9.2.40 - Metals and Other Elements at Trace Levels in Foods / Single Element Methods

AOAC Official Method 993.14
Trace Elements in Waters and Wastewaters

Inductively Coupled Plasma-Mass Spectrometric Method
First Action 1993

(Applicable to determination of 20 trace elements, at concentrations of 0.8-200 µg/L, in finished drinking water, groundwater, and wastewaters.)

Caution: The following reagents are highly toxic: antimony, arsenic trioxide, beryllium sulfate, cadmium, chromium trioxide, lead nitrate, selenium dioxide, thallium nitrate, and uranium nitrate.

Results of interlaboratory study:

See Table **993.14A** for interlaboratory study data.

A. Principle

Method describes multielement determination of trace elements by inductively coupled plasma-mass spectrometry (ICP-MS). Elements are digested in a nitric-hydrochloric acid solution. Sample material in solution is introduced by pneumatic nebulization into radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. Ions are extracted from plasma through differentially pumped vacuum interface and are separated on the basis of mass-to-charge ratio by a quadrupole mass spectrometer having minimum resolution capability of 1 amu peak width at 5% peak height. Ions transmitted through quadrupole are detected by continuous dynode electron multiplier assembly, and ion information is processed by data handling system.

B. Apparatus

(**a**) *Inductively coupled plasma-mass spectrometer*.—(*1*) Instrument capable of scanning mass range 5-250 amu with minimum resolution capability of 1 amu peak width at 5% peak height and that may be fitted with conventional or extended

dynamic range detection system. (*2*) Argon gas supply (high-purity grade, 99.99%). (*3*) Variable-speed peristaltic pump required for solution delivery to nebulizer. (*4*) Mass-flow controller on nebulizer gas supply may be required. Water-cooled spray chamber beneficial in reducing interferences. Operating conditions: Because of diversity in instrumentation, manufacturer-provided operating conditions should be followed.

(**b**) *Glassware*.—Volumetric flasks, graduated cylinders, funnels, centrifuge tubes, and calibrated pipets.

(**c**) *Beakers*.—250 mL conical Phillips with 50 mm watch glasses and 250 mL Griffin with 75 mm watch glasses.

(**d**) *Storage bottles.*—125 and 250 mL, narrow mouth, Teflon FEP (fluorinated ethylene propylene), with Tefzel ETFE (ethylene tetrafluorethylene) screw caps.

(**e**) *Air displacement pipetter*.—Digital, capable of 10-2500 µL range and disposable pipet tips.

(**f**) *Analytical balance.*—Sensitivity ±0.1 mg.

(**g**) *Hot plate.*—With variable temperature, controllable to ±3°C.

(**h**) *Centrifuge.*—Steel cabinet with guard bowl, electric timer, and brake, capable of 2000 *g.*

(**i**) *Drying oven*.—Gravity convection oven with thermostatic control capable of maintaining 105° ± 5°C.

C. Reagents

(**a**) *Nitric acid (HNO_3) solutions.*—(*1*) *HNO_3.*—Concentrated, specific gravity 1.41. (*2*) *HNO_3 solution (1 + 1).*—Add 500 mL HNO_3 to 400 mL reagent water and dilute to 1 L. (*3*) *HNO_3 solution (1 + 9).*—Add 100 mL HNO_3 to 400 mL reagent water and dilute to 1 L. (*4*) *1% (v/v) HNO_3 solution*. (*5*) *2% (v/v) HNO_3 solution*.

(**b**) *Hydrochloric acid (HCl) solutions.*—(*1*) *HCl.*—Concentrated, specific gravity 1.41. (*2*) *HCl solution (1 + 1).*—Add 500 mL HCl to 400 mL reagent water and dilute to 1 L.

(**c**) *Ammonium hydroxide (NH_4OH).*—Concentrated, specific gravity 0.902.

(**d**) *Tartaric acid.*

(**e**) *Reagent water.*—ASTM type I water (ASTM D1193) is required. Prepare water by distillation, polishing with mixed bed of ion exchange material, and filtration through 0.2 m membrane filter.

(**f**) *Standard solutions.*—Purchase or prepare from ultra high-purity chemicals or metals (99.99-99.999% pure). Pickle metals (where indicated), to clean surfaces and reduce mass, by adding 20% excess of metal to acid; dry, weigh, and repeat process until desired weight is achieved. Dry salts 1 h at 105°C, except where noted. Use reagent water, (**e**), for all dilutions unless otherwise specified. Store stock solutions in Teflon bottles, **B**(**d**). Accurately weigh all amounts to nearest 0.1 mg.

(*1*) *Aluminum stock solution (1000 µg Al/mL).*—Pickle Al metal in 75-80°C (1 + 1) HCl solution, (**b**)(*2*), to 0.100 g. Dissolve metal in 10 mL HCl, (**b**)(*1*), and 2 mL HNO_3, (**a**)(*1*), by heating ca 30 min at 75-80°C. Continue heating until solution has evaporated to 4 mL. Cool to room temperature and add 4 mL reagent water. Evaporate to 2 mL by heating. Cool to room temperature and dilute to 100 mL.

(*2*) *Antimony stock solution (1000 µg Sb/mL).*—Dissolve 0.100 g Sb powder in 2 mL (1 + 1) HNO_3 solution, (**a**)(*2*), and 0.5 mL HCl. Heat at 75-80°C to dissolve, cool to room temperature, and add 20 mL reagent water and 0.15 g tartaric acid, (**d**). Warm solution to dissolve white precipitate. Cool and dilute to 100 mL.

(*3*) *Arsenic stock solution (1000 g As/mL).*—Dissolve 0.1320 g As_2O_3 in mixture of 50 mL reagent water and 1 mL NH_4OH, (**c**), by heating at 75-80°C; cool to room temperature; and acidify with 2 mL HNO_3. Dilute to 100 mL.

(*4*) *Barium stock solution (1000 g Ba/mL).*—Dissolve 0.1437 g $BaCO_3$ in mixture of 10 mL reagent water and 2 mL HNO_3 by heating while stiring. Dilute to 100 mL.

(*5*) *Beryllium stock solution (1000 g Be/mL).*—Dissolve 1.965 g $BeSO_4 \cdot 4H_2O$ (*do not dry*) in 50 mL reagent water. Add 1 mL HNO_3. Dilute to 100 mL.

(*6*) *Bismuth stock solution (1000 g Bi/mL).*—Dissolve 0.1115 g Bi_2O_3 in 5 mL HNO_3 by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*7*) *Cadmium stock solution (1000 g Cd/mL).*—Pickle Cd metal in (1 + 9) HNO_3 solution, (**a**)(*3*), to 0.100 g. Dissolve in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*8*) *Chromium stock solution (1000 g Cr/mL).*—Dissolve 0.1923 g CrO_3 in mixture of 10 mL reagent water and 1 mL HNO_3. Dilute to 100 mL.

(*9*) *Cobalt stock solution (1000 g Co/mL).*—Pickle Co metal in (1 + 9) HNO_3 solution to 0.100 g. Dissolve in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*10*) *Copper stock solution (1000 g Cu/mL).*—Pickle Cu metal in (1 + 9) HNO_3 solution to 0.100 g. Dissolve in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*11*) *Indium stock solution (1000 g In/mL).*—Pickle In metal in (1 + 1) HNO_3 solution to 0.100 g. Dissolve in 10 mL (1 + 1) HNO_3 solution by heating at 75-80°C , cool to room temperature, and dilute to 100 mL.

(*12*) *Lead stock solution (1000 g Pb/mL).*—Dissolve 0.1599 g $Pb(NO_3)_2$ in 5 mL (1 + 1) HNO_3 solution. Dilute to 100 mL.

(*13*) *Magnesium stock solution (1000 g Mg/mL).*—Dissolve 0.1658 g MgO in 10 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*14*) *Manganese stock solution (1000 g Mn/mL).*—Pickle Mn flake in (1 + 9) HNO_3 solution to 0.100 g. Dissolve in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*15*) *Molybdenum stock solution (1000 g Mo/mL).*—Dissolve 0.1500 g MoO_3 in mixture of 10 mL reagent water and 1 mL NH_4OH by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*16*) *Nickel stock solution (1000 g Ni/mL).*—Dissolve 0.100 g Ni powder in 5 mL HNO_3 by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*17*) *Scandium stock solution (1000 µg Sc/mL).*—Dissolve 0.1534 g Sc_2O_3 in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*18*) *Selenium stock solution (1000 g Se/mL).*—Dissolve 0.1405 g SeO_2 in 20 mL reagent water. Dilute to 100 mL.

(*19*) *Silver stock solution (1000 g Ag/mL).*—Dissolve 0.100 g Ag metal in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL. Store in amber container.

(*20*) *Terbium stock solution (1000 g Tb/mL).*—Dissolve 0.1176 g Tb_4O_7 in 5 mL HNO_3 by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*21*) *Thallium stock solution (1000 g Tl/mL).*—Dissolve 0.1303 g $TlNO_3$ in mixture of 10 mL reagent water and 1 mL HNO_3. Dilute to 100 mL.

(*22*) *Thorium stock solution (1000 g Th/mL).*—Dissolve 0.2380 g $Th(NO_3)_4 \cdot 4H_2O$ (*do not dry*) in 20 mL reagent water. Dilute to 100 mL.

(*23*) *Uranium stock solution (1000 g U/mL).*—Dissolve 0.2110 g $UO_2(NO_3)_2 \cdot 6H_2O$ (*do not dry*) in 20 mL reagent water. Dilute to 100 mL.

(*24*) *Vanadium stock solution (1000 g V/mL).*—Pickle V metal in (1 + 9) HNO_3 solution to 0.100 g. Dissolve in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*25*) *Yttrium stock solution (1000 g Y/mL).*—Dissolve 0.1270 g Y_2O_3 in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(*26*) *Zinc stock solution (1000 g Zn/mL).*—Pickle Zn metal in (1 + 9) HNO_3 solution to 0.100 g. Dissolve in 5 mL (1 + 1) HNO_3 solution by heating at 75-80°C, cool to room temperature, and dilute to 100 mL.

(**g**) *Calibration standard solutions (10 g/mL).*—(*1*) *Standard solution A.*—Combine 1 mL each (**f**)(*1*)-(*3*), (*5*), (*7*)-(*10*), (*12*), (*14*)-(*16*), (*18*), (*21*)-(*24*), and (*26*) and dilute mixture to 100 mL with 1% (v/v) HNO_3, (**a**)(*4*). (*2*) *Standard solution B.*—Combine 1 mL each (**f**)(*4*) and (*19*) and dilute to 100 mL with reagent water with 1% (v/v) HNO_3, (**a**)(*4*).

(**h**) *Internal standard solution (100 g/mL).*—Combine 10 mL (**f**)(*6*), (*11*), (*17*), (*20*), and (25) and dilute to 100 mL with reagent water, (**e**). If internal standards are added by peristaltic pump, dilute using 1% (v/v) HNO_3, (**a**)(*4*). Store in Teflon bottle.

(**i**) *Blanks.*—(*1*) *Calibration blank.*—1% (v/v) HNO_3, (**a**)(*4*), in reagent water, (**e**). (*2*) *Laboratory reagent blank (LRB).*—Containing reagents in same volumes used in processing samples. (*3*) *Rinse blank.*—2% (v/v) HNO_3, (**a**)(*5*), in reagent water, (**e**).

(**j**) *Tuning solution (100 g/L).*—Combine 10 mL of (**f**)(*5*), (*9*), and (*11*)-(*13*) and dilute to 100 mL with 1% (v/v) HNO_3, (**a**)(*4*). Internal standards are not added to this solution.

(**k**) *Quality control sample (QCS; 100 g/L).*—Prepare as directed by diluting USEPA (U.S. Environmental Protection Agency), Certified Quality Control Sample (SPEX Industries is suitable source), or equivalent, in reagent water.

(**l**) *Laboratory fortified blank (LFB).*—Combine portions from multielement stock standard solutions A, (**g**)(*1*), and B, (**g**)(*2*), to reagent water, (**e**), diluting 1:100 to produce final concentration 100 g/L for each analyte. LFB must be carried through entire test sample digestion and preparation scheme. Add internal standards to LFB if direct addition procedure is used.

D. Material Collection and Preservation

For total dissolved elements, filter material through 0.45 µm membrane filter. Acidify filtrate with (1 + 1) HNO_3 solution, **C**(**a**)(*2*), to pH < 2 at time of collection.

For total recoverable elements, acidify material with (1 + 1) HNO_3 solution to pH < 2 at time of collection.

Hold materials ca 16 h prior to analysis.

E. Material Preparation

For dissolved elements, add 1 mL HNO_3, **C**(**a**)(*1*), to 100 mL filtered, acid-preserved test portion.

For total recoverable elements, transfer 100 mL well-mixed, acid-preserved test portion containing 0.25% (w/v) total solids to 250 mL Griffin beaker. Add 1 mL HNO_3 and 0.5 mL HCl, **C**(**b**)(*1*). Heat on hot plate without boiling until volume is reduced to 15-20 mL. Reflux 30 min (very slight boiling may occur). Cool and transfer to 50 mL volumetric flask or 50 mL class A stoppered graduated cylinder. Dilute to volume with reagent water, **C**(**e**), and mix. Let insoluble material separate. Pipet 20 mL into 50 mL volumetric flask, dilute to volume with reagent water, and mix well. Analyze as soon as possible because effects of various matrices on diluted test solution stability cannot be characterized. Dilute original test sample to contain <100 g/L Ag and digest if analyses indicate Ag concentration in test sample is >100 g/L.

F. Calibration

Initiate proper operating configuration of instrument and data system. Conduct mass calibration and resolution checks using tuning solution, **C**(**j**). Resolution at low mass is indicated by Mg isotopes 24, 25, and 26; resolution at high mass is indicated by Pb

isotopes 206, 207, and 208. Adjust spectrometer resolution to produce 0.75 amu peak width at 5% peak height. Adjust mass calibration if any Mg or Pb isotope mass is shifted by more than 0.1 amu from unit mass. Analyze tuning solution 5 times to demonstrate instrument stability (relative standard deviations should be <5%). Calibrate instrument for analytes using calibration blank, **C**(**i**)(*1*), and calibration standard solutions A, **C**(**g**)(*1*), and B, **C**(**g**)(*2*), prepared at one or more concentration levels. *See* Table **993.14B** for recommended masses and elemental equations for data calculations. Report data as average of 3 replicate integrations. *See* Table **993.14C** for common molecular ion interferences. Flush system between solution changes using rinse blank, **C**(**i**)(*3*).

Internal standardization.—For full mass range scans, 3 internal standards are required. For general application, use 5 internal standards: Sc, Y, In, Tb, and Bi. Internal standards must be present in test portions, standards, and blanks (200 g/L is recommended).

Instrument performance.—After calibration, analyze QCS, **C**(**k**). If measurements exceed ±10% QCS limits, terminate analysis, identify and correct source of problem, recalibrate instrument, and reverify calibration before continuing analyses. To verify instrument calibration on continuing basis, run calibration blank and calibration standard as surrogate test samples after every 10 analyses. If indicated concentration deviates from true concentration by >10%, recalibrate instrument and reanalyze last 10 test portions.

G. Quality Control

Minimum quality control requirements for this method include: (*1*) initial demonstration of method performance; (*2*) monitoring of internal standard area counts in each test solution (area of internal standard within 60-125% area in calibration blank); (*3*) analysis of 1 LRB, **C**(**i**)(*2*), with each set of test solutions as continuing check on test solution contamination; (*4*) analysis of QCS, **C**(**k**), with each set of test solutions as continuing check on method recovery; and (*5*) analysis of calibration standards, **C**(**g**), every 10 analyses as continuing check on calibration curve (measured values should not exceed ±10% concentration).

Demonstrate initial, and continuing, method performance every 6 months by digesting 7 spiked reagent water test samples at 2-5 estimated detection limit to determine method detection limits (MDL). Calculate MDL and compare to results in Table **993.14D**.

$$\text{MDL} = t \quad S$$

where t = Student's t value for 99% confidence level with n - 1 degrees of freedom (t = 3.14 for 7 replicates) and S = standard deviation of the 7 replicate analyses.

Demonstrate continuing check on method recovery by digesting and analyzing 1 QCS with each set of samples and compare recovery to performance-based acceptance limits presented in Table **993.14D**. If indicated concentration of any analyte deviates from acceptance limits, reanalyze QCS for that analyte. Recalibrate for all analytes still outside acceptance limits.

Reference:
J. AOAC Int. **77,** 1004(1994).

Table 993.14A: Interlaboratory study results for trace elements in water, inductively coupled plasma-mass spectrometric method

Table 993.14A: (*continued*)

Table 993.14A: (*continued*)

Table 993.14A: (*continued*)

Table 993.14A: (*continued*)

Table 993.14A: (*continued*)

Table 993.14B: Recommended masses and elemental equations

Table 993.14C: Common molecular ion interferences in ICP-MS

Table 993.14D: Total recoverable method detection limits and acceptance limits for QC check sample