

# STANDARD OPERATING PROCEDURE

## For

### USEPA METHOD 200.8, Rev. 5.4

#### Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Mass Spectrometry

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SOP #: EPA 200.8

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Page 1 of 33

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# MassDEP

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## TABLE OF CONTENTS

	Page
LIST OF REVISIONS .....	3
LIST OF TABLES .....	4
1.0 SCOPE AND APPLICATION .....	5
2.0 SUMMARY OF METHOD .....	7
3.0 DEFINITIONS.....	7
4.0 INTERFERENCES .....	9
5.0 SAFETY .....	10
6.0 EQUIPMENT AND SUPPLIES .....	11
7.0 REAGENTS AND STANDARDS.....	12
8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE .....	14
9.0 QUALITY CONTROL.....	14
10.0 CALIBRATION AND STANDARDIZATION .....	17
11.0 PROCEDURE .....	17
12.0 DATA ANALYSIS AND CALCULATIONS.....	24
13.0 METHOD PERFORMANCE .....	24
14.0 POLLUTION PREVENTION .....	24
15.0 WASTE MANAGEMENT .....	24
16.0 REFERENCES.....	25
17.0 TABLES, FORMS, FIGURES, AND VALIDATION DATA.....	26



## LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	November 2006	None	
1.0	July 2007	Added Section 3.15 – Definition of Minimum Reporting Limit (MRL)  Several other minor edits  Table 2 – Adjusted the experimentally determined MDL values with 2 significant figures, added the MRLs, and adjusted the LDRs with the new MDLs	8  Throughout Document  26
1.5	January 2008	Section 11.5.4 – Changed analytical sequence  Table 1 – Updated	20  24
1.6	January 2010	Minor updates to Sections 3.0 – Definitions; Section 7.0 – Reagents and Standards; Section 9.3 – Assessing Laboratory Performance; and List of Tables.  Substantial updates to Section 11.4 – Sample Analysis  Updated Table 2 – MDL data  Added Table 4 – SmartTune Acceptance Criteria  Added Form 1 – Standard Preparation Form.	7, 12, 13 & 16  19-21  28  31  32
1.7	April 2011	Table 2 – Updated MDL data	28-29
1.8	December 2012	Table 2 – Updated MDL data  Section 16 – Added references 4 through 10	



## LIST OF TABLES

	Page
TABLE 1. QUALITY CONTROL ELEMENTS AND ACCEPTANCE LIMITS FOR EPA METHOD 200.8 – DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY .....	26
TABLE 2. MASS, METHOD DETECTION LIMITS (MDLS), MINIMUM REPORTING LIMITS (MRLS), AND LINEAR DYNAMIC RANGES (LDRS) IN REAGENT WATER FOR METHOD EPA 200.8, (3-1-2011 – 2-23-2012) .....	29
TABLE 3. ACCEPTANCE LIMITS FOR QC CHECK SAMPLE (9.2.3) .....	31
TABLE 4. SMARTTUNE ACCEPTANCE CRITERIA .....	32
FORM 1: BENCH DATA COLLECTION FORMS\200-8 STD PREP .....	33



## 1.0 SCOPE AND APPLICATION

- 1.1 Inductively coupled plasma- mass spectrometry (ICP- MS) is used to determine metals and some nonmetals in solution. ICP-MS may be used for the determination of dissolved elements in drinking water, surface water, and ground water. Total recoverable elements may be determined in these matrices as well as wastewaters, sludges, and soils. This method is applicable to the following analytes:

<u>Analyte</u>		<b>Chemical Abstract Services Registry Numbers (CASRN)</b>
Aluminum	(Al)	7429-90-5
Antimony *	(Sb)	7440-36-0
Arsenic*	(As)	7440-38-2
Barium*	(Ba)	7440-39-3
Beryllium*	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium*	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium*	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper*	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead*	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury*	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel*	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium*	(Se)	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium*	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Uranium*	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

**\*The elements designated with an asterisk in the above table are the SDWA (Safe Drinking Water Act) analytes, which may be tested for using this method. Annual proficiency tests and U.S. EPA certification for the analysis of drinking water by this method is limited to these elements.**



- 1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)], consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.
- 1.3 ICP-MS is used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be < 0.2% (w/v) (Sect. 4.1.4).
- 1.4 With the exception of silver, all metals determined with this method are analyzed directly by pneumatic nebulization without acid digestion only if the sample has been properly preserved with acid and has a turbidity of < 1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis."
- 1.5 For the determination of total recoverable analytes in aqueous and solid samples, a digestion/extraction is performed prior to analysis when the elements are not in solution (e.g., fish/biological tissues, soils, sludges, sediments, and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material  $\geq 1\%$  (w/v) are extracted as a solid type sample.
- 1.6 When determining boron or silica in aqueous samples, only plastic, PTFE, or quartz labware is used from the time of sample collection to completion of analysis. For the accurate determination of boron or silica in solid samples, only PTFE beakers are used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. Borosilicate glass is avoided to prevent contamination of boron or silica.
- 1.7 The total recoverable sample digestion procedure in this method results in the loss of the volatile organo-mercury compounds and is therefore unsuitable for the determination of these compounds. However, for drinking waters suitable for direct analysis (NTU < 1), the combined concentration of inorganic and organo-mercury compounds can be determined by direct analysis pneumatic nebulization if gold is added to the sample(s), standards, and rinse solution to eliminate memory interference.
- 1.8 Low silver recoveries for samples with high chloride concentrations are avoided by digesting these samples prior to analysis. The total recoverable sample digestion procedure given in this method is performed for the determination of silver in aqueous samples containing concentrations up to 0.1mg/L Ag. Wastewater and other samples that contain higher concentrations of silver are diluted prior to digestion by taking decreasingly smaller aliquots of the well mixed sample until the analysis solutions contains < 0.1mg/L Ag. Also, the extraction of tin from solid samples is performed using aliquots < 1 g when determined sample concentrations exceed 1%.
- 1.9 The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis is completed as soon as possible after sample preparation.
- 1.10 Method detection limits (MDLs), minimum reporting limits (MRLs), and linear dynamic ranges (LDRs) for the elements will vary with the mass selected and the matrix. Listed in Table 2 are the MDLs, MRLs, and LDRs for selected masses in reagent water. However, actual MDLs, MRLs, and LDRs will be dependent on the sample matrix and selected operating conditions.
- 1.11 Users of the method data should state the data-quality objectives prior to the commencement of analysis. Initial demonstration performance data described in Section 9.2 was performed and is documented and kept on file.



## 2.0 SUMMARY OF METHOD

- 2.1 An aliquot of a well-mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are first digested in a microwave digestion system, in a hot block, or on a hot plate. After cooling, the sample is made up to volume, mixed, and filtered, centrifuged, or left to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is  $< 1$  NTU, the sample is made ready for analysis by the appropriate addition of nitric acid to  $\leq$  pH 2.
- 2.2 The analysis described in this method involves multi-elemental determinations by ICP-MS using a sequential instrument. The instrument measures characteristic mass-to-charge spectra. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific mass to charge spectra are produced by radio frequency inductively coupled plasma. The ions are pumped through a vacuum interface into a quadrupole and separated on the basis of their mass-to-charge ratio. The transmitted ions are detected by an electron multiplier capable of operating in both a digital and analog mode. The detector information is processed and controlled by a computer system. Interferences inherent in this technique must be recognized and corrected for. Interferences are considered and addressed in Sections 4.7.9 and 11.

## 3.0 DEFINITIONS

- 3.1 Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.
- 3.2 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.3 Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45- $\mu$ m membrane filter assembly prior to sample acidification.
- 3.4 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sample site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.
- 3.5 Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same mass.
- 3.6 Instrument Performance Check (IPC) Solution - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria. Depending on when it is run following instrument calibration, it may also be called an Initial Calibration Verification (ICV) or Continuing Calibration Verification (CCV) – See Table 1.
- 3.7 Internal Standard(s) - Pure analyte(s) added to a sample, extract, and standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard(s) element must be an analyte that is not a sample component and behave in a manner similar to the element of interest. The internal standard is used to correct for matrix effects and instrument drift.



- 3.8 Laboratory Duplicates (Sample and Sample Duplicate) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of Sample and Sample Duplicate indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.9 Laboratory Fortified Blank (LFB) - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.10 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.11 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.
- 3.12 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear – also referred to as the Linear Calibration Range (LCR).
- 3.13 Mass - The mass to charge ratio of a single or polyatomic ion.
- 3.14 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.15 Minimum Reporting Limit (MRL) - The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the MRL check standard for that analyte and can only be used if acceptable quality control criteria for the analyte at this concentration are met.
- 3.16 Quality Control Sample (QCS) - A solution of method analytes of known concentrations, which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.
- 3.17 Quality Control Sample (Standard Reference Material – Solids Matrix Only) (QCS<sub>SRM</sub>) - A sample of a matrix similar to the sample being analyzed which contains analytes of a known or accepted concentration. The QCS<sub>SRM</sub> is obtained from a source external to the laboratory and contains the analytes of interest at certified concentrations for the method of interest. This QCS<sub>SRM</sub> is processed in the same manner as the sample, unlike the QCS in 3.16, and is used to check method performance.
- 3.18 Solid Sample - For the purpose of this method, a sample taken from material classified as fish/biological tissue, soil, sediment, or sludge.
- 3.19 Standard Addition - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.





- 3.20 Stock Standard Solution - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.21 Total Recoverable Analyte - The concentration of analyte determined either by "direct analysis" of an unfiltered acid-preserved drinking water sample with turbidity of < 1 NTU or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method.
- 3.22 Tuning Solution - Solution used to determine if the instrument performance is acceptable. It is analyzed prior to calibration and sample analysis.
- 3.23 Water Sample - For the purpose of this method, a sample taken from one of the following sources: drinking water, surface water, ground water, storm water, or industrial or domestic wastewater.

#### 4.0 INTERFERENCES

- 4.1 The following interferences may cause inaccuracies in the determination of elements by ICP-MS.
- 4.1.1 Isobaric elemental interferences occur when isotopes of different elements form singly or doubly charged ions of the same nominal mass-to-charge ratio, which the instrument cannot resolve. Most elements have at least one isotope free of isobaric interference and this isotope may be used if it provides sufficient sensitivity, does not suffer from interference, and is otherwise acceptable for the analyses. Note, however, that selenium-82 suffers from an isobaric interference from Krypton, a potential contaminant in the Argon gas used to generate the plasma. Molybdenum-98 also suffers from ruthenium interference. Isobaric interferences must be corrected for by measuring the concentration of another isotope of the interfering isotope and correcting for its concentration. For the common interferences the software provided by the manufacturer performs this correction automatically.
- 4.1.2 Abundance sensitivity occurs when the wings of a mass peak overlap with one or more adjacent mass peaks. Under these conditions the wings contribute to the amount measured in the adjacent peak and cause an erroneously high concentration measurement. This may be a particularly troublesome problem when measuring the concentration of a small peak adjacent to a large peak. Overlap is an effect of the ions' energies and the quadrupole operating pressure. The potential for these interferences should be recognized and the spectrometer resolution should be adjusted to try and minimize this effect.
- 4.1.3 Isobaric polyatomic interferences occur when polyatomic ions form singly or doubly charged ions of the same mass-to-charge ratio as the element of interest and the instrument is unable to discriminate between them. These ions form in the plasma or interface system from interactions within and between the plasma gases, support gases, and sample components. Most of the common interferences have been identified and are automatically corrected for by the manufacturer's software. Of particular interest is the Krypton-82 isobaric elemental interference with Selenium and the resultant isobaric polyatomic interference with Arsenic as Krypton contamination of the Argon gas used to generate the plasma may occur. If such interferences are suspected alternate interference-free isotopes should be used if possible.
- 4.1.4 Physical interferences result from differences between the calibration standards and sample's matrix or digested solution. Differences in the way standards and samples are transported to the plasma, react in the plasma, and are transported through the plasma



quadrupole interface can create differences in the instrument's response when measuring a standard compared to a sample. High levels of dissolved solids in the sample may form deposits on the skimmer cones reducing the orifice diameter and potentially decreasing the ions transmitted. For this reason, it is recommended that dissolved solids not exceed 0.2%w/v whenever possible. The use of internal standards may effectively compensate for these differences and is required for SDWA analyses.

- 4.1.5 Memory interferences occur when isotopes of elements in a previously analyzed sample contribute to the signal detected in a following sample, standard, or QC sample. Memory effects can result from buildup of material on or in the skimmer cones, torch, tubing, spray chamber, or nebulizer. Memory interferences can be minimized by the use of a suitable rinse time. The rinse time can be initially estimated by aspirating the highest calibration standard or a standard higher than the expected highest sample concentration for the normal sample analysis period, then analyzing a blank solution until the analyte signal returns to baseline. Further adjustments of rinse time may be required when analyzing samples. Memory interferences can also be assessed by noting the results of triplicate integrations during data acquisition. If the consecutive integrations decrease in several samples or standards, memory interference should be suspected and rinse time adjusted. Memory interference from the rinse solution can also occur. If the three consecutive integrations' concentrations increase over time suspect interference from the rinse solution and increase the read delay time. Note that mercury determinations suffer from severe memory interferences, which can be alleviated by the addition of gold to the rinse. At 100  $\mu\text{g/L}$  gold, the recommended concentration, 5  $\mu\text{g/L}$  mercury will be rinsed out in approximately 2 minutes. For higher mercury concentrations, increase the rinse time.

## 5.0 SAFETY

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. All laboratory personnel are trained on the applicable laboratory safety procedures, and the OSHA and other regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. These reagents are used in a fume hood and if skin or eye contact occurs, large volumes of water are applied to flush the area of contact. An emergency shower and eyewash station are located in the laboratory. Safety glasses are used for eye protection and protective clothing is worn.
- 5.2 Acidification of samples is done in a fume hood to prevent the inhalation of toxic gases, such as cyanide or sulfide, volatile organic compounds, microbiological components, or radiological components.
- 5.3 All personnel handling potentially infectious environmental samples are immunized against known disease causative agents.
- 5.4 Caution is used when viewing the plasma. All instrument interlocks must be engaged for plasma to ignite, which provides the user of the method some protection from exposure to ultraviolet emissions.
- 5.5 All laboratory personnel fully comply with all relevant federal, state, and local waste management and disposal regulations. (Sect 14.0 and 15.0)



## 6.0 EQUIPMENT AND SUPPLIES

### 6.1 Inductively coupled plasma - mass spectrometer

6.1.1 Instrumentation: Perkin-Elmer Elan DRC-e, Serial # AH0100770602. Quadrupole Mass Spectrometer with dual mode (analog and digital) detector and dynamic reaction cell (DRC). DRC not currently accepted for SDWA analyses.

6.1.2 Computer: Dell Optiplex GX620

6.1.2.1 Software: Elan Instrument Software Version 3.3, Build 3.3.16.167e

6.1.3 Torch Module: The quick-change torch module is the quartz torch, torch block, spray chamber, and nebulizer/end cap, all in one assembly. This module can be quickly removed from the sample compartment for cleaning or replacement of new torch. The torch has an alumina injector with a 2.0-mm I.D. The load coil is water-cooled. Refer to Hardware Guide for the Elan DRC-e.

6.1.4 Spray Chamber: A Scott double-pass spray chamber and Gem Tip cross-flow pneumatic nebulizer are currently in use. Other spray chambers and nebulizers are available.

6.1.5 Peristaltic Pump: The peristaltic pump is integral to the ICP-MS and fully computer-controlled. Pump speeds are programmable in the Method Editor, Calibration page and QC Autosampler page and the Sample Information File. Coupled with the pump is the mixing block, where standards and samples are mixed with the internal standard.

6.1.6 Autosampler: The AS-93 plus Autosampler, serial number 933S5111305, is configured for this instrument. It is computer controlled and programmable. This system uses Tray F; it has 149 sample locations (15 mL) and 8 standard locations (50 mL).

6.1.7 Recirculator: Polyscience recirculator Model 3370, Serial # G56386

6.2 General Maintenance Procedure for Inductively Coupled Plasma - Mass Spectrometer - ICP maintenance is performed on a daily basis by the lead analyst (See Section 11). Major maintenance operations are performed by a Perkin-Elmer Customer Service Engineer. Service calls are placed to the company only when the lead analyst is not capable of performing the required maintenance. Service call reports are kept on file.

6.3 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

6.4 Equipment suitable for heating samples to temperature and under conditions specified by digestion procedure(s)

6.4.1 A temperature-adjustable hot plate capable of maintaining a temperature of 95°C

6.4.2 A laboratory microwave oven suitable for performing sample digestions

6.5 A gravity convection-drying oven with thermostatic control capable of maintaining 180 ± 5°C.

6.6 An assortment of air displacement pipettors and high-quality metal-free tips appropriate for the pipettors.

6.7 Polypropylene sieve, 5-mesh (4-mm opening).

6.8 Labware - For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory



work area is designated for trace element sample handling. Sample containers used in the determination of trace elements are sufficiently cleaned. Sample cleaning procedure involves washing with a detergent solution, rinsing with tap water, soaking for 4 h or more in 20% (v/v) nitric acid or a mixture of  $\text{HNO}_3$  and  $\text{HCl}$  (1+2+9), rinsing with reagent water and storing clean. Chromic acid must never be used to clean the glassware. Disposable pre-cleaned or metal-free labware does not require laboratory cleaning. Microwave digestion vessels are cleaned twice through their cleaning procedure with a reagent water rinse between and after each cleaning.

- 6.8.1 Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).
- 6.8.2 Assorted calibrated glass Type A volumetric pipettes.
- 6.8.3 Conical Phillips beakers (Corning): 250 mL with 50-mm ribbed watch glasses.
- 6.9 Argon Gas, compressed, high purity.
- 6.10 Semi-automatic change panel. Change panel capable of using two Argon cylinders.
- 6.11 Microwave digestion vessels made of PTFE.

## 7.0 REAGENTS AND STANDARDS

- 7.1 Only high-purity reagents suitable for trace metal analysis are used. All acids used for this method are equivalent to trace metal or better grade.
- 7.2 Hydrochloric acid, concentrated (sp. gr. 1.19) ( $\text{HCl}$ )
  - 7.2.1 Hydrochloric acid (1+1) - Add 500 mL concentrated  $\text{HCl}$  diluted to 1 L with reagent water.
  - 7.2.2 Hydrochloric Acid (1+4) - Add 200 mL concentrated  $\text{HCl}$  diluted to 1 L with reagent water.
- 7.3 Nitric acid, concentrated (sp. gr. 1.41) ( $\text{HNO}_3$ )
  - 7.3.1 Nitric Acid (1+1) - Add 500 mL concentrated  $\text{HNO}_3$  to 400 mL of reagent water and dilute to 1 L.
  - 7.3.2 Nitric acid (1+2) - Add 100 mL concentrated  $\text{HNO}_3$  to 200-mL of reagent water.
- 7.4 Reagent water - ASTM Type I reagent-grade water
- 7.5 Ammonium hydroxide, concentrated.
- 7.6 Standard Stock Solutions - Stock standards are purchased as both single and multi-element solutions. They are replaced when the expiration date is exceeded.
- 7.7 Preparation of Working Calibration Standard Solutions - Calibration standard solutions are prepared every two weeks or as necessary. Standards' concentrations will vary from analysis to analysis depending upon the analytes requested and expected range of sample concentrations. Dilutions of the stock solutions appropriate for the test being performed shall be made into 1%  $\text{HNO}_3$  v/v unless the standards are unstable in the resulting solution. Under those circumstances an alternate diluent may be used. The most commonly used standards and QC samples are prepared as described in Form 1.
- 7.8 Blanks - Four types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure, the laboratory fortified blank is used to



assess routine laboratory performance and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

- 7.8.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards, usually 1%  $\text{HNO}_3$ , unless an alternate diluent is used.
- 7.8.2 Laboratory reagent blank (LRB) contains all the reagents in the same concentrations as used in the processing of the samples. The LRB is carried through the same preparation scheme as the samples, including sample digestion.
- 7.8.3 Rinse blank is prepared by acidifying reagent water to 2%  $\text{HNO}_3$  unless the standards are prepared in an alternate diluent. In the latter case, the rinse blank shall be similar to the alternate diluent used.
- Note: Since mercury is to be determined in some samples, it is necessary to add gold to a concentration of 100  $\mu\text{g/L}$  in all rinse blanks except for alternate rinse blanks.
- 7.8.4 Laboratory Fortified Blank (LFB) is prepared by spiking an aliquot of LRB with one or more single or multi-element stock solution(s). The analyst will spike with a concentration above the RDL but not above the calibration. The LFB must be carried through the same procedure as the samples, including digestion if required.
- 7.9 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It is prepared in the same mixture as the calibration standards by combining method analytes at appropriate concentrations. The IPC is prepared from the same standard stock solutions used to prepare the calibration standards. Depending on its use, it may also be called an Initial Calibration Verification (ICV) or Continuing Calibration Verification (CCV).
- 7.10 Quality Control Sample (QCS) - Analysis of a QCS is performed for initial verification of calibration standards in order to verify instrument performance. The QCS is obtained from an outside source different from the standard stock solutions and prepared in the same mixture as the calibration standards, see 3.16. Not to be confused with the QCS 3.17.
- 7.11 Tuning Solution - This solution is used for tuning and mass calibration of the instrument prior to analysis. This solution is purchased and according to manufacturer's requirements contains 10  $\mu\text{g/L}$  of Magnesium, Indium, Lead, and Uranium
- 7.12 Internal Standards Solution - The Internal Standards Solution is added to all standards, samples, and QC samples by the peristaltic pump through a mixing block. Using the current pump tubing configuration of black-black internal diameter (ID) 0.030 inch for the sample, and orange-green ID 0.015 inch for the Internal Standard, the Internal Standard is diluted in a 1 to 5 ratio. To obtain a final concentration of 10  $\mu\text{g/L}$ , the Internal Standards Solution is made at a concentration of 50  $\mu\text{g/L}$  for one or more of the following commonly used Internal Standard elements: scandium, yttrium, indium, rhodium, terbium, holmium, germanium, or lutetium. Other elements may be used if they meet the requirements of behaving in a manner similar to the analytes of interest and are not contained in the sample. Note that lithium and yttrium may occur naturally in the samples, indium suffers isobaric interference from tin, and scandium may suffer from polyatomic interference. Additionally, yttrium may form a mass 105 yttrium oxygen ion and mass 106 yttrium hydroxide ion.





## **8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE**

- 8.1 Appropriate preservation and pretreatment steps are performed on all samples analyzed by this method. The pH of all aqueous samples is tested immediately prior to the direct analysis of any sample.
- 8.2 For the determination of the dissolved elements, the sample is filtered through a 0.45- $\mu$ m pore diameter membrane filter at the time of collection or soon thereafter. The sample is acidified to pH < 2 with 1+1 or concentrated nitric acid immediately following filtration.
- 8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with 1+1 or concentrated nitric acid to pH < 2. The sample is held for sixteen hours and then verified to be pH < 2 just prior to analysis. Preservation of the sample may be done at the time of collection in the field or the sample may be delivered to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Unless the sample is known to be non-hazardous, it is to be acidified in a fume hood.
- 8.4 Solid samples do not require preservation other than storage at 4°C. There is no established holding time for solid samples.
- 8.5 For aqueous samples, a field blank should be prepared and analyzed if required by the data user. The blank shall be treated identical to the samples including the same sample containers and acid.
- 8.6 Fish/biological tissue samples should be stored at -10°C to -20°C.

## **9.0 QUALITY CONTROL**

- 9.1 The quality control program for this method consists of an initial demonstration of laboratory capability and the periodic analysis of laboratory reagent blanks, fortified blanks, and quality control standards as a continuous check on laboratory performance. Records of these data are maintained and kept on file.
- 9.2 Initial Demonstration of Performance
- 9.2.1 Initial demonstration of performance is conducted prior to analysis of samples. At minimum, the LDR and MDL are produced prior to any analysis of environmental samples.
- 9.2.2 The Linear Dynamic Range (LDR) is established for each mass utilized (See Table 2) and is determined from a linear calibration prepared in the normal manner and composed of a calibration blank and at least two calibration standards using the established analytical operating procedure for the instrument. The LDR is determined by analyzing increasingly higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. The LDRs are documented and kept on file. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit are diluted and reanalyzed. The LDRs are verified annually or whenever a change in analytical or instrument performance occurs, which would then dictate that the LDRs be re-determined.
- 9.2.3 The Quality control sample (QCS) (Section 3.16) is analyzed with every analytical run to verify the calibration standards. To verify the calibration standards, the mean concentrations from at least three analyses of the QCS must be within  $\pm 10\%$  of the stated values. If the QCS is used to verify acceptable on-going instrument performance,



it must be within  $\pm 10\%$  or within the stated limits in Table 3, whichever is greater. If the calibration standards are not verified, performance is unacceptable, and the determination of analytes is not continued. The source of the problem is identified and corrected before proceeding on with any analyses.

- 9.2.4 Method detection limits (MDLs) are established for all masses utilized, using reagent water (blank) fortified at a concentration of two to five times the estimated method detection limit (see Table 2). To determine MDL values, seven replicate aliquots of the fortified reagent water are processed through the entire analytical method. Calculations of the MDL are as follows:

$$MDL = (t) \times (S)$$

Where:

t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

If desired, MDLs may be confirmed by reanalysis of seven aliquots on three nonconsecutive days. The MDL value for each day is calculated. The average of the three MDLs may provide a more appropriate MDL estimate.

It is preferred that the MDL solution be within two to five times the calculated MDL. If the MDL solution is greater than ten times the calculated MDL the test shall be rerun using a lower concentration standard in an appropriate range. Failure to do this may result in an unrealistically low MDL value.

Calculation of the MDL in reagent water is a best-case scenario and may not reflect the real world effect of a sample's matrix.

The MDLs must be sufficiently low to detect regulated analytes at or below the level required by the appropriate regulation(s). MDLs should be determined annually, when a new operator begins working, or whenever, in the judgment of the analyst, a change in the performance of the instrument occurs.

### 9.3 Assessing Laboratory Performance

- 9.3.1 Laboratory reagent blank (LRB): The laboratory analyzes one LRB with every batch of 20 or fewer samples of the same matrix. LRB data is used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination. If LRB values equal or exceed 10% of the sample's value or are 2.2 times the MDL a fresh aliquot of sample and LRB should be sampled, prepared, and analyzed after correcting the source of contamination. For SDWA analyses this is required.
- 9.3.2 Laboratory fortified blank (LFB): The laboratory analyzes one LFB with each batch of samples. The LFB accuracy is calculated as percent recovery using the following equation:

$$R = \frac{LFB - LRB}{s} \times 100$$

Where:

R = Percent recovery



- LRB = Laboratory reagent blank.  
LFB = Laboratory fortified blank.  
S = Concentration equivalent of analyte added to fortify the LRB solution.

If the recovery of the analyte falls outside the required control limits of 85 - 115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

- 9.3.3 The LFB analyses data are used to assess laboratory performance against the required control limits of 85-115%. When sufficient internal performance data become available (usually a minimum of twenty to thirty analyses), optional control limits may be developed from the mean percent recovery ( $\bar{x}$ ) and the standard deviation (S) of the mean percent recovery. These data are used to establish the upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{x} + 3S$$

$$\text{LOWER CONTROL LIMIT} = \bar{x} - 3S$$

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits are calculated using the most recent twenty to thirty data points. The standard deviation (S) data are used to establish an on-going precision statement for the level of concentrations included in the LFB. These data are kept on file and available for review.

- 9.3.4 Instrument performance check (IPC) solution: IPC is analyzed with every analytical run, immediately after calibration and at the end of the analytical run. The IPC, immediately after calibration, is analyzed to verify that the instrument is within  $\pm 10\%$  of calibration. This is also called the ICV. Subsequent analyses of the IPC solution, also called CCV, must be within  $\pm 15\%$  of calibration. If the calibration cannot be verified within the specified limits, the IPC and the calibration blank are reanalyzed. If analysis of the IPC solution or the calibration blank is outside the limits, sample analysis is discontinued, and the cause of the problem is determined, corrected, and/or the instrument recalibrated. All samples following the last acceptable IPC solution are reanalyzed. The analysis data of the calibration blank and IPC solution are kept on file with the sample analyses data.

#### 9.4 Assessing Analyte Recovery and Data Quality

- 9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Laboratory fortified matrix (LFM) samples and duplicate samples are processed to assess matrix effects.
- 9.4.2 The laboratory adds a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot is a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration is the same as that used in the laboratory-fortified blank (Sect. 7.8). Whenever possible, for solid samples, however, the concentration added is expressed as mg/kg
- 9.4.3 Percent recovery for each analyte is calculated using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

Where:





- R = Percent recovery
- $C_s$  = Fortified sample concentration.
- C = Sample background concentration.
- s = Concentration equivalent of analyte added to fortify the sample.

9.4.3.1 The analyst will spike a sample with a concentration above the RDL but not above the LDR of calibration. If normal spike concentrations do not meet this criterion, on-line spikes may be prepared and analyzed.

9.4.3.2 LFM recovery range is 70% to 130%. If the analyte spiked is < 30% of the sample's background concentration, the percent recovery calculation is not required.

9.4.4 If the recovery of the analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user will be informed that the result for that analyte is suspect due to lack of sample homogeneity or matrix effects.

9.4.5 Reference materials are utilized for every analytical run unless unavailable. They are analyzed to provide additional performance data, and demonstrate the ability to perform the method on a particular matrix.

9.5 Internal standards responses are monitored throughout the analysis. The absolute response of any one internal standard shall be within 60% to 125% of the response in the calibration blank; deviations greater than this may indicate a matrix effect. Flush the instrument with rinse blank until internal standard response in the calibration blank returns to its original value. Dilute the sample by a factor of two and reanalyze. If flushing the instrument fails to return calibration blank values to their original value, determine the cause of the drift. Suspect partially blocked sampling cone or sample delivery system. The ratios of the internal standard elements to each other are also monitored. A change in the ratio may indicate the sample contains one or more of the internal standard elements. For full mass range scans, a minimum of three internal standards is required.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Plasma operating conditions are determined by the user and then stored by the instrument. The instrument then automatically adjusts the system conditions to remain within the prescribed operational settings and makes continuous diagnostic adjustments.

10.2 After the plasma has been "conditioned" for 30 minutes, a calibration blank is aspirated followed by the calibration standards. The instrument is calibrated with single element or mixed calibration standard solutions as appropriate for the analysis. Stock standards and dilutions are recorded in the Standard Preparation Logbook.

## 11.0 PROCEDURE

**Instrument Operating Procedure & Daily Maintenance** – The following actions are performed on days that the instrument is used. All maintenance performed, except daily tubing replacements, is logged in the ICP-MS maintenance logbook.



## 11.1 Standard Operating Procedure for ICP-MS

11.1.1 Turn on Computer and Screen. Login name Runinstrument, Password Runinstrument#1.

11.1.2 Switch on the Ventilation Hood, Recirculator, and the Air Conditioner to highest setting.

11.1.3 Gas Supply: Make sure both Argon tanks are open; one tank should always be in use. If using DRC mode, make sure reaction gas cylinder is open.

11.1.3.1 Argon cylinders are attached to the semi-automatic change panel. When changing a cylinder, be certain the "in use" arrow points to the cylinder not being exchanged. This prevents most of the system from becoming contaminated with room air and allows the instrument to continue to run while tanks are exchanged. The second stage pressure should be about 80 pounds per square inch (psi).

11.1.3.2 The reaction gas has a separate regulator; the second stage pressure should be eight to nine psi. There are several possible reaction gases; the one in use depends upon the interference to be resolved. Several of these gases are hazardous and appropriate precautions must be taken.

11.1.4 Maintenance of Sample Introduction System: Check Autosampler activity, probe location, and draining of waste. Align Peristaltic Pump tubes on rollers and check for tube flattening, abrasion, stretching and change peristaltic pump tubes if necessary, check magazine fittings and adjust if necessary. The sample and internal standard tubing should be changed daily. The rinse blank tubing has three bridges so two sections of tubing can be used before it is required to be changed.

11.1.5 Insert Internal Standard line and check internal standard solution for sufficient volume for analysis. Prepare new solution if necessary and record solution preparation in Standard Preparation Logbook. Insert rinse blank line into the rinse solution; be sure there is sufficient solution volume for analysis.

11.1.6 On the computer screen, you will see the Windows Icons. Activate the Elan Icon once for the active software window and a second time for an off-line window. All Elan functions are controlled through the use of workspaces. A workspace contains the various files necessary to perform a particular analysis. Certain workspaces are manufacturer defined and read only, the contents of these workspaces cannot be changed, e.g. Daily Performance, Tuning, and Optimization. Other workspaces contain methods for particular analysis types, e.g. EPA 200.8 or 6020. Within these latter, it is possible to modify the method or use more than one method depending upon the analyses required.

11.2 Elan Instrument Control Session Window opens. The default workspace may be used to check on the instrument's status and start the instrument or another workspace may be chosen as follows.

11.2.1 Click on Workspace Icon (upper left green folder icon) or choose File-Open Workspace.

11.2.2 Choose the workspace of interest, e.g. Daily Performance, EPA200.8, etc.

11.2.3 Click on the Instrument icon if the Instrument window is not already there. The vacuum system should always be on and ready unless maintenance is being performed, the left vacuum pump, gas connections, quadrupole, and turbo pumps displays should be green. If they are any other colors the system is not ready. Do not ignite the plasma. Determine the reason the system is not ready, correct it, turn on the pumps, and wait for the system to pump down to the necessary vacuum before proceeding.



- 11.3 Igniting Plasma – In the Quantitative Analysis Window (Click Method or File-Open Method-choose a method), Sampling tab click Probe. When the Autosampler Probe Control box appears click the Go to Rinse button. Make sure probe goes to the rinse station, the autosampler pump is running, and rinse solution is filling the rinse station. In the Instrument Window on the Front Panel tab, click on the Start button to ignite the plasma. The ignition of the plasma takes 90 seconds or so. Pumps, gases and nebulizer are now activated and all displays on the Instrument window should turn green in a few seconds. The analyst should visually check to be sure the plasma ignited, it is visible either at the torch mounts connection to the spray chamber or through the small window on the upper right of the instrument. Analyst should check the mixing block, peristaltic pumps, tubing, exhaust system, cooling system, and solutions to assure all components are operating correctly.
- 11.3.1 If there is a problem with ignition, the plasma will not light and the “button” will be turned off. Also, Instrument window displays should turn yellow or red to indicate a potential source of the problem. Plasma ignition should occur on demand. Occasionally two or three attempts are required, especially if room air has entered the gas lines. If not, check those areas indicated in the Instrument window display, Front Panel, or Diagnostics tabs as possible trouble sources. If the instrument has been in use for some time without torch maintenance or unusually dirty samples have been run, open torch assembly compartment and check nebulizer and spray chamber for residue buildup, check for leaks and replace O-rings if showing signs of wear. Clean or replace torch components. Reassemble torch and attempt plasma ignition again.
- 11.3.2 The fume exhaust system on this instrument also acts to remove excess heat. Be sure the system is working correctly, especially if the Plasma System section of the Diagnostics tab on the Instrument window indicates a heat buildup.
- 11.3.3 The Water Re-circulator is an important accessory for the ICP. Check the operation of this unit; especially if the Cooling System information on the Diagnostics tab of the Instrument window indicates a problem.
- 11.3.4 The plasma needs to be “conditioned” for approximately 30 minutes before you can analyze any standards or samples.
- 11.4 Sample Analysis – Before analysis can be performed, the analyst should perform the following maintenance as needed:
- 11.4.1 Spectrophotometer XY Alignment: To be done when the torch is removed, or the cones are removed or cleaned. To perform this, go to the X-Y workspace. Aspirate a solution of 10- $\mu$ g/L Magnesium, Indium, and Uranium in 0.5% nitric acid. Click Analyze Sample. Open the Real Time window – be sure the analytes of interest are displayed. Open the ICP-MS cover and turn the Y adjustment knob until maximum signal is detected. Then turn the X adjustment knob until maximum signal is detected. Repeat to be sure maximum signal is detected.
- 11.4.2 If performing analyses that must meet EPA requirements (e.g., SDWA testing), use the SmartTune wizard to perform the required pre-analysis testing.
1. Click on the SmartTune icon. Check that C:\Elandata\Wizard\SmartTune\DailyOpt.swz has been selected as the SmartTune file.
  2. Aspirate a 10  $\mu$ g/L solution of barium, beryllium, cadmium, cerium, cobalt, copper, indium, magnesium, lead, rhodium, and uranium in 1% nitric acid.
  3. Wait for the solution to reach the torch and then click Optimize.



4. When SmartTune has finished, check that the results for all options are acceptable – See Table 4.
  5. To repeat one of the procedures, highlight it under the Optimization Setup in the left pane of the SmartTune.
  6. Save the Optimization files when leaving this workspace.
  7. SmartTune performs the following: Mass Calibration and Resolution, Lens voltage, Auto Lens Calibration, and Daily Performance Check. Date and initial this report. Save it in the Daily Summary Reports binder. Include a copy in the QC batch(s) folder.
- 11.4.3 Daily Performance Check: If a daily performance check is sufficient, perform the following pre-analysis testing.
1. Open the Daily Performance workspace.
  2. Aspirate a solution of 10-µg/L magnesium, indium, cerium, barium, and uranium in 1% nitric acid.
  3. Click Analyze Sample.
  4. Compare the results of the Daily Performance Report to the expected results in the online software.
  5. If the report values are acceptable, proceed.
  6. Date and Initial this report.
  7. Save in the Daily Summary Reports binder and include a copy in the QC batches folder.
- 11.4.4 Optimizing Nebulizer Gas Flow for 3% Oxides:
- To reduce nebulizer gas flow:**
1. On the **File** menu, click **Open Workspace**.
  2. Select **Optimizing Nebulizer Gas Flow.wrk**, and then click **Open**.
  3. In the Optimization window, click the **Auto Optimize** tab. In the **Parameter Description** list box, click **ICP RF Power**.
  4. In the **Current Value** field, type the power (in watts) you want to use, and then click **Set**. (**Current Value** is 1300 at this time).
  5. In the **Parameter Description** list box, click **Nebulizer Gas Flow (NEB)**.
  6. Click **Get Analyte List**. The ELAN software gets the list of analytes from the method in the workspace, and displays the analytes in the **Analyte** drop-down list.
  7. Click **Get Defaults**.
  8. In the **Optimization Criteria** group, click **Formula**.
  9. Fill in the formula drop-down menu boxes with the following expression:  
$$\text{CeO } 156 / \text{Ce } 140 < .03$$

**NOTE:** The last box contains the criterion .03 which means 3%.
  10. Aspirate a 10-µg/L solution of barium, beryllium, cadmium, cerium, cobalt, copper, indium, magnesium, lead, rhodium, and uranium in 1% nitric acid.



11. Click **Optimize**
12. Save the Optimization file when leaving this workspace
13. If the oxide ratio is greater than 3% at a given RF power and range of nebulizer gas flows, reduce the **Start Value** in the Parameter Range group on the **Auto Optimize** tab and repeat steps 10-12;

Or

If the oxide ratio is less than 3% BUT the sensitivity is poor and/or the noise at mass 8.5 and 220 does not meet specification (that is, less than 1.5 and 2.0 cps, respectively), increase the RF power by 25 watts and repeat steps 10 and 11. Repeat this step to achieve the desired sensitivity, oxide, and background response. Typically, it is not recommended to exceed 1300 watts during this optimization. If the background is still too high, optimize the cell path voltage and repeat nebulizer gas flow optimization.

11.4.5 Detector Optimization: This service is under service contract. All detector optimizations are performed by a Perkin-Elmer Service Engineer.

11.4.6 Using the Workspace to analyze samples:

- 11.4.6.1 Open the workspace that contains the method of interest, e.g. EPA200.8, 6020, etc. If not already done, make new files for the Calibration View, Dataset, and Samples files. Make active the file of interest and click File-New on the menu. Some files will ask for a new name immediately, others require the new file to be saved by clicking File-Save as. Note: these files do not automatically appear in the workspace unless you save this particular version of the workspace. A workspace always displays the files present the last time the workspace was saved. These files can be retrieved by making active the file type of interest, e.g. Dataset, clicking on File-Open, and then choosing the file you wish to use.
- 11.4.6.2 Open the Method and check that it is the method you wish to use. If not, click File-Open and choose the appropriate method. Check the method to be sure the information contained in it is correct. Be especially careful that the various times and pump speeds match on the Sampling and QC-Autosampler pages as this information is not readily apparent while running the samples. There is a column fill function for these columns. Note that all analytes in the method will be tested for, so if the analysis requires only one or a few elements to be tested for it may be advantageous to create a new method.
- 11.4.6.3 Make active the Sample window. Fill in the sample information, including the autosampler position. There is a fill dialog box but it is unlikely to be of use unless all the samples are sequential. Be certain the pump speeds and times match those in the method. This information does not default even if the method column is filled in. There is a column fill function for these columns. Make sure the first sample's Measurement Action is Run Blank, Stds, and Sample or no calibration will be performed. Subsequent sample runs using the existing calibration need only have Run Sample in the first sample's Measurement Action. Save the modified sample file.
- 11.4.6.4 Highlight the samples to be analyzed in the Sample window and click Build Run List. A list of the analysis order (Batch) will appear. Click Print List to obtain a hard copy of this list. If Print List does not work, do a Screen Print of the list. Load the autosampler according to the list. Date and initial this list and keep with the paper copy of the analysis run if a paper copy is kept.



## 11.5 Sample Analysis, Automated Analysis

11.5.1 Automated analysis may be started by clicking Analyze Batch on the Run List window or the Samples window. A Batch box will appear which indicates the sample currently being analyzed as well as the analysis progress.

11.5.2 Priority Sample(s): To insert a priority sample, click the Priority box and fill in the sample's information. Note that the term "next sample" does not necessarily mean the one about to be run. It may be two or three samples before the Priority sample is run.

11.5.3 Append Samples: To append one or more samples to the Batch click the Append button and fill in the sample(s)' information. There must be at least three samples left in the Batch for this to work.

### 11.5.4 Analytical Sequence:

An example tray protocol for an EPA 200.8 analysis follows.

Sequence	Sample ID
1	Calibration Blank
2	Calibration Standard Solutions
3	Quality Control Sample(s) (QCS $\pm$ 10%) – Performance Check Standard(s)
4	Minimum Reporting Limit (MRL) Standard(s) – Performance Check Standard(s)
5	IPC(s) ( $\pm$ 10%) – Performance Check Standard(s)
6	Continuous Calibration Blank (CCB)
7	10 or fewer samples which may include LRB(s), LFB(s), Matrix QCS (s) (QCS <sub>SRM</sub> ), Sample Duplicate(s), LFM(s), Performance Check QCS(s) as necessary
8	Continuing Calibration Check CCC(s) $\pm$ 15% - Performance Check Standard(s)
9	CCB
10	10 or fewer samples which may include LRB(s), LFB(s), Matrix QCS(s), Sample Duplicate(s), LFM(s), Performance Check QCS(s) as necessary.
11	QCS(s) $\pm$ 10%, Optional Performance Check Standard(s)
12	CCC(s) $\pm$ 15%
13	CCB

11.6 Results Data File In the Elan software – Other than as each sample's results are shown on the computer monitor, results can only be viewed by printing the results' report. Be sure the Quantitative Analysis Method Report tab has Send to printer checked and the Report Options Template box contains a report format, usually quant summary.rop. If the Report View window is





blank, there is no report format in the method. Note: the software currently contains a bug, which occasionally deletes the print information in the method for any workspace opened. Filling in the report information and saving the workspace usually fixes the problem for some time.

11.7 Retrieving Data Files – In the Elan software, the contents of the data files can only be retrieved and viewed by Re-processing the data with the original conditions.

11.7.1 If the desired data are not active, load the desired data set by making the window Dataset active, then click File-Open and choose the desired data set. In the Dataset window check the box Use Original Conditions, choose the results to be printed, and click Reprocess.

11.8 Re-processing data – If there are minor changes to be made to the method, calibration, or sample information it is possible to reprocess the data instead of rerunning the samples. This may be acceptable under such conditions as one calibration standard's results are obviously incorrect and should not be included in the calibration curve; the curve does not go through zero but the original curve type was Linear Thru Zero; some part or parts of the samples' information was incorrect, e.g. volume, sample Log-in number; the standard(s) concentrations are not the defaults in the method used; etc. Re-processing is not a substitute for correcting problems with digestions, contamination, incorrect use of the instrument, or other major issues. Re-processing does not alter the acquired data just the results obtained from these data.

11.8.1 If the desired data are not active, load the desired data set by making the window Dataset active. Click File-Open then choose the desired data set.

11.8.2 To exclude a calibration point, click on the point in the Calibration View window.

11.8.3 To change sample information, type the correct information in the Dataset window. Note: after Re-processing the original values for the changed data will re-appear in the original data lines. The corrected information will appear in the Re-processed data's line.

11.8.4 Highlight the samples to be re-processed. Check save Re-processed Data if you wish to save the results. The re-processed data will be appended to the Dataset in a color other than the original color.

11.8.5 Click Reprocess: The re-processing will start and the results reports will be printed.

11.9 Sample Preparation – Typical sample preparation methods are listed below.

SDWA Metals	Method 200.2
Rivers/Ponds Total	Method 3015
Total Recoverable	Method 3005
Total Suspended -0.45 µm	Method 3005
Dissolved -0.45 µm	Method 3005
Total TCLP Extracts	Method 3015
Total High TDS	Method 3010B
RCRA	Method 3051
Total for Wastes Liquid/Solid	Method 3051
Total for Soil, Sludge, Sediment	Method 3051
Fish/Biological Tissue	Method 3052



Other matrices and sample preparation methods are acceptable if they meet the data quality objectives and satisfy the appropriate regulatory requirements.

## 12.0 DATA ANALYSIS AND CALCULATIONS

- 12.1 Sample data are reported in units of mg/L for aqueous samples and mg/kg dry weight for solid samples.
- 12.2 For dissolved aqueous analytes, report the data generated directly from the instrument with allowance for sample dilution. Concentrations below the MDL are reported as ND (not detected) with the MDL concentration stated.
- 12.3 For total recoverable aqueous analytes, multiply solution analyte concentrations by the dilution factor and report data to the proper significant figures.
- 12.4 For total recoverable analytes in solid samples, round the solution analyte concentrations to the proper significant figures in mg/L.
- 12.5 For total recoverable analytes in solid samples, the (C) concentration in mg/kg is calculated as follows:

$$\text{Sample Conc. (mg / kg) dry weight basis} = \frac{C \times V \times D}{W}$$

Where:

- C = Concentration in extract (mg/L)
- V = Volume of extract (L)
- D = Dilution factor (undiluted = 1)
- W = Weight of sample aliquot extracted (kg)

## 13.0 METHOD PERFORMANCE

Listed in Table 2 are the MDLs for total recoverable metals determined for the masses used in this method. The MDLs were determined in reagent water blank matrix.

## 14.0 POLLUTION PREVENTION

- 14.1 Refer to the WES Environmental Management System (EMS) policy and SOPs regarding pollution prevention.
- 14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

## 15.0 WASTE MANAGEMENT

- 15.1 WES laboratories fully comply with all applicable federal, state, and local environmental regulations. WES is also committed to protecting the air, water, and land by minimizing and
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controlling all chemical releases from fume hoods, biological safety cabinets, and bench operations. Refer to the WES EMS policy and SOPs regarding waste management.

- 15.2 All chemical waste is collected in sealed waste containers. Once the waste containers reach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste drum (organic or inorganic). Within 180-days of waste accumulation, the waste drum is transported off the premises by a licensed hazardous waste management contractor. Under the WES EMS, a chemical inventory database has been developed to track purchases and use of chemicals and other hazardous materials, and the waste generated by the use of these chemicals.

## 16.0 REFERENCES

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## 17.0 TABLES, FORMS, FIGURES, AND VALIDATION DATA

**TABLE 1. Quality Control Elements and Acceptance Limits for EPA Method 200.8 – Determination of Metals and Trace Elements in Water And Wastes By Inductively Coupled Plasma-Mass Spectrometry**

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Linear Calibration Range (LCR)	Change in instrument hardware or operating conditions, by judgment of analyst.	Three standards, one of which is close to the upper limit of the LDR or up to any standard which when run as a sample is $\pm 10\%$ of the true value.	If change in instrument, change LCR to new values. If no change in instrument, check/service instrument. If instrument functioning correctly, change LCR.
Method Detection Limit (MDL)	Every year or when there is a new operator or at the preference of the analyst.	Target analyte concentration spiked into the blank matrix should not exceed 10 times (1 to 5x ideally) the experimentally determined MDL	Repeat MDL study spiking the blank matrix with lower concentration of the target analyte.
Instrument Stability	45-minute warm-up	RSD < 5% for five replicates of all analytes in Tuning solution	Determine and correct the cause, recalibrate before analyzing samples
Initial Calibration	Every run	$r^2 > 0.995$	Determine the cause and recalibrate with new standards
Internal Standard	Every run. Internal Standard is added to all standards and sample solutions.	Monitor Internal Standards for ratio differences. Responses outside 60% to 125% of response found in Calibration Blank are outside Acceptance Criteria.	Ratio variation may indicate Internal Standard element in sample, choose alternate Internal Standard element. Response outside 60% to 125% may indicate matrix effect, dilute sample and reanalyze.
Instrument Performance Check Sol. (IPC, ICV, CCC, CCV)	Immediately following each calibration (IPC, ICV), after every tenth sample (CCC, CCV) and at the end of the run (CCC, CCV)	ICV ( $\pm 10\%$ ) Concentration = the midpoint calibration standard. CCV ( $\pm 15\%$ ) Concentration = midpoint of calibration.	Reanalyze IPC, if outside range, recalibrate and re-analyze sample(s) since last successful CCC, or discontinue & recalibrate instrument if necessary.



**TABLE 1. Quality Control Elements and Acceptance Limits for EPA Method 200.8 – Determination of Metals and Trace Elements in Water And Wastes By Inductively Coupled Plasma-Mass Spectrometry**

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Calibration Blank (CCB)	Immediately following each IPC, after every CCV and at the end of the run	< MDL, but > a negative signal in concentration units equal to the MDL. If there is no MDL, < ½ the MRL.	Determine cause and reanalyze, or recalibrate instrument. If it is not possible to reanalyze, qualify the data if sample concentration is < 10 times the CCB. If the sample's concentration is "Not Detected" or greater than or equal to 10 times the CCB, no qualification is needed.
Quality Control Sample (QCS) - from a source external to the laboratory (See Sect. 3.16)	After calibration, optional at the end of the run.	90 – 110 % Recovery from triplicate readings	Acceptable range should be met before continuing with sample analysis. Recalibrate and repeat. If reanalysis is not possible, the data may be qualified.
Laboratory Reagent Blank (LRB)	One with each batch of 20 or fewer samples	< 2.2 times the analyte MDL or 10% of the analyte level measured in the sample	Determine and eliminate the source of contamination and then repeat sample analysis if possible. If problem cannot be corrected, qualify samples with concentrations < 10 times the LRB. If the sample's concentration is "Not Detected" or greater than or equal to 10 times the LRB, no qualification is required.
Laboratory duplicate	Every 10 samples or less	Relative percent difference among duplicates (RPD) ≤ 20 for SDWA analyses. For other matrices, see LIMS limits.	Repeat analysis with new aliquots if suspect result in error or qualify the data. If the sample is non-homogenous, note this with the duplicate's result in the LIMS report. If reanalysis is not possible, the data may be qualified.
Laboratory Fortified	Every 10 samples or less	70 – 130%	If laboratory



**TABLE 1. Quality Control Elements and Acceptance Limits for EPA Method 200.8 – Determination of Metals and Trace Elements in Water And Wastes By Inductively Coupled Plasma-Mass Spectrometry**

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Matrix (LFM)		Note: Recovery calculation is not required if the concentration added is less than 30% of the unfortified sample concentration	performance shown to be in control, LRB and LFB or QCS within acceptance criteria, problem is a matrix effect – qualify data.
Laboratory Fortified Blank (LFB)	One with each batch of 20 samples	85 – 115%	Source of the problem should be identified and resolved before continuing analysis. If reanalysis is not possible, the data are qualified.
MRL Check Standard	At the beginning of every analytical run	$\pm 20\%$	Acceptable range should be met before reporting data for SDWA analyses. If not acceptable, then recalibrate and repeat or, for that analysis run, raise the MRL to the lowest standard which meets the MRL criteria. If the problem persists, suspect the MDL and MRL are too low for the analysis conditions.



**TABLE 2. Mass, Method Detection Limits (MDLs), Minimum Reporting Limits (MRLs), and Linear Dynamic Ranges (LDRs) in Reagent Water for Method EPA 200.8, (3-1-2011 – 2-23-2012)**

Analyte	Mass	MDL ( $\mu\text{g/L}$ )	MRL ( $\mu\text{g/L}$ )	LDR ( $\mu\text{g/L}$ )
Aluminum	27	NA	50	50 – 1000
Antimony	123	0.03	0.10	0.03 – 1000
Antimony	121	0.03	0.10	0.03 – 1000
Arsenic	75	0.15	0.50	0.15 – 1000
Barium	137	0.04	0.50	0.04 – 1000
Barium	135	0.10	0.50	0.10 – 1000
Beryllium	9	0.02	0.10	0.02 – 1000
Boron	11	ND	ND	ND
Cadmium	111	0.03	0.10	0.03 – 1000
Cadmium	114	0.03	0.10	0.03 – 1000
Calcium	43	ND	ND	ND – 1000
Chromium	52	0.07	0.50	0.07 – 1000
Chromium	53	0.21	0.90	0.21 – 1000
Cobalt	59	0.01	0.10	0.01 – 1000
Copper	63	0.51	2.0	0.51 – 1000
Copper	65	0.51	2.0	0.51 – 1000
Iron	56	ND	ND	ND – 200
Lead	208	0.28	0.90	0.28 – 200
Magnesium	24	0.96	5.0	0.96 – 1000
Manganese	55	0.08	0.50	0.08 – 1000
Molybdenum	98	0.03	0.10	0.03 – 1000
Nickel	60	0.04	0.50	0.04 – 1000
Potassium	39	ND	ND	ND – 10000
Selenium	82	0.20	0.90	0.20 – 1000
Selenium	77	1.2	5.0	1.20 – 1000
Silver	107	0.23	0.90	0.23 – 1000
Sodium	23	NA	50	50 – 1000
Strontium	88	ND	ND	ND
Thallium	205	0.02	0.10	0.02 – 1000
Thallium	203	0.04	0.50	0.04 – 1000
Tin	118	ND	ND	ND



**TABLE 2. Mass, Method Detection Limits (MDLs), Minimum Reporting Limits (MRLs), and Linear Dynamic Ranges (LDRs) in Reagent Water for Method EPA 200.8, (3-1-2011 – 2-23-2012)**

Analyte	Mass	MDL ( $\mu\text{g/L}$ )	MRL ( $\mu\text{g/L}$ )	LDR ( $\mu\text{g/L}$ )
Titanium	47	ND	ND	ND
Uranium	238	0.01	0.10	0.01 – 1000
Vanadium	51	0.04	0.50	0.04 – 1000
Zinc	66	0.46	2.0	0.46 – 1000
Zinc	67	0.59	2.0	0.59 – 1000
Zinc	68	0.46	2.0	0.46 – 1000

NA: Not Applicable. An MDL cannot be determined for these analytes due to preservative or other matrix interference(s).

ND: Not Determined. These analytes have not been requested so MDLs, MRLs, and LDRs have not been determined. When determined, these data will be added to the table.

The MRL is usually set at three to approximately five times the MDL. However, due to the large number of analytes, this is not always feasible. In some instances the lowest MRL standard that is at least three times the MDL is also greater than five times the MDL.



**TABLE 3. Acceptance Limits for QC Check Sample (9.2.3)**  
**Method Performance ( $\mu\text{g/L}$ )**

Element	Acceptance Limits <sup>(1)</sup> %
Aluminum	84-117
Antimony	93-107
Arsenic	91-113
Barium	92-108
Beryllium	88-112 <sup>2</sup>
Cadmium	94-108
Chromium	91-114
Cobalt	90-106
Copper	94-107
Lead	94-114
Manganese	90-106
Molybdenum	94-108
Nickel	94-106
Selenium	86-121
Silver	91-111
Thallium	90-107
Thorium	94-109
Uranium	94-111
Vanadium	90-110
Zinc	91-119
<sup>1</sup> Acceptance limits calculated as average recovery $\pm$ 3 standard deviations	
<sup>2</sup> Acceptance limits centered at 100% recovery.	



**TABLE 4. SmartTune Acceptance Criteria**

QC Element	Acceptance Criteria		
Sensitivity	Analyte	Mass	Measured Intensity cps/10- $\mu$ g/L Standard
	Mg	24.0	> 50,000
	In	114.9	> 250,000
	U	238.1	> 200,000
Background	220 < 2 ups		
Doubly Charged	$Ba^{++}/Ba < 3\%$		
Oxides	$CeO/Ce < 3\%$		
Mass Calibration	$\pm 0.1$ amu from stated mass of analyte		
Resolution	0.65 amu $\pm$ 0.1 amu at 10% peak height		
Instrument Stability	RSD < 5% for five readings of Mg, In, and U		





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SOP #: EPA 200.8  
SOP Rev. #: 1.8  
Date: December 2012  
Page: 33 of 33

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**FORM 1: Bench Data Collection Forms\200-8 Std Prep**

[See "Standards Preparation for EPA Method 200.8" Bench Data Collection Form](#)