Advances in Nutrient Metals Digestion using Open and Closed Vessel Microwave Systems

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Abstract

Rapid technologically evolution in sensor, computer, and vessel enhancements have led to lower detection limits and residual carbon values for both open and closed vessel microwave techniques. Application of these technologies to the determination of nutrient metals (as well as nitrogen content) of food and feeds has shown that both high level (Fe, Zn, Cu) and important trace (Se, As, Co) metals can be prepared in a variety of matrices including accepted Standard Reference Materials (SRM) provided by the National Institute for Standards and Technology as a benchmark for success.

The addition of microwave transparent temperature sensors, slope control technology, and acoustic safety devices have made closed vessel microwave digestion a safe and effective option for both routine and trace work. Development of new open vessel systems using slot technology[1] has allowed the use of larger sample sizes for matrices that are not easily dealt with at the 0.5 gram level.

Paired with modem ICP-OE, or ICP-MS; these sample preparation technologies can help provide rapid turnaround for quality control or to solve nutritional or toxicity anomalies

Introduction

One of the earliest accepted applications of closed vessel microwave digestion was food and fecal analysis for nutrient and trace metals [Milne, et al., 1988]. Good recoveries with lower time and labor costs and better organic destruction and retention of volatile elements were reasons cited for using this technique instead of conventional hot plate or bomb methods for sample preparation. The latest work by another well-known Federal agency indicates that open vessel, automated microwave digestion can expand the sample size range and therefore the detection limit for trace metals, especially by ICP-MS.

Methods

Closed Vessel

Closed vessel microwave digestion utilized advanced composite or Teflon® PFA vessels in a specialized laboratory microwave oven (Today's Chemist at Work, July/ Aug 96) using direct pressure and temperature feedback control and precise power delivery (CEM MDS-2000T, Matthews, NC). These capabilities separate laboratory microwave systems for food analysis from those used for domestic cooking applications. Safety is a major issue since finely divided foodstuffs can react with superheated acids and cause explosions if proper control systems are not in place [Kingston, et al.] Matrices can be as varied as orange juice [Rezaaiyan, R, et al. 1990], seafood [McCarthy, et al. 1991], and foliage [Finch, et al., 1990] with analytes including virtually the entire periodic table (e.g. sulfur, selenium, lead, cadmium, zinc, as well as nutrient metals). The technique takes

advantage of the rapid absorption of microwave energy by food components including fats, carbohydrates, and proteins and the superheated temperatures attained when using closed vessels (microwave 'pressure cooking').

Open Vessel

Recent developments in open vessel microwave technology include 'slot technology[1]', infrared (IR) temperature feedback control, and automatic 'on the fly' reagent addition. The basic technique is similar to hotplate digestions but is designed to be faster, cleaner, and more controlled. The steam and carbon dioxide evolved during the acid digestion of organic foodstuffs limits the sample size on closed vessel systems. In an open vessel system these gases can be routed thru a scrubber device allowing much larger samples to be digested without the carbon dioxide 'cap' .

A one gram sample of milk powder, SRM 8435 was placed in a CEM STAR 2 (CEM Corp, Matthews, NC) and the following program entered:

Initial Reagent: 2.5mL Sulfuric, 12mL Nitric

Stage	Ramp Time	Temp. (C	Time at Parameter	Reagent	Aliquot Size (mL)	Added du TAP
1	3 min	130		None	None	No
2	2 min	200	1 min	2mL nitric	1mL	Yes
3	2 min	250	5 min	10mL nitric	1mL	Yes
4	0	200	10 min	20mL peroxide	1mL	Yes

Each program stage consists of a time to temperature (TimeWave™) stage along with reagents to be added during this ramp.

[1] Slot technology positions the sample cells along the edge of a microwave waveguide and gates the microwave energy to each cell in a controlled fashion without varying the output of the microwave device itself. Patent pending.

Results

The results from this run are listed below along with the certified reference values:

Analyte	Mn	Cu	Ca	Pb	Se	Fe
Units	ppm	ppm	wt%	ppm	ppm	ppm
Concn	0.19	0.52	0.88	.0.9	0.16	1.50
Ref Value	0.12-0.22	0.38-0.54	0.87-0.97	0.06-0.16	0.12-0.15	0.70-2.90

In addition, work was performed in cooperation with a Federal laboratory using the STAR System with a simple nitric acid/hydrogen peroxide digestion of various Standard Reference Materials using advanced Inductively-Coupled Plasma-Mass Spectroscopy (ICP-MS) technology:

Element/unit	**Tomato Leaf SRM 1573a Ref Value**	**CEM/Federal Lab ICP-MS Value**
Ca mg/100 g	5050 ± 90	4950
Mg mg/100 g	1200	1154
Na mg/100 g	13.6 ± 0.4	10.0
K mg/100 g	2700 ± 50	2554
P mg/100 g	216 ± 4	230.
Cu mg/100 g	0.47 ± 0.014	0.44
Mn mg/100 g	24.6 ± 0.8	22.38
Zn mg/100 g	3.09 ± 0.07	2.95
Cd ug/100 g	152.0 ± 4	139.
Co ug/100 g	57 ± 2	67.0
Pb ug/100 g	N/A	69.9
Hg ug/100 g	3.4 ± 0.4	N/A
Lobster NRC Tort-2	**NIST**	**CEM/Federal Lab ICP-MS Value**
Cu mg/100 g	10.6 ± 1.0	10.08
Fe mg/100 g	10.5 ± 1.3	9.93
Mn mg/100 g	1.36 ± 0.12	1.22
Zn mg/100 g	18 ± 0.6	17.63
Co ug/100 g	51 ± 9	52.41
Ni ug/100 g	250. ± 19	256.

Discussion

The use of ICP-OE and ICP-MS extend the detectable range of nutrient and toxic metals into the parts per million to parts per trillion range. Conventional sample preparation techniques would require clean room conditions to meet the ppt range at the very best. A combination of closed and open vessel microwave options was developed in order to offer the analyst a clean option for this type of work. Published results on the closed vessel system have demonstrated that it is capable of reproducible work in this range provided that careful reagent selection and sample handling are used. However samples sizes for the closed vessel technique are generally limited to 0.1 to 0.5 grams .

Preliminary work indicates that use of pure reagent grade nitric acid and hydrogen peroxide can permit open vessel microwave to address these same sample types with sample sizes ranging from one gram to 10 grams. Use of high boiling acids such as sulfuric or perchloric may also be possible in open vessel/slot systems, however these are not often available in the requisite purities for ultra-trace work.

Additional work will need to be performed in order to validate the open vessel/slot technology for all food matrices (as well as fecal, hair, and related materials of nutritional interest).

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