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# Investigation of analyte losses using microwave-assisted sample digestion and closed vessels with venting



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## ABSTRACT

Microwave-assisted sample digestion using closed vessels is becoming the standard for trace analysis because contamination and losses can be better controlled. Gases are generated during digestion and there is an increment of the internal vessel pressure. Consequently, vessels venting may occur depending on the design of the vessel and the maximum pressure it can stand for. In the present work it was observed that it is possible to allow venting during the digestion without losing volatile analytes, such as As, when properly controlling heating and chemical conditions. Recoveries for As in certified reference materials of animal tissues ranged from 94 to 112% despite mass losses as high as 62%  $\text{mm}^{-1}$  observed in the digests. However, for Hg(II) in medium containing chlorides recoveries were poor. The efficiency of digestion was measured by determination of organic carbon contents in digests and they ranged from 0.10 to 0.19% for plant and animal tissues. The temperature gradient along the vessel height is important for avoiding losses of volatile elements.

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## 1. Introduction

Sample preparation is a critical step in the development of an analytical procedure because samples frequently should be digested to a representative solution [1]. The Analytical Methods Committee AMCTB N° 56 [2] published a technical statement pointing out that errors in chemical analysis are often discussed but seldom reliably attributed to their specific causes. The feedback from participants in proficiency testing is a good source of information and in AMCTB N° 56 was shown that sample preparation was the most critical step. In this context efficient sample preparation is essential in any trustable analytical procedure. The resulting digest for subsequent determinations by ICP-MS and/or ICP OES should not contain solids, which could cause clogging of the nebulizer, or high residual carbon contents which may cause transport effects, charge-transfer reactions [3], plasma spectral interferences [4] and plasma instability [5,6].

Microwave-assisted sample preparation with cavity oven and closed vessels are increasingly being used due to its compatibility with most modern instrumental methods, once it promotes better analytical blank control, use of smaller volume of acids, improved safety conditions, and avoid losses by volatilization or

contaminations commonly present in open systems [7–9]. Several acid mixtures can be employed depending on the type of sample and further steps of analysis. However, sample preparation involving microwave-assisted digestion in closed vessels offer limitations such as the mass of sample, which in general should not exceed 0.5 g for a sample containing high amounts of organic compounds. As the sample mass increases, there is an increment of the internal vessel pressure and, consequently, vessels venting may occur. This is important for safety reasons and avoids that the closed vessels reach too high pressures that may be harmful [10]. On the other hand, it is believed that venting cause losses and quantitative recoveries of volatile analytes are not possible after venting. However, if the venting process is controlled as well as the chemical reactions, losses of volatile elements can be avoided; moreover, vessels with higher height increased the gradient of temperature along its column and this effect will help to promote condensation processes and to keep ions into solution. Nevertheless, analysts must be careful because the determination of elements, such as Hg in water samples, requires addition of chloride in order to preserve dissolved mercury and avoid memory effects when solutions are introduced using pneumatic nebulization in ICP techniques. On the other hand, the presence of chloride may facilitate losses by volatilization [11].

Microwave-assisted digestion can be performed using dilute acid solutions without any significant negative influence on the digestion efficiency, which improves analytical blanks, and

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decreases costs and residues generation [12]. Additionally, temperature is a critical parameter for efficient sample digestion of organic samples in order to achieve activation energies necessary for promoting oxidation processes [13,14]. Such temperatures are easily and safely obtained and monitored using microwave-assisted digestions in closed vessels, which also offer accurate and precise results [15].

The aim of the study here described was to demonstrate that by controlling both heating and chemical conditions it is possible to allow venting during digestions without losses of analytes, even the ones considered as easily lost by volatilization. By confirming this hypothesis, it will be possible to work with dilute solutions of nitric acid and higher masses of samples without losses of analytes. By allowing controlled venting during digestion, the developed analytical procedure will be suitable for trace analysis applications and safety conditions will also be improved because closed vessels do not need to be designed to stand for too high pressures when working at too high temperatures.

## 2. Materials and methods

### 2.1. Instrumentation

A microwave oven model Ethos UP (Milestone MLS, Sorisole, BG, Italy) equipped with a medium pressure rotor with 44 TFM vessels (MAXI-44) with 'vent-and-reseal' technology was used for sample digestion. Vessel volume is 100 mL, internal diameter is 25 mm and height is 23.5 cm. The vessel dimensions were designed aiming higher temperature gradient which improves acid regeneration. It means that vessel internal diameter was decreased for putting more vessels in the rotor and at the same time its height was increased for increasing the temperature gradient between the bottom of the vessel and its top. This system is ideal for condensation of vaporized acids, especially in the regeneration of diluted nitric acid by condensation processes and reaction with oxygen, easily generated by H<sub>2</sub>O<sub>2</sub> addition [16–18]. The rotor is totally controlled by contactless infrared sensor (T2) for temperature control of each single vessel. This is a medium pressure rotor for acid digestion of easy to medium-difficult samples. The temperature inside the tube should not exceed 200 °C and the pressure must be kept below 35 bar. Additionally, a large cavity equipped with powerful exhaust system allows safe removal of gases escaping from vessels [10].

The measurements of analytes were performed by ICP OES or ICP-MS depending on the concentration of each analyte. An ICP OES iCAP 6500 Duo (Thermo Fisher Scientific, Madison, WI, USA) was used for monitoring emission lines (nm) in axial<sup>a</sup> and radial<sup>b</sup> viewing as follows: As I 193.759<sup>a</sup>, C I 193.091<sup>b</sup>, Ca II 396.847<sup>b</sup>, Cd II 226.502<sup>a</sup>, Cr II 283.563<sup>a</sup>, Fe II 238.204<sup>b</sup>, Hg II 194.227<sup>a</sup>, Mg II 279.553<sup>b</sup>, P I 178.766<sup>b</sup>, Pb II 220.353<sup>a</sup>, S I 182.624<sup>b</sup>, and Zn I 213.856<sup>b</sup>. Atomic lines are designed as I and ionic as II. The sample introduction system was composed by a glass concentric nebulizer and a cyclonic spray chamber. An ICP-MS/MS (Agilent Technologies, Model 8800, Tokyo, Japan) was used for determination of the isotopes <sup>57</sup>Fe<sup>+</sup>, <sup>68</sup>Zn<sup>+</sup>, <sup>75</sup>As<sup>+</sup>, <sup>111</sup>Cd<sup>+</sup>, <sup>112</sup>Cd<sup>+</sup>, <sup>206</sup>Pb<sup>+</sup> and <sup>201</sup>Hg<sup>+</sup> operated in single quadrupole mode with 7 mm of sampling depth. The sample introduction system consisted of a glass concentric nebulizer and a Scott type – double path spray chamber. Instruments operational parameters for ICP OES and ICP-MS are presented in Table 1.

### 2.2. Reagents and analytical solutions

Distilled-deionized water (resistivity higher than 18.2 MΩ cm) obtained from Milli-Q<sup>®</sup> Plus (Millipore Corp., Bedford, MA, USA)

**Table 1**  
ICP OES and ICP-MS operating parameters.

Instrument Parameter	Operating condition	
	ICP OES	ICP-MS
RF applied power (kW)	1.15	1.55
Plasma gas flow rate (L min <sup>-1</sup> )	12.0	12.0
Auxiliary gas flow rate (L min <sup>-1</sup> )	0.5	1.8
Nebulizer gas flow rate (L min <sup>-1</sup> )	0.70	1.05
Sample flow rate (mL min <sup>-1</sup> )	1.1	1.0

system was used to prepare all solutions. Nitric and hydrochloric concentrated acids (Merck, Darmstadt, Germany) previously purified by a quartz sub-boiling distillation apparatus (Milestone), and 30% mm<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (Labsynth, Diadema, SP, Brazil) were used to digest plant and animal tissues. Monoelement stock solutions of 1000 mg L<sup>-1</sup> of As, Cd, Cr, Hg, Pb, Zn, Ca, Fe, Mg, P, and S (Qhemis, São Paulo, SP, Brasil) were appropriately diluted to obtain analytical calibration solutions and to prepare spiked solutions. The residual acidity of the digests was determined by acid–base titration using sodium hydroxide solution standardized with potassium hydrogen phthalate.

### 2.3. Spiked solutions

Solutions containing 1.0 or 2.0 mg L<sup>-1</sup> of As, Cd, Cr, Hg, Pb and Zn, were subjected to the heating program to evaluate the effect of venting on analytes recoveries in the following media: 14 mol L<sup>-1</sup> HNO<sub>3</sub>, 12 mol L<sup>-1</sup> HCl and aqua regia. A volume of 10 mL of the respective solution was added to each digestion vessel and 100 or 200 μL of the analytes As, Cd, Pb, Zn, Cr and Hg 1000 mg L<sup>-1</sup> was added to obtain solutions containing 1.0 or 2.0 mg L<sup>-1</sup>, respectively.

### 2.4. Certified reference materials

The following certified reference materials (CRM) produced by the National Research Council Canada (NRCC Ottawa, Ontario, Canada): Dogfish Liver (DOLT-5) and Lobster Hepatopancreas (TORT-3); and by the National Institute of Standards and Technology, (NIST, Gaithersburg, MD, USA): Bovine Muscle Powder (RM 8414) and Trace Elements in Spinach Leaves (1570a), were used to evaluate the accuracy of the microwave-assisted sample preparation procedure.

Masses of 0.20 or 0.50 g of the CRMs were accurately weighted and transferred to digestion vessels, followed by the addition of 10 mL of 14 mol L<sup>-1</sup> HNO<sub>3</sub>. The goal here was to evaluate the venting effect when working with different masses of samples.

In order to check the recoveries for the CRMs, aliquots of approximately 0.20 g of each CRM were weighted and microwave-assisted digested using (I) 10 mL of 14 mol L<sup>-1</sup> HNO<sub>3</sub> or (II) 5 mL of 14 mol L<sup>-1</sup> HNO<sub>3</sub> plus 5 mL of H<sub>2</sub>O<sub>2</sub> 30% mm<sup>-1</sup> or (III) 10 mL of 7 mol L<sup>-1</sup> HNO<sub>3</sub>. Final volumes were made up to 50.0 mL with distilled-deionized water. An additional 4-fold dilution was performed before ICP-MS measurements in order to adjust the total dissolved solids contents.

### 2.5. Microwave-assisted heating program

The heating program at 1800 W of applied power was performed in two steps: 1st step: 5 min to reach 140 °C and 5 min at 140 °C, and 2nd step 10 min to reach 180 °C and 10 min at 180 °C. Afterwards, a ventilation step of 30 min was added to the heating program for vessels cooling. The vessels were removed from the rotor and cooled down to room temperature. The digestion

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