure inside the SRC avoids contamination and losses by volatilization. Compared to conventional digestions using concentrated nitric acid solutions, we may emphasize that all obtained digests are fully compatible with conditions required by pneumatic nebulization in ICPs and all limits of detection were improved proportionally to the decrease of the dilution factor. These data are not shown here, but as expected lower dilution of the digests and

Table 4
Determined concentrations of metals and Se (mean ± standard deviation, $n=3$) in certified reference materials.

Analyte	Certified values (mg kg^{-1})			Determined values (mg kg^{-1})		
	Apple leaves	Bovine liver	Whole milk powder	Apple leaves	Bovine liver	Whole milk powder
Al[f]	286 ± 9	3[a]	0.9[b]	268.6 ± 8.7[d]	2.38 ± 0.19[d]	1.2 ± 0.1[e]
Cu[f]	5.64 ± 0.24	160 ± 8	0.46 ± 0.08[c]	5.8 ± 0.1[d]	163.5 ± 0.01[d]	0.56 ± 0.10[e]
Fe	83 ± 5	184 ± 15	1.8 ± 1.1[c]	83.5 ± 9.9[d]	162.1 ± 5.9[d]	ND
Mn[g]	54 ± 3	10.5 ± 1.7	0.17 ± 0.05[c]	49.1 ± 3.0[d]	9.6 ± 0.4[d]	0.20 ± 0.01[e]
Mo[g]	0.094 ± 0.013	3.5 ± 0.3	0.29 ± 0.13[c]	0.080 ± 0.003[e]	3.6 ± 0.4[e]	0.33 ± 0.02[e]
Rb	10.2 ± 1.5	13.7 ± 1.1	16[b]	12.3 ± 0.1[d]	17.1 ± 2.0[d]	18.1 ± 1.1[d]
Se	0.050 ± 0.009	0.73 ± 0.06	0.131 ± 0.014[c]	ND	0.75 ± 0.02[e]	ND
Sr	25 ± 2	0.136 ± 0.001	4.35 ± 0.50[c]	23.8 ± 2.8[d]	0.22 ± 0.03[d]	4.5 ± 0.2[d]
Zn	12.5 ± 0.3	127 ± 16	28.0 ± 3.1[c]	10.8 ± 0.1[d]	97.0 ± 1.8[d]	25.0 ± 2.1[d]

ND—not determined.

[a] Noncertified values.
[b] Information concentrations.
[c] Reference concentrations.
[d] Measurement performed by ICP OES.
[e] Measurement performed by ICP-MS.
[f] Y was used as internal standard.
[g] Rh was used as internal standard.

Table 5
Residual carbon contents (%) and residual acidities (mol L^{-1}) for digestions of mixed batch samples with concentrated nitric acid in TFM vials (mean ± standard deviation, $n=3$).

Sample	RCC	Residual acidity
Grass	0.080 ± 0.050	7.5 ± 0.3
Bovine semen	0.075 ± 0.020	8.5 ± 0.1
Apple leaves	< 0.013	7.6 ± 0.2
Bovine kidney	0.130 ± 0.040	7.4 ± 0.1
Bovine liver	0.120 ± 0.020	6.6 ± 0.2
Whole milk powder	< 0.013	6.42 ± 0.05

Table 6
Residual carbon contents (%) and residual acidities (mol L^{-1}) for digestions of mixed batch samples with concentrated nitric acid in quartz vials.

Sample	RCC	Residual acidity
Polymer	2.59	3.4
Biodiesel	0.93	3.3
Lubricant oil	1.60	4.1
Lubricant oil + Biodiesel	1.74	3.3

blanks obtained using low volume and concentration of subdistilled nitric acid led to better detection power.

The next step for moving forward microwave-assisted sample preparation procedures would be the development of digestion procedures that could be simultaneously applied for samples with completely different composition. The conventional technology based on closed vessels microwave-assisted heated for promoting digestions does not allow running mixed batches of samples because of the critical conditions of pressure that can be reached in vessels containing samples with higher amounts of organic compounds. Of course, this is a limitation in laboratories coping with large batches of samples with different characteristics. This is not the case for vessels in the rack of a SRC because all they are submitted to the same external pressure and temperature conditions into the microwave chamber. We have tested the ability of SRC for running mixed batches of samples by simultaneously digesting samples of grass, bovine semen, apple leaves, bovine kidney, bovine liver, and whole milk powder using TFM vials (Table 5) and samples of polymer, biodiesel, lubricant oil and lubricant oil mixed with biodiesel using quartz vials (Table 6). The heating program was implemented by adding concentrated nitric acid and the maximum temperature was set at 250 °C. It can be seen that efficient digestions were promoted for all samples. Additionally, it can be inferred from the relatively high residual acidities that it is probably possible to run mixed batch of samples using diluted nitric acid solutions as demonstrated for whole milk powder, apple leaves, and bovine liver. However, this aspect was not investigated here for samples of polymers and oils. Of course, all digests obtained should be further diluted before introducing them in ICPs using pneumatic nebulizers.

This is clearly a step ahead for simplifying the application of microwave-assisted digestion procedures and makes them compatible with complex routine analysis of laboratories with challenging demands for different types of samples. Additionally, the simplicity of operation with vials and racks used in the UltraWAVE™ microwave oven helps to increase sample throughput compared to conventional closed vessel microwave technology. Using the SRC approach there is no need to assemble and disassemble vessels and all analytical operations can be carried out in one single vessel.

4. Conclusions

This work demonstrates the potentialities of the SRC approach for performing routine digestions of samples using concentrated or diluted solutions of nitric acid and extremely simple heating programs. All sample preparation steps for each sample were carried out in only one vial decreasing possibilities of losses of analytes and contamination. Sample throughput is improved owing to the easy operation of vials and racks. The developed procedures are fully suitable for high demanding analytical laboratories and did not require any extensive training of technical personal. Surely we may conclude that sample preparation is becoming simple and compatible with analytical capability of modern instrumentation.

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