

An application of pressure/temperature-controlled microwave heating curves for the mineralization of tuna material prior to spectrometric quantification of mercury

Jorge E. Tahán, José M. Sánchez, Minerva C. Rodríguez, Hernán S. Cubillán
Víctor A. Granadillo and Romer A. Romero*

Laboratorio de Instrumentación Analítica, Facultad Experimental de Ciencias
La Universidad del Zulia, Maracaibo, Venezuela

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Abstract

This work presents an application of pressure/temperature-controlled microwave heating curves for monitoring the mineralization the Standard Reference Material of Albacore Tuna RM 50 for the subsequent flow injection cold vapor atomic absorption spectrometric (FI-CVAAS) determination of total mercury (Hg). Mineralizations were performed using a CEM Model MDS-2100 laboratory microwave oven (950 W for 100% power) provided with pressure sensing tube and fiberoptic temperature probe to monitor and control pressure and temperature conditions inside the lined digestion vessels. A Perkin-Elmer Model 5100 PC atomic absorption spectrometer equipped with an electrodeless discharge lamp for Hg, was used in the flow injection mode. A Perkin-Elmer Model FIAS-400 system with an AS-90 autosampler were connected to the spectrometer. Initially, approximately 500 mg of standard test portion were digested with 15 mL of concentrated nitric acid. The mineralization time was 4 min. For nitric acid mineralization, one control vessel, two sample vessels and one blank vessel were employed for simultaneous digestion. After 2.5 min of mineralization time, pressure was kept at approximately 190 psi and temperature decreased down to 150°C. Unfortunately, not more than 20% of the total Hg was recovered. The mineralization of 300 mg of lyophilized test portion with 15 mL of concentrated nitric acid followed. These conditions favored the FI-CVAAS evaluation of total Hg (ca. more than 80% was recovered). The best results were obtained using less sample weight and fewer microwave digestion vessels under the following conditions: addition of 15 mL of concentrated nitric acid to 200 mg of test portion weight, using three digestion vessels (one control vessel, one sample vessel and one blank vessel) irradiated for 4 min. Under these conditions, the FI-CVAAS Hg concentration ($0.87 \pm 0.03 \mu\text{g/g}$) correlated statistically with the certified value ($0.95 \pm 0.10 \mu\text{g/g}$) reported for the reference material Albacore Tuna. The amount of Hg required to give 1% absorption was 314 pg. The detection limit, defined as twice the standard deviation of the blanks, was 164 ng/L which corresponds to 82 pg of Hg for 500 μL of solution undergoing analysis. Precision (R.S.D.) was better than 3%. In conclusion, monitoring and controlling pressure and temperature inside the digestion vessels guaranteed a much safer mineralization, avoiding chance for explosion of the reactor system and potential injuries to the analyst. In general,

* Author to whom correspondence should be addressed: Apartado Postal 15202, Las Delicias, Maracaibo 4003-A, Venezuela. e-mail: rromero@dino.conicit.ve.

pressure/temperature controlled microwave mineralization seems to be reliable alternative for sample decomposition.

Key words: Flow injection cold vapor atomic absorption spectrometry; pressure/temperature-controlled microwave mineralization; standard reference material albacore tuna; total mercury.

Aplicación de curvas de calentamiento por microondas con control de presión y temperatura para la mineralización de atún previo a la cuantificación espectrométrica del mercurio

Resumen

Se presenta una aplicación metodológica en el uso de curvas de calentamiento por microondas con control de presión y temperatura para monitorear la mineralización del material certificado Albacore Tuna RM 50, para la determinación posterior del mercurio (Hg) total empleando la técnica de la espectrometría de absorción atómica con vapor frío, en el modo de inyección en flujo continuo (FI-CVAAS). El material de referencia se mineralizó empleando un horno de microondas CEM Modelo MDS-2100 (950 W para 100% de potencia) con sensores de presión y temperatura. El Hg total se determinó empleando un espectrómetro de absorción atómica Perkin-Elmer Modelo 5100 PC equipado con una lámpara de descarga sin electrodo para Hg, al cual se le acopló un sistema de flujo continuo Perkin-Elmer Modelo FIAS-400, con muestreador automático AS-90. Inicialmente, ca. 500 mg del material certificado se digirieron con 15 mL de ácido nítrico concentrado por 4 min. Luego de 2,5 min de mineralización, la presión se mantuvo hasta ca. 190 psi y la temperatura disminuyó a 150°C. Desafortunadamente, menos del 20% del mercurio total pudo cuantificarse. La mineralización de 300 mg del material de referencia con 15 mL de ácido nítrico concentrado favoreció la evaluación total del Hg en un 80%. Finalmente, la mineralización de 200 mg del material de referencia con 15 mL de ácido nítrico concentrado irradiados por 4 min permitió correlacionar estadísticamente las concentraciones de Hg determinadas por FI-CVAAS ($0,87 \pm 0,03 \mu\text{g/g}$) con las reportadas para el material certificado ($0,95 \pm 0,10 \mu\text{g/g}$). La cantidad de Hg requerida para dar 1% de absorción fue 314 pg. El límite de detección, definido como dos veces la desviación standard del blanco, fue 164 ng/L la cual correspondió a 82 pg de Hg para 500 μL de solución inyectada. La precisión (R.S.D.) fue menor del 3%. El monitoreo y control de la presión y la temperatura dentro de los recipientes de digestión garantizó una mineralización más segura, evitando riesgos de explosión y peligro para el analista. En forma general, la mineralización en microondas con control de presión y temperatura constituye una alternativa confiable para la descomposición de muestras biológicas.

Palabras claves: Mercurio total; mineralización por microondas con control de presión y temperatura; espectrometría de absorción atómica con vapor frío con inyección en flujo continuo; material de referencia standard Albacore Tuna.

Introduction

Numerous reliable microwave mineralization methods have been developed over the years, as analytical approaches for determining trace metals in biological, environmental and food samples, employing voltammetric and spectrometric techniques (1-5). The use of microwave heating for sample dissolution was first reported in 1975 (6), showing a possible alternative for the classical open air hot plate digestion procedure (7). Open vessel work requires special hoods, can lead to corrosion of equipment, is open to potential contamination of the sample, and does not take into account the risk of metal losses by volatilization (8). Moreover, the most striking disadvantage of all dissolution procedures with conductive heat as an energy source is that they are time-consuming because a temperature gradient evolves from the oven via the vessel walls to the sample (8). Additionally, reaction temperature is limited to the atmospheric boiling point of the acid mixture. Microwave-based digestion techniques have been successfully employed due to the fact that they are faster. Microwave radiation can pass vessel walls (e.g., fluoropolymers) without substantial loss, offering a reduced risk of contamination and volatilization of the metal when closed-vessel reactors are used (4). A test portion sample placed inside a microwave-transparent vessel with a polar liquid or ionic solution (usually an acid) is subjected to rapid heating and elevated pressures, causing the test portion sample to digest in a short time. Microwave mineralizations have been reported using high pressure microwave digestion bombs and microwave digestion vessels with pressure relief valves (9-13). Tahán *et al.* (12) cited the spectrometric determination of total aluminum, chromium, copper, iron, mercury, sodium, lead and zinc concentrations in commercial canned seafood samples after microwave mineralizations by using microwave acid

digestion bombs and 120-mL Teflon PFA microwave digestion vessels with pressure relief valves. Mineralizations were performed in a laboratory microwave oven with conventional microwave heating power (ca. 600 W of full power).

Microwave mineralization can be done with high intensity microwaves (950 W of microwave energy, at full power, at a frequency of 2450 MHz) in closed-vessels reactors whose inside pressure and temperature conditions are controlled and monitored from an oven microcomputer board (14, 15). This novelty approach differs widely from the traditional microwave mineralization systems and may constitute an alternative to understand how efficient could be the mineralization procedure, once pressure and temperature reach maximal values.

Mercury (Hg) is usually determined using cold vapor atomic absorption spectrometry (CVAAS), and the introduction of flow injection (FI) technique for automated solution handling has further increased the reliability and attractiveness of CVAAS (16). However, the direct spectrometric determination of total Hg in biological materials is interfered with the presence of organic matter (15); this may bind mercury, modifying the metal speciation and, therefore, avoiding analyte reduction by sodium borohydride (12). Hence, the spectrometric procedure requires a preliminary destruction of organic matter to free the analyte metal from organic ligands. This may be done easily by monitoring pressure and temperature inside the reactor until optimal mineralization conditions are obtained.

We present an application of pressure/temperature-controlled microwave heating curves for monitoring the mineralization of tuna samples prior to the FI-CVAAS determination of total Hg.

Materials and Methods

Apparatus

A Perkin-Elmer Model 5100 PC atomic absorption spectrometer (*Überlingen, Germany*), equipped with an electrodeless discharge lamp for mercury, operated at 170 mA from an external power supply, was used in the flow injection mode. A 0.7 nm spectral slit-width was selected to isolate the 253.7 nm mercury resonance line; the temperature of the quartz tube atomizer was set to 20°C. A Perkin-Elmer Model FIAS-400 system equipped with two programmable peristaltic pumps and Tygon pump tubes were used in this study. An AS-90 autosampler was connected to the spectrometer. Nitrogen (inlet pressure of 52 psi) was the carrier gas. Instrumental conditions are shown in Table 1. The spectrometer, the flow injection system and the autosampler were controlled from a computer based on the Intel 80486 microprocessor running the 6.22 MS-DOS operating system (IBM Personal System/ValuePoint) and the GEM/3 Desktop operating system interface software. Microwave mineralizations were performed for the Albacore Tuna RM 50 Standard Reference Material (National Institute of Standards and Technology, US Department of Commerce, Gaithersburg MD, USA) using a CEM Model MDS-2100 laboratory microwave oven (950 W for 100% power) provided with pressure sensing tube and fiberoptic temperature probe to monitor and control pressure and temperature conditions inside the lined digestion vessels (Figure 1a). This type of vessel consists of a 100-mL Teflon PFA inner linner and a Teflon PFA cover; the casing and cap of the lined digestion vessel are made from microwave-transparent polymer (polyth-erimide). The collection vessel placed in the center of the turntable collects, condenses and vents vapors released when the rupture membrane breaks down (Figure 1b). In this system, pressure tubing attached to a sam-

Table 1
Instrumental conditions for the FI-CVAAS
determination of total mercury
in Albacore Tuna

Wavelength/nm	253.6
Electrodeless discharge lamp current/mA	170
Slit-width/nm	0.7
Absorbance measured	Peak height
Measurement time/s	25
Nitrogen carrier gas pressure/psi	52
Flow rate of reducing agent/ mL/min	10
Flow rate of carrier agent/mL/min	6

ple vessel (control vessel) is routed outside the microwave cavity of the CEM Model MDS-2100 laboratory microwave oven (950 W for 100% power) through one of the inlet/outlet ports; pressure is sensed by a transducer and displayed graphically and digitally on the display screen of the oven. The microwave transparent fiberoptic temperature probe is inserted into the thermowell of the control vessel and exits the microwave cavity via a bulkhead connector and leads to a special temperature control PC board mounted on the system CPU board; the temperature sensor is a phosphor located at the tip of the probe (Figure 1b).

Reagents

All chemicals used were of analytical reagent grade. The sodium tetrahydroborate solution (0.4% m/v) was prepared by dissolving sodium tetrahydroborate powder (Riedel-de Haën, Hannover, Germany) in appropriate amounts of grade 1 [as established by the American Society for Testing and Materials (ASTM), electrical resistivity

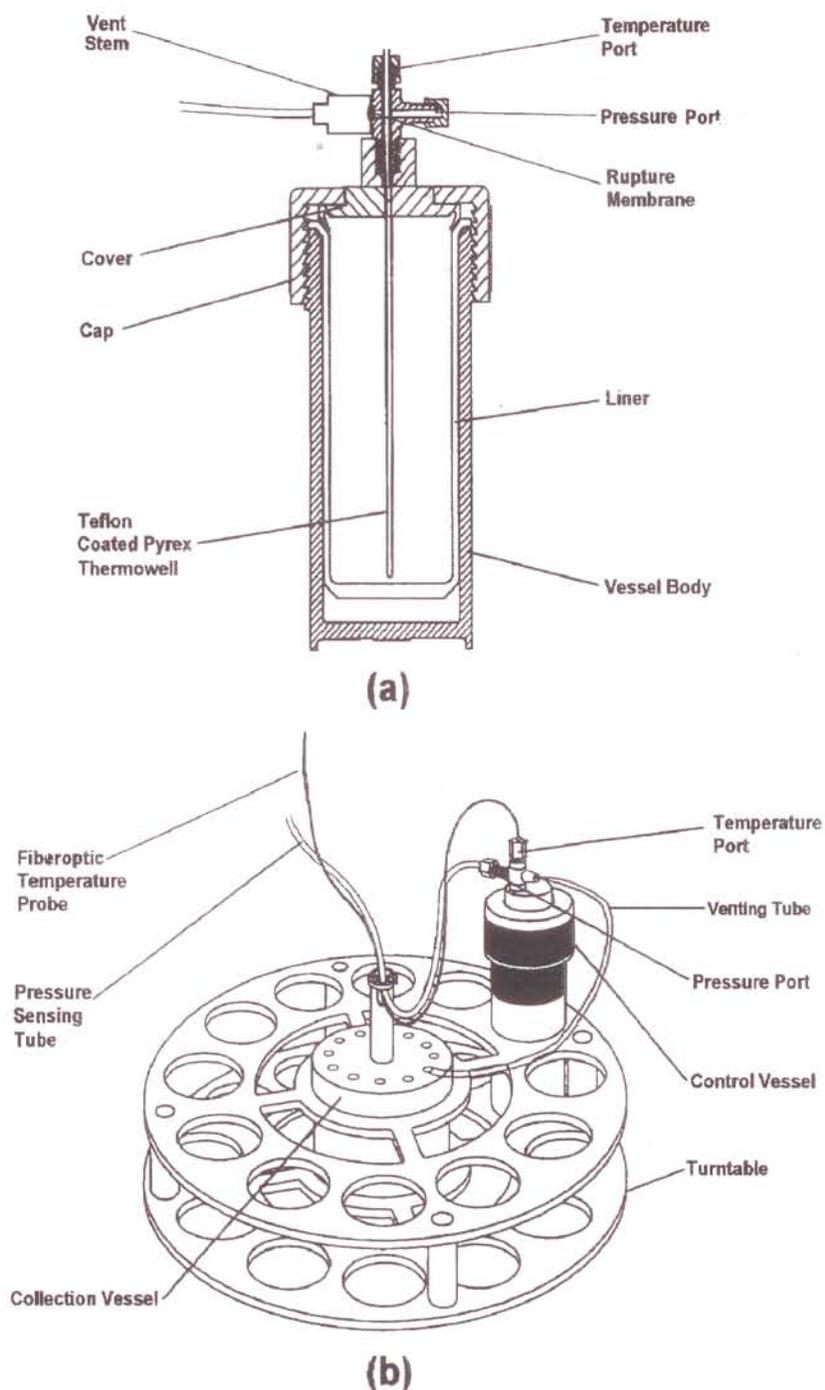


Figure 1: Microwave sample digestion system. (a) Lined digestion vessel for pressure and temperature control. (b) Routing of pressure sensing tube, fiberoptic temperature probe and vent tube connected to collection vessel.

16.6 M Ω /cm at 25°C) (17) triply-distilled and de-ionized water, then stabilized with 0.2% m/v sodium hydroxide (Merck). This solution was prepared daily before use. Concentrated nitric acid (Merck) was used during the digestion procedures. The stock solution (1,000 mg/L of Hg) was prepared from Atomic Absorption Standard (J.T. Baker, Phillipsburg, NJ, USA) concentrates. Standard solutions were freshly prepared by serial dilution of the stock with 0.01 mol/L nitric acid.

Closed-vessel microwave mineralization of Albacore Tuna

Approximately 200 mg of the Standard Reference Material Albacore Tuna RM 50 and 15 mL of concentrated nitric acid were placed into the vessel liner and capped with a cover that employs pressure assisted type seal for leak-free operation (e.g., as internal vapor pressure rises from microwave heating of the liquid, the seal is energized, forming a progressively tighter seal with increasing pressure). The capped liner was put into the microwave-transparent body of the lined digestion vessel and closed by tightening the cap. Three samples and one blank were routinely prepared for simultaneous digestion. The four vessels (including the control vessel which always contained the largest test portion to mineralize) were placed on the turntable, inserted in the oven, and irradiated for 4 min (at 100% power, equivalent to 950 W and 2450 MHz); the optimized conditions for maximal pressure and temperature were 190 psi and 190°C. The turntable was rotated continuously. After cooling to ambient temperature, caps were removed and contents were transferred quantitatively into 25-mL calibrated flasks and diluted to volume with grade I ASTM triply-distilled, deionized water. Blanks were prepared with the same reagent, without the sample, undergoing a similar high-pressure closed-vessel decomposition treatment by microwave heating.

Mercury determination by FI-CVAAS

For mercury quantification, the sample loop had a volume of 500 μ L. Triplicate determinations were always done, for every program sequence tested. The tygon pump tubes with the following color codes and inner diameters were used: red-red (1.14 mm) for sodium tetrahydroborate, yellow-blue (1.52 mm) for the carrier and black-white (3.18 mm) for sample waste.

Results and Discussion

During the microwave mineralization procedure, Hg losses by volatilization were eliminated by carrying out the acid mineralization in sealed vessels. The microwave mineralizations were performed for the Standard Reference Material Albacore Tuna RM 50; the final digestion solution was suitable for the subsequent FI-CVAAS determination of total Hg. Figure 2 details different mineralization curves used to provide the final optim mineralization conditions. Initially, approximately 500 mg of standard test portion were digested with 15 mL of concentrated nitric acid. The mineralization time was 4 min; the maximal pressure and temperature inside the digestion vessels were set up at 190 psi and 190°C. For nitric acid mineralization, one control vessel, two sample vessels and one blank vessel were employed for simultaneous digestion. Figure 2a shows the monitoring of the pressure and temperature inside the sample vessel. Initially, the temperature was increased after 15 s of mineralization while pressure required 1 min to obtain a competitive increment. After 2.5 min of mineralization time, pressure was kept at ca. 190 psi and temperature decreased down to 150°C. Unfortunately, not more than 20 % of the total mercury was recovered. As a consequence, the ability of obtaining and maintaining maximal pressure (190 psi) and temperature (190°C) conditions at the beginning of

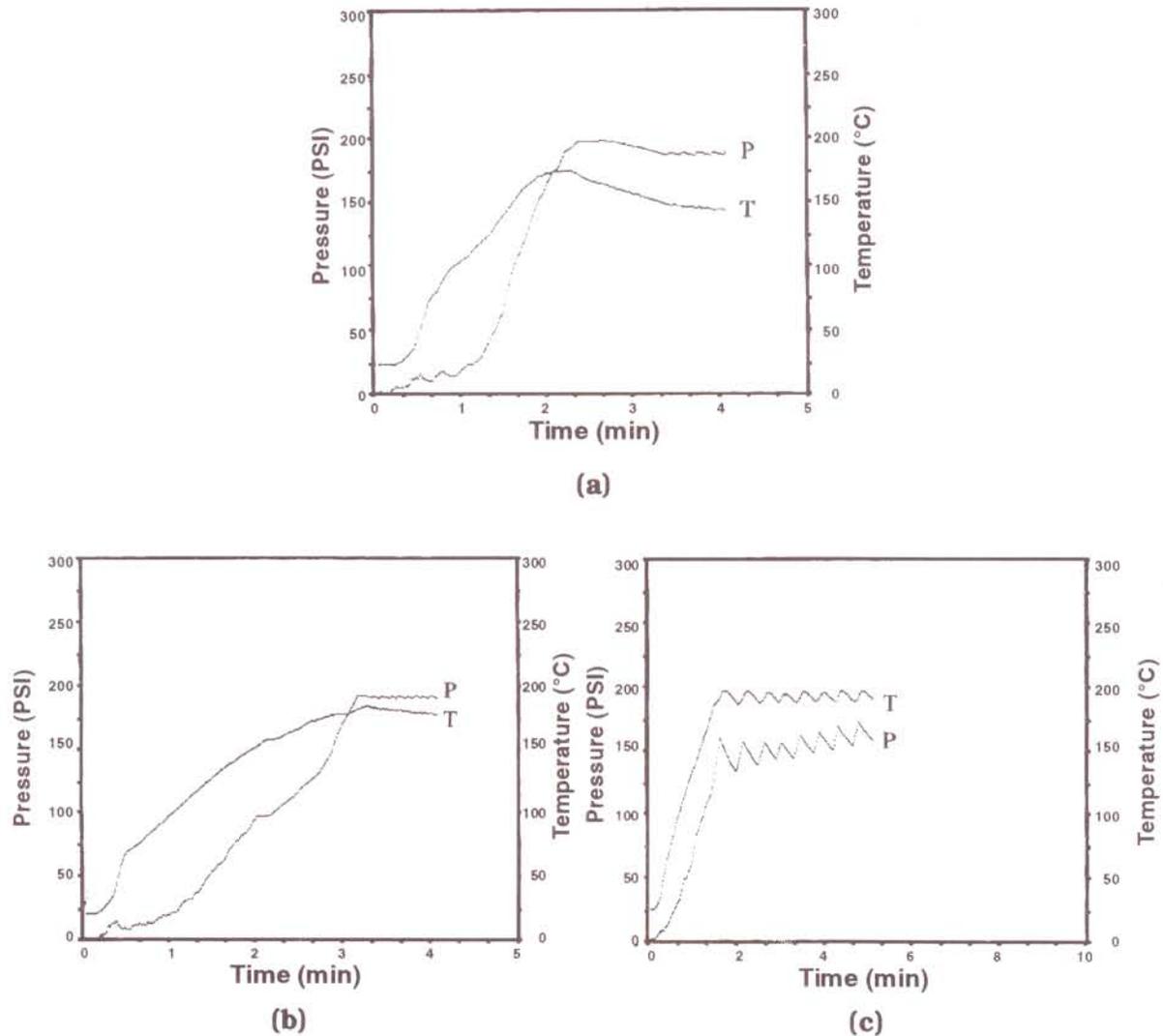


Figure 2: Monitoring pressure (P) and temperature (T) inside the lined digestion vessel heated by microwave irradiation. (a) Sample weight, 500 mg of reference material Albacore Tuna; nitric acid volume, 15 mL. (b) Sample weight, 300 mg of reference material; nitric acid volume, 15 mL. (c) Sample weight, 200 mg of reference material; nitric acid volume, 15 mL. In all cases, pressure and temperature were set up at 190 psi and 190°C. For cases (a) and (b), one control vessel, two sample vessels and one blank vessel employed. For case (c), one control vessel, one sample vessel and one blank vessel employed.

the process was not accomplished. Additional oven time periods (ca. 10, 15, 20 min) were tried to ensure the quantitative destruction of the organic concomitants but total mercury quantification was still not satisfactory.

In efforts to determine the total mercury concentration in the reference material, the mineralization of 300 mg of lyophilized test portion with 15 mL of concentrated nitric acid followed. These conditions favored the FI-CVAAS evaluation of total mercury (ca. more than 80% was recovered). Figure 2b shows the typical traces for the pressure and temperature, obtained under the experimental conditions mentioned. Maximal pressure (190 psi) and temperature (180°C) values were achieved after 3 min of microwave mineralization. Pressure increased slowly due to the fact that the sample weight was decreased to 300 mg. The best results were obtained using less sample weight and fewer microwave digestion vessels under the following conditions: addition of 15 mL of concentrated nitric acid to 200 mg of test portion weight, using three digestion vessels (one control vessel, one sample vessel and one blank vessel) irradiated for 4 min (Figure 2c). Under these conditions, the FI-CVAAS mercury concentration ($0.87 \pm 0.03 \mu\text{g/g}$) correlated statistically with the certified value ($0.95 \pm 0.10 \mu\text{g/g}$) reported for the reference material Albacore Tuna.

Peak height absorbance readings (A_p) increased linearly in relation to the mass (in ng) of mercury (C) present according to the equation $A_p = 0.0146 C - 0.0002$ (correlation coefficient $r = 0.9994$). The amount of Hg required to give 1% absorption was 314 pg. The detection limit, defined as twice the standard deviation of the blanks, was 164 ng/L which corresponds to 82 pg of mercury for 500 μL of solution undergoing analysis. Precision (R.S.D.) was better than 3%. These results can be considered adequate for this kind of analysis. For 70 mg of bio-

logical material mineralized and deluted to produce 10 mL of solution, the detection limit was 1.14 ng/g of Hg (dry-mass) in the original solid samples.

In pressure/temperature-controlled microwave mineralization experiments, the best mineralization conditions are obtained once pressure and temperature reach maximal values; in general, the faster in reaching maximal values the better the oxidizing agent (14). In addition, pressure inside the digestion vessel increased when the sample weight added decreased.

In conclusion, monitoring and controlling pressure and temperature inside the digestion vessels guarantee a much safer mineralization than those reported previously (10), avoiding chances for explosion of the reactor system and potential injuries to the analyst. The risk of analyte losses by volatilization and of contamination are lessened because pressurized vessels are employed. Furthermore, lined digestion vessels are able to deal with a large organic sample size (ca. < 0.2 g). In general, pressure/temperature-controlled microwave mineralization seems to be reliable alternative for sample decomposition.

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