3125 B. Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) Method

1. General Discussion

a. Principle: Sample material is introduced into an argon-based, high-temperature radio-frequency plasma, usually by pneumatic nebulization. Energy transfer from the plasma to the sample stream causes desolvation, atomization, and ionization of target elements. Ions generated by these energy-transfer processes are extracted from the plasma through a differential vacuum interface, and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The mass spectrometer usually is of the quadrupole or magnetic sector type. The ions passing through the mass spectrometer are counted, usually by an electron multiplier detector, and the resulting information processed by a computer-based data-handling system.

b. Applicable elements and analytical limits: This method is suitable for aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, vanadium, and zinc. The method is also acceptable for other elemental analytes as long as the same quality assurance practices are followed. The basic element suite and recommended analytical masses are given in Table 3125:I.

Typical instrument detection limits (IDL)[1,2] for method analytes are presented in Table 3125:I. Determine the IDL and method detection level (or limit) (MDL) for all analytes before method implementation. Section 1030 contains additional information and approaches for the evaluation of detection capabilities.

The MDL is defined in Section 1010C and elsewhere.[2] Determination of the MDL for each element is critical for complex matrices such as seawater, brines, and industrial effluents. The MDL will typically be higher than the IDL, because of background analyte in metals preparation and analysis laboratories and matrix-based interferences. Determine both IDL and MDL upon initial implementation of this method, and then yearly or whenever the instrument configuration changes or major maintenance occurs, whichever comes first.

Determine linear dynamic ranges (LDR) for all method analytes. LDR is defined as the maximum concentration of analyte above the highest calibration point where analyte response is within ±10% of the theoretical response. When determining linear dynamic ranges, avoid using unduly high concentrations of analyte that might damage the detector. Determine LDR on multielement mixtures, to account for possible interelement effects. Determine LDR on initial implementation of this method, and then yearly.

c. Interferences: ICP/MS is subject to several types of interferences.

1) Isotopes of different elements that form ions of the same nominal mass-to-charge ratio are not resolved by the quadrupole mass spectrometer, and cause isobaric elemental interferences. Typically, ICP/MS instrument operating software will have all known isobaric interferences

entered, and will perform necessary calculations automatically. Table 3125:II shows many of the commonly used corrections. Monitor the following additional masses: ^{83}Kr, ^{99}Ru, ^{118}Sn, and ^{125}Te. It is necessary to monitor these masses to correct for isobaric interference caused by ^{82}Kr on ^{82}Se, by ^{98}Ru on ^{98}Mo, by ^{114}Sn on ^{114}Cd, and by ^{123}Te on ^{123}Sb. Monitor ArCl at mass 77, to estimate chloride interferences. Verify that all elemental and molecular correction equations used in this method are correct and appropriate for the mass spectrometer used and sample matrix.

2) Abundance sensitivity is an analytical condition in which the tails of an abundant mass peak contribute to or obscure adjacent masses. Adjust spectrometer resolution to minimize these interferences.

3) Polyatomic (molecular) ion interferences are caused by ions consisting of more than one atom and having the same nominal mass-to-charge ratio as the isotope of interest. Most of the common molecular ion interferences have been identified and are listed in Table 3125:III. Because of the severity of chloride ion interference on important analytes, particularly arsenic and selenium, hydrochloric acid is not recommended for use in preparation of any samples to be analyzed by ICP/MS. The mathematical corrections for chloride interferences only correct chloride to a concentration of 0.4%. Because chloride ion is present in most environmental samples, it is critical to use chloride correction equations for affected masses. A high-resolution ICP/MS may be used to resolve interferences caused by polyatomic ions. Polyatomic interferences are strongly influenced by instrument design and plasma operating conditions, and can be reduced in some cases by careful adjustment of nebulizer gas flow and other instrument operating parameters.

4) Physical interferences include differences in viscosity, surface tension, and dissolved solids between samples and calibration standards. To minimize these effects, dissolved solid levels in analytical samples should not exceed 0.5%. Dilute water and wastewater samples containing dissolved solids at or above 0.5% before analysis. Use internal standards for correction of physical interferences. Any internal standards used should demonstrate comparable analytical behavior to the elements being determined.

5) Memory interferences occur when analytes from a previous sample or standard are measured in the current sample. Use a sufficiently long rinse or flush between samples to minimize this type of interference. If memory interferences persist, they may be indications of problems in the sample introduction system. Severe memory interferences may require disassembly and cleaning of the entire sample introduction system, including the plasma torch, and the sampler and skimmer cones.

6) Ionization interferences result when moderate (0.1 to 1%) amounts of a matrix ion change the analyte signal. This effect, which usually reduces the analyte signal, also is known as ‘‘suppression.’’ Correct for suppression by use of internal standardization techniques.

2. Apparatus

a. Inductively coupled plasma/mass spectrometer: Instrumentation, available from several manufacturers, includes a mass spectrometer detector, inductively coupled plasma source, mass flow controllers for regulation of ICP gas flows, peristaltic pump for sample introduction, and a computerized data acquisition and instrument control system. An x-y autosampler also may be used with appropriate control software.

b. Laboratory ware: Use precleaned plastic laboratory ware for standard and sample preparation. Teflon,*#(1) either tetrafluoroethylene hexafluoropropylene-copolymer (FEP), polytetrafluoroethylene (PTFE), or perfluoroalkoxy PTFE (PFA) is preferred for standard preparation and sample digestion, while high-density polyethylene (HDPE) and other dense, metal-free plastics may be acceptable for internal standards, known-addition solutions, etc. Check each new lot of autosampler tubes for suitability, and preclean autosampler tubes and pipettor tips (see Section 3010C.2).

c. Air displacement pipets, 10 to 100 µL, 100 to 1000 µL, and 1 to 10 mL size.

d. Analytical balance, accurate to 0.1 mg.

e. Sample preparation apparatus, such as hot plates, microwave digestors, and heated sand baths. Any sample preparation device has the potential to introduce trace levels of target analytes to the sample.

f. Clean hood (optional), Class 100 (certified to contain less than 100 particles/m^3), for sample preparation and manipulation. Preferably perform all sample manipulations, digestions, dilutions, etc. in a certified Class 100 environment. Alternatively, handle samples in glove boxes, plastic fume hoods, or other environments where random contamination by trace metals can be minimized.

3. Reagents

a. Acids: Use ultra-high-purity grade (or equivalent) acids to prepare standards and to process sample. Redistilled acids are acceptable if each batch is demonstrated to be free from contamination by target analytes. Use extreme care in the handling of acids in the laboratory to avoid contamination of the acids with trace levels of metals.

1) *Nitric acid,* HNO_3, conc (specific gravity 1.41).

2) *Nitric acid,* 1 + 1: Add 500 mL conc HNO_3 to 500 mL reagent water.

3) *Nitric acid,* 2%: Add 20 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

4) *Nitric acid,* 1%: Add 10 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

b. Reagent water: Use water of the highest possible purity for blank, standard, and sample preparation (see Section 1080). Alternatively, use the procedure described below to produce water of acceptable quality. Other water preparation regimes may be used, provided that the water produced is metal-free. Reagent water containing trace amounts of analyte elements will cause erroneous results.

Produce reagent water using a softener/reverse osmosis unit with subsequent UV sterilization. After the general deionization system use a dual-column strong acid/strong base ion exchange system to polish laboratory reagent water before production of metal-free water. Use a multi-stage reagent water system, with two strong acid/strong base ion exchange columns and an activated carbon filter for organics removal for final polishing of laboratory reagent water. Use only high-purity water for preparation of samples and standards.

c. Stock, standard, and other required solutions: See Section 3120B.3*d* for preparation of standard stock solutions from elemental materials (pure metals, salts). Preferably, purchase high-purity commercially prepared stock solutions and dilute to required concentrations. Single- or multi-element stock solutions (1000 mg/L) of the following elements are required: aluminum, antimony, arsenic, barium, beryllium, cerium, cadmium, chromium, cobalt, copper, germanium, indium, lead, magnesium, manganese, molybdenum, nickel, rhodium, scandium, selenium, silver, strontium, terbium, thallium, thorium, uranium, vanadium, and zinc. Prepare internal standard stock separately from target element stock solution. The potential for incompatibility between target elements and/or internal standards exists, and could cause precipitation or other solution instability.

1) *Internal standard stock solution:* Lithium, scandium, germanium, indium, and thorium are suggested as internal standards. The following masses are monitored: ^{6}Li, ^{45}Sc, ^{72}Ge, ^{115}In, and ^{232}Th. Add to all samples, standards, and quality control (QC) samples a level of internal standard that will give a suitable counts/second (cps) signal (for most internal standards, 200 000 to 500 000 cps; for lithium, 20 000 to 70 000 cps). Minimize error introduced by dilution during this addition by using an appropriately high concentration of internal standard mix solution. Maintain volume ratio for all internal standard additions.

Prepare internal standard mix as follows: Prepare a nominal 50-mg/L solution of ^{6}Li by dissolving 0.15 g $^{6}Li_2CO_3$ (isotopically pure, i.e., 95% or greater purity†#(2)) in a minimal amount of 1:1 HNO_3. Pipet 5.0 mL 1000-mg/L scandium, germanium, indium, and thorium standards into the lithium solution, dilute resulting solution to 500.0 mL, and mix thoroughly. The resultant concentration of Sc, Ge, In, and Th will be 10 mg/L. Older instruments may require higher levels of internal standard to achieve acceptable levels of precision.

Other internal standards, such as rhodium, yttrium, terbium, holmium, and bismuth may also be used in this method. Ensure that internal standard mix used is stable and that there are no undesired interactions between elements.

Screen all samples for internal standard elements before analysis. The analysis of a few representative samples for internal standards should be sufficient. Analyze samples ‘‘as received’’ or ‘‘as digested’’ (before addition of internal standard), then add internal standard mix and reanalyze. Monitor counts at the internal standard masses. If the ‘‘as received’’ or ‘‘as digested’’ samples show appreciable detector counts (10% or higher of samples with added internal standard), dilute sample or use an alternate internal standard. If the internal standard response of the sample with the addition is not within 70 to 125% of the response for a

calibration blank with the internal standard added, either dilute the sample before analysis, or use an alternate internal standard. During actual analysis, monitor internal standard masses and note all internal standard recoveries over 125% of internal standard response in calibration blank. Interpret results for these samples with caution.

The internal standard mix may be added to blanks, standards, and samples by pumping the solution so it is mixed with the sample stream in the sample introduction process.

2) *Instrument optimization/tuning solution,* containing the following elements: barium, beryllium, cadmium, cerium, cobalt, copper, germanium, indium, magnesium, rhodium, scandium, terbium, thallium, and lead. Prepare this solution in 2% HNO_3. This mix includes all common elements used in optimization and tuning of the various ICP/MS operational parameters. It may be possible to use fewer elements in this solution, depending on the instrument manufacturer's recommendations.

3) *Calibration standards,* 0, 5, 10, 20, 50, and 100 µg/L.‡#(3) Other calibration regimes are acceptable, provided the full suite of quality assurance samples and standards is run to validate these method changes. Fewer standards may be used, and a two-point blank/mid-range calibration technique commonly used in ICP optical methods should also produce acceptable results. Calibrate all analytes using the selected concentrations. Prepare all calibration standards and blanks in a matrix of 2% nitric acid. Add internal standard mix to all calibration standards to provide appropriate count rates for interference correction. NOTE: All standards and blanks used in this method have the internal standard mix added at the same ratio.

4) *Method blank,* consisting of reagent water (¶ 3*b*) taken through entire sample preparation process. For dissolved samples, take reagent water through same filtration and preservation processes used for samples. For samples requiring digestion, process reagent water with the same digestion techniques as samples. Add internal standard mix to method blank.

5) *Calibration verification standard:* Prepare a mid-range standard, from a source different from the source of the calibration standards, in 2% HNO_3, with equivalent addition of internal standard.

6) *Calibration verification blank:* Use 2% HNO_3.

7) *Laboratory fortified blank* (optional)*:* Prepare solution with 2% nitric acid and method analytes added at about 50 µg/L. This standard, sometimes called a laboratory control sample (LCS), is used to validate digestion techniques and known-addition levels.

8) *Reference materials:* Externally prepared reference material, preferably from National Institute of Standards and Technology (NIST) 1643 series or equivalent.

9) *Known-addition solution for samples:* Add stock standard to sample in such a way that volume change is less than 5%. In the absence of information on analyte levels in the sample, prepare known additions at around 50 µg/L. If analyte concentration levels are known, add at 50 to 200% of the sample levels. For samples undergoing digestion, make additions before digestion. For the determination of dissolved metals, make additions after filtration, preferably

immediately before analysis.

10) *Low-level standards:* Use both a 0.3- and a 1.0-µg/L standard when expected analyte concentration is below 5 µg/L. Prepare both these standards in 2% nitric acid.

Prepare volumetrically a mixed standard containing the method analytes at desired concentration(s) (0.30 µg/L, 1.0 µg/L, or both). Prepare weekly in 100-mL quantities.

d. Argon: Use a prepurified grade of argon unless it can be demonstrated that other grades can be used successfully. The use of prepurified argon is usually necessary because of the presence of krypton as an impurity in technical argon. ^{82}Kr interferes with the determination of ^{82}Se. Monitor ^{83}Kr at all times.

4. Procedures

a. Sample preparation: See Section 3010 and Section 3020 for general guidance regarding sampling and quality control. See Section 3030E for recommended sample digestion technique for all analytes except silver and antimony. If silver and antimony are target analytes, use method given in 3030F, paying special attention to interferences caused by chloride ion, and using all applicable elemental corrections. Alternative digestion techniques and additional guidance on sample preparation are available.[3,4]

Ideally use a ‘‘clean’’ environment for any sample handling, manipulation, or preparation. Preferably perform all sample manipulations in a Class 100 clean hood or room to minimize potential contamination artifacts in digested or filtered samples.

b. Instrument operating conditions: Follow manufacturer’s standard operating procedures for initialization, mass calibration, gas flow optimization, and other instrument operating conditions. Maintain complete and detailed information on the operational status of the instrument whenever it is used.

c. Analytical run sequence: A suggested analytical run sequence, including instrument tuning/optimization, checking of reagent blanks, instrument calibration and calibration verification, analysis of samples, and analysis of quality control samples and blanks, is given in Table 3125:IV.

d. Instrument tuning and optimization: Follow manufacturer’s instructions for optimizing instrument performance. The most important optimization criteria include nebulizer gas flows, detector and lens voltages, radio-frequency forward power, and mass calibration. Periodically check mass calibration and instrument resolution. Ideally, optimize the instrument to minimize oxide formation and doubly-charged species formation. Measure the CeO/Ce ratio to monitor oxide formation, and measure doubly-charged species by determination of the Ba^{2+}/Ba^{+} ratio. Both these ratios should meet the manufacturer’s criteria before instrument calibration. Monitor background counts at mass 220 after optimization and compare with manufacturer’s criteria. A summary of performance criteria related to optimization and tuning, calibration, and analytical performance for this method is given in Table 3125:V.

e. Instrument calibration: After optimization and tuning, calibrate instrument using an appropriate range of calibration standards. Use appropriate regression techniques to determine calibration lines or curves for each analyte. For acceptable calibrations, correlation coefficients for regression curves are ideally 0.995 or greater.

Immediately after calibration, run initial calibration verification standard, ¶ 3*c*5); acceptance criteria are ±10% of known analyte concentration. Next run initial calibration verification blank, ¶ 3*c*6); acceptance criteria are ideally ± the absolute value of the instrument detection limit for each analyte, but in practice, ± the absolute value of the laboratory reporting limit or the laboratory method detection limit for each analyte is acceptable. Verify low-level calibration by running 0.3- and/or 1.0-µg/L standards, if analyte concentrations are less than 5 µg/L.

f. Sample analysis: Ensure that all vessels and reagents are free from contamination. During analytical run (see Table 3125:IV), include quality control analyses according to schedule of Table 3125:VI, or follow project-specific QA/QC protocols.

Internal standard recoveries must be between 70% and 125% of internal standard response in the laboratory-fortified blank; otherwise, dilute sample, add internal standard mix, and reanalyze.

Make known-addition analyses for each separate matrix in a digestion or filtration batch.

5. Calculations and Corrections

Configure instrument software to report internal standard corrected results. For water samples, preferably report results in micrograms per liter. Report appropriate number of significant figures.

a. Correction for dilutions and solids: Correct all results for dilutions, and raise reporting limit for all analytes reported from the diluted sample by a corresponding amount. Similarly, if results for solid samples are to be determined, use Method 2540B to determine total solids. Report results for solid samples as micrograms per kilogram, dry weight. Correct all results for solids content of solid samples. Use the following equation to correct solid or sediment sample results for dilution during digestion and moisture content:

$$R_{corr} = \frac{R_{uncorr} \times V}{W \times \%\ TS/100}$$

where:

R_{corr} = corrected result, µg/kg,
R_{uncorr} = uncorrected elemental result, µg/L,
V = volume of digestate (after digestion), L,
W = mass of the wet sample, kg, and
$\%\ TS$ = percent total solids determined in the solid sample.

b. Compensation for interferences: Use instrument software to correct for interferences listed previously for this method. See Table 3125:III for a listing of the most common molecular ion interferences.

c. Data reporting: Establish appropriate reporting limits for method analytes based on instrument detection limits and the laboratory blank. For regulatory programs, ensure that reporting limits for method analytes are a factor of three below relevant regulatory criteria.

If method blank contamination is typically random, sporadic, or otherwise not in statistical control, do not correct results for the method blank. Consider the correction of results for laboratory method blanks only if it can be demonstrated that the concentration of analytes in the method blank is within statistical control over a period of months. Report all method blank data explicitly in a manner identical to sample reporting procedures.

d. Documentation: Maintain documentation for the following (where applicable): instrument tuning, mass calibration, calibration verification, analyses of blanks (method, field, calibration, and equipment blanks), IDL and MDL studies, analyses of samples and duplicates with known additions, laboratory and field duplicate information, serial dilutions, internal standard recoveries, and any relevant quality control charts.

Also maintain, and keep available for review, all raw data generated in support of the method.[5]

6. Method Performance

Table 3125:I presents instrument detection limit (IDL) data generated by this method; this represents optimal state-of-the-art instrument detection capabilities, not recommended method detection or reporting limits. Table 3125:VII through IX contain single-laboratory, single-operator, single-instrument performance data generated by this method for calibration verification standards, low-level standards, and known-addition recoveries for fresh-water matrices. Performance data for this method for some analytes are not currently available. However, performance data for similar ICP/MS methods are available in the literature.[1,4]

7. References

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Endnotes

1 (Popup - Footnote)
* Or equivalent.
2 (Popup - Footnote)
† Cambridge Isotope Laboratories or equivalent.
3 (Popup - Footnote)
‡ Performance data for the method were obtained with these concentrations.