

# 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-Mass Spectrometry

SOP #: EPA 200.8

SOP REVISION #: 4.2

DATE: December 2022

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# MassDEP

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## LIST OF REVISIONS

Rev. #	Date	Description of Revision	Section #
0	November 2006	None	
1.0	July 2007	Added Section – Definition of Minimum Reporting Level (MRL)  Several other minor edits throughout document  Table 2 – Adjusted the experimentally determined MDL values with 2 significant figures, added the MRLs, and adjusted the LDRs with the new MDLs	3.15   17.0
1.5	January 2008	Changed analytical sequence  Updated Table 1	11.5.4 17.0
1.6	January 2010	Minor updates to:  Definitions  Reagents and Standards  Assessing Laboratory Performance; and List of Tables  Substantial updates to Sample Analysis  Updated Table 2 – Updated MDL data  Added Table 4 – SmartTune Acceptance Criteria  Added Form 1 – Standard Preparation Form	  3.0 7.0 9.3 11.4 17.0 17.0 18.0
1.7	April 2011	Updated Table 2 – Updated MDL data	17.0
1.8	December 2012	Added References 4 through 10  Updated Table 2 – Updated MDL data	16.0 17.0
2.0	February 2016	Changed division name from Division of Environmental Analysis (DEA) to Division of Environmental Laboratory Sciences (DELS) and made other minor clarifications throughout to update document.  Updated software, hardware, equipment, & supplies  Clarified calibration standards preparation  Clarified MDL determination  Updated to reflect changes in facility, hardware, and software  Corrected typographical errors	6.0  7.0 9.2.4 11.0 12.0
2.1	September 2017	Included the number of replicates per analysis  Clarified and combined Section 12.3  Section Deleted  Table 3 – Deleted	11.4.6.2 12.2 12.3 17.0



3.0	November 2018	Equipment and Supplies Updated	6.0
		MDL Procedure Updated	9.0
		Updated Tuning Procedure	11.0
		Table 1 – LRB Acceptance Criteria Updated	17.0
		Updated Table 2	17.0
3.1	February 2019	Deleted Table 2 (MDLs) & Table 3 (QCS Check Std Acceptance Criteria)	17.0
		Table 4 renumbered to Table 2	17.0
		Forms Section removed	18.0
4.0	April 2020	Changed Page #(s) to Section #(s)	List of Revisions
		Equipment and Supplies updated for new Perkin Elmer NexION 1000 ICP-MS instrument	6.0
		Reagents and Standards – Minor edits throughout	7.0
		Calibration and Standardization updated for NexION 1000 ICP-MS	10.0
		Procedure updated for new instrument	11.0
		Table 2 – SmartTune Daily Performance Check Acceptance Criteria updated for NexION	17.0
		Table 3 – KED Daily Performance Check Criteria added	17.0
		Table 4 – Elemental Equations for Data Corrections added	17.0
4.1	October 2021	Changes made in response to EPA review of Rev. 4.0:	
		Thermostatic control – typographical error corrected	6.5
		Added KED prohibition for use with drinking water samples	7.12
		Clarified sample acidification requirements	8.4
		Added that MDL standard is prepared over 3 separate days	9.2.4.1
		Added Proficiency Testing section	9.3.5
		Added monitoring Internal Standard RSDs	9.5
		Added RSD% and replicate requirements	11.2.1
		Corrected NexION Set-up solution analyte list	11.2.9
		Added monitoring Internal Standard RSDs	Table 1
		Added Concentration of Daily Performance Check Solution	Table 2



4.2	December 2022	<p>Sections 6.1.6.1 and 6.1.6.2 – Added Autosampler Default Method Sampling Settings.</p> <p>Section 8.4 – Clarified Potable vs. Non-Potable Water Acid Preservation.</p> <p>Section 9.1 – Added overview of quality control.</p> <p>Section 9.2.1 – Updated Linear Calibration Range and Carryover.</p> <p>Section 9.2.2 – Added IDC QCS Replicates.</p> <p>Section 9.3.2 – Added IDC LFB Replicates.</p> <p>Section 10.2 – Added Calibration Blank.</p> <p>Section 11.2.11 – Clarified AMS Flow Rate Procedure.</p> <p>Section 11.4.3 – Clarified procedure to append samples.</p> <p>Section 11.4.4 – Added new section explaining the Run List Pause Feature.</p> <p>Section 11.4.6 – Updated analytical sequence.</p> <p>Section 12.3 – Clarified solid sample calculations.</p> <p>Section 12.5 – Added new section listing the documentation to be included in data packet for QA L1 and L2 reviews.</p>	
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## 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 in wastewaters, sludges, and soils. This method is applicable to the following analytes:

<u>Analyte</u>		<u>Chemical Abstract Services Registry Numbers (CASRN)</u>
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
Cadmium*	(Cd)	7440-43-9
Chromium*	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper*	(Cu)	7440-50-8
Lead*	(Pb)	7439-92-1
Manganese	(Mn)	7439-96-5
Mercury*	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel*	(Ni)	7440-02-0
Selenium*	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium*	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
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). This method uses aerosol dilution, referred to as All Matrix Solution (AMS) by the manufacturer, to dilute sample analytes and total dissolved solids. AMS dilution takes place



inside the cyclonic spray chamber and helps maintain the plasma's ionizing effectiveness while reducing the likelihood of forming insoluble precipitates in the interface region.

- 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 sample.
- 1.6 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. The addition of gold must be added at the time of sample and standard preparation to stabilize mercury.
- 1.7 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 0.1 mg/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  $< 0.1$  mg/L Ag
- 1.8 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 varied and unknown concentrations of sulfate, analysis is completed as soon as possible after sample preparation.
- 1.9 Method detection limits (MDLs), minimum reporting levels (MRLs), and linear dynamic ranges (LDRs) for the elements will vary with the mass selected and the matrix. For MDLs, MRLs, and LDRs, for selected masses in reagent water, see the most recent MDL study at [WES SharePoint: \DELS\DELS-QAP\IDC, MDL & MRL Data\IOC Lab\EPA Method 200.8](#). Note that actual MDLs, MRLs, and LDRs will be dependent on the sample matrix and selected operating conditions.
- 1.10 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 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 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 Section 4.

### 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) (IS) - 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) (Lab Dup) - 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)/ Laboratory Control Sample (LCS) - 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)/ Matrix Spike (MS) - 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 monoatomic 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 Level (MRL) - The lowest analyte concentration that can be quantitated with acceptable accuracy and precision under stated analytical conditions.
- 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 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 (See Table 4 for manufacturer-generated correction equations for those elements that require correction).
- 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 (See Table 4).
- 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 µg/L gold, the recommended concentration, 5 µg/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 Safety Data Sheets (SDS) 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 while wearing gloves, 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 Instrumentation: Inductively Coupled Plasma - Mass Spectrometer
  - 6.1.1 Perkin Elmer NexION 1000, Serial # 815N9022804X, Mass Spectrometer with dual mode (analog and pulse) detector, Universal Cell Technology (UCT) capable of Kinetic Energy Discrimination (KED), Dynamic Reaction Cell (DRC), and Standard Mode Operation. KED and DRC are not currently accepted for SDWA analyses.
    - 6.1.1.1 Computer: Dell OptiPlex 3050, Service Tag 15RT0Q2
    - 6.1.1.2 Operating System: Windows 10 2016 LTSB, 64 bit



6.1.1.3 Software: Syngistix Version 2.5, Build 2.5.1902.5377

6.1.2 Torch Module: SMARTintro Sample Introduction Module, Purple Cassette, with One-Piece 2.0-mm I.D. Quartz Torch-Injector.

6.1.3 LumiCoil™ RF coil: Requires no maintenance or cooling.

6.1.4 Spray Chamber: Glass Cyclonic C3 High Sensitivity Spray Chamber with matrix port (AMS) with high sensitivity ST3 PFA MicroFlow Nebulizer. PC<sup>3</sup>X Peltier Cooler/Heater: Heats or cools the NexION cyclonic chamber from -10°C to +80°C, thermal stabilization of the spray chamber improves long-term stability, oxide performance, and is controlled directly through the Syngistix software.

6.1.5 Peristaltic Pump: The peristaltic pump is integral to the ICP-MS and is fully computer-controlled from the method's sampling tab, the device window, or from the SmartTune file. The peristaltic pump controls carrier transport, internal standard transport, and cyclonic chamber drainage.

6.1.6 Autosampler: SC40X ESI Fast Autosampler, Serial # SC4-190069, is paired with the NexION 1000. It is computer controlled and programmable. This system has 10 positions for standard (50-mL) solutions plus four user configurable trays: one 21-position rack for 50-mL tubes, and three 60-position racks for 15-mL tubes. A fast-switching valve minimizes sample uptake and washout time, eliminates contact with peristaltic tubing, and reduces stabilization time. Internal to the Fast-Switching Valve design is a feature that adds and mixes the internal standard to all standards and samples.

6.1.6.1 Default Syngistix Sampling Settings for Metals/Uranium Method

- Sample Flush: 1 sec
- Read Delay: 17 sec
- Wash: 12 sec

6.1.6.2 Default Syngistix Sampling Settings for Mercury Method

- Sample Flush: 1 sec
- Read Delay: 30 sec
- Wash: 30 sec

6.1.7 Chiller: Polyscience Whisper Cool, Model N0772046, Serial # 1902-02864, PE Sciex Coolant (WE016558, 1L)

6.1.8 Printer: Either dedicated or networked.

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, calibrating pipettes for standard preparation, 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 block 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  $105 \pm 5^\circ\text{C}$ .
- 6.6 An assortment of air displacement pipettes and high-quality metal-free pipette tips.
- 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. Laboratory 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.
- Note: Samples are not collected by laboratory personnel. As a result, laboratory has no control over sample bottles, other supplies and consumables, or techniques used in the field.
- 6.8.1 Glassware – Class A 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 Pre-cleaned 50-mL polypropylene or polyethylene digestion tubes with cap, matching reflux caps.
- 6.8.4 Pre-cleaned 15-mL sample tubes.
- 6.9 Argon Gas, cryogenic and compressed, ultra-high purity (99.999%).
- 6.10 Automatic Gas Switching Panel: Switching panel capable of using one high-pressure Argon Dewar and two high-pressure Argon cylinders.
- 6.11 Microwave digestion vessels made of PTFE.
- 6.12 Narrow-mouth storage bottles, polypropylene, polyethylene, or FEP (fluorinated ethylene propylene) with ETFE (ethylene tetrafluoroethylene) screw closure, 250-mL capacity.





#### 6.13 Peristaltic Pump Tubing

- 6.13.1 Carrier Black/black tubing – MP2 PVC flared 0.76-mm ID, 72-mm between bridges, Part # N8145197.
- 6.13.2 Internal Standard orange/green tubing – MP2 PVC flared 0.38-mm ID, 72-mm between bridges, Part # N8145202,
- 6.13.3 Cyclonic Chamber Waste tubing grey/grey – MP2 Santoprene 1.30-mm ID, 82-mm between bridges, Part # N8145173,

### 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.

**Reagents and Standards Preparation Bench Sheets for this method are standalone documents found in the Forms Folder for this method in the WES W drive at W:/DELS/Inorganic Chemistry Lab/Standard and Reagent Prep Forms. Different forms exist for making the internal standard, the rinse and carrier solution, and standard solutions, including calibrators, QC elements, the NexION setup solution, the KED Daily Performance Check, and the Dual Detector solution.**

#### 7.2 Hydrochloric acid, concentrated (sp. gr. 1.19) (HCl)

- 7.2.1 Hydrochloric acid (1+1) – Add 500 mL of concentrated HCl diluted to 1 L with reagent water.
- 7.2.2 Hydrochloric Acid (1+4) – Add 200 mL of concentrated HCl diluted to 1 L with reagent water.

#### 7.3 Nitric acid, concentrated (sp. gr. 1.41) (HNO<sub>3</sub>)

- 7.3.1 Nitric Acid (1+1) – Add 500 mL of concentrated HNO<sub>3</sub> to approximately 400 mL of reagent water and dilute to 1 L.
- 7.3.2 Nitric acid (1+2) – Add 100 mL of concentrated HNO<sub>3</sub> 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 prior to or at the expiration date.

#### 7.7 Preparation of Working Calibration Standard Solutions: Calibration standard solutions are prepared every two weeks for SDWA analyses, or as necessary for all other analyses. 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% HNO<sub>3</sub> (v/v) unless the standards are unstable in the resulting solution. Under those circumstances, an alternate diluent may be used.



- 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. For mercury analysis, gold is added to a final concentration of 100  $\mu\text{g/L}$  during preparation.
- 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. For mercury analysis, gold is added to a final concentration of 100  $\mu\text{g/L}$  during preparation.
- 7.8.3 Rinse blank and carrier are prepared by acidifying reagent water to 2%  $\text{HNO}_3$  prepared with 100  $\mu\text{g/L}$  of gold unless the standards are prepared in an alternate diluent. In the latter case, the rinse and carrier blank shall be similar to the alternate diluent used.
- 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 MRL but not above the calibration. The LFB must be carried through the same procedure as the samples, including digestion if required. For mercury analysis, gold is added to a final concentration of 100  $\mu\text{g/L}$  during preparation.
- 7.9 Instrument Performance Check (IPC) Solution: The IPC solution is used to periodically verify instrument performance during analysis. It is prepared from the same multi-element 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 manner as the calibration standards. Not to be confused with the QCS-SRM.
- 7.11 Tuning Solution: This is a multi-purpose solution and has been renamed by the manufacturer as the NexION Setup Solution. As a tuning solution, it is used to calibrate the mass spectrometer to ensure correct mass assignment and unit mass resolution. Target sensitivity levels are also influenced by other components of the ICP-MS besides the quadrupole. Therefore, the Setup Solution is also used for individual optimizations (torch, nebulizer, QID, and Detector) to ultimately meet the manufacturer's target abundance, oxide, double charge, precision, and background noise levels in the Daily Performance Check.
- 7.12 Internal Standards Solution: The Internal Standards Solution is added to all calibration standards, samples, and QC standards 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. Prepare internal standards according to the specific bench sheet required: Internal Standard Preparation for EPA 200.8 using AMS or AMS with KED. NOTE: KED is not used for the analysis of drinking water samples. Internal standard concentrations are experimentally determined by





obtaining counts between 300,000 and 500,000 for one or more of the following commonly used Internal Standard elements: gallium, rhodium, terbium, iridium, 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 as yttrium oxygen ion and mass 106 as yttrium hydroxide ion, a secondary mass for cadmium.

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 When requested, the laboratory provides appropriate pre-cleaned samples bottles for Method 200.8 analysis; and appropriate sample bottle specifications for clients who supply their own bottles. Samples are not collected by laboratory personnel. The laboratory has no control over sample bottles, other supplies and consumables, or techniques used in the field.
- 8.2 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. A minimum of 250 mL of liquid sample or > 200 g of solid sample is required to perform all analyses and meet QC requirements.
- 8.3 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.
- 8.4 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 at least 16 hours for potable water, 24 hours for non-potable water, and then verified to be pH < 2 just prior to processing. If the pH is > 2 after 16 (or 24) hours, acidify to pH < 2 again and wait another 16 (or 24) hours before retesting the pH and continuing with post-acid turbidity. Immediately before instrumental analysis, confirm that the pH is < 2 for non-digested samples with turbidity NTU < 1. 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 acid preserved upon receipt in the laboratory. Unless the sample is known to be non-hazardous, it is to be acidified in a fume hood. Field and laboratory samples are stored at  $4 \pm 2^{\circ}\text{C}$ .
- 8.5 Solid samples do not require preservation other than storage at  $4 \pm 2^{\circ}\text{C}$ .
- 8.6 For aqueous samples, a field reagent 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.
- 8.7 Fish/biological tissue samples are stored at  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$ .

## 9.0 QUALITY CONTROL

- 9.1 The quality control (QC) requirements of this method include initial and ongoing elements: instrument calibration and verification (ICV, CCV & QCS), evaluating analyst and method accuracy/precision (LFB/QCS % recovery/RSD, sample duplicate RPD), MDL/MRL determination for sensitivity/reporting levels, method and instrument contamination (ICB, CCB, LRB), participation in annual proficiency testing, and examining contribution of sample bias on data quality results (LFM). This section details the specific requirements for each of these QC elements. The laboratory is required to maintain performance records that define the quality of the data that are generated.



## 9.2 Initial Demonstration of Performance

9.2.1 The Linear Dynamic Range (LDR) is established for each mass utilized 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. If the LDR is not determined for each analyte, a linear calibration range is established for sample analysis. Sample concentrations can only be reported if they lie within the linear calibration range. If a sample is over the highest calibrator, the following sample could be suspect, especially if it has a very low concentration. For such a situation, retest the suspect sample. Inspect RSDs carefully for all samples after a high sample and repeat if carryover is suspected. If the next bracketing CCV/CCB exceeds acceptance limits, repeat all samples in the bracket. Alternatively, demonstrate the absence of carryover with a check standard above the highest calibrator. **Make certain high check standards do not come immediately after a sample with a high chloride concentration and that the system has been properly rinsed to avoid permanent instrument contamination. Do not check the LDR/presence of carryover over 500 µg/L with AMS on.**

9.2.2 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 1, 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. As part of the IDC, run seven QCS replicates for accuracy and precision using three separate standard preparations that are analyzed on different days.

9.2.3 Method Detection Limit (MDL) – The MDL is determined for each mass utilized using both reagent water replicates (MDL<sub>b</sub>) and fortified reagent water replicates (MDL<sub>s</sub>).

9.2.3.1 Determination of Method Detection Limit (MDL<sub>s</sub>): MDLs are established for all analytes using reagent water fortified at a concentration of 2.5 to 5 times the estimated instrument detection limit (IDL), but no more than 10 times the IDL or previously established MDL. The IDL concentration is estimated based on:

- The instrument manufacturer's IDL or from previous MDL studies using a similar LDR.

MDL standards are prepared on 3 separate calendar days. To determine MDL values, take seven replicate aliquots of the fortified reagent water along with seven method blanks and process through the entire analytical method over at least three separate days.

$$\text{MDL}_s = (t) \times (S)$$

Where:



$t$  = Students'  $t$  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.

$$MDL_b = \bar{X} + t_{(n-1, 1-\alpha=0.99)} S_b$$

$MDL_b$  = The MDL based on method blanks

$\bar{X}$  = mean of the method blank results (use zero in place of the mean if the mean is negative)

$t_{(n-1, 1-\alpha=0.99)}$  = the student  $t$ -value appropriate for the single-tailed 99<sup>th</sup> percentile  $t$  statistics and a standard deviation estimate with  $n-1$  degrees of freedom.

$S_b$  = sample standard deviation of the replicate method blank sample analyses.

Select the greater of  $MDL_s$  or  $MDL_b$  as the initial MDL.

The following inequalities are useful when evaluating a calculated MDL.  
Calculated MDL < Spike Level < 10 X Calculated MDL or Spike Level/MDL < 10.

As per EPA-NE (Region 1), it is important to evaluate the average percent recovery of the replicates to determine if it meets the minimum acceptance criteria for low-level measurements. The laboratory will keep on file the MDL study and the MDL study performed as per EPA-NE (Region 1) recommendations. The later MDL study will be used to derive MRL values.

After the initial MDL is established, the MDL study may take place over a two-year period.

9.2.3.2 On-going Data Collection: During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples. If any analytes are repeatedly not detected in the quarterly spiked sample analyses, or do not meet the qualitative identification criteria of the method, then this is an indication that the spiking level is not high enough and should be adjusted upward. Note that it is not necessary to analyze additional method blanks together with the spiked samples since routine method blanks are analyzed with each batch during sample analysis. Ensure that at least seven spiked samples and seven method blanks are completed for the annual verification. If only one instrument is in use, a minimum of seven spikes are still required, but they may be drawn from the last two years of data collection. At least once per year, re-evaluate the spiking level. If more than 5% of the spiked samples do not return positive numerical results that meet all method qualitative identification criteria, then the spiking level must be increased, and the initial MDL re-determined.

9.2.3.3 Ongoing Annual Verification: At least once every thirteen months, re-calculate  $MDL_s$  and  $MDL_b$  from the collected spiked samples and method blank results. Include data generated within the last twenty-four months, but only data with the same spiking level. If the laboratory believes the sensitivity of the method



has changed significantly, then the most recent data available may be used, maintaining compliance with the requirement for at least seven replicates in three separate batches on three separate days. Only use data associated with acceptable calibrations and batch QC. Include all routine data, except for batches that are rejected, and the associated samples reanalyzed.

Ideally, use all method blank results from the last 24 months for the MDL<sub>b</sub> calculation. The laboratory has the option to use only the last six months of method blank data or the fifty most recent method blanks, whichever criteria yields the greater number of method blanks. If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL. Note that the range of 0.5 to 2.0 approximates the 95th percentile confidence interval for the initial MDL determination with six degrees of freedom.

With sample results no longer reported below the MRL, the procedure and frequency for determining MDL<sub>s</sub> is determined by the U.S. EPA to satisfy the legal requirements of the method. Refer to the 2017 CWA Method Update Rule (MUR) that includes revisions to the original 40 CFR Appendix B to Part 136, Rev 1.11, Definition and Procedure for the Determination of the Method Detection Limit (MDL), that are now included in Rev 2, 12/13/16. The MDLs and MRLs must be sufficiently low to detect regulated analytes at or below the level required by the appropriate regulation(s). MDLs should be determined as specified above, 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 are 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 ¼ of the MRL (equivalent to 2.2 times the MDL), a fresh aliquot of sample and LRB should be sampled, prepared, and analyzed after correcting the source of contamination. This is required for SDWA analyses.

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. As part of the IDC, run seven LFB replicates for accuracy and precision using three separate standard preparations and that are analyzed on different days.

- 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, after every ten samples 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.
- 9.3.5 Proficiency Testing: Analyze an externally generated, single-blind quality control sample (QCS of unknown concentration) annually. Obtain this sample from a source external to the laboratory and compare results to that laboratory's acceptance results. If testing results do not pass acceptance criteria, investigate why, take corrective action, and analyze a new QCS. Repeat this process until results meet the acceptance criteria.

#### 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, this also applies to 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<sub>s</sub> = 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 MRL 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.

In addition to internal standard recoveries, monitor internal standard RSDs throughout the run. RSDs should be less than 5%. When internal standard RSDs are above 5%, take action to determine if an underlying sample introduction problem exists. When diagnosing the problem, consider internal standard RSDs, internal standard recovery trends, Daily Performance Check results and RSDs, as well as the accuracy of QC standards. QC standards outside of acceptance limits could indicate a problem with mixing in the ESI FAST valve or with the carrier/internal





standard pump tubing. If QC standards pass but internal standard RSDs/recoveries become an issue, suspect problem with argon delivery to the nebulizer or a defective nebulizer.

## 10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Plasma operating conditions are determined by the user and then stored in the Conditions window. 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 30-60 minutes, tune the instrument as described in the Procedure Section (Section 11.0). Then proceed to calibrate the instrument by aspirating the subtraction blank, followed by the calibration blank, and then the calibration standards. The instrument is calibrated with single element or with a multi-element standard as appropriate for the analysis. Stock standards and dilutions are recorded on the Standard Preparation Bench Sheets.

### 10.3 Summary of NexION 1000 ICP-MS Routine Maintenance and Inspection

- 10.3.1 Replace the carrier, internal standard, and cyclonic chamber waste tubing daily. To reduce changes in analyte intensity and degradation in short term stability, manually stretch the tubing before installation. Maintain proper tension on the tubing to establish constant flow.
- 10.3.2 In the Syngistix software (circle in upper left corner, replaces term “File” in other software) menu, the Videos section contains various maintenance video clips. They provide step-by-step instructions on how to remove, clean, assemble, and reinstall the torch and cones. Supplemental cleaning instructions are also available in the Perkin Elmer Training Manual for the nebulizer, spray chamber, torch, and interface cones. Routine maintenance is performed when the end user’s data quality objectives cannot be achieved.

Open the instruments interface door using Devices→ICP-MS→Cone Access or the instrument’s front panel. Visually inspect the torch and check that there is not excessive discoloration or buildup. Excessive torch buildup can create arcing with the Rf coil and lead to overheating/melting/damage to either the torch or coil. Visually inspect the cones. Replace cones if the orifice size or shape is altered. Cones may need cleaning if there is an increase in the background signal, poor long-term stability, memory effect, loss of sensitivity or distorted peak shape. Changes in vacuum pressure could indicate a cone blockage (pressure decrease) and a pressure increase could indicate a worn orifice that has increased in size. Never insert a wire into the orifice of the cones as it could damage the size/uniformity of the opening.

Rarely, a new cone will not function properly. To test whether a new or used cone may be the source of the problem, it is suggested to keep a set of still properly functioning used cones on hand for short-term testing of instrument parameters. It is important to condition new or cleaned cones to decrease signal drift due to the initial deposition of sample matrix onto the cone surface. See the Perkin Elmer Training Manual for various conditioning techniques.

- 10.3.3 Peristaltic Tubing and Cyclonic Inspections: With the placement of air bubbles into the peristaltic tubing, verify the liquid travels smoothly and at a constant rate. The cyclonic waste line should have a consistent bubble pattern and steady flow rate. Blockages or crimped tubing can interfere with maintaining a constant, steady state condition. With the plasma on, inspect the nebulizer and spray chamber daily for an even spray pattern with



minimal pulsation. Pulsation could indicate the nebulizer has a blockage. If mist does not evenly cover the walls of the cyclonic spray chamber or if large droplets are observed, the spray chamber may need cleaning, especially if memory effect problems are observed.

- 10.3.4 Pre-Run Conditioning: To routinely clean the ESI Fast Autosampler probe, transfer line, sample loop, and switching valve before an analytical run, use the 2% nitric acid rinse fortified with gold to washout the sample introduction system. Activate the Control icon in the upper left corner of the menu bar and select Autosampler → ESI settings in the Device window. All the autosampler positions will be visible in a schematic window of the ESI autosampler. Right click the rinse positions and select Perform Rinse in each position. As an additional precaution, insert a few rinse samples to the run list before the calibration blank. Note: Prime and condition the autosampler **before** placing samples into the autosampler racks. The pump that initially fills the autosampler rinse positions may have entrained air in the lines, causing rinse to spray up into the right side of cabinet and potentially contaminating samples.
- 10.3.5 Replace rough pump oil (Leybonol Fomblin PFPE LVO 420, PE Part# N8145003) every 12 months. The vacuum pump for the ICP interface region may need more frequent replacement during periods of heavy use due to greater sample contamination. If the oil does not appear colorless, replace sooner. Maintain the oil level between the minimum and maximum level, ideally between the halfway and maximum level.
- 10.3.6 If air entrainment is suspected in the argon delivery lines, a purge valve exists near the wall valve to flush the argon lines.
- 10.3.7 Check chiller coolant level daily and top off (Perkin-Elmer Sciex Coolant, Part# WE016558 Rev D) if necessary.
- 10.3.8 Check the argon Dewar daily for capacity and to adjust the pressure builder to achieve approximately 250-320 PSI at the panel entry point.

## 11.0 PROCEDURE

- 11.1 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. For certain diagnostic purposes, the analyst must be in Service mode. Caution: It is possible to permanently disable the instrument in Service mode. Do not enter Service mode unless necessary, do not change settings unless current settings are recorded, do not change settings unless absolutely necessary.
- 11.1.1 Turn on the power to the computer and monitor. The Syngistix icon will appear on the desktop.
- 11.1.2. Check that the chiller is on, and the coolant level is in the normal operating range before igniting the plasma. Normal chiller operating temperature and pressure readings are approximately 15°C at 47 psi. Check that the rough pump's oil level is in the normal operating range and that no oil leaks are present in the retaining pan.
- 11.1.3 Gas Supply: Check that the argon Dewar is sufficiently full and producing enough gas to maintain pressure, back-up cylinders contain sufficient argon, and switching panel indicates sufficient pressure to distribute argon to the building. With the plasma turned on, the pressure builder will likely need to be opened. When the plasma is turned off, the





pressure builder can be closed. If using KED or DRC mode, make sure the respective gas cylinder is open.

11.1.3.1 Argon Dewar and cylinders are attached to the automatic switching panel. When changing a Dewar or the cylinders, be certain the valve between the pigtails and the panel is closed. This prevents most of the system from becoming contaminated with room air and allows the instrument to continue to run while the Dewar or tanks are exchanged. The pressure at the instrument's wall regulators should be about 90-100 pounds per square inch (psi).

11.1.3.2 The helium KED and DRC gases have separate regulators; the second stage pressure regulator should be set at 50 psi and stepped down to 15-20 psi at the instrument's wall regulator. 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 On the computer's desktop screen, a Syngistix icon starts the Syngistix ICP-MS software. Once opened, the software's Control window is activated by default. The Control window is comprised of three windows: Devices, System Status, and System View. In the device screen, manual control of various instrument components is possible: ICP-MS, Pump, Autosampler, and PC3. The ICP-MS icon controls plasma ignition, control of the vacuum pumps, and operation of the interface access door. The pump icon controls functions related to the peristaltic pump: the on/off switch, speed, direction of rotation, tubing saver options, and startup options when the plasma is ignited. The autosampler icon allows manual control of autosampler, access to configuration settings, the ability to rinse the autosampler probe, and the sample introduction system, calibration of the probe's X-Y-Z coordinates and initialization. PC3 controls temperature settings for the Peltier heater/cooler and on/off power options. System Status displays alerts for overdue scheduled instrument maintenance. System Status alerts are linked to the maintenance tab where users can view, edit, and define maintenance reminders. Featured on top of the System View window are the instrument's vacuum pressure display and a schematic of the instrument, consisting of the detector, quadrupole, universal cell, quadrupole ion deflector (QID), and torch. When operating, the ion path in these components becomes animated. Selecting any of these components will also display diagnostic settings. System View also displays the diagnostic status of other important instrument conditions related to the instrument's ventilation, power, vacuum, gases, Rf generator, cooling, and torch alignment. Clicking on one these components will display its status and operating conditions, such as set point values, read back (RB) values, voltages, pressure readings, and temperature. The torch position tab is used to view, define, and edit torch X, Y, and Z individual motor positions. In most cases, X, Y, and Z torch settings are adjusted using SmartTune's torch alignment and Torch Sampling Depth optimization functions.

11.1.5 Transfer the internal standard and carrier line probes from reagent water to the 2% nitric acid rinse solution. Replace the peristaltic pump tubing: carrier, internal standard, and cyclonic spray chamber waste tubing. Properly align the tubing on the rollers and start the pump using the Device window. Set the peristaltic pump speed to -32 rpm. Snap the tubing clamps into position and observe if liquid is being drawn into the carrier and internal standard tubing.

11.1.6 The cyclonic spray chamber and nebulizer combination is self-aspirating once the plasma is ignited. Therefore, fluid flows must be checked before igniting the plasma.

11.1.7 Once liquid has reached the spray chamber and the waste is being removed properly (smoothly, with segments of liquid and air), double check the flow by inserting air



segments into both the carrier and internal standard lines. Check that liquid is traveling smoothly through the carrier and internal standard lines. Adjust pressure on peristaltic tubing if necessary. Note that smoothest flow is before the peristaltic pump and is usually achieved by loosening the set screw until the flow just stops, tightening the screw until forward flow is just established, then tightening the screw an additional  $\frac{1}{4}$  to  $\frac{1}{2}$  turn.

- 11.1.8 Once proper liquid transfer is established the plasma can be ignited. In the Device Window, click on the ICP-MS icon and then the power button to ignite the plasma. The ignition of the plasma typically takes no more than 60 seconds. The peristaltic pump can remain on before igniting the plasma. If the operator prefers to turn the peristaltic pump off, it will turn on automatically after the plasma is established, using the speed setting from the current method loaded or the optional value entered into the device's pump speed after plasma ignition. The generated plasma is created using the settings stored in the Default Conditions file. In the laboratory notebook, note the vacuum pressure before and after igniting the plasma. If the pressure varies from historical operating conditions, it could indicate defective cones, improperly installed cones, or a sample introduction leak.
- 11.1.9 If there is a problem with ignition, the plasma will not light, and the power "button" will be turned off. Check that the argon pressure is high enough to sustain the plasma. Check that the cyclonic spray chamber is draining properly, and that excessive liquid is not building up in the cyclonic spray chamber due to improperly installed tubing in the peristaltic pump. Examine the System View window for any system failures or diagnostic alerts. Check for a possible air leak or if the cyclonic spray chamber is not properly installed into the torch cassette. Make sure the torch cassette locks are in the correct position. Open the interface region and inspect the torch, clean torch components if dirty or excessive carbon buildup is present. Check that all the connections to cyclonic chamber and nebulizer are tight and secure. In the Syngistix software drop down menu, examine the events history log for clues.
- 11.1.10 The fume exhaust system on this instrument also acts to remove excess heat. Be sure the system is working correctly, especially if the Plasma diagnostic window of System View indicates heat buildup. The instrument exhaust needs 650 LFM and the autosampler exhaust needs 50 LFM.
- 11.1.11 The water re-circulator (chiller) is an important accessory for the ICP. Check the operation of this unit, especially if the Cooling System diagnostic window in System View indicates a problem. Periodically check that the fluid level is in the normal operating range and that the pressure is around  $47 \pm 5$  psi at  $15 \pm 2^{\circ}\text{C}$ . The approximate interface temperature should be  $55^{\circ}\text{C}$  and the torch box temperature should be  $59^{\circ}\text{C}$ . Insufficient flow may display itself with the plasma lighting but immediately extinguishing.
- 11.1.12 With the plasma on, visually inspect that a constant nebulizer spray pattern produces a steady mist pattern in the spray chamber. A clean cyclonic chamber will not collect large droplets on the wall. Before tuning the instrument or analyzing any samples, the plasma needs to be "conditioned" for a minimum of 30-60 minutes to achieve thermal equilibrium.
- 11.2. Pre-Analysis Routine: Before an analysis can be performed, the instrument needs to be optimized for proper operation. Click on the SmartTune icon located on the top of the menu bar. Load the file SmartTune Daily \_DEP\_ EPA 200.8 file.
- 11.2.1 The manufacturer recommends starting with a Daily Performance Check to determine which optimizations are necessary before performing the final Daily Performance Check. The Daily Performance Check tests the instruments sensitivity, interference levels from



oxides and double charges, the detector's background noise, and the instruments precision. Optimizations to the following instrument systems are routinely performed: XY torch alignment, quadrupole mass calibration and resolution, nebulizer flow, QID voltages, KED QID voltages, detector voltages, and dual detector calibration. Daily performance checks exist for when the instrument is run in standard, KED and DRC mode. Only standard mode and KED mode will be discussed in this SOP. The standard mode Daily Performance Check method acquires 5 replicates of a 1-µg/L solution and RSD readings must be below 5%. The Daily Performance Check with AMS off is used to determine if the instrument is working properly. The Daily Performance Check with AMS on is used to monitor sensitivity trends. The pass/fail comment for the Performance Check with AMS on can be ignored.

11.2.2 XY Torch Alignment: Maximizes ion transmission to sensitivity based on the torches relative position to the interface and ion optics. Can be performed daily or at minimum when the torch is removed, cones are removed for cleaning, or when the interface door is opened.

11.2.3 Mass Calibration and Resolution: Optimizes quadrupole voltages to establish mass accuracy and peak resolution. EPA 200.8 requires a Mass Calibration and Resolution optimization for each analytical run.

Peak Accuracy  $\pm 0.05$  amu

Resolution:  $0.75 \pm 0.03$  amu at 5% height

11.2.4 Nebulizer Gas Flow Optimization: Recommended to achieve Ce/CeO levels below 2.5% while maximizing indium counts. This optimization will reduce polyatomic interferences and may help with double charges. Too high a flow cools the plasma, decreases ionization efficiency, and increases molecular ion formation. Too low a nebulizer flow will heat the plasma, reduce analyte signal, and increase double charged ions.

11.2.5 QID (Quadrupole Ion Deflector) Optimization: Separates ionized species from photons and neutrals, thereby lowering background noise. The QID function compensates for matrix suppression and space charge effects in the ion optics. Can be performed daily or when sensitivity targets are low or if the nebulizer flow rate is changed.

11.2.6 Detector Voltage Optimization: Optimizes voltages to both the pulse and analog stages in the detector. Detector voltages should be checked when degradation in the signal occurs that cannot be resolved with the typical adjustments above. Anytime detector voltages are adjusted, a dual detector calibration must be performed. The tuning solution is not required for this optimization.

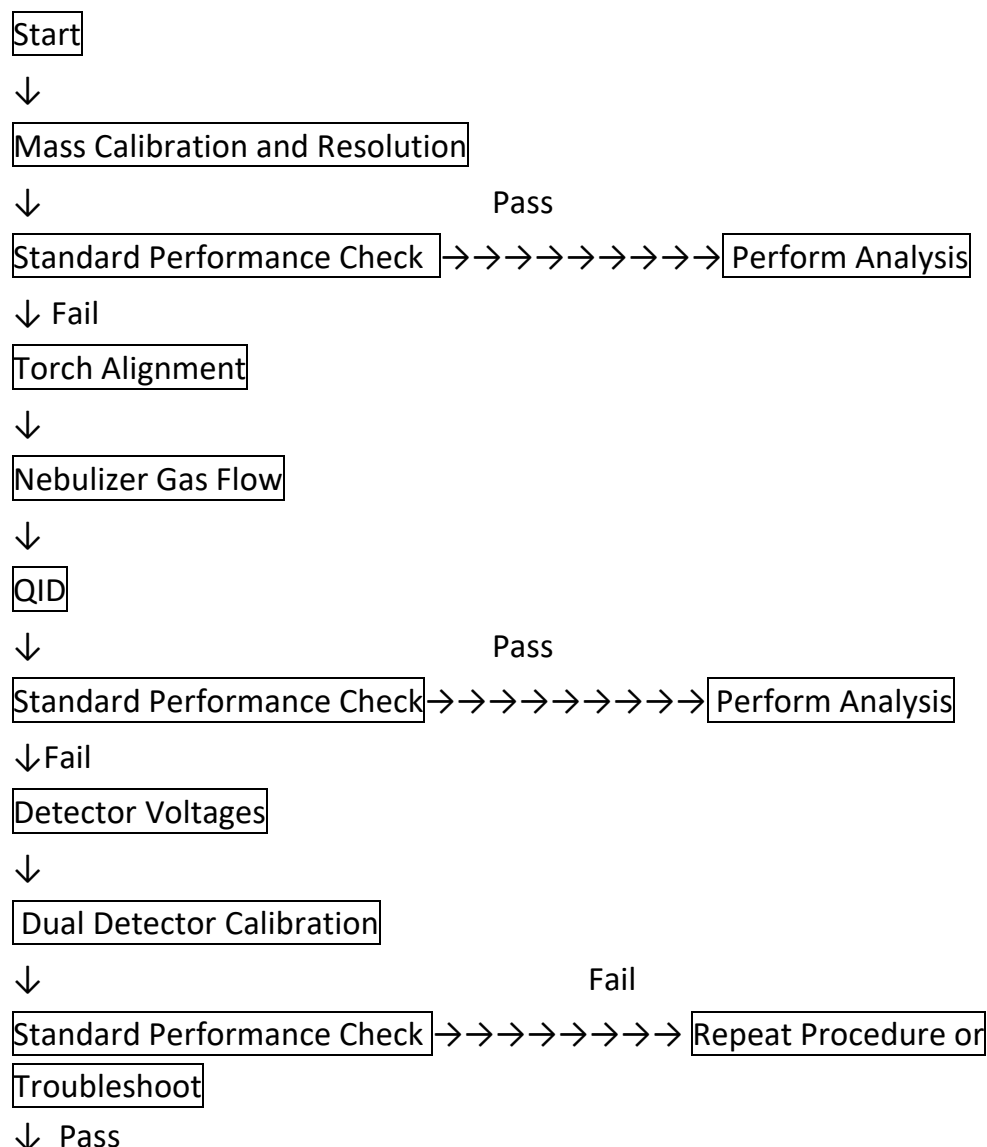
11.2.7 Dual Detector Calibration: Optimizes the linearity of the pulse to analog switchover in the detector. Dual detector calibrations are necessary for analytes whose counts are close to or greater than 2,000,000 cps or for analyses that require intensity measurements of matrix elements for interference corrections. The dual detector optimization uses a 200-µg/L standard solution and should contain as many of the analytical method analytes, the internal standard analytes, and the interference correction analytes as possible. Analytes not physically acquired during the calibration are interpolated using the nearest two acquired masses. The closer these two masses are, the better the interpolated accuracy. Typical calibration correlation coefficient values are 0.999. To print the results of the Dual Detector Calibration, enter the Reporter's Current Sample tab and print the report from the Syngistix software drop down menu using the Dual Detector report template. The



report can also be printed by reprocessing from the Dataset. This optimization is performed with a 200- $\mu$ g/L standard.

- 11.2.8 EPA 200.8 for drinking water does not allow use of the instrument's DRC (Dynamic Reaction Cell) and the DBT (Dynamic Bandpass Tuning) features. A typical suggested Daily SmartTune Optimizations order could start with a mass calibration & resolution, Daily Performance Check, torch alignment, nebulizer Gas Flow, QID, and Daily Performance Check. If the first Daily Performance Check passes, further optimizations are not required. For a Full SmartTune Optimization, a suggested order is mass calibration & resolution, torch alignment, Nebulizer Gas Flow, QID, Detector Voltages, Dual Detector Calibration, and the Daily Performance Check. As the number of elements to be analyzed increases, it is highly recommended to calibrate the dual detector daily.

### Typical SmartTune Optimization Order





## Perform Analysis

- 11.2.9 Load the SmartTune file C:\data\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz for optimizations. This file combines optimizations normally found in both the daily and full optimization. All optimizations and performance checks are configured for manual sampling. The user can manually pick and choose which optimizations are required based on the performance of the instrument. Place the carrier line and the internal standard line in the NexION Setup Solution. Aspirate the 1- $\mu$ g/L setup solution containing beryllium, cerium, cobalt, indium, iron, lithium, magnesium, lead, and uranium in 1% nitric acid. Allow enough time for both solutions to reach the detector and for flow rates to stabilize if the peristaltic pump speed is varied. If not enough time is allowed to equilibrate the system, RSD results will be high.
- 11.2.10 To perform only a single optimization, such as Mass Calibration and Resolution, highlight it under Optimization in the left pane of the SmartTune window, right click, and select quick optimization. The same quick optimization can be performed on any other optimization procedure or for the Daily Performance Check. The following SmartTune screenshots display setup parameters for each optimization.

### Optimization View

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\ICPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual

☒ Use Manual Sampling (no autosampler) ☐ Stop if Optimization Fails  
☐ Use Smart Sampling ☒ Send Results to Printer

**Optimization**

- ... Torch Alignment
- ... Mass Calibration and Resolution
- ... [STD] Performance Check
- ... [STD/KED] Nebulizer Gas Flow
- ... [STD/DRC] QID
- ... [KED] QID
- ... [STD] Performance Check
- ... Detector Voltages
- ... Dual Detector Calibration
- ... [Helium KED] Performance Check

**Autosampler**

Procedure	A/S Loc.
Torch Alignment	1
Mass Calibration and Resolution	1
[STD] Performance Check	1
[STD/KED] Nebulizer Gas Flow	1

**Peristaltic Pump**

	Time (sec)	Speed (+/- rpm)
Sample Flush	35	-18.0
Read Delay	15	-18.0
Analysis		-18.0
Wash	45	-18.0

**Files**

Conditions  
Default.dac

MassCal  
Default.tun

DataSet  
C:\Users\Public\Documents\PerkinElmer Syngistix\ICPMS\DataSet\Default





## Daily Performance Check

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\ICPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual

Edit List ...

Optimization

- Torch Alignment
- Mass Calibration and Resolution
- [STD] Performance Check
- [STD/KED] Nebulizer Gas Flow
- [STD/DRC] QID
- [KED] QID
- [STD] Performance Check
- Detector Voltages
- Dual Detector Calibration
- [Helium KED] Performance Check

Method

Method File

STD Performance Check.mth Browse...

Criteria

	Analyte	Comparator	Target	RSD <	RSD Target
1	<input checked="" type="checkbox"/> Be 9.0122	>	4500	<input type="checkbox"/>	0.00
2	<input checked="" type="checkbox"/> In 114.904	>	80000	<input type="checkbox"/>	0.00
3	<input checked="" type="checkbox"/> U 238.05	>	60000	<input type="checkbox"/>	0.00
4	<input type="checkbox"/> CeO 155.9	>	0	<input type="checkbox"/>	0.00
5	<input type="checkbox"/> Ce 139.905	>	0	<input type="checkbox"/>	0.00
6	<input type="checkbox"/> Ce++ 69.9527	>	0	<input type="checkbox"/>	
7	<input checked="" type="checkbox"/> Bkgd 220	<=	3	<input type="checkbox"/>	0.00
8	<input checked="" type="checkbox"/> CeO 155.9/Ce 139.905	<=	0.025	<input type="checkbox"/>	
9	<input checked="" type="checkbox"/> Ce++ 69.9527/Ce 139.905	<=	0.03	<input type="checkbox"/>	

☒ Stop SmartTune if the criteria are achieved

## Mass Calibration and Resolution

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\ICPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual

Edit List ...

Optimization

- Torch Alignment
- Mass Calibration and Resolution
- [STD] Performance Check
- [STD/KED] Nebulizer Gas Flow
- [STD/DRC] QID
- [KED] QID
- [STD] Performance Check
- Detector Voltages
- Dual Detector Calibration
- [Helium KED] Performance Check

Method

Method File

C:\Users\Public\Documents\PerkinElmer Syngistix\ICPMS\Method\Tuning20 Browse...

Criteria

	Target Accuracy (+/- amu)	Peak Height(%)	Target Resolution (amu)	Number of Iterations
Mass Calibration	0.05			
Resolution	0.03	5	0.75	6

☐ Peak Width Only



## Torch Alignment

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual ▾

Edit List ...

Optimization

- Torch Alignment
- Mass Calibration and Resolution
- [STD] Performance Check
- [STD/KED] Nebulizer Gas Flow
- [STD/DRC] QID
- [KED] QID
- [STD] Performance Check
- Detector Voltages
- Dual Detector Calibration
- [Helium KED] Performance Check

Method

Method File

Torch Alignment.mth Browse...

Criteria

	Analyte	Operator	Analyte	Comparator	Target
Intensity	In 114.904 ▾			Maximum	0.00

## Nebulizer

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual ▾

Edit List ...

Optimization

- Torch Alignment
- Mass Calibration and Resolution
- [STD] Performance Check
- (STD/KED) Nebulizer Gas Flow
- [STD/DRC] QID
- [KED] QID
- [STD] Performance Check
- Detector Voltages
- Dual Detector Calibration
- [Helium KED] Performance Check

Method

Method File

Optimize.mth Browse...

Criteria

		Analyte	Operator	Analyte	Comparator	Target
Intensity	<input checked="" type="checkbox"/>	In 114.904 ▾			Maximum ▾	0.00
Background	<input type="checkbox"/>				<= ▾	0
Formula	<input checked="" type="checkbox"/>	CeO 155.9 ▾	/ ▾	Ce 139.905 ▾	<= ▾	0.025

☐ Ramp ☒ Apply results to all modes

Range

Pass	Start	End	Step
Initial	0.940	1.060	0.020

Get Defaults

Add Retry...

Remove Retry



## QID

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual

Edit List ...

Optimization

- ... Torch Alignment
- ... Mass Calibration and Resolution
- ... [STD] Performance Check
- ... [STD/KED] Nebulizer Gas Flow
- ... [STD/DRC] QID
- [KED] QID**
- ... [STD] Performance Check
- ... Detector Voltages
- ... Dual Detector Calibration
- ... [Helium KED] Performance Check

Method

Method File

QID Calibration.mth Browse...

Range

Pass	Start	End	Step
Initial	-20.000	0.000	0.500

Get Defaults

## KED QID

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual

Edit List ...

Optimization

- ... Torch Alignment
- ... Mass Calibration and Resolution
- ... [STD] Performance Check
- ... [STD/KED] Nebulizer Gas Flow
- ... [STD/DRC] QID
- [KED] QID**
- ... [STD] Performance Check
- ... Detector Voltages
- ... Dual Detector Calibration
- ... [Helium KED] Performance Check

Method

Method File

QID Calibration.mth Browse...

Range

Pass	Start	End	Step
Initial	-20.000	0.000	0.500

Get Defaults





## KED Daily Performance Check

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual  
Edit List ...

Optimization

- Torch Alignment
- Mass Calibration and Resolution
- [STD] Performance Check
- [STD/KED] Nebulizer Gas Flow
- [STD/DRC] QID
- [KED] QID
- [STD] Performance Check
- Detector Voltages
- Dual Detector Calibration
- [Helium KED] Performance Check**

Method  
Method File  
KED Performance Check.mth Browse...

Criteria

		Analyte	Comparator	Target	RSD <	RSD Target
1	<input type="checkbox"/>	ClO-hi 50.9638	>	0	<input type="checkbox"/>	0.00
2	<input checked="" type="checkbox"/>	Co-hi 58.9332	>	25000	<input type="checkbox"/>	0.00
3	<input type="checkbox"/>	CeO-hi 155.9	>	0	<input type="checkbox"/>	0.00
4	<input type="checkbox"/>	Ce-hi 139.905	>	0	<input type="checkbox"/>	0.00
5	<input type="checkbox"/>	ClO-lo 50.97	>	0	<input type="checkbox"/>	0.00
6	<input type="checkbox"/>	Co-lo 58.94	>	0	<input type="checkbox"/>	0.00
7	<input checked="" type="checkbox"/>	Ar2-hi 77.9173	<=	30	<input type="checkbox"/>	0.00
8	<input checked="" type="checkbox"/>	Kr-hi 82.9141	<=	300	<input type="checkbox"/>	0.00
9	<input checked="" type="checkbox"/>	ClO-hi 50.9638/Co-hi 58.933	<=	0.005	<input type="checkbox"/>	
10	<input checked="" type="checkbox"/>	CeO-hi 155.9/Ce-hi 139.905	<=	0.01	<input type="checkbox"/>	

☒ Stop SmartTune if the criteria are achieved

## Detector Voltages

SmartTune Wizard - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\Wizard\SmartTune\SmartTune Daily\_DEP\_200.8.swz

Optimize SmartTune Manual  
Edit List ...

Optimization

- Torch Alignment
- Mass Calibration and Resolution
- [STD] Performance Check
- [STD/KED] Nebulizer Gas Flow
- [STD/DRC] QID
- [KED] QID
- [STD] Performance Check
- Detector Voltages**
- Dual Detector Calibration
- [Helium KED] Performance Check

Method  
Pulse Method File  
Pulse Stage Optimization.mth Browse...

Analog Method File  
Analog Stage Optimization.mth Browse...

Criteria

	Analyte	Method	Value
Pulse	Pulse 76	Intensity Change (%)	10
Analog	Analog 80	Gain	10000

Advanced

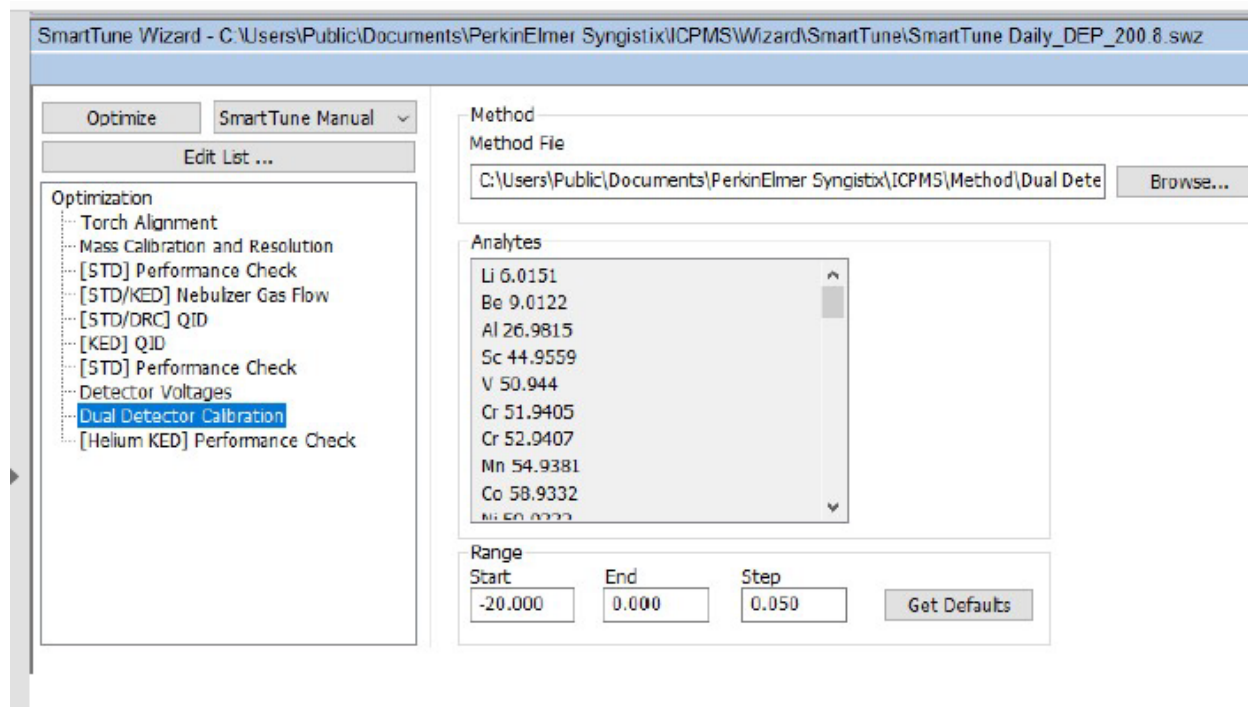
Range

	Pulse			Analog	
	Start	End	Step	Start	End
Initial	600	1300	50	-1600	-1900
Retry 1	600	1800	50	-1600	-2400

Get Defaults  
Add Retry  
Remove Retry



## Dual Detector Calibration



11.2.11 When all the desired quick optimizations are complete, perform the final Daily Performance Check and confirm the results are acceptable. See Table 2 for Standard Mode operation and Table 3 for KED mode acceptance criteria. If using AMS aerosol dilution, navigate to Conditions window in the top menu bar and select the Manual Adjust tab. AMS works by adding an argon diluting gas to the cyclonic chamber. The AMS flow must be subtracted from the nebulizer flow, so the sum of AMS flow plus nebulizer flow equals the original nebulizer flow used in the Daily Performance Check with AMS off. To dilute all samples and standards by approximately 2x, adjust the AMS Gas Flow to achieve Indium counts that are approximately half the counts achieved with AMS off. **Significant advances in instrument sensitivity allow the use of AMS to safely extend the method's LCR to 200 µg/L. With AMS, a 200-µg/L sample is effectively reduced to approximately 100 µg/L. In doing so, we reduce the chance of creating insoluble precipitates (i.e., AgCl) inside the instrument that could lead to permanent contamination and elevated reporting limits.** For experiments using KED mode, optimize the instrument using standard KED mode first. Then in the Conditions window, switch to helium KED mode. Run the KED Daily Performance Check using a 10-µg/L cobalt solution in 1% HCl.

11.2.12 Timing is a tab in the method, along with equations, calibration, QC, reports, etc. The method's Timing Tab must use the same tuning and Conditions file that SmartTune used during optimizations.



## Method - Timing View

Quantitative Analysis Method - C:\Users\Public\Documents\PerkinElmer Syngistix\ICPMS\Method\WES Methods\EPA200.8 26ElementStd.

Timing | Processing | Equation | Calibration | Sampling | Devices... | QC... | Report | Notes

Sweeps / Reading: 20      Est. Reading Time: 0:00:32.664      MassCal File: default.tun      Browse...

Readings / Replicate: 1      Est. Replicate Time: 0:00:32.664      Conditions File: c:\users\public\documents\perkinel...      Browse...

Replicates: 3      Est. Sample Time: 0:01:37.992      ☒ Enable QC Checking

	Int Std	Analyte	Mass (amu)	Scan Mode (*)	MCA Channels	Dwell Time per AMU (ms)	Integration Time (ms)	Corrections	Profile (*)	
1		Li	6.0151	Peak Hopping	1	25	500		Standard	0
2		Be	9.0122	Peak Hopping	1	25	500		Standard	0
3		Al	26.9815	Peak Hopping	1	25	500		Standard	0
4		Ti	47.948	Peak Hopping	1	25	500	Ca	Standard	0
5		Sc	44.9559	Peak Hopping	1	25	500		Standard	0
6		V	50.944	Peak Hopping	1	25	500	ClO, Cr	Standard	0
7		Cr	51.9405	Peak Hopping	1	25	500		Standard	0
8		Mn	54.9380	Peak Hopping	1	25	500		Standard	0

11.2.13 Save any optimization and tuning files before leaving the SmartTune workspace. Click on the "Conditions" icon in the toolbar and then selecting the file and save. To save the Mass Calibration and Resolution file, click on the arrow below the Conditions Icon and select file/save. Save any changes to the SmartTune file.

11.2.14 Date and initial the first page of every optimization and include all printouts in the WinLIMS WL batch folder. The final report or paper packet to be presented for verification and approval should also include initialed and date copies of the run list (add the LIMS sample ID to the QC elements), a Summary Report for every sample in the run list (QC elements need their WinLIMS sample ID documented), a calibration report, standard and reagent preparation sheets, a sample dilution preparation sheet, the Reporter's QC Internal Standard numerical results that charts every sample's internal standard recovery, and the WorkList's page count documented on the first page of the report.

11.2.15 After tuning and optimizing instrument parameters, clean the internal standard and carrier line probes before placement in their respective solutions to prevent contamination. Rinse the probes first in a container of reagent water and then rinse in 2% nitric acid. Likewise, clean the probes after performing the dual detector calibration.

## 11.3. Using the Workspace to Analyze Samples

11.3.1 Open the workspace that contains the method of interest, e.g., SDWA EPA 200.8, CWA EPA 200.8, etc., or use the Syngistix ribbon menu to manually load the analytical method and associated files. The method file path is C:\Users\Public\Documents\PerkinElmer Syngistix\ICPMS\Method\WES Methods\EPA200.8 26Element. A workspace always displays the files present the last time the workspace was saved. A new sample



information file and dataset file need to be created with each run and saved to the workspace. Otherwise, manually load the method, sample, and data file individually. It is best to open the sample Workspace immediately before running samples. Depending on what operations the user performs **after** opening/saving the sample analysis workspace, the default files that were initially loaded may not still be active. For example, if any type of optimization is performed in the SmartTune Window after opening the sample Workspace, the active Dataset file will change to Default. Before running the instrument, manually make sure the correct method, sample information file, dataset file, and the correct default Conditions are loaded.

- 11.3.2 Create a new Sample file and Dataset file for running the sample Workspace for a given day. The lab's naming convention for sample and dataset file is the year followed by the month and day (20200727 for 07/27/2020). Methods are stored in the WES Methods folder; Sample files and Dataset files are stored according to the year. Save the new Workspace by clicking on the Syngistix ball and selecting Workspace, save workspace. By selecting the Review icon in the Syngistix ribbon, a window will open to display all files currently in use for a given workspace. These files can also be retrieved by making active the icon of interest, e.g., Dataset, Sample, or Method file. If any are incorrect, click on the Syngistix software menu and open the file you wish to use; resave the workspace.
- 11.3.3 Make active the Method window and check that it is the method you wish to use for the runlist. If not, click the Syngistix software menu and open the appropriate method. Check the method to be sure the information contained in it is correct and has not changed from reprocessing. In the timing tab, check that the method includes three replicates per analysis, with 10 sweeps/reading, and 1 reading/replicate. In the Processing tab, QID should be activated, and the detector should be operating in Dual mode. 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, it may be advantageous to create a new method. Using only the desired standards may also help reduce the possibility of instrument contamination.
- 11.3.4 Make active the Sample window and the batch tab. Fill in the information required to populate the instrument's run list, including the autosampler position, sample description, method, measurement action, and sample type. Place a few rinse samples before creating the calibration table. Make sure the first true sample's (excluding rinses) Measurement Action is Run Blank, Standards, and Sample or no calibration will be performed. Subsequent samples will be analyzed using the existing calibration and need only have Run Sample for the Measurement Action. Save the new sample file.
- 11.3.5 Click on the Batch Index box or highlight the samples to be analyzed in the Sample window and then select Build Run List. A list of the analysis order (Batch) will appear. Select Printable View and then right click the mouse to print a hard copy of the run list. Load the autosampler according to the run list. Date and initial this list and keep with the paper copy of the analysis run if a paper copy is kept. If a run list is appended during a run or if priority sample(s) is added that changes the run list, reprint, date, and initial the final run list as well.

#### 11.4 Automated Sample Analysis

- 11.4.1 Automated analysis may be started by clicking Analyze Batch on the Run List window. A Batch box will appear which indicates the sample currently being analyzed as well as the analysis progress of each replicate.





- 11.4.2 Priority Sample(s): To insert a priority sample, click the Priority box and fill in the sample's information. Note that the term priority does not necessarily mean the next sample about to be run. It may take two or three samples before the Priority sample is run.
- 11.4.3 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. Note: When samples are appended to the end of the table, bracketing QC is not automatically added. The operator must include the final CCV/CCB as appended samples if what is being added exceeds 10 samples. If a run list finishes before samples can be appended, create a new run list to extend the run. Begin with a CCV/CCB, followed by the samples, and ending with a closing CCV/CCB to bracket the samples.
- 11.4.4 Pause: The run table can be paused for numerous reasons to assist the analyst. For example, it can be used to add priority samples, append the table, to give the operator time to make dilutions or remake check standards, if necessary.
- 11.4.5 When the batch is done running, do not close the Syngistix software until the calibration file is saved and the calibration report is printed out using the Quant Calibration report template. Activate the Calibration View window in the Syngistix ribbon and then save in the Syngistix software drop down menu. In the same menu, select print and choose the calibration report template to print the summary report of all the correlation coefficients. Make sure to also print out a hard copy of all the sample files in the batch using the quant summary+qc\_lawrence template since all the original conditions are active and loaded.
- 11.4.6 Analytical Sequence: Below is an example of a tray protocol for EPA 200.8 analysis. Rinses before the calibration or after a potentially concentrated sample should be referred to as a 1% Nitric Acid Rinse. This implies method blank acceptance criteria do not apply.

Sequence Sample ID

1. 1% Nitric Acid Rinse
2. 1% Nitric Acid Rinse
3. Subtraction Blank
4. Calibration Blank
5. Calibration Standard Solutions
6. LRB - Performance Check Standard
7. Quality Control Sample(s) [QCS  $\pm$  10% of True Value (TV)] - Performance Check Standard(s)
8. Minimum Reporting Level (MRL) Standard(s) - Performance Check Standards(s)
9. IPC(s) or ICV(s) ( $\pm$  10% of TV) - Performance Check Standard(s)
10. Initial Calibration Blank (ICB) - Performance Check Standard
11.  $\leq$  10 Samples which may include LFB(s) ( $\pm$  15% of TV), Matrix QCS(s) (QCS SRM), Sample Duplicate(s), LFM(s), Performance Check QCS(s) as necessary
12. Continuing Calibration Check(s) ( $\pm$  15% of TV) - Performance Check Standard(s)
13. CCB
14.  $\leq$  10 Samples which may include LRB(s), LFB(s) ( $\pm$  15% of TV), Matrix QCS(s) (QCS SRM), Sample Duplicate(s), LFM(s), Performance Check QCS(s) as necessary
15. CCC(s) ( $\pm$  15% of TV)
16. CCB
17. Repeat 13-15 as necessary



- 11.4.7 Viewing Data Files In Real Time: After the instrument begins analyzing a batch, the operator can view real-time results in the Reporter window for each acquired mass. The Reporter has tabs to view the results in different formats: raw intensities (with and without RSDs), a concentration view, a graphic representation of internal standards plotted over time, and a Quality Control View.

Clicking on a particular mass' calibration curve in the concentration tab opens a more detailed view for that analyte's calibration. Details include a larger calibration graph, the final concentration for each calibration standard of that analyte, the Background Equivalent Concentration (BEC), the correlation coefficient, and the curve's best fit linear regression equation. This detailed view is particularly helpful to view the final concentration value for each calibrator since the main Reporter screen only gives calibrator results *before* the curve is completely created along with pass/fail calibration results based on the correlation coefficient. Note: If the detail view is printed, certain unique identifiers are not included, such as Batch ID, run date, print date, etc. These must be added by the analyst.

- 11.5. Retrieving Data Files and Reprocessing: In the Syngistix software, the contents of the original data files can only be retrieved (printed) and viewed by Re-processing the data files with the original conditions.

- 11.5.1 To retrieve the correct results for a dataset, one must use the original default Condition from that day. If reprocessing does not require any modifications to the method, calibration, or sample ID; reprocess by checking the box Use Original Conditions. This will automatically reprocess the results as they originally appeared in the Reporter and the software rebuilds the calibration curve from the dataset. The calibrators will not have the true read back results in this round of reprocessing if the report is printed out. To print out the calibrators with the correct read back values, save the calibration curve as the default calibration. Highlight all the data files again, uncheck original conditions, and reprocess a second time now that the curve has been regenerated. Alternatively, if the calibration file for the batch was originally saved, the second round of reprocessing can be omitted. Just load the calibration file before reprocessing and reprocess using Original Conditions.

- 11.5.2 Re-Processing Data: If there are minor changes to be made to the method, calibration, or sample ID, it is possible to reprocess data to correct these issues. Some examples could include correcting the following issues: an improperly prepared calibrator needs to be removed from the calibration curve; calibration levels were incorrectly assigned; method QC nomenclature may need correcting; a different internal standard may need to be used; or QC limits, method integration parameters, etc., need to be corrected. Reprocessing is not a substitute for correcting problems with digestions, contamination, incorrect use of the instrument, or other major issues. Reprocessing does not alter the acquired data, just the results. Reprocessing must only use original conditions and not conditions from a different day or even a different dual detector.

- 11.5.3 When reprocessing involves correcting some of the issues mentioned above, first make corrections in the appropriate file and save where appropriate. When reprocessing a dataset after subsequent runs have been performed, the following must be done. Highlight one of the data files in the dataset batch (see example Dataset below) and click on the arrow to open the drop-down menu next to the load button. Select Conditions and then click on Load. This will overwrite all the current Default Conditions in the Conditions window to how they existed when the batch was acquired, including the Mass Calibration and Resolution file, parameters in the Condition's Manual Adjust tab, and the Dual Detector Calibration file (see example Conditions below). Save the new Conditions file.



## Dataset View

Dataset - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\DataSet\2020 DataSet\20200505 Uranium PT\				
<div>Reprocess Summary Report... Conditions Load</div> <div><input type="checkbox"/> Use Original Conditions <input type="checkbox"/> Save Reprocessed Data</div>				
	Batch ID	Sample ID	Acquisition Date/Time	Method
1	2020 Uranium PT	Blank	5/5/2020 2:00:08 PM	C:\Users\Public\Documents\PerkinElmer
2	2020 Uranium PT	Blank	5/5/2020 2:02:27 PM	C:\Users\Public\Documents\PerkinElmer
3		Calibration Blank	5/5/2020 2:04:47 PM	C:\Users\Public\Documents\PerkinElmer
4		Level 1- 10 ppb	5/5/2020 2:07:05 PM	C:\Users\Public\Documents\PerkinElmer
5		Level 2- 20 ppb	5/5/2020 2:09:24 PM	C:\Users\Public\Documents\PerkinElmer
6		Level 3- 50 ppb	5/5/2020 2:11:43 PM	C:\Users\Public\Documents\PerkinElmer
7		Level 4- 100 ppb	5/5/2020 2:14:02 PM	C:\Users\Public\Documents\PerkinElmer

## Conditions - Manual Adjustment View

Conditions - C:\Users\Public\Documents\PerkinElmer Syngistix\CPMS\Conditions\Default.dac

QIDDual DetectorManual AdjustAdvanced OptimizeCell Parameters

Profile

Standard

View DAC Values

☐ Active

☒ All

DAC

0.93

Nebulizer Gas Flow [NEB]

	Standard	Helium KED	Description	Stop Value	Setting Time (sec.)	Minimum Value	Maximum Value
1	0.93	0.93	Nebulizer Gas Flow [NEB]	0.02	10	0	1.5
2	0.1	0.1	AMS Gas Flow	0.005	10	0	0.9
3	1.1	1.1	Auxiliary Gas Flow	0.025	10	0.6	2
4	15	15	Plasma Gas Flow	0.5	10	10	20
5	1600	1600	ICP RF Power	50	15	400	1600
6	-1750	-1750	Analog Stage Voltage	-100	2	-3000	0
7	1000	1000	Pulse Stage Voltage	50	2	0	2500
8	12	12	Discriminator Threshold	5	0	0	1000
9	-12	-12	Deflector Voltage	0.25	0	-100	20
10	0	-10.5	Quadrupole Rod Offset [QRO]	0.5	1	-26	26
11	-1	-10	Cell Entrance Voltage	1	1	-60	20
12	-1	-31	Cell Exit Voltage	1	1	-60	20
13	-6	-12	Cell Rod Offset [CRO]	1	1	-40	10
14		500	Axial Field Voltage [AFT]				
15		0	RPa				
16		0.25	RPq				

Hover over the CalibView icon in the top ribbon and click on the down arrow. Select **Clear Calibration and Blank** to remove any existing calibration. Reprocess twice without checking the box "Use Original Conditions". Reprocessing the first time builds the curve. Save the calibration as the default calibration. Reprocessing the second time will generate concentrations for the calibrators. Before reprocessing the second time, return



to the Method's Report tab and check the box to send the report template (Quant Summary + QC\_Lawrence) to the printer.

11.5.4 After reprocessing an old dataset is complete, the user can reload and save the most recent default Conditions by retrieving the conditions from the most recent dataset. Similarly, if a method becomes corrupted, it can be restored by retrieving the method from the last successful dataset. Users can quickly reconstruct methods, conditions, MassCal, calibration curves, report options, instrument configuration, diagnostic parameter, and more.

11.6 Sample Preparation: Typical sample preparation methods are listed below (see separate SOPs).

SDWA Metals	Method 200.2
Rivers/Ponds Total	Method 3015
Total Recoverable	Method 3005
Total Suspended (0.45- $\mu$ m Filter)	Method 3005
Dissolved (0.45- $\mu$ m Filter)	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 end user's data quality objectives and satisfy the appropriate regulatory requirements.

11.7 Replacement of Consumable Parts: When at all possible, it is a good practice to condition parts by running the instrument with 2% nitric acid and by injecting consecutive mid-level standards prior to using the instrument for an actual analysis.

11.8 Data Backup and Storage: In the event the dedicated computer for the NexION 1000 malfunctions, data files are manually backed up on the network drive at WES SharePoint: /DELS/InorganicChemistryLab/DataBackup/ICP-MS/Users/Public/Documents/PerkinElmerSyngistix/ICPMS/DataSet.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Sample data are reported in units of  $\mu$ g/L for aqueous samples and  $\mu$ g/kg wet or dry weight, as appropriate, for solid samples.

12.2 Concentrations below the MRL are reported as < MRL in WinLIMS, with the MRL concentration stated. Enter raw results and dilution factors into WinLIMS. WinLIMS reports final results and dilution adjusted MRLs to the appropriate number of significant figures.





- 12.3 For total recoverable analytes in solid samples, the sample concentration in  $\mu\text{g}/\text{kg}$  wet weight is calculated as follows:

$$\text{Sample Conc. (}\mu\text{g / kg)} = \frac{C \times V \times D}{W}$$

Where:

- C = Concentration in extract ( $\mu\text{g}/\text{L}$ )  
V = Volume of extract (L)  
D = Dilution factor (undiluted = 1)  
W = Wet weight of sample aliquot extracted (kg)

For solid samples, if needed, the result in  $\mu\text{g}/\text{kg}$  dry weight can be obtained by dividing the wet weight result above by the percent solid expressed as a decimal.

- 12.4 If the MRL or method blank(s) fail for an analyte, raise the MRL to the next highest level if the end users' data quality objectives are still met.

- 12.5 Documentation to be included in data packet for QA Level 1 and Level 2 reviews:

- 12.5.1 Digestion Sheet
- 12.5.2 pH Checks documented on Login Preservation Sheet
- 12.5.3 Post-Acid Turbidity Checks using Turbidity Bench Sheet
- 12.5.4 Mass Calibration and Resolution Optimization
- 12.5.5 Optimizations: Torch Alignment/Nebulizer/QID/Dual Detector/etc.
- 12.5.6 Daily Performance Check
- 12.5.7 Standard/Reagent/Internal Standard/Dual Detector Preparation Sheets
- 12.5.8 Summary Calibration Report
- 12.5.9 Sample Dilution Sheet
- 12.5.10 Sequence Table(s): Intended run list and if different, the actual run list

## 13.0 METHOD PERFORMANCE

MDLs for total recoverable metals determined for the masses used in this method are on file. The MDLs were determined in spiked 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 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 approach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste drum (organic or inorganic, as appropriate). 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 using these chemicals.

## 16.0 REFERENCES

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  13. Perkin Elmer Training Manual, NexION Operation with Syngistix Software, N0220193, Rev. G.
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## 17.0 TABLES

**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 a significant change in the analytical system. Values may be taken from up to two years of analyses.	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	30- to 60-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. RSDs should be less than 5%.	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. Suspect a sample introduction issue if RSDs are high.
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
Continuing Calibration Blank (CCB)	Immediately following each IPC, after every CCV, and at the end of the run	< 2.2 times the analyte MDL (3/4 the MRL) or < 10% of the analyte level measured in the sample	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 (3/4 the MRL) 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) $\leq$ 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.



**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
Laboratory-Fortified Matrix (LFM)	Every 10 samples or less	70-130% Recovery Note: Recovery calculation is not required if the concentration added is less than 30% of the unfortified sample concentration	If laboratory 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% Recovery	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	$\pm 20\%$ of true value for SDWA analyses. Acceptance Criteria according to end users' specifications for other analyses.	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. NexION 1000 Daily Performance Check Acceptance Criteria**

QC Element	Acceptance Criteria (1-µg/L Solution)		
Sensitivity	Analyte	Mass	Measured Intensity cps/10-µg/L Standard
	Be	9.0	> 4,500
	In	114.9	> 80,000
	U	238.1	> 60,000
	Co	58.9	NA
	Pb	208.0	NA
	Mg	24	NA
Background	220 < 3 cps (Check vacuum or skimmer cone installation if elevated)		
Doubly Charged	Ce <sup>++</sup> /Ce < 3%		
Oxides	CeO/Ce < 2.5%		
Mass Calibration	± 0.05 amu from stated mass of analyte		
Resolution	0.75 amu ± 0.03 amu at 5% peak height		
Instrument Stability	RSD < 3% for five replicates of Be, Mg, Co, In, Pb, and U EPA 200.8 requires RSD < 5%		



**TABLE 3. NexION 1000 KED Daily Performance Check Acceptance Criteria**

QC Element	Acceptance Criteria
Co-hi 59	> 25,000 cps
Ar2-hi 78	$\leq 30$ cps
Kr-hi 83	$\leq 300$ cps
CIO-hi 51/Co-hi 59	$\leq 0.005$
CeO-hi 156/Ce-hi 140	$\leq 0.01$
CIO-lo 51/Co-lo 59	$\leq 0.02$



**TABLE 4. Elemental Equations for Data Corrections**

Element	Mass	Elemental Equation
V	50.944	$-3.127 * (\text{ClO } 53 - (0.113 * \text{Cr } 52))$
As	74.9216	$-3.127 * (\text{ArCl } 77 - (0.815 * \text{Se } 82))$
Se	81.9167	$-1.007833 * \text{Kr } 83$
Mo	97.9055	$-0.109613 * \text{Ru } 101$
Cd	110.904	$-1.073 * (\text{MoO } 108 - (0.712 * \text{Pd } 106))$
In	114.904	$-0.014038 * \text{Sn } 118$
Sb	122.904	$-0.125884 * \text{Te } 125$
Pb	207.977	$+1 * \text{Pb } 206 + 1 * \text{Pb } 207$
Fe	53.9396	$-0.028226 * \text{Cr } 52$
Se	77.9173	$-0.030461 * \text{Kr } 83$
Cd	105.907	$-1.223914 * \text{Pd } 105$
Cd	107.904	$-1.184953 * \text{Pd } 105$
Cd	113.904	$-0.027250 * \text{Sn } 118$
Kr	82.9141	$-0.006781 * \text{Sr } 88$
Ru	98.9061	$-0.045678 * \text{Pd } 105$
Pd	104.905	$-0.097656 * \text{Cd } 111$
W	183.951	$-0.001238 * \text{Os } 189$