

# Elemental Analysis Manual

## for Food and Related Products

### Archive Notes

This is an archived file provided for historical reference purposes only. Links to sites external to this file are not maintained and have therefore been removed. For the most recent information, readers are directed to the current [EAM](#).

## 4.4 Inductively Coupled Plasma-Atomic Emission Spectrometric Determination of Elements in Food Using Microwave Assisted Digestion

Version 1.0 (June 2008)  
Authors: William R. Mindak  
Scott P. Dolan

GLOSSARY

### 4.4.1 SCOPE AND APPLICATION

This method describes procedures for using inductively coupled plasma-atomic emission spectrometry (ICP-AES) for determination of total element concentration (mass fraction) in food. The method was validated with the following foods: milk, cheese, bacon, tuna, eggs, peanut butter, corn, bread, pancakes, cereal, prune juice, lemonade, broccoli, sweet potato, spaghetti & meatballs, mayonnaise, beer, beef baby food, haddock and pears. Other matrices may be analyzed by these procedures if performance is demonstrated for an applicable analyte in the matrix of interest, at the concentration levels of interest. This method using pneumatic nebulization is applicable to the analytes listed in 4.4 Table 1. It should be noted that aluminum results could be biased low in some samples because of insoluble aluminum compounds

especially if silica is present. Thallium is listed conditionally because although fortification recoveries were acceptable during method validation, no reference materials were available.

**4.4 Table 1. Analytical Limits**

| Element   | Symbol | ASDL <sup>a</sup><br>(mg/L) | LOD <sup>b</sup><br>(mg/kg) | LOQ <sup>b</sup><br>(mg/kg) |
|---|--------|-----------------------------|-----------------------------|-----------------------------|
| Aluminum  | Al     | 0.054                       | 0.8                         | 2                           |
| Arsenic   | As     | 0.086                       | 2                           | 4                           |
| Barium  | Ba     | 0.0033                      | 0.05                        | 0.2                         |
| Boron   | B      | 0.021                       | 0.3                         | 0.8                         |
| Cadmium   | Cd     | 0.023                       | 0.3                         | 0.9                         |
| Calcium   | Ca     | 0.63                        | 8                           | 30                          |
| Chromium  | Cr     | 0.13                        | 2                           | 5                           |
| Cobalt  | Co     | 0.021                       | 0.3                         | 0.8                         |
| Copper  | Cu     | 0.0079                      | 0.1                         | 0.3                         |
| Iron  | Fe     | 0.0083                      | 0.2                         | 0.3                         |
| Lead  | Pb     | 0.17                        | 3                           | 6                           |
| Magnesium   | Mg     | 0.16                        | 2                           | 6                           |
| Manganese   | Mn     | 0.0099                      | 0.2                         | 0.4                         |
| Molybdenum  | Mo     | 0.027                       | 0.4                         | 1                           |
| Nickel  | Ni     | 0.066                       | 0.9                         | 3                           |
| Phosphorus  | P      | 0.16                        | 2                           | 6                           |
| Potassium   | K      | 1.1                         | 20                          | 40                          |
| Sodium  | Na     | 0.12                        | 2                           | 5                           |
| Strontium   | Sr     | 0.0019                      | 0.03                        | 0.07                        |
| Thallium  | Tl     | 0.16                        | 2                           | 6                           |
| Vanadium  | V      | 0.014                       | 0.2                         | 0.5                         |
| Zinc  | Zn     | 0.023                       | 0.3                         | 0.8                         |
| <sup>a</sup> Based on 3×σ of method blanks using pneumatic nebulization.                            |        |                             |                             |                             |
| <sup>b</sup> Based on 10×σ of method blanks, 4 g analytical portion, and 50 mL analytical solution. |        |                             |                             |                             |

The limits listed in 4.4 Table 1 are intended as a guide and actual limits are dependent on the sample matrix, instrumentation and selected operating conditions.

---

*Note: When the method was developed, the protocol at the time required ASQL and LOQ be calculated based on 10 times the standard deviation of the blank. The values reported in 4.4 Table 1 thus reflect “10×σ” values rather than the current protocol of “30×σ”.*

---

Aluminum concentrations using the method do not account for aluminum bound to silicates. The method, especially using pneumatic nebulization, may not achieve quantitative measurement of typical concentrations in some foods for some elements. Using ultrasonic nebulization will improve analytical limits for most elements. The following elements appear prone to laboratory environmental contamination and therefore require extensive assessment of contamination control: aluminum, chromium, and lead. Successful application of the method must match the purpose of the food analysis with the laboratory’s analytical limits. A subset of the elements may be selected for analysis.

This method should only be used by analysts experienced in the use of inductively coupled plasma atomic emission spectrometry, including the interpretation of spectral and matrix interferences, and procedures for their correction, and should be used only by personnel thoroughly trained in the handling and analysis of samples for determination of trace elements in

food products.

#### 4.4.2 SUMMARY OF METHOD

An analytical portion (0.4 to 5 g dependent on food composition) is decomposed with nitric acid and hydrogen peroxide in a high-pressure Teflon<sup>®</sup> lined digestion vessel using microwave heating and a feedback program to control temperature and pressure. A 50 mL analytical solution is prepared from the digest. Analytical solutions are nebulized and aerosol is transported to a plasma where desolvation and excitation occur. Either pneumatic or ultrasonic nebulization sample introduction is used. Characteristic atomic emission spectra are produced by radio frequency inductively coupled plasma. Spectra are dispersed by a grating spectrometer, and line intensities are measured with a light sensitive detector such as a photomultiplier tube or charge transfer device. Photocurrents are processed by a computer system. A background correction technique is required to compensate for variable background emission contribution to analyte signal and should be applied except in cases of line broadening. Extensive quality control procedures are incorporated for monitoring laboratory contamination and food matrix interference to ensure data quality. The application of microwave assisted decomposition sample preparation to ICP-AES determination of elements is well documented in the literature<sup>1-10</sup>.

#### 4.4.3 EQUIPMENT AND SUPPLIES

---

*Disclaimer: The use of trade names in this method constitutes neither endorsement nor recommendation by the U. S. Food and Drug Administration. Equivalent performance may be achievable using apparatus and materials other than those cited here.*

---

- (1) Inductively coupled plasma atomic emission spectrometer (ICP-AES)—Simultaneous or sequential ICP-AES with associated glassware, which uses a mass flow controller to regulate argon nebulizer flow rate supplied by a Dewar of liquid argon or tank of gaseous argon. A variable speed peristaltic pump to deliver all solutions to nebulizer. Pneumatic nebulizer which can aspirate high dissolved solids (*e.g.*, V-groove, cross flow, etc.) or an ultrasonic nebulizer.

---

*Safety Note: Inductively coupled plasmas should only be viewed with proper eye protection from ultraviolet emissions.*

---

- (2) Microwave decomposition system—Requires temperature control to 200 °C, pressure control to at least 600 psi, power range of 0-100% in 1% increments, minimum 1000 watts for 12 position carousel, feedback control of temperature and pressure and multi-step programming with ramp to temperature capability. Digestion vessels must be TEM Teflon<sup>®</sup> lined. System must be able to reach at least 200 °C and at least 600 psi. Vessels designed to vent and reseal can be used provided they vent at pressures >300 psi. Directions on use of microwave digestion equipment are specific to CEM Corporation brand equipment and assume familiarity. Use of the method with other brands of equipment may require procedural modifications.

---

*Safety Note: Microwave digestion systems are dangerous. Vessels contain concentrated nitric acid at high temperatures and pressures. Analyst must be familiar with manufacturer's recommended safety precautions.*

---

#### 4.4.4 REAGENTS AND STANDARDS

Reagents may contain elemental impurities that can affect the quality of analytical results. Reagents should be sought that minimize analyte contamination (ideally, analyte level is below the IDL). Use of high purity or trace element (i.e., metals) grade reagents is usually required.

---

*Safety Note: Reagents should be regarded as potential health hazards and exposure to these compounds should be limited. Material safety data sheets for these chemicals are to be available to the user.*

---

- (1) Reagent water—Water that meets specifications for ASTM Type I water<sup>11</sup>.
- (2) High purity nitric acid—Concentrated (sp gr 1.41), trace element grade or double distilled.
- (3) Nitric acid—Concentrated (sp gr 1.41), ACS reagent grade.
- (4) Nitric acid 1% (v/v)—Dilute 10 mL high purity nitric acid to 1000 mL with reagent water.
- (5) Nitric acid 10% (v/v)—Dilute 100 mL high purity nitric acid to 1000 mL with reagent water.
- (6) Hydrogen peroxide—30% H<sub>2</sub>O<sub>2</sub> solution. High purity or trace metals grade.
- (7) Stock standard solutions—Commercially prepared single element solutions prepared specifically for spectrometric analysis (usually 1000 or 10,000 mg/L). Stock standard solutions may also be prepared in the laboratory from high purity (≥99.99%) metals or salts. Alternatively, commercial multi-element solutions prepared specifically for spectrometric analysis can be used. These multi-element solutions will be much lower in concentration (typically 10-500 mg/L) than single element solutions to avoid compatibility problems.
- (8) Intermediate standard solution(s)—Prepared to contain appropriate concentration(s) of analytes for preparation of standard solutions. Pipet an appropriate volume of stock standard solution(s) into an acid rinsed volumetric flask and dilute to volume with 10% nitric acid. Alternatively, intermediate standard solutions may be prepared gravimetrically by measuring stock standard solution and 10% nitric acid masses multiplied by solution density in a 125 or 250 mL plastic bottle. The density of 10% (v/v) nitric acid is 1.04 g/mL and stock standard solution densities are provided by their commercial sources. Store prepared intermediate standard solutions in plastic bottles. Alternatively, commercial multi-element solutions prepared specifically for spectrometric analysis can be used.
- (9) Standard solutions—Prepare at least 3 standard solutions by combining appropriate volumes of stock standard solutions or intermediate standard solutions in volumetric flasks. Analyte concentration range should cover the LDR or a portion thereof. Lowest standard should be near the ASQL. Dilute to volume with 10% nitric acid. Many of the elements (cadmium, cobalt, molybdenum, etc.) have LDRs that far exceed the values expected in food analytical solutions. In addition, line-rich elements like iron may cause spectral interference on other emission lines if high concentrations are used to standardize the instrument. Therefore, the analyst may choose to work within part of the LDR. A recommended maximum concentration of an element in a standard solution is 10 mg/L. Exceptions would be elements usually present at high concentrations for example, calcium, sodium, potassium, magnesium and phosphorus. For convenience, each standard

solution should contain all the analytes to be determined. Chemical compatibility (i.e., of analytes, acids, etc.) must be considered to avoid the formation of analyte precipitates when mixing single element stock solutions to prepare standard solutions. High quality custom-made multi-element solutions are commercially available and are recommended. Transfer prepared standard solutions to acid cleaned plastic bottles (Teflon<sup>®</sup> FEP is preferred) for storage. Standard solutions may also be prepared by gravimetric dilution. Gravimetric dilution can be performed by measuring mass of stock or intermediate standard solution and 10% nitric acid masses in a 125 or 250 mL plastic bottle. Volumes are calculated from solution densities. At typical laboratory temperatures, the density of 10% (v/v) nitric acid is 1.04 g/mL and stock standard densities are provided by their commercial sources. Do not use standard solutions that are more than 30 days old since element concentrations can change with age.

- (10) Standard blank—10% nitric acid. Prepare sufficient amount for use in standardization, determination of IDLs, and for nebulizer rinse between each measurement.
- (11) Independent check solution (ICS)—Dilute appropriate volumes of analyte stock solutions or intermediate standard solutions obtained from a different source than used to prepare standard solutions with 10% nitric acid so analyte concentration will be several times the ASQL or in the range of 0.5 to 10 mg/L for most elements. Do not use ICS that is more than 30 days old since element concentrations can change with age.
- (12) Check solution—Use mid-concentration multi-analyte standard solution for the check solution.
- (13) Fortification solution—Prepared such that, when 1 mL is diluted to analytical solution volume (initial analytical solution volume usually 50 mL), analyte concentration is approximately at the middle of the LDR or appropriate for the expected sample analyte concentration. A fortification solution should not be prepared that would result in an analyte concentration in the analytical solution that is less than 10 times the ASQL. In addition, the fortification solution should not increase any analyte's concentration by more than 40 mg/L relative to the analytical solution because of potential problems caused by high analyte levels (nebulizer transport effects and spectral interference, etc.) and the challenge of minimizing the fortification solution volume. Pipet an appropriate volume of stock standard solution(s) or intermediate standard solution(s) into an acid rinsed volumetric flask and dilute to volume with 10% nitric acid. Alternatively, fortification solution may be prepared gravimetrically.

---

*Note: The concentration of analytes in the fortification solution should be adjusted based on experience and knowledge on the native analyte levels for the types of samples analyzed. Ideally, the fortification level should be 1 to 3 times the sample's native analyte concentration. However, determining ideal fortification levels is encumbered by the number of analytes, wide range of analyte concentrations found in foods, and unknown analyte concentration in the sample. For microwave digestion, it is important to control the amount of solution added to the decomposition vessel to minimize dilution of the nitric acid for a more consistent decomposition. Therefore, the total volume of fortification solution(s) added to the analytical portion must be no more than 1 mL.*

*Note: A fortification solution may also be used to prepare the ICS. However, in this case the stock and intermediate standard solutions used to prepare the fortification solution would have to be from a source independent from those used to prepare standard solutions. When the ICS is prepared from the fortification*

*solution then ICS also serves to check the fortification level.*

---

#### 4.4.5 DIGESTION PROCEDURE

The following operations should be performed in a clean environment to reduce contamination. An exhausting hood must be used when working with nitric acid. See §2.3.1 for additional information on performing microwave digestions.

- (1) Weigh analytical portion into clean vessel liner and determine mass of analytical portion to  $\pm 0.001$  g. For samples of unknown composition, limit portion to the equivalent of about 0.5 g dry material. If maximum pressure attained for this unknown is less than the vessel limit, then make a notation that for this food matrix a greater mass may be analyzed. However, less than the maximum mass should be used for samples high in salt content. A maximum analytical portion of 5 g should not be exceeded even if calculations based on the food's energy indicate that a larger portion could be taken. Use 1 g reagent water for method blanks (MBKs).
- (2) Wash down any material on walls and wet sample with 1 to 2 mL reagent water. Do not add more than 2 mL of water. Pipet 7.0 mL or weigh 10.0 g of high purity nitric acid into vessel liner.
- (3) If foaming or reaction with the acid is observed (usually foods high in sugar), let the vessels sit uncovered for 20 minutes or until reaction subsides. If a clean air hood is unavailable for this operation, place caps on vessels without pressing down fully or, if so equipped, cap vessels and loosen the pressure relief safety membrane nut to allow pressure to escape.
- (4) Seal vessels, (tighten pressure relief nuts if equipped) and run the digestion program in 4.4 Table 2.

**4.4 Table 2. Microwave Digestion Programs**

| <i>Digestion Programs for CEM MARS 5 with 12-Position Carousel<br/>with Ramp to Temperature Feature</i>  |           |                       |
|--|-----------|-----------------------|
| <i>Power is applied for the Ramp Time minutes or until Control Pressure or Control Temperature is met. If Control Pressure or Control Temperature are met before end of Ramp Time then program proceeds to Hold Time</i> |           |                       |
|  | Digestion | Peroxide<br>Oxidation |
| Maximum Power (Watts)  | 1200      | 1200                  |
| Control Pressure (psi) <sup>a</sup>  | 800       | 800                   |
| Ramp Time (min)  | 25        | 10                    |
| Hold Time (min)  | 10        | 5                     |
| Control Temperature (°C)   | 200       | 200                   |
| <sup>a</sup> Only use with non-venting vessels.  |           |                       |

- (5) After vessels have cooled to less than 50 °C move them to an exhausting hood and vent excess pressure slowly. Open vessels and add 2 mL 30% hydrogen peroxide. Reseal vessels (tighten pressure relief nuts if equipped) and run peroxide oxidation program in 4.4 Table 2.
- (6) After vessels have cooled to less than 50 °C move them to an exhausting clean hood and vent excess pressure slowly. Quantitatively transfer and dilute digestion solution to 50

mL with reagent water. This analytical solution should be transferred to a plastic bottle or a capped polypropylene centrifuge tube for storage.

#### 4.4.6 DETERMINATION PROCEDURE

The determination procedure was developed using an Applied Research Laboratories Model 3580 inductively coupled plasma atomic emission spectrometer. 4.4 Table 3a lists conditions used with this instrument. The optimum conditions must be determined for the equipment used. Quantification is performed by standard curve. However, complex matrices may require additional dilution or the determination to be made by standard additions.

##### **Instrument Setup**

- (1) Setup inductively coupled plasma atomic emission spectrometer according to the manufacturer's recommendations and with the following attributes:
  - Set rinse time to at least 60 sec.
  - Program instrument method for the analytes of interest. Include the following elements even if they are not analytes of interest to allow for interference correction: Al, Ca, Fe, Cr, Cu, Mn, Ti, and V.
  - Suggested emission line wavelengths are listed in 4.4 Table 3b. Other wavelengths may be used but they may not achieve the same sensitivities.
  - Use background correction.
  - Configure instrument for 3 integrations of emission. Use integration time appropriate for the particular instrument and emission line. Allow at least 10 sec after the solution reaches the plasma before starting integration. Report each emission reading and the mean and RSD.
  - Program instrument to use a linear, least squares calculated intercept, curve fit algorithm for converting emission values to mg/L concentration units. Do not subtract standard blank response from standard solution response. Use the mean of the emission integrations to calculate concentration of analyte.
- (2) Optimize instrument
  - Follow manufacturer's recommendations for optimizing the emission spectrometer.
  - After instrument warm-up, perform optical profiling. Optical profiling is performed either with a built-in mercury lamp, a 2 mg/L Mn solution, or procedure recommended by instrument manufacturer.
- (3) Check instrument performance
  - Verify emission counts are within 80-100% of expected value with a mid-range standard.
  - Verify short term precision is less than 5% relative standard deviation with a mid-range standard (n=5).
  - Verify IDL is within a factor of 3 of expected value.

**4.4 Table 3a. Typical ICP-AES Instrument Conditions**

|   |   |
|---|---|
| Conditions for Applied Research Laboratories (ARL) Model 3580 |   |
| <i>Plasma</i>   |   |
|   | Incident RF power: 1200 watts<br>Reflected RF power: <10 watts<br>Viewing height above work coil: 15 mm<br>Argon pressure: >90 psi<br>Injector tube orifice internal diameter: 1 mm<br>Coolant argon flow rate: 12 L/min<br>Auxiliary (plasma) argon flow rate: 1 L/min<br>Aerosol carrier Ar flow rate: 0.85 L/min |
| <i>Pneumatic Nebulizer</i>                                    |   |
|   | ARL Maximum Dissolved Solids Nebulizer (V-groove):<br>Sample uptake rate controlled to 2.5 mL/min   |
| <i>Ultrasonic Nebulizer</i>                                   |   |
|   | CETAC U-5000AT:<br>Heating Temperature: 140 °C<br>Sample uptake rate controlled to 1 mL/min<br>Cooling Temperature: 0.5 °C  |
| <i>Data Acquisition Parameters</i>                            |   |
|   | Integration Time: 10 sec<br>Number of Integrations: 3   |

**4.4 Table 3b. Typical ICP-AES Instrument Conditions: Wavelengths**

| Conditions for Applied Research Laboratories (ARL) Model 3580               |   |            |   |
|---|---|------------|---|
| Element   | Wavelength (nm)<br>x Order <sup>a</sup> | Element    | Wavelength (nm)<br>x Order <sup>a</sup> |
| Aluminum  | 308.22x2                                | Magnesium  | 383.83x1 <sup>b</sup>                   |
| Arsenic   | 189.04x3                                | Manganese  | 257.61x3                                |
| Barium  | 493.41x1                                | Molybdenum | 202.03x3                                |
| Boron   | 249.68x3                                | Nickel     | 231.60x3                                |
| Cadmium   | 226.50x3                                | Phosphorus | 178.29x3 <sup>b</sup>                   |
| Calcium   | 317.93x2 <sup>b</sup>                   | Potassium  | 766.49x1 <sup>b</sup>                   |
| Chromium  | 267.72x3                                | Sodium     | 589.59x1 <sup>b</sup>                   |
| Cobalt  | 228.62x3                                | Strontium  | 407.77x1 <sup>b</sup>                   |
| Copper  | 324.75x2                                | Thallium   | 190.86x3                                |
| Iron  | 259.94x2                                | Vanadium   | 292.40x2                                |
| Lead  | 220.35x3                                | Zinc       | 213.86x2                                |
| <sup>a</sup> Background corrections performed at ± 0.070 nm except as noted |   |            |   |
| <sup>b</sup> No background correction performed.                            |   |            |   |

## Determination of Analyte Concentration Using Standard Curve

- (1) Standardize the instrument using the standard blank and at least 3 standard solution concentration levels. Allow at least 10 sec after the standard solution reaches the plasma before starting integration. Flush system with standard blank for at least 60 sec between each standard solution.
- (2) Check Standardization Performance
  - Correlation coefficient (r) of linear regression (emission intensity verses concentration) is  $\geq 0.998$ .
  - ICS recovery within  $100 \pm 5\%$  (initial calibration verification).
  - Standard blank  $< \text{ASDL}$ .
- (3) Analyze analytical solutions and quality control solutions. Interpolate analyte concentration from standard curve. A typical sequence for an analytical run is listed in 4.4 Table 4. Rinse sample introduction system by aspirating standard blank for a minimum of 60 sec between all analyses (or longer if necessary). Rinse time is appropriate if results of a standard blank are  $< \text{ASDL}$  when analyzed immediately after a high standard.
- (4) Check Instrument Measurement Performance
  - RSD of replicate integrations  $\leq 7\%$  for all solutions when instrument response  $\geq \text{ASQL}$ .
  - Check solution analyzed at a frequency of 10% and at the end of the analytical run has a recovery of  $100 \pm 10\%$  (continuing calibration verification).
  - Standard blank analyzed at a frequency of 10% and at the end of the analytical run  $< \text{ASDL}$  (continuing calibration blank).
  - Measurements are below highest standard solution. Dilute analytical solution with standard blank if necessary to comply with criteria.
  - Wavelength scan indicates absence of spectral interference that is not corrected for by background correction or inter-element correction factors.
- (5) Inter-element Correction Factors
  - If analytical solution has or is expected to have Al, Ca, Fe, Cr, Cu, Mn, Ti or V at concentrations  $> 20 \text{ mg/L}$  then inter-element correction factors must be determined as outlined in manufacturer's Instructions. Program instrument to use these factors.
  - Analyze the solution(s) used to determine the inter-element correction factors as a sample to demonstrate proper correction for interference.

---

*Note: Each analytical solution must be checked for spectral interference by performing a wavelength scan. An intensity (emission counts) verses wavelength scan must be recorded for each element for each analytical solution. Depending on ICP-AES instrument software, these scans can be incorporated into the ICP-AES analytical run or performed in a separate "scan" run. An appropriate standard solution must be scanned and the result overlaid with the scan of the analytical solution. A standard solution close in element concentration to the analytical solution should be chosen. A broad or double peak indicates an unresolved peak that may result in a positive bias. Interfering peaks could be from*

*elements not being quantified. Peaks in the area of the background correction point(s) may result in a negative bias. Background correction points should be chosen in an area(s) free from other peaks.*

---

**4.4 Table 4. Typical Analytical Sequence**

| Auto-Sampler<br>Tube # | Solution                  | Quality Control Criteria                    |
|------------------------|---------------------------|---|
|                        | sensitivity check         | Emission counts 80-100% of historical value |
|                        | precision check           | n=5, RSD ≤5%                                |
|                        | standard curve check      | r ≥ 0.998                                   |
|                        | analyze std blank 5 times | IDL ≤ 3 × historical IDL                    |
| 1                      | ICS                       | Recovery 95-105%, RSD <7%                   |
| 2                      | standard blank            | <ASDL                                       |
| 3                      | MBK 1                     | ≤MBK <sub>C</sub>                           |
| 4                      | MBK 2                     | ≤MBK <sub>C</sub>                           |
| 5                      | MBK 3                     | ≤MBK <sub>C</sub>                           |
| 6                      | RM                        | Conc < high std, recovery 80-120%, RSD <7%  |
| 7                      | sample 1                  | Conc < high std, RSD <7%                    |
| 8                      | sample 1 FAP              | Conc < high std, recovery 80-120%, RSD <7%  |
| 9                      | sample 2                  | Conc < high std, RSD <7%                    |
| 10                     | check solution            | Recovery 90-110%, RSD <7%                   |
| 11                     | standard blank            | <ASDL                                       |
| 12                     | sample 3                  | Conc < high std, RSD <7%                    |
| 13                     | sample 4                  | Conc < high std, RSD <7%                    |
| 14                     | sample 5 #1               | Conc < high std, RSD <7%                    |
| 15                     | sample 5 #2               | Conc < high std, RSD <7%                    |
| 16                     | sample 6                  | Conc < high std, RSD <7%                    |
| 17                     | sample 7                  | Conc < high std, RSD <7%                    |
| 18                     | sample 8                  | Conc < high std, RSD <7%                    |
| 19                     | sample 9                  | Conc < high std, RSD <7%                    |
| 20                     | sample 10                 | Conc < high std, RSD <7%                    |
| 21                     | sample 11                 | Conc < high std, RSD <7%                    |
| 22                     | check solution            | Recovery 90-110%, RSD <7%                   |
| 23                     | standard blank            | <ASDL                                       |
| 24                     | sample 12                 | Conc < high std, RSD <7%                    |
| 25                     | sample 13                 | Conc < high std, RSD <7%                    |
| 26                     | sample 14                 | Conc < high std, RSD <7%                    |
| 27                     | check solution            | Recovery 90-110%, RSD <7%                   |
| 28                     | standard blank            | <ASDL                                       |

#### 4.4.7 CALCULATIONS

Calculate the concentration (mass fraction) of the analyte in the analytical portion according to the formula

$$\text{Concentration (mg/kg)} = \left[ (S \times DF) - \text{MBK}_L \right] \times \frac{V}{m \times \text{MCF}}$$

where

S = concentration of analyte in analytical solution (or diluted analytical solution) (mg/L)

MBK<sub>L</sub> = laboratory MBK (mg/L)

V = volume (L) of analytical solution (usually 0.050 L)

m = mass of analytical portion (kg)

DF = dilution factor (1 if analytical solution not diluted)

MCF = mass correction factor (1 if no water or other solvent was added to aid homogenization)

Round calculated concentration to at most 3 significant figures. Concentration may be converted to other convenient units (*e.g.*, µg/kg, ng/kg).

#### 4.4.8 METHOD VERIFICATION

The following is the minimum number of quality control samples to be analyzed with each batch of samples: 1 reference material (RM), 1 fortified analytical portion (FAP), 3 MBKs, and 1 replicate. Analysis of replicate analytical portions is encouraged for all samples but replicates should be analyzed whenever analyte nonhomogeneity may be an issue.

##### **Reference Material**

Control limits for RM Recovery are  $100 \pm 20\%$  or within concentration uncertainty (converted to percent relative uncertainty) supplied on certificate, whichever is greater. The z-score procedure, which allows for greater deviation and is discussed in §3.5.3, may also be used, although it requires additional calculations. If three or more RMs are analyzed then only two-thirds of an element's RM recovery results must meet the control limit.

##### **FAP Recovery**

Control limit for FAP recovery is  $100 \pm 20\%$ .

##### **Method Blanks (MBK)**

Minimum of 2 MBKs analyzed and concentration of both MBKs are  $\leq \text{MBK}_C$ . If 3 or more MBKs are analyzed then at least two-thirds of MBKs are  $\leq \text{MBK}_C$ .

##### **Relative Percent Difference (RPD) of Two Replicate Analytical Portions**

Control limit for RPD is 20%.

#### 4.4.9 REPORT

Report results only when quality control criteria for a batch have been satisfactorily met. Report results that are  $\geq \text{LOQ}$  as the mass fraction determined followed by the units of measurement. Report results that are  $\geq \text{LOD}$  and  $< \text{LOQ}$  as the mass fraction determined followed by the units of

measurement and the qualifier that indicates analyte is present at a trace level that is below the limit of reliable quantification (TR). Report results that are <LOD as 0 followed by the units of measurement and the qualifier that indicates analyte is below the level of reliable detection or is not detected (ND).

---

*Example: LOQ = 6 mg/kg; LOD = 3 mg/kg. Levels found for three different samples were 10 mg/kg, 5 mg/kg and 2 mg/kg.*

*10 mg/kg is  $\geq$ LOQ; report 10 mg/kg*

*5 mg/kg is  $\geq$ LOD but also <LOQ; report 5 mg/kg (TR)*

*2 mg/kg is <LOD; report 0 mg/kg (ND)*

---

#### 4.4.10 METHOD VALIDATION

Closed-vessel microwave digestion procedures are commonly applied to trace element analysis of food samples because of superior contamination control, speed and ease of use<sup>12-13</sup>. Combining microwave digestion and ICP-AES for food analysis has been demonstrated<sup>1-10</sup>.

*In-house validation.* Results of an FDA in-house validation of the method are presented in Appendix A. In addition, these in-house validation results using ultrasonic nebulization were published<sup>10</sup>. In general, the recovery results for RMs using pneumatic nebulization are good except for aluminum and no assessment can be made for chromium, cobalt, molybdenum, nickel and thallium due to lack of reference value data. As expected, aluminum recovery results for RMs were low especially in materials containing appreciable levels of silicon. Low recovery of aluminum appears to be associated with incomplete dissolution of samples containing silica and requires the use of hydrofluoric acid to obtain complete recovery.

The results of replicate FAP analyses of 20 foods using ultrasonic nebulization were used to assess analyte recovery and matrix induced interference. FAPs were analyzed for all elements except calcium, magnesium, phosphorus, potassium and sodium. All foods had been prepared and analyzed for 14 elements under FDA's Total Diet Study program<sup>14</sup> enabling comparison of analytical results for some elements. FAP recoveries for all foods were acceptable (80-120%) for arsenic, barium, cadmium, chromium, copper, iron, manganese, molybdenum, nickel, strontium, thallium, and vanadium. FAP recoveries for most foods were acceptable for all other elements (aluminum, boron, lead, selenium, sodium and zinc). The precision of replicate analysis of unfortified portions was 15% or less for all element concentration measurements above LOQ except for cadmium in spaghetti (19%), calcium in haddock (30%), copper in cheddar cheese (16%), iron in cheddar cheese (19%) and mayonnaise (17%), nickel in prune juice (16%), potassium in mayonnaise (17%), and selenium in haddock (20%). FDA Total Diet Study results were available for comparison for all elements except barium, boron, chromium, molybdenum, strontium, and thallium. A majority of the results were in agreement with Total Diet Study results.

The in-house validation results for analysis of foods using microwave decomposition and element detection using ICP-AES indicate the following elements can be reliably measured at concentrations above LOQ: arsenic, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, sodium, strontium, vanadium and zinc. Thallium appears to be reliably measured but accuracy assessment is hindered by the lack of appropriate reference materials. Aluminum can be

measured but the analyst must realize that the results might be biased low if some of the aluminum is bound to silica.

*Uncertainty.* A result above LOQ has an estimated combined uncertainty of 10%. Use of a coverage factor of 2 to give an expanded uncertainty at about 95% confidence corresponds with the RM Recovery control limit of  $\pm 20\%$ . A result above LOD but below LOQ is considered qualitative and is not reported with an uncertainty.

A detailed discussion of method uncertainty is presented in §3.3. This method conforms to the information contained in that discussion. Derivation of an estimated uncertainty specific to an analysis is discussed §3.3.2.

*Interlaboratory trial.* [Under development]

## REFERENCES

- (1) Xu, L., and Shen, W. (1988) Study on the PTFE Closed-Vessel Microwave Digestion Method in Food Elemental Analysis, *Fresenius' Z. Anal. Chem.* **332**, 45-47.
- (2) Shiraishi, K., McNroy, J. F., and Igarashi, Y. (1990) Simultaneous Multielement Analysis of Diet Samples by Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry, *J. Nutr. Sci. Vitaminol.* **36**, 81-86.
- (3) Krushevska, A., Barnes, R. M., Amarasiriwaradena, C. J., Foner, H., and Martines, L. (1992) Comparison of Sample Decomposition Procedures for the Determination of Zinc in Milk by Inductively Coupled Plasma Atomic Emission Spectrometry, *J. Anal. At. Spectrom.* **7**, 851-858.
- (4) Sheppard, B. S., Heitkemper, D. T., and Gaston, C. M. (1994) Microwave Digestion for the Determination of Arsenic, Cadmium and Lead in Seafood Products by Inductively Coupled Plasma Atomic Emission and Mass Spectrometry, *Analyst* **119**, 1683-1686.
- (5) Negretti de Bratter, V. E., Bratter, P., Reinicke, A., Schulze, G., Walter, O. L., and Alvarez, N. (1995) Determination of Mineral and Trace Elements in Total Diet by Inductively Coupled Plasma Atomic Emission Spectrometry: Comparison of Microwave-Based Digestion and Pressurized Ashing Systems Using Different Acid Mixtures, *J. Anal. At. Spectrom.* **10**, 487-491.
- (6) Sun, D., Waters, J. K., and Mawhinney, T. P. (1997) Microwave Digestion for Determination of Aluminum, Boron, and 13 Other Elements in Plants by Inductively Coupled Plasma Atomic Emission Spectrometry, *J. AOAC Int.* **80**, 647-650.
- (7) Barnes, K. W. (1998) A Streamlined Approach to the Determination of Trace Elements in Foods, *At. Spectrosc.* **19**, 31-39.
- (8) Sun, D., Waters, J. K., and Mawhinney, T. P. (2000) Determination of Thirteen Common Elements in Food Samples by Inductively Coupled Plasma Atomic Emission Spectrometry: Comparison of Five Digestion Methods, *J. AOAC Int.* **83**, 1218-1224.
- (9) Carrilho, E. N. V. M., Gonzalez, M. H., Nogueira, A. R. A., Cruz, G. M., and Nobrega, J. A. (2002) Microwave-Assisted Acid Decomposition of Animal- and Plant-Derived Samples for Element Analysis, *J. Agric. Food Chem.* **50**, 4164-4168.
- (10) Dolan, S. P., and Capar, S. G. (2002) Multi-element Analysis of Food by Microwave Decomposition and Inductively Coupled Plasma-Atomic Emission Spectrometry, *J. Food Compos. Anal.* **15**, 593-615.
- (11) ASTM International (2006) ASTM D 1193-06, "Standard Specification for Reagent Water". Available from ASTM ([link removed](#)).
- (12) Environmental Protection Agency (1996) SW-846 EPA Method 3052 rev. 0, Microwave assisted acid digestion of siliceous and organically based matrices, Test Methods for Evaluating Solid Waste, 3rd ed., 3rd update, U.S. EPA, Washington, DC. Available from EPA (27 April 2008) ([link removed](#)).
- (13) Lamble, K. L. and Hill, S. J. (1998) Microwave digestion procedures for environmental matrices, *Analyst* **123**, 103R-133R.
- (14) U.S. Food and Drug Administration (2001) (INTERNET) FDA Total Diet Study Home Page. Available from FDA. (22 January 2010) ([link removed](#)).