

# STANDARD OPERATING PROCEDURE

For

USEPA METHOD 200.7, Rev. 4.4

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

SOP #: EPA 200.7

SOP REVISION #: 7.0

DATE: December 2022

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# MassDEP

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## LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	March 1999	None	
1.0	October 2000	New ICP software Iron accuracy, precision, and MDL data updated (9/15/2000 data)	11 30-33
1.1	November 2000	Accuracy, precision, and MDL data updated (Tables 6,7, & 8)	30-33
1.2	December 2001	Table 2 – Table 8 renumbered to Table 3 – Table 9 New Table 2	26 – 33 26
2.0	March 2003	Addition of new matrix – fish biota  Table 6 deleted, Table 7-9 renumbered to Table 6-8 Table 8 values updated Table 9 added Table 10 added	Throughout document 31 – 33 33 34 34
2.1	January 2004	Section 1.1 – Identified the elements that are analyzed by this method in drinking water samples	5
2.2	April 2004	Section 6.2 – ICP general maintenance procedures added Section 7.7 – Standards preparation revised Section 7.8.4 – Added MRL (RDL) check standard prep Section 9.3.2 – LFB preparation and calculation Section 9.4.3 – MRL check std and LFM preparation Section 10.2 – Instrument calibration procedure updated Section 11.0 – Instrument daily and monthly maintenance added Section 11.5.8 – Analytical sequence added Table 2 – QC elements and acceptance criteria updated Table 8 – Updated MDL data (3/16/2004)	11 12 13 15 17 18 18-19  20 28-29
3.0	December 2006	Replaced old DEP Logo with state seal + MassDEP  Numerous minor revisions throughout New ICP instrument and operating software (Section 6.1) New instrument and software operating procedures (Section 11.0) 2006 MDL data (Table 8) 2006 SDWA interelement correction factors (Table 11)	Title page & header  11 19 38 40



Rev. #	Date	Description of Revision	Page #
3.1	January 2008	Section 7.7.1 – Standards preparation revised.	14
		Section 7.13 – Revised plasma solutions to include 10 mg/L Mn for axial and radial optimization.	16
		Section 8.1 – Included pH log sheet as part of sample collection, preservation, and storage.	16
		Section 9.2.4 – MDL preparation and calculations.	17
		Section 11.1.3 – Took out WinLab offline; step may cause data management problems.	21
		Section 11.4.7 – Added time needed for machine to stabilize before starting calibration sequence.	23
		Section 11.5.1– Added axial and radial alignment instructions	23
		New Section 11.5.2 – Added mercury alignment instructions	23
		Old Sections 11.5.2 and 11.5.3 – Renumbered to 11.5.3 and 11.5.4, respectively	23
		Section 11.6.7 – Changed analytical sequence	23
3.2	March 2010	Table 2 – Updated	32
		Section 6.9.3 – Changed from Conical Phillips beakers to Environmental Express.	12
		Section 7.7.1.7 – Change in standard preparation	13
		Section 11.5.2 – Mercury alignment deleted	22
		Renumbered sections 11.5.3 and 11.5.4 to 11.5.2 and 11.5.3	22
		Table 5 – Updated MDL data	35



Rev. #	Date	Description of Revision	Page #
4.0	September 2010	Added definitions of IEC, MRL, MRL check standard, and QCS-SRM in Sections 3.7, 3.14, 3.15, and 3.17, respectively	9 & 10
		Deleted definition of solid sample in Section 3.19 – Method no longer used in our laboratory to test solid samples	10
		Section 6.9 – Revised lab-ware cleaning procedure	13
		Section 7.1 & Forms Section – Added links to Standard-Reagent Preparation Bench Sheets	14 & 38
		Section 9.2.4 – Added procedure for use of QCS-SRM	17
		Section 9.2.5 – Updated MDL procedure	17
		Section 11.1.1.3 – Removed old air compressor from service; now using new building-wide compressed air system	21
		Section 11.4.3 – Updated location and temperature set point of water re-circulator	22
		Section 13.0 – Deleted reference to MDLs for fish/biological tissue; method no longer used to test fish/biological tissue	29
		Section 16.0 – Added Reference # 5	30
		Table 2 – Updated	32
		Deleted Tables 3 (IDLs), 6 (old accuracy data), 7 (old precision data), 9 (MDL 2.0 g fish/biological tissue), and 10 (MDL 5.0 g fish/biological tissue) – renumbered remaining tables	34-38
4.1	April 2011	Table 2 – Internal Standard acceptance criteria – added number range for Y	32
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		Table 5 – Updated MDL data	36
		Table 6 – Updated ICF data	37
		Section 11.1 – New gas delivery system in new laboratory wing	21
		Section 11.3 – New exhaust system in new laboratory wing	22
4.2	December 2012	Section 7.7 – Specify Bench Form for recording Calibration Std information/preparation Section 10.2 – Specify Bench Form for recording Calibration Std information/preparation Section 11.4.6 – Specify Form for recording QC Std information/preparation Section 11.5.2 – Describe data backup procedure Section 17.0 – Added references 6 - 9 Section 18.0 – Table 5 – Updated MDL Table and added MDLs for Boron and Lead Section 18.0 – Table 6 – Updated Interelement Correction Table	



Rev. #	Date	Description of Revision	Page #
5.0	February 2016	<p>Changed division name from Division of Environmental Analysis (DEA) to Division of Environmental Laboratory Sciences (DELS), and made other minor changes to update document</p> <p>Section 11.4.3 – Temperature changed from 18 to 17°C and pressure reading added 56 to 57 psi</p> <p>Section 2.1 – Removed microwave digestion and added digestion/extraction</p> <p>Section 6.4 – Added quartz inserts</p> <p>Section 6.9 – Removed twice for rinsing with reagent water in between cleaning cycles. Added quartz inserts.</p> <p>Section 6.9.4 – Added quartz inserts</p> <p>Sections 6.10 to 6.13 – Updated Dewars and change panel for Argon and Nitrogen.</p> <p>Sections 7.2.1, 7.2.2, 7.3.1, &amp; 7.3.2 – Removed these sections.</p> <p>Section 7.7.1 – Added to see Forms 1 to 5 Sections 7.7.1.1 to 7.7.1.10 – Removed</p> <p>Section 7.10 – Added to see Form 1</p> <p>Section 7.14 – Added to see Form 2</p> <p>Section 8.2 – Nitric acid added to dissolved sample preparation and described how to have the ICP calculate the dilution factor.</p> <p>Section 9.4.2 – Clarified equation.</p> <p>Section 9.5.1 – Removed Method of Standard Additions</p> <p>Section 11.4.3 – Temperature 17°C, pressure 56-57 psi</p> <p>Section 11.6.7 – Sequence removed 22 QCS</p> <p>Section 18.0 – Table 2 – Removed QCS at end of run</p> <p>Section 18.0 – Table 4 – Added 80-mg/L, 50-mg/L, 40-mg/L, and 20-mg/L solutions.</p> <p>Form 4 – Added Combined</p> <p>Form 5 – Added Form – Single SIC (IEC) Standards Preparation for EPA 200.7 and EPA 6010C</p>	Throughout document
5.1	September 2017	Section 10.3.2 – Added number of replicates per reading	



Rev. #	Date	Description of Revision	Page #
6.0	January – February 2019	Section 3.5 – Removed IDL from definitions. Section 4.1.5. – IEC additions. Section 6.0 – Updated equipment – new ICP and prep <b>FAST</b> autosampler. Section 11 – Updated procedures for new ICP and new software. Removed procedures for old ICP and its software. Section 11.11 – Clarified sample preparation procedure. Section 16.0 – Added references for Hardware and Software Guides for the Optima and prep <b>FAST</b> found on the LENOVO computer, and user guides in pamphlet form located in the laboratory. Section 18.0 – Removed 3 Tables, including Table of MDLs; List of Tables updated.	
7.0	December 2022	Section 1.1 – Added Cerium (Ce), Lithium (Li), Phosphorus (P), and Silica (SiO <sub>2</sub> ) as target analytes. Sections 3.19 and 3.20 – Added definitions for Solid Sample and Spectral Interference Check (SIC) Solution. Section 4.0 – Updated. Section 6.0 – Updated equipment and supplies. Section 6.2 – General equipment maintenance moved to Section 11.10. Section 7.0 – Updated reagents and standards; added Spectral Interference Check Solutions and Interelement Corrections. Section 8.0 – Updated. Sections 9.0, 10.0 & 11.0 – Extensive revisions; expanded procedures. Section 11.0 – Added Figures 1 through 11 to show key software screens. Section 12.0 – Updated. Section 14.0 – Added new section on major instrument maintenance. Section 17.0 – Updated references. Section 18.0 – Deleted Table 1 and renumbered Table 2 to Table 1 and updated table. Added new Tables 2A, 2B, and 3.	



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## 1.0 SCOPE AND APPLICATION

- 1.1 Dual View inductively coupled plasma-atomic emission spectrometry (ICP-AES) or optical emission spectrometry (ICP-OES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, fish/biological tissue, and solid wastes. This method is applicable to the following analytes:

<b>Chemical Abstract Services Registry Numbers (CASRN)</b>		
<b>Analyte</b>		
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium*	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Cerium	(Ce)	7440-45-1
Chromium*	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper*	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-2
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel*	(Ni)	7440-02-0
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica	(SiO <sub>2</sub> )	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

\* In our laboratory, this method is used to test drinking water samples only for the elements designated with an asterisk in the above table (i.e., barium, chromium, copper, and nickel). 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-AES 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) (Section 4.2).
- 1.4 With the exception of silver, all metals determined with this method are analyzed directly by pneumatic nebulization without acid digestion only if the sample has been properly preserved with acid and has a turbidity of < 1 NTU at the time of analysis; this total recoverable determination procedure is referred to as "direct analysis."
- 1.5 For the determination of total recoverable analytes in aqueous and solid samples, a digestion/extraction is performed prior to analysis when the elements are not in solution (e.g., fish/biological tissues, soils, sludges, sediments, and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material  $\geq 1\%$  (w/v) are extracted as a solid type sample.
- 1.6 When determining boron in aqueous samples, only plastic, PTFE is used from the time of sample collection to completion of analysis. For the accurate determination of boron in solid samples, only PTFE beakers are used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. Borosilicate glass is avoided to prevent contamination of boron.
- 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 silver. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains < 0.1 mg/L silver. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples is performed using aliquots < 1 g when determined sample concentrations exceed 1%.
- 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 varying 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 wavelength selected, the spectrometer, the matrix, and the selected operating conditions. For MDLs, MRLs, and LDRs, for selected wavelengths in reagent water, see the most recent MDL study at MassDEP Wall Experiment Station - DELS\DELS-QAP\IDC, MDL & MRL Data\IOC Lab\EPA Method 200.7.
- 1.10 Initial Demonstration of Capability data, described in Section 9.2, are 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 un-dissolved material, a digestion/extraction is performed prior to analysis. After



cooling, the sample is made up to volume and filtered. 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 first preserved with nitric acid to pH < 2 and then adjusted to 1% nitric acid.

- 2.2 The analysis described in this method involves multi-elemental determinations by inductively coupled plasma optical emission spectrometry (ICP-OES) using a simultaneous instrument. The instrument measures characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the dual view configured plasma torch. Element-specific emission spectra are produced by radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction (BGC) technique is used to compensate for variable background contribution to the determination of the analytes. Background is measured adjacent to the analyte wavelength during analysis. Interferences are considered and addressed in Sections 4.0, 7.0, 9.0, 10.0, and 11.0.

### 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 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 – See Table 1.
- 3.6 Interelement Correction (IEC) - A method of correcting for spectral interferences. It uses mathematical correction factors to reallocate emission intensities.
- 3.7 Internal Standard (IS) - Pure analyte (s) added to a sample, extract, or 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 must be an analyte that is not a sample component and behaves in a manner similar to the element of interest. The internal standard is used to correct for matrix effects and instrument drift.
- 3.8 Laboratory Duplicates (Sample and Sample Duplicate) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of the Sample and the Sample Duplicate indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.



- 3.9 Laboratory Fortified Blank (LFB) - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.10 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.11 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.
- 3.12 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.
- 3.13 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.
- 3.14 Minimum Reporting Level (MRL) - The lowest analyte concentration that can be quantitated with acceptable accuracy and precision under stated analytical conditions. This defined concentration can be no lower than the concentration of the MRL check standard for that analyte and can only be used if acceptable quality control criteria for the analyte at this concentration are met.
- 3.15 MRL Check Standard - Low-level standard with concentration at least 3 to 5 times the MDL value. The standard is analyzed at the beginning of each analytical run before the samples are run.
- 3.16 Plasma Solution - A solution that is used to determine the optimum orientation of the quartz torch for viewing the plasma.
- 3.17 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.
- 3.18 Quality Control Sample - Standard Reference Material (QCS-SRM) [Solid Matrix Only] - A Sample of a matrix similar to the sample being analyzed, which contains analytes of a known or accepted concentration. The QCS-SRM is obtained from a source external to the laboratory and contains the analytes of interest at certified concentrations for the method of interest. The QCS-SRM is processed in the same manner as the sample, unlike the QCS in Section 3.17, and is used to check method performance.
- 3.19 Solid Sample - For this method, a sample taken from material classified as fish/biological tissue, soil, sediment, or sludge.
- 3.20 Spectral Interference Check (SIC) Solution - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria. Two types of spectral interference solutions are used in this method: single element and multielement.



- 3.21 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.
- 3.22 Total Recoverable Analyte - The concentration of analyte determined either by "direct analysis" of an unfiltered acid-preserved 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.
- 3.23 Water Sample - For this method, a sample taken from one of the following sources: drinking water, surface water, ground water, storm water runoff, or industrial or domestic wastewater.

#### 4.0 INTERFERENCES

- 4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.
- 4.1.1 Background emission and stray light are compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity is determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement is free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.
- 4.1.2 Spectral overlaps are avoided by using an alternate wavelength; or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements near the upper end of its LDR. Some potential on-line spectral interferences observed for the recommended and secondary wavelengths are given in Tables 2A and 2B, respectively. When uncorrected, these interferences will not produce accurate analyte concentrations. The interferences listed are only those that occur between method analytes. Interelement correction factors determined on the Optima 8300 DV, within tested concentration ranges, are applied to compensate for the effects of interfering elements.
- 4.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.11. Additionally, re-evaluation of spectral interferences is mandatory whenever any major change is made to the instrument, including changes to the nebulizer, spray chamber, torch, plasma optimization, and background correction (BGC) points. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections are dependent on the selection of background correction points. Selecting a BGC point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.





- 4.1.4 Spectral interference effects are evaluated for the instrument used in this method. Instrument operating conditions (such as power, torch x-y viewing position, and argon flow rate) change emission intensities. The wavelengths used in this method have interferences that are documented and kept on file, an example is given in Tables 2A and 2B. The IEC (Inter-element Correction) model builder in the PerkinElmer Syngistix software is used to create an IEC table for the automatic correction of interferences on all analyses. To determine the appropriate location for off-line BGC, the user scans the area on either side adjacent to the wavelength and records the apparent emission intensity from all other analytes. The location selected for BGC must be either free of off-line inter-element spectral interference or alternately, the Syngistix software can be used to assign automatic BGC on all determinations. For all the secondary wavelengths used, both the on-line and off-line spectral interferences from all method analytes must be determined and documented and provided for their automatic correction on all analyses. Tests are done to determine the spectral interference using analyte concentrations that adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient. However, for analytes such as iron, that may be found at higher concentrations, a more appropriate test would be to use a concentration near the upper LDR limit.
- 4.1.5 Samples that are analyzed with the IEC table activated will have the interferences mathematically corrected. If an analysis is done with the IEC off, it can be reprocessed with the IEC on and the IEC model will apply to the sample results. Remember to give a different name to the reprocessed data file as to not overwrite the original data file. SIC solutions are routinely analyzed to verify the absence of inter-element spectral interference.
- 4.2 Physical interferences are effects associated with sample transport and nebulization. Physical interferences associated with samples containing high dissolved solids or changing viscosity are corrected by using an internal standard. An internal standard is mixed with all samples prior to entering the plasma and the relative emission intensity of the internal standard is used to calculate the corrected sample concentration.
- 4.3 Chemical interferences from molecular compound formation or ionization effects are reduced by the axial configuration of the plasma and the use of a shear gas that eliminates the cooler region of the plasma where emission from easily ionized elements (EIEs) like potassium and sodium take place. In samples that contain high concentrations (greater than 1,000 mg/L) of EIEs like lithium, sodium and potassium, suppression or enhancement of emission signals, depending on the analyte species, is possible.
- 4.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. A rinse period of at least 30 seconds is run between samples and standards. An initial calibration blank (ICB) is analyzed after calibration and continuing calibration blank (CCBs) are analyzed after every 10 or fewer samples, and at the end of the analytical run. The analyst monitors the concentration of the CCB to ensure analyte signals are less than  $\frac{3}{4}$  the absolute value of the minimum reporting level (MRL).

## 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 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.
- 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 the 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. (Sections 15.0 and 16.0)

## 6.0 EQUIPMENT AND SUPPLIES

### 6.1 Instrumentation: Inductively Coupled Plasma - Optical Emission Spectrometer

6.1.1 PerkinElmer Optima 8300 DV ICP-OES, Serial # 078S1603284. Emission spectrometer with dual viewing mode (axial and radial) detector. The UV detector covers an extended ultraviolet wavelength range from 165 to 403 nm. The VIS detector covers the visible wavelength range from 404 to 782 nm.

6.1.1.1 Software: Syngistix for ICP, Version 5.1.0.0293

6.1.1.2 User guides with instructions on how to use the instrument and software, are stored in the instrument computer and can be found under **Desktop> Manuals**

6.1.1.2.1 Customer Hardware and Service Guide (7)

6.1.1.2.2 Syngistix Software Guide (8)

6.1.1.2.3 Syngistix Data Management Software (9)

6.1.2 Computer: Dell OptiPlex XE3, Serial # WCAPELB6R3KD3

6.1.2.1 Operating System: Windows 10 Enterprise LTSC, 64 bit

6.1.3 Printer: Either dedicated or network.

6.1.4 Torch Module: (Quartz Torch PerkinElmer Part # N0780130, Sapphire Injector PerkinElmer Part # N0782005) The quick-change adjustable torch module is an all-in-one assembly composed of the quartz torch, injector, spray chamber, and nebulizer/end cap. This module can be quickly removed from the sample compartment for cleaning or replacement of torch. This adjustable mount allows the torch on adjustment of up to 5 mm. The torch has a 1.8-mm sapphire injector for PE Optima 8000 series ICP with an ESI spray chamber. Refer to the Hardware and Service Guide for the Optima 8300 DV.



- 6.1.5 Dual Spray Chamber: (PerkinElmer Part # N0782014) A quartz hydride C2 dual cyclonic spray chamber consisting of an un-baffled lower chamber with 7-mm ID baffle in the upper chamber and a 4-mm ID baffle in the transfer tube between chambers. It includes dual drain lines for C2 chamber using gray/gray santoprene tubing.
- 6.1.5.1 Nebulizer: (PerkinElmer Part # N8145368) A PFA-ST self-aspirating MicroFlow nebulizer for prepFAST systems connected to the dual cyclonic spray chamber.
- 6.1.6 Autosampler: Elemental Scientific prepFAST 4DX inline syringe-driven autodilution system with mobile cart. The autosampler is computer controlled and programmable. This system has 5 possible tray positions. Tray 0 has a 9 position standards-rack that fits 125-mL bottles. This tray is not routinely changed out and currently only holds the blank solutions, since the working standards are prepared manually. Trays 1-4 are either set for 21 positions (3x7) for 50-mL vials or 60 positions (5x12) for 15-mL vials. The racks are updated depending on the number of samples for each analytical run. The calibration standards positions are programmed into the Calibration tab of the Method Editor and the positions for samples are entered into the Sample Information File.
- 6.1.6.1 FAST DXi Dual Valve Module – Four channel precision micro peristaltic pump, one P6 valve and one P7+ valve. The P7+ valve can be in either the “Load” or “Inject” position. The “Load” position indicates that the valve is ready to be filled with a new sample or rinse solution when cleaning the valve. The “Inject” position indicates that the sample is being injected into the internal standard and diluent flow. The P6 valve also has the “Load” or “Inject” sample option and it behaves similarly to the sampling P7+ valve. Refer to the prepFAST S400V Basic Operation Manual (10) for detailed information on the probe, valve, and syringe positions during common operations of the autosampler.
- 6.1.6.2 Peristaltic Pump: The peristaltic pump is fully computer-controlled. Pump speeds are programmable in the Method Editor. The sampling flow rate is set to 0.30 mL/min and the wash flow rate is set to 0.40 mL/min.
- 6.1.6.3 Peristaltic Pump Tubing:
- 6.1.6.3.1 Carrier tubing – Flared PVC MP<sup>2</sup> Two-Stop, 0.76-mm ID, 72-mm between bridges, Black/Black, PerkinElmer Part # N8145202.
- 6.1.6.3.2 Waste tubing – Non-Flared Santoprene MP<sup>2</sup> Two-Stop, 1.30-mm ID, 82-mm between bridges, Gray/Gray, PerkinElmer Part # N8145173.
- 6.1.6.4 S400V Syringe Pump – Automated four syringe pump unit with FAST actuator and a 12-port valve. The unit includes one 12-mL CTFE syringe with PTFE plunger (PerkinElmer Part # N8145227) and three 3-mL quartz syringes with PFA plunger (PerkinElmer Part # N8145223). The syringe pump directs the carrier, diluent, and internal standard solutions during analysis. When the valve is in the “Fill” position as indicated by the illuminated LED, the flow is directed into the syringe from the reagent bottles. When the valve is in the “Dispense” position as indicated by the illuminated LED, the flow is directed from the syringes to the sampling P7+ valve and instrument.
- 6.1.6.5 Software: ESI SC/FAST, Version 2.9.0.202
- 6.1.7 Chiller: PolyScience WhisperCool™ Chiller, Model N0772046, Serial # 5U1652289, polyclear MIX 30 PLUS Fluid (PE # N0776200, 0.5 gal)





- 6.1.8 Two - Fully Automatic Universal Gas Management Systems capable of providing continuous supply of gas from either cryogenic liquid cylinders or high-pressure gas cylinders, or any combination of both. The devices are used to monitor, control, and switch the flow of gas from cryogenic or high-pressure cylinders from either of two independent sources while maintaining a settable, constant delivery pressure.
- 6.1.8.1 One – Ultra High Purity (UHP) Argon cryogenic liquid cylinder (Dewar), 230 Liter: 99.999% Purity
- 6.1.8.2 Two – UHP Argon high-pressure cylinder backups, Size 300: 99.999% Purity
- 6.1.8.3 One – Ultra High Purity (UHP) Nitrogen cryogenic liquid cylinder (Dewar), 230 Liter: 99.999% Purity
- 6.1.8.4 Two – UHP Nitrogen high-pressure cylinder backups, Size 300: 99.999% Purity
- 6.1.9 In-house Air Compressor:
- 6.1.9.1 One – Air Dryer Filter Assembly with R250 Regulator (PerkinElmer Part #N0775325)
- 6.1.9.2 Two – SPEEDAIRE Compressed Air Filter for Particulates, 5-micron (Grainger Part # 4ZL49)
- 6.2 Analytical balance, with capability to measure to 0.1 mg, for determining dissolved solids in digests or extracts.
- 6.3 A temperature adjustable hot plate or HotBlock® Heating Block capable of maintaining a temperature of 95°C, or a microwave digestion system.
- 6.3.1 Disposable digestion tubes, disposable reflux caps, disposable watch glasses and filters.
- 6.3.2 PTFE microwave digestion vessels and quartz inserts.
- 6.4 A gravity-convection drying oven with thermostatic control capable of maintaining a temperature of  $180 \pm 5^\circ\text{C}$ .
- 6.5 Assortment of air displacement pipettors capable of delivering volumes ranging from 100  $\mu\text{L}$  to 10 mL with corresponding metals-free high-quality disposable pipette tips.
- 6.6 Mortar and pestle, ceramic or nonmetallic material.
- 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 concern. 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. Field sample containers used in the determination of trace elements are purchased as pre-cleaned glass or HDPE containers. Laboratory containers for sample handling and storage are bought trace metal-free or pre-cleaned. Volumetric flasks and other glassware used to make standards, etc., are initially cleaned as follows: glassware is washed with a detergent solution made from Citramax, rinsed with tap water, soaked



for four or more hours in 20% (v/v) nitric acid or hydrochloric acid, rinsed with reagent water, and stored in a clean cabinet. While in use, glassware is triple rinsed with reagent water, and stored in 5% (v/v) nitric acid. Microwave digestion vessels and inserts are run through the microwave cleaning cycle.

**Note:** Samples are not collected by laboratory personnel. As a result, the laboratory has no control over sample bottles, other supplies and consumables, or techniques used in the field.

- 6.8.1 Glassware: Volumetric flasks, graduated cylinders, funnels, and centrifuge tubes (glass and/or metal-free plastic).
- 6.8.2 Assorted glass calibrated Type A volumetric pipettes.
- 6.8.3 Narrow-mouth storage bottles with screw closure, HDPE or LDPE, 125-mL to 2-L capacities.

## 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 greater than or equivalent to trace metal purity grade.

**Reagent and Standard Preparation Bench Sheets for this method are standalone documents found in the EICL Forms folder for EPA Method 200.7 in the WES SharePoint site.**

- 7.2 Hydrochloric acid, concentrated (sp. Gr. 1.19) (HCl)

- 7.2.1 Hydrochloric acid (1:4) – Add 2 mL of *conc.* HCl to 4 mL reagent water and dilute to 10 mL.

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

- 7.3.1 Nitric acid (1:1) – Add 5 mL of *conc.* HNO<sub>3</sub> to 4 mL reagent water and dilute to 10 mL.

- 7.4 Reagent water: ASTM Type I reagent-grade water

- 7.5 Hydrogen Peroxide, 30%, (H<sub>2</sub>O<sub>2</sub>): Stabilized certified reagent grade.

- 7.6 Standard Stock Solutions: Single element stock standards are purchased for all the analytes tabulated in Section 1.1. These stock standards are replaced prior to or at the expiration date.

- 7.7 Mixed Calibration Stock Standard Solutions: A set of seven mixed calibration standard solutions are purchased from Inorganic Ventures because their mixtures most closely compare to the solutions recommended in EPA Method 200.7, Table 3.

- 7.7.1 Preparation of Working Calibration Standard Solutions: Calibration standard solutions are prepared every two weeks for SDWA analyses, or as necessary for all other analyses. Inorganic Ventures prepares the mixed calibration stock standards so that a 100X dilution yields the recommended maximum calibration standard in Table 1 of EPA Method 200.7. For this method, it was decided to start with a four-point calibration curve: blank, a 400X dilution, 200X dilution, and a 100X dilution for the highest calibration standard. The number of standards included in the calibration curve for each wavelength in this method were optimized for the sensitivity of our current instrument and for the expected concentration range of the most commonly requested analytes. The working calibration standard solutions are prepared in 2% HNO<sub>3</sub> (v/v).



- 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.
- 7.8.2 The laboratory reagent blank (LRB) contains all the reagents in the same volumes as used in the processing of the samples. The LRB is carried through the same entire preparation scheme as the samples, including sample digestion, when applicable.
- 7.8.3 The laboratory fortified blank (LFB) is prepared by spiking an aliquot of the laboratory reagent blank with a single element or multi-element standard solution. The concentrations of the analytes in the LFB should mirror the expected analyte concentration in the samples. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.
- 7.8.4 The rinse blank is prepared by acidifying reagent water to the same concentrations of acids as used in the calibration blank.
- 7.9 Instrument Performance Check (IPC) Solution: The IPC solution is used to periodically verify instrument performance during analysis. It is prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. Depending on when it is run, the IPC may also be called an Initial Calibration Verification (IPC-ICV) or Continuing Calibration Verification (IPC-CCV). The IPC-ICV is prepared from the same stock standard solutions used to prepare the calibration standards. Hence, for the IPC-ICV, there are seven different solutions free of spectral interferences from analytes in the respective solutions. The IPC-ICV has analyte concentrations at half of the suggested concentration for instrument calibration from EPA Method 200.7 Table 1. The IPC-CCV are two solutions purchased from Inorganic Ventures, the same vendor used for the calibration standards. The IPC-CCV is a different solution from the IPC-ICV because the method allows for a wider acceptance range for the IPC-CCV. Furthermore, reducing the solutions from seven to two for the IPC-CCV reduces analysis time. The IPC-CCV have a concentration of 2 mg/L for all analytes, except silver is at 0.25 mg/L and potassium, phosphorus and silica are at 10 mg/L. Silver must be limited to < 0.5 mg/L for solution stability. Potassium and phosphorus are higher because of higher MDL values and silica is higher because of potential contamination.
- 7.10 Quality Control Sample (QCS): Analysis of a QCS is performed for verification of calibration standards in order to verify instrument performance. The QCS must be obtained from an outside source different from the stock calibration standard solutions and prepared in the same acid mixture as the calibration standards. Currently, the seven QCS stock standards are a custom order from Environmental Express to match the stock standards used for the IPC-ICV. The working QCS solutions are diluted in the same matrix as the calibration standards and IPC, namely 2% HNO<sub>3</sub>.
- 7.11 Spectral Interference Check (SIC) Solutions: When interelement corrections are applied, SIC solutions containing the interfering element, at levels that will provide an adequate test of the correction factors, are analyzed.
- 7.11.1 For analytes with documented interferences, the appropriate single element SIC solution(s) are analyzed with every analytical batch. Usually a 50-mg/L concentration of the interferent suffices, however, for interferences due to elements like iron, a higher concentration would be more appropriate.



- 7.11.2 Multi-element SIC solutions or interference check solutions (ICS) may be substituted for the single element SIC solutions provided an analyte is not subject to interference from more than one interferant in the solution. Multi-element SIC or ICS solutions can assess the accuracy of the correction routine and can help detect if analytes have overly positive or overly negative results indicated by apparent analyte concentrations exceeding the absolute value of the MRL. However, because multi-element SIC solutions are mixtures, and possibly contain multiple interferents on a given analyte, they do not pinpoint which correction factor is causing the over or under correction on the analyte.
- 7.11.3 If the correction routine is operating properly, the determined apparent analyte(s) concentration resulting from each SIC solution should be  $< |MRL|$  for the un-spiked analyte being interfered upon. If the apparent analyte concentration is outside this range, the cause of the exceedance should be determined and corrected, and the correction factor updated if necessary.
- Note: The SIC solution should be analyzed more than once, with adequate rinse time between solutions, to confirm a change has indeed occurred.
- 7.12 For recommended and secondary wavelengths in this method, on-line and off-line spectral interferences from all method analytes need to be determined and documented, and an interelement correction routine created to provide for their automatic correction. Thus, on all analyses of this method, interelement corrections should be used. If for some reason, interelement corrections cannot be used, SIC solutions can serve to verify if interference is significant. If the SIC solution confirms an operative interference that is  $\geq 10\%$  of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure.
- 7.13 Plasma Solution: Plasma solutions are used to optimize the plasma viewing positions for maximum light throughput to the detector. A 1.0-mg/L Mn solution is used for axial view and a 10.0-mg/L Mn solution is used for radial view.
- 7.14 Internal Standard (IS) Solution: The internal standard is a 10 mg/L solution of yttrium (Y) in the same acid mixture as the calibration standards (2% HNO<sub>3</sub>). Prepare the internal standard solution according to the specific bench sheet. The IS solution is added to all calibration standards, samples, and QC standards by the peristaltic pump through a mixing block.

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 When requested, the laboratory provides appropriate pre-cleaned samples bottles for Method 200.7 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 (pH is recorded on a preservation sheet that is included with the sample reports). If properly acid preserved, the sample can be held up to six months before analysis. 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 as soon thereafter. The sample is acidified with (1+1) or *conc.* nitric acid immediately following filtration to pH  $< 2$ .



- 8.4 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) or *conc.* 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 for post-acid turbidity analysis. If the pH is > 2 after 16 (24) hours, acidify to pH < 2 again and wait another 16 (24) hours before retesting the pH and continuing with turbidity analysis. 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  $4 \pm 2^{\circ}\text{C}$ . There is no established holding time limitation for solid samples.
- 8.6 For aqueous samples, a field blank should be prepared and analyzed as required by the data user.
- 8.7 Fish/biological tissue samples should be stored frozen 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 components: 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, spectral interference checks (single element or multi-element SIC), method and instrument contamination checks (ICB,CCB, LRB), participation in annual proficiency testing, and contribution of sample bias (LFM) on data quality results. QC records are maintained and kept on file. This section details the specific requirements for each of these QC elements.

### 9.2 Initial Demonstration of Capability (IDC)

- 9.2.1 The initial demonstration of performance or capability is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits). Each analyst using this method must conduct all the components of the IDC in the order given below prior to any analysis of environmental samples.
- 9.2.2 Mixed Calibration Standards Design – Prior to using mixed calibration standards, each element in the calibration solution mixture needs to be analyzed separately to determine possible spectral interferences between the components of the mixture and to ensure compatibility with the other analytes in calibration solution. The EPA recommended mixed calibration standards were designed for the wavelengths suggested in the method. If different wavelengths or different combinations of the mixed calibration standards are to be used, great care should be taken when preparing the mixed standards to ensure that the elements are compatible, stable together, and do not significantly interfere with the other analytes in mixture.

**Note:** This step was already done once for the Optima 8300 DV in-house and for the wavelengths listed in Tables 2A and 2B. The resulting mixed calibration standard solutions are listed in Table 3. **The design of the mixed calibrations standards needs to be performed only if there is a new instrument or different secondary wavelengths are to be used.**





9.2.2.1 Perform a qualitative run to determine the extent to which an analyte interferes on another analyte's wavelength. A calibration curve composed of a blank and a high-level single element stock standard needs to be analyzed for each analyte in the proposed calibration mixture. Once a calibration curve is created for all the analytes, then single element standards at the intended concentration of the mixed calibration solution need to be analyzed. The single element standard is then assessed for false positive or negative concentrations on the other analytes in the intended mixed calibration standard. A single element stock standard having a concentration on another analyte in its proposed calibration mixture of more than  $\pm 0.2\%$  should be labeled as a noteworthy interference and the analytes should not put together in the calibration mixture. However, if the historical MRL of an analyte being interfered upon is greater than the observed interference, then the interference is deemed insignificant since it is below the analyte's reporting limit. The interference percentage was calculated using the equation below:

$$\frac{\text{Apparent Analyte Concentration}}{\text{Measured Concentration of Single Element Standard}} \times 100\%$$

9.2.3 Linear Dynamic Range (LDR) – The upper limit of the LDR must be established for each wavelength utilized and determined from a linear calibration prepared in the normal manner composed of a calibration blank and at least one calibration standard using the established analytical operating procedure for the instrument. The LDR is determined by analyzing increasingly higher standard concentrations of the analyte until recoveries exceed 90-110%. The LDRs are documented and kept on file. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit are diluted and reanalyzed. The LDRs are verified annually or whenever a change in analytical or instrument performance occurs, which would then dictate that the LDRs be re-determined.

9.2.3.1 The instrument was calibrated using the working calibration standards discussed in Section 7.7.1 and prepared from the mixed calibration standards shown in Table 3. Immediately following calibration, 7 IPC-ICV standards, 1 ICB and 7 QCSs were analyzed. There are 7 IPC-ICV, 7 QCS and 7 IPC-CCV standards because there is 1 per calibration group, usually at the mid-point level of the calibration curve. The quality control standards and LDR standards were prepared in groups rather than using multi-element mixed standards because the inter-element correction (IEC) routine had not been established at this point. Without the use of IECs, the multi-element mixed standards could have spectral interferences that result in improper quantitation. Furthermore, the LDR for each analyte must be established before creating an IEC table because the single element standard concentration used to generate the table cannot exceed the dynamic range.

9.2.3.2 For each mixed calibration group, at least three succeeding higher standards were prepared and analyzed until the observed analyte concentration was outside 90-110% of the stated concentration of the standard. For some analytes, the observed analyte concentration was well within the 10% criteria, however, higher concentrations were not analyzed since such elevated concentrations are not expected in the samples intended for this method. Normally 100 mg/L is sufficient for the upper limit of LDR, except for As, Ca, Fe, Mg, K, P, Pb and Na.



- 9.2.4 Interelement Correction (IEC) Table – An interelement spectral interference correction routine must be established for sample analysis. PerkinElmer refers to the correction routine as an Interelement Corrections (IEC) table. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration on the analyte that exceeds  $\frac{1}{2}$  MRL of the analyte. Once established, the entire routine must be initially verified, and recreated whenever there is a change in instrument operating conditions. Major changes to the instrument configuration which require re-evaluation of interferences include changes to nebulizer, spray chamber, torch optimization, and background correction points. Only a portion of the correction routine, i.e., the determined interferences of the target analytes, must be verified on a daily basis. Test criteria and required solutions are described in Section 7.11. Initial and periodic verification data of the routine are kept on file.
- 9.2.4.1 The instrument was calibrated using the working calibration standards discussed in Section 7.7.1 and prepared from the mixed calibration standards shown in Table 3. Immediately following calibration, 7 IPC-ICV standards, 1 ICB and 7 QCSs were analyzed. After the initial QC samples, the 31 method analytes were each tested as single element standards. The correction routine for this method is complex because there is one instrument method with the 31 analytes listed in Section 1.1. Thus, each analyte is a potential spectral interferent on the other analytes. For most analytes, a concentration just below the upper limit of the LDR was chosen for the interferent standard concentration to build the IEC table. For data quality purposes, the interferent standard concentration for a specific wavelength should not exceed its maximum LDR value. The success of an IEC table is heavily dependent on the placement of background points, integration areas, plasma, and sample uptake conditions. If these conditions change due to instrument maintenance or any other reason, a new IEC table must be created.
- 9.2.4.2 Prior to creating an IEC table, the appropriate location of the BGC points must be determined. The placement of the points is based on peak definition and any spectral interference from adjacent wavelengths. Since there are so many analytes in this method, the selection of BGC points at certain wavelengths may be too convoluted. Also, negative correction factors occur when the interfering peak is at the background correction position. For these reasons, automatic background correction was selected for all wavelengths in the instrument method.
- 9.2.4.3 The instrument method has two wavelength lines for some analytes. The PerkinElmer IEC Model Builder does not allow for a given analyte to have IEC factors from more than one wavelength per interferent. For example, Fe interferes on Mn, and Fe has two wavelength lines in the instrument method but only one of the Fe lines can have an IEC factor for Mn. The wavelengths chosen for the IEC factors table were the recommend lines in EPA Method 200.7.
- 9.2.4.4 In order to create the IEC table, an estimated MRL for each wavelength in the method is needed. The MRL is needed to set the minimum concentration limit for interference correction. The MRLs were first determined without the use of corrections and an IEC table. However, in the future, historical MRL values or estimates may be used to create the IEC table. The IEC table is only preliminary at this point and must be updated with the determined MRL values.
- 9.2.4.4.1 The instrument method must be updated to include the use of the preliminary IEC table. This updated instrument method is then used to



acquire the seven replicates of method detection level (MDL) standards and to calculate the method reporting limit (MRL) for each wavelength, see Section 9.2.5. Single element SIC solutions for the 31 potential interferents **must** be included in each analytical run. The concentration limit for a blank is  $< \frac{3}{4} \text{ MRL}$ . To ensure the blank criteria is met, the minimum concentration limit for interference correction in the IEC table is set as  $\frac{1}{2} \text{ MRL}$  for each wavelength. Once, the minimum concentration limit in the IEC table is updated with the calculated MRL, each MDL standard run is then reprocessed with the updated IEC table.

9.2.4.4.2 The correction factors in the IEC table are derived using single element standards from one run. In theory, if the plasma conditions and the background points stay the same then the correction factors should remain consistent day to day leading to values very close to zero for unspiked analytes in interference check solutions. In actuality, daily variations in instrument conditions lead to slight variations with correction factors.

9.2.4.4.3 If an apparent analyte concentration (concentration measured at the analyte line, but its due to the interferent instead of the analyte) is greater than or equal to the analyte's minimum IEC concentration limit, an IEC factor for the analyte/interferent pair is calculated and entered into the IEC factors table. However, if the apparent analyte concentration is found to be less than the correction limit, the IEC factor entered into the IEC table for the analyte/interferent pair is zero. The effect of the interferent on the analyte is not sufficient to warrant a correction.

9.2.4.4.4 The value of each IEC factor is equal to the apparent analyte concentration divided by the interferent concentration. The apparent analyte concentration is the concentration measured at the analyte line, but due to the interferent instead of the analyte.

$$\text{IEC Factor} = \frac{\text{Apparent concentration of the analyte due to the interfering element measured at the analyte wavelength in } \frac{\text{mg}}{\text{L}}}{\text{Actual concentration of interfering element measured at another wavelength characteristic of the interfering element in } \frac{\text{mg}}{\text{L}}} \times 1,000$$

9.2.4.5 The SIC standards in the reprocessed MDL standards runs from Section 9.2.4.4.1 are then assessed to determine the accuracy of the IEC factors. The single element in the SIC should have a recovery of 90-110%. The other 30 analytes not spiked into SIC standard should have concentration values less than the absolute value of its MRL, i.e.,  $< |\text{MRL}|$ .

9.2.4.5.1 If the IEC table has a correction factor for an analyte and after the IEC correction has been applied that analyte still has a false positive in a SIC standard, the only option left to meet the SIC acceptance criteria is to increase the analyte's MRL.





9.2.4.5.2 If the IEC table does not have a correction factor for an analyte and that analyte has a false positive in a SIC standard, then the minimum concentration limit for interference correction in the IEC table for that analyte may be set lower than  $\frac{1}{2}$  MRL to try and generate a correction factor for that analyte.

9.2.4.5.3 The reason these two scenarios occur is because the correction factors in the IEC table are not averaged, instead they are derived from one run from one day. As a result, the MRL values need to be set high enough to account for the correction factors set in the IEC table.

9.2.4.9 PerkinElmer allows for manual entry of correction factors in the IEC model. However, it is not customary for our program to use this feature. Only automatically generated correction factors are used.

#### 9.2.5 MDL Determination – USEPA MDL Procedure Revision 2 (11)

9.2.5.1 The MDL must be determined for all wavelengths utilized using both method blank replicates ( $MDL_b$ ) and spiked reagent water replicates ( $MDL_s$ ). MDL values determined for this method must be sufficiently low to satisfy compliance monitoring regulations.

9.2.5.2 To determine an MDL, analyze at least seven aliquots of both method blanks ( $MDL_b$ ) and low-level spiked standards in reagent water ( $MDL_s$ ). The replicate aliquots should be processed through the entire analytical method over at least three separate days, with different standards prepared each day. The spiked reagent water standard should be at a concentration of 2 to 10 times the estimated instrument detection limit (IDL) or previously established MDL using a similar linear calibration range (LCR). Recoveries for low-level spiked standards must be within 80 to 120%. If this criterion is not met, the spiking level is too low and the determinations must be repeated at a higher concentration.

9.2.5.3 Calculate the  $MDL_s$  (the MDL based on low-level spiked reagent water standards) as follows:

$$MDL_s = (t) \times S_s$$

where,

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]  
 $S_s$  = standard deviation of the replicate spiked analyses

9.2.5.4 Calculate the  $MDL_b$  (the MDL based on method blank samples) as follows:

$$MDL_b = X_b + (t) \times S_b$$

where,

$X_b$  = mean of method blank results  
t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]  
 $S_b$  = standard deviation of replicate method blank analyses

9.2.5.5 The MDL then equals whichever is greater:  $MDL_s$  or  $MDL_b$ .



9.2.5.6 The MRL of an analyte is chosen as the spike standard level that gives acceptable accuracy and precision. Each replicate has recoveries within  $\pm 20\%$  of the spiked amount and the spike level is typically less than ten times (preferably within two to five times) the calculated MDL. If the spike level was found to be greater than ten times the calculated MDL, then a lower spike level is tested. However, a lower spike level could have calculated MDL values within the appropriate range but fail the recovery criterion. The final MRL may also need to be raised to satisfy the unspiked analyte criteria of the SIC standards, see Section 9.2.4.5.

9.2.6 Accuracy and Precision – Analyze at least seven aliquots of both the QCS and LFB in three separate batches on three separate days. The purpose of these replicates is to show whether the laboratory is capable of making accurate (percent recovery) and precise (RSDs) measurements for this method.

9.2.6.1 Quality Control Sample (QCS) – A second source laboratory control sample used to verify the calibration standards. Analyzed with every analytical batch. The concentrations from the QCS must be within  $\pm 5\%$  of the stated values. If the calibration standards are not verified, performance is unacceptable, and analysis is discontinued. The source of the problem is identified and corrected before proceeding with any analyses.

9.2.6.2 Laboratory Fortified Blank (LFB) – A laboratory sample used to evaluate laboratory performance and analyte recovery in a blank matrix. The LFB accuracy is calculated as percent recovery, comparing the measured concentration values to the stated values. If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

### 9.3 Ongoing Demonstration of Capability

***See Section 11.8 for a sample run list. The analysis data for all QC solutions are to be kept on file with the sample analyses data.***

9.3.1 Internal Standard (IS) Response (Initial & Ongoing) – The response of the yttrium internal standard must be monitored in the axial and radial viewing modes throughout the analysis with every analytical run. The use of an internal standard solution eliminates the need for the method of standard additions (MSA). The absolute response of the yttrium internal standard in axial mode and radial mode should be within 80% to 120% of the response in the calibration blank. Additionally, the internal standard relative standard deviation (RSDs) throughout the run should be  $< 3\%$ .

9.3.1.1 IS responses exceeding method limits may indicate a matrix effect. If the IS response is outside the specified range, flush the instrument with rinse blank until the IS response returns to acceptable levels. Dilute the sample by a factor of two and reanalyze. If flushing the instrument fails to return IS responses to their original levels, determine the cause of the drift.

9.3.1.2 If the internal standard RSD/recovery uncharacteristically spike, suspect a possible issue with the nebulizer.

9.3.2 Instrument Performance Check (IPC) – The IPC is analyzed with every analytical run, immediately after calibration, after every ten samples and at the end of the analytical run.



The IPC-ICV, run immediately after calibration, must verify that the instrument is within  $\pm 5\%$  of initial calibration with an RSD  $< 3\%$ . The IPC-CCV must be within  $\pm 10\%$  of calibration. If the calibration cannot be verified within the specified limits, the IPC and the calibration blank (see Section 9.3.3) are reanalyzed. If the second analysis of the IPC solution or the calibration blank is outside of 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.

- 9.3.3 Calibration Blank (CB) – The calibration blank is the zero standard for all calibration curves and depending on when it is run following instrument calibration, it may also be called an Initial Calibration Blank (ICB) or Continuing Calibration Blank (CCB). The ICB is required immediately after the IPC-ICV and before the analysis of samples. The CCB is required immediately after every IPC-CCV. Analyte concentrations in the CB must be  $< \frac{1}{4}$  MRL. If any analyte has CB concentrations outside this criterion, a second determination of the CB can be performed by running another IPC/CB pair.
- 9.3.4 Quality Control Sample (QCS) – A second source laboratory control sample analyzed immediately following the ICB with every analytical run. The concentrations from the QCS must be within  $\pm 5\%$  of the stated values. 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 with any analyses.
- 9.3.5 Laboratory Reagent Blank (LRB) – The LRB is carried through the same entire preparation scheme as the samples including sample digestion, when applicable. 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. Analyte concentrations in the LRB must be  $< \frac{1}{4}$  MRL (equivalent to 2.2 times the MDL). If any analyte has LRB values outside this criterion, fresh aliquots of samples and LRB should be sampled, prepared, and reanalyzed after correcting the source of contamination. This is required for SDWA analyses.
- 9.3.6 Laboratory Fortified Blank (LFB) – The laboratory analyzes one LFB with every batch of 20 or fewer samples of the same matrix. Process the LFB through all sample preparation and analysis steps (i.e., LFB counts as a sample). Higher or lower LFBs may be prepared to correspond with the range of the sample concentrations. The LFB analysis data are used to assess laboratory performance against the required control limits of 85-115%. If LFB results are out of control, take corrective action, including re-analysis of the opening QC and/or recalibration of the instrument.
- 9.3.7 Method Reporting Level (MRL) Check – Low-level standard with concentration at least 3 to 5 times the MDL value. The check standard is analyzed at the beginning of each analytical run prior to the LFB and before the samples are analyzed. The results must be within 20% of the true value. The acceptable range must be met before reporting data. If unacceptable, then repeat the analysis. If the problem persists, consider if the instrument's sensitivity has changed or if the MDL and MRL are too low for the analytical conditions. The MRL may be raised to the next highest level if the end users' data quality objectives are still met.
- 9.3.8 Sample and Sample Duplicate (Lab Dup) – A randomly selected sample that is analyzed in duplicate with every 10 or fewer samples. The sample/sample duplicate assesses the laboratory's ability to produce reproducible results but also assesses sample homogeneity. The duplicate samples are to be independently prepared and analyzed.



The relative percent difference (RPD) must be less than 20%. If duplicate results are out of control for dissolved samples, determine the cause, reanalyze samples, and the sample duplicate(s). For total recoverable samples, the duplicate can be repeated if the sample was prepared in error. If the duplicate was prepared correctly, properly qualify results and indicate the sample is not homogenous.

9.3.9 Laboratory Fortified Sample Matrix (LFM) – The laboratory adds a known amount of each analyte to a sample (typically the same sample used for the Lab Dup) with every 10 or fewer samples. LFM samples and duplicate samples are processed to assess matrix effects. The LFM aliquot is a duplicate of the aliquot used for sample analysis and for total recoverable determinations with the NTU >1, the spike is added prior to digesting the sample.

9.3.9.1 For aqueous samples, the added analyte concentration is the same as that used in the LFB (Section 7.8.3). The spiked concentration must be above the MRL but not greater than the upper limit of the LDR for any given analyte. If the LFB concentration does not represent 30% of the native sample concentration, on-line spikes will be prepared and analyzed. For solid samples, the concentration added is expressed as mg/kg and is calculated as follows:

$$C_{digestate} = \frac{V_{spike} \times C_{spike}}{V_{i_{digestate}}}$$

where,

$C_{digestate}$  = spike concentration in the digestate (µg/mL)  
 $V_{spike}$  = volume of spike solution added (mL)  
 $C_{spike}$  = concentration of spike solution (µg/mL)  
 $V_{i_{digestate}}$  = initial volume of digestate (mL)

$$C_{solid}(WW) = \frac{V_{f_{digestate}} \times C_{digestate}}{W}$$

where,

$C_{solid}$  = spike concentration in solid sample, wet weight (µg/g = mg/kg)  
 $V_{f_{digestate}}$  = final volume of digestate (mL)  
 $C_{digestate}$  = spike concentration in the digestate (µg/mL)  
 $W$  = weight of sample used in digestion (g)

9.3.9.2 For solid samples, the result in µg/g dry weight can be obtained by dividing the wet weight result by the percent solids expressed as a decimal, see Section 12.4.

9.3.9.3 The LFM percent recovery for each analyte is calculated using this equation:

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

where,

$R$  = percent recovery  
 $C_s$  = fortified sample concentration  
 $C$  = sample native concentration  
 $s$  = concentration equivalent of analyte added to fortify the sample



9.3.9.4 The acceptable LFM recovery range is 70% to 130%. If the spiked concentration is < 30% of the sample's native concentration, NCH is entered for the LFM result.

9.3.9.5 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, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or matrix effects.

9.3.10 Spectral Interference Check (SIC) – Single element and multi-element spectral interference check solutions are to be analyzed with every analytical run. SIC solutions may be run before or after samples. The SIC solutions should be composed of the known interferences for all the applicable analytes. The interferences in the SIC solutions should recover 90-110% of their stated values. The target analytes not present in the SIC solutions should not have concentrations that exceed the absolute value of the MRL or < | MRL|. In other words, analytes not spiked into the SIC solutions should not be observed at levels significantly different than that of a blank. SIC solutions are processed to test the correction efficacy of the IEC table and if working correctly, there should be no false positives/false negatives caused by spectral interferences.

9.3.11 Linear Dynamic Range (LDR) Check – If all samples have concentrations within the calibration curve, then the LDR check can be omitted. If the analyte concentration exceeds the established upper limit of the LDR, then the sample must be diluted to fall within the analyte's LDR and reanalyzed. If there are samples with analyte concentrations above the highest calibration standard and within 90% of the established upper limit of the LDR, then a LDR check must be included with the analytical run. It is recommended to analyze the LDR check after all samples have been analyzed. The percent recovery of the LDR check must be 90% to 110%.

9.3.11.1 If a sample is over the upper limit of the LDR, 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.

9.3.12 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably. Reference materials containing high concentrations of analytes can provide additional information on the performance of the spectral interference correction routine.

#### 9.4 Ongoing Annual Verification

9.4.1 MDL Determination – At least once every thirteen months, re-calculate MDL<sub>s</sub> and MDL<sub>b</sub> from the collected spiked samples and method blank results using the equations in Sections 9.2.5.3 and 9.2.5.4. Ensure that at least seven spiked samples and seven method blanks are completed for the annual verification. The verified MDL is the greater of the MDL<sub>s</sub> or MDL<sub>b</sub>.

9.4.1.1 Include data generated within the last twenty-four months, but only data with the same spiking level. If 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.

9.4.1.2 Only use data associated with acceptable calibrations and batch QC. Include all routine data, with the exception of batches that are rejected, and the associated samples reanalyzed. If the method has been altered in a way that can be reasonably expected to change its sensitivity, then use only data collected after the change.

9.4.2 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 the PT provider's acceptance range. If results are not within acceptance limits, investigate why, take corrective action, and analyze a new PT. Repeat this process until results meet the acceptance criteria.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Specific wavelengths used for this method are listed in Tables 2A and 2B. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. The instrument and operating conditions utilized for determinations is capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task.

10.1.1 The current operating conditions for the ICP-OES instrument are 1500 watts radio frequency (RF) power, the plasma viewing height for the X-position is set to 0.0 mm and 15.0 mm for the Y-position. The plasma flow is 10 L/min, the auxiliary flow is 0.2 L/min, and the nebulizer flow is 0.6 L/min. The torch position is -3 and the plasma equilibration time is 15 secs. The sampling pumping rate is 0.30 mL/min with at least 25 sec. flush time with the carrier after each determination. An additional 10 sec. rinse is added after a sample with any analyte concentration over 10 mg/L.

10.2 Plasma operating conditions were determined by the PerkinElmer service engineer application specialist and the user, then stored to the instrument. The instrument automatically adjusts the system conditions to remain within the prescribed operational settings and makes continuous diagnostic adjustments.

10.2.1 Whenever the torch is removed, the plasma and plasma viewing height must be reoptimized. Perform a torch alignment of the axial and radial views for maximum light throughput to the detector. **If the torch is removed, the IEC table must be rebuilt.**

10.2.1.1 Axial Mode Alignment – Place the carrier probe in the 1.0-mg/L Mn solution and allow for the solution to be aspirated for a couple of minutes. In the Syngistix software, click on the **Instrument** tab. In the **Spectrometer** group, click **Align View** and both the **Spectrometer Control** and **Align View** dialogs appear. By default, the radio button for **Axial** is selected in the **Spectrometer Control** dialog. In the **Align View** dialog, ensure the selected analyte is Mn 257.610 and that the instructions say to aspirate a 1-mg/L Mn solution. Then click **Align** in the **Align View** dialog. The instrument will then begin to optimize the axial viewing position. Once it is complete, manually rinse the outside of the carrier probe and place in the carrier probe in the carrier acid solution.





- 10.2.1.2 Radial Mode Alignment – Place the carrier probe in the 10.0-mg/L Mn solution and allow for the solution to be aspirated for a couple of minutes. In the Syngistix software, click on the **Instrument** tab. In the **Spectrometer** group, click **Align View** and both the **Spectrometer Control** and **Align View** dialogs appear. Since the **Axial** radio button is selected by default in the **Align View** dialog, close that dialog box and click on the **Radial** radio button in the **Spectrometer Control** dialog box. The dialog box refreshes and becomes grayed out for a few seconds. Once it is engaged again, click **Align View**. The **Align View** dialog reappears and ensure the selected analyte is Mn 257.610 and that the instructions say to aspirate a 10-mg/L Mn solution. Then click **Align** in the **Align View** dialog. The instrument will then begin to optimize the radial viewing position. Once it is complete, manually rinse the outside of the carrier probe and place in the carrier probe in the carrier acid solution. Print the results and keep on file.
- 10.2.1.3 The software will determine the maximum emission intensity. The axial and radial alignment of the torch are automatically adjusted and accepted. On a daily basis, the maximum intensity in axial and radial viewing position for the X-position should be set to 0.0 mm and 15.0 mm for the Y-position in axial viewing mode.
- 10.3 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure are described in Section 9.2. These data must be generated using the same instrument operating conditions and calibration routine to be used for sample analysis. Documented data must be kept on file and be available for review by the data user.
- 10.4 As part of the IDC, an interelement spectral interference correction routine must be established and initially verified to be used during sample analysis. A general description concerning the development of an IEC table are given in Section 9.2.4. Once established, for analyte wavelengths with documented interferences (See Tables 2A and 2B), the appropriate single element SIC solution(s) are analyzed with every analytical batch. Additionally, all interelement spectral correction factors must be updated annually or when necessary.
- 10.4.1 If a new IEC table is created and it is not part of an IDC study or annual MDL study, then one run of single element interference check standards is needed to verify the accuracy of the newly created correction factors. A separate run is needed from the run used to create the IEC table because if the IEC table run is reprocessed with the IEC table on then all the SIC standards will have passing values for the un-spiked analytes, i.e., a perfect correction will occur.
- 10.4.2 When samples are analyzed and the IEC table is in use, the software multiplies the interferent concentration by the IEC factor. It then subtracts this product from the measured analyte concentration to report the corrected analyte concentration.
- Corrected Analyte Conc. = Measured Analyte Conc. – (IEC Factor x Interferent Conc.)*
- 10.4.3 Interference correction is only valid for a given interferent at levels up to the single element standard used to create the IEC table. If an interferent is found at a level above the concentration of single element standard level tested, the sample must be diluted until the interferent is below the tested level.



## 11.0 PROCEDURE

### 11.1 Aqueous Sample Preparation – Dissolved Analytes

- 11.1.1 Pour 50 mL of the filtered, acid-preserved sample into a 50-mL polypropylene centrifuge tube. Then add 0.5 mL of *conc.* nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid. Cap the tube and mix. The sample dilution factor is 1.01 and calculations must account for this dilution factor. The sample is now ready for analysis. The pH of the sample must be checked immediately prior to analysis to confirm a pH < 2.

**Note:** If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using EPA Method 200.2.

### 11.2 Aqueous Sample Preparation – Total Recoverable Analytes

- 11.2.1 For the “direct analysis” of total recoverable analytes in aqueous samples containing turbidity < 1 NTU, treat an unfiltered acid-preserved sample aliquot using the sample preparation procedure described in Section 11.1.1 while making allowance for sample dilution in the data calculation.
- 11.2.2 For the determination of total recoverable analytes in aqueous samples with >1 NTU, samples must be digested by EPA Method 200.2 (Refer to SOP # EPA 200.2 Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements).

### 11.3 Solid Sample Preparation – Total Recoverable Analytes

- 11.3.1 For the determination of total recoverable analytes in solid samples, refer to Section 11.2 SOP # EPA 200.2 Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements.

### 11.4 Instrument Operating Procedure: Pre-ignition Checks

- 11.4.1 Ventilation – Ensure that ventilation is active and stable. The ICP torch vent required flow rate is 5,660 liters/min (200 cubic feet/min) at the end of the venting hood.
- 11.4.2 Gases – Verify gas pressure, quantity, and purity. Check that the argon and nitrogen Dewars are sufficiently full and producing enough gas to maintain pressure, ensure back-up cylinders contain sufficient gas, and that the switching panel indicates sufficient pressure to distribute gas to the building.
- 11.4.2.1 Nitrogen, UHP ≥ 99.999%, used for purging spectrometer optics. The supply should be on at all times. The nitrogen supply regulator is set to 60 PSI, the available pressure should be between 40 and 120 PSI.
- 11.4.2.2 Argon, UHP ≥ 99.996%, used for plasma generation and sample transport. The supply should be on at all times. The argon supply regulator is set to 100 PSI, the available pressure should be between 80 and 120 PSI.
- 11.4.2.3 Compressed Air, used for producing shear gas. The compressed air regulator is set to 100 PSI, the available pressure should be between 80 and 120 PSI. Verify that the compressed air supply is free of water. If water is introduced into the supply line, then the filters may not be effective. This in turn can





damage the ICP-OES. Once the plasma is lit, make sure that the air pressure remains constant. If pressure decreases, there could be a blockage in the Air Dryer Filter Assembly, or the in-house air compressor may need maintenance.

- 11.4.3 Coolant – The Poly Science Whisper Cool Chiller is in the Equipment Room, across from the Elemental Analysis Laboratory. The temperature is set at 15.1°C and the pressure range is 71 to 73 PSI. Check coolant levels daily and top off using polyclear Mix 30, if necessary. Routinely check and clean the strainer in the coolant input and vacuum the front of grill to remove dust, as needed. Coolant fluid should be changed out every 6 to 12 months and is usually performed during the Annual Preventative Maintenance visit by a PerkinElmer service engineer.
- 11.4.4 Cleanliness of Torch and Windows – Open the torch box and inspect the injector, torch, and axial and radial for cleanliness. Examine the RF coil for deposits and ensure that it is clean and dry. If any components show signs of build-up or staining, remove them, and clean them as prescribed by the manufacturer. After the components are reinstalled, the axial and radial alignment must be performed as described in Section 10.2.1 and the IEC table must be rebuilt and reverified. Close the torch box carefully and ensure it is sealed. The plasma will not ignite if the torch box is not closed correctly.
- 11.4.5 Instrument Online – The ICP should always stay on standby, unless it has to be completely powered down for a facilities-related issue. If the ICP has been turned all the way off, the on switch is found on the right side of the instrument. Turn it on and let the ICP equilibrate for at least two hours before turning on the plasma. The computer is turned off at the end of the day to conserve energy. Turn on the computer.
- 11.4.6 prepFAST Autosampler – Verify the autosampler is powered on.
- 11.4.6.1 Fill the 2-L “prepFAST Internal Standard” reagent bottle with a 10-mg/L Y Standard in 2% HNO<sub>3</sub> (See bench sheet - ICP IS and Nitric Acid Rinse Prep). Make sure that the tubing is submerged in the bottle and well below the liquid surface.
- 11.4.6.2 Fill the 2-L “prepFAST Carrier/Diluent” and the 2-L “prepFAST Rinse” reagent bottles with 2% HNO<sub>3</sub> (See bench sheet - ICP IS and Nitric Acid Rinse Prep). Make sure that the tubing is submerged in the bottle and well below the liquid surface.
- 11.4.6.3 Double click on the **ESI SC** icon (Stands for Elemental Scientific-Sample Introduction System). The ESI SC/FAST software **MUST** be initialized first before opening the Syngistix for ICP software. Communication errors will occur if the ESI SC/FAST software is not loaded before the Syngistix software. The autosampler will initialize, the sample probe will move to the Home position and the “Fill” and “Dispense” LED lights on the S400V Syringe Pump will toggle on and off. Confirm that the bottom screen has *Autosampler Initialized* and *Instrument Comm Port Opened* in green before you proceed to other commands. If the autosampler is not properly initialized, the text will be in red, and the syringe pump should be power cycled to re-establish communication. The FAST Method File is called *prepFAST-2\_1500\_Loop.txt*. If the FAST method is edited or changed, the analysis can be drastically affected since the method is optimized for the required sample loop and number of analytes in the method.

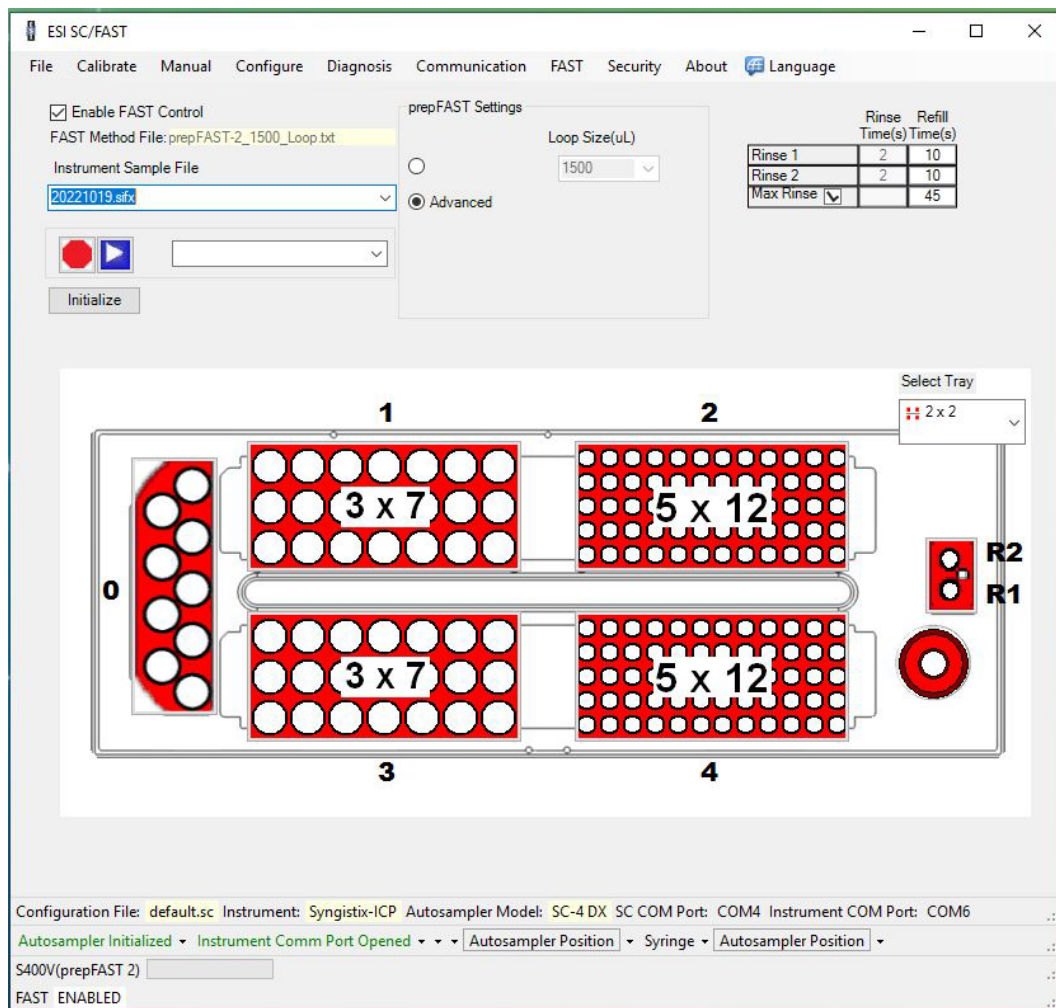
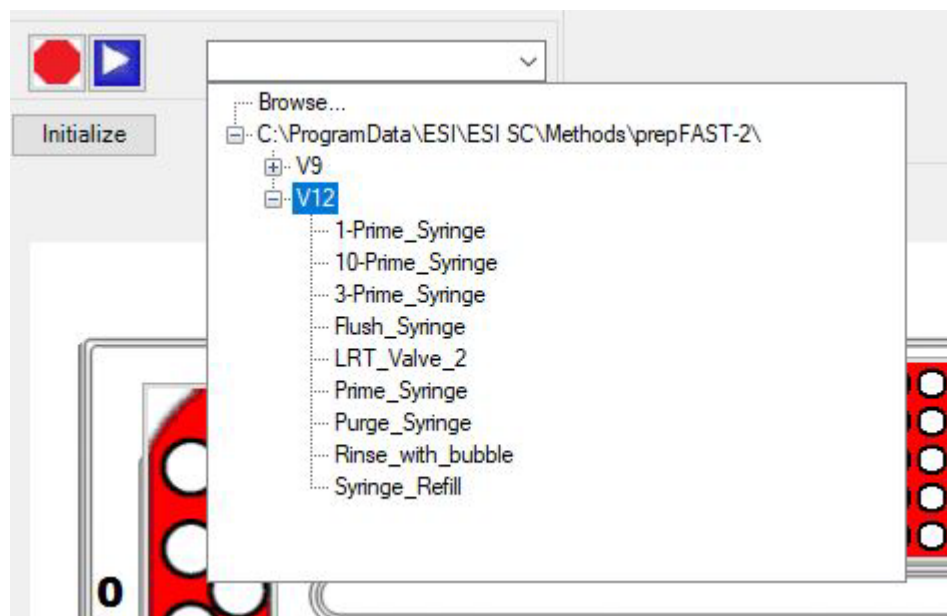


Figure 1. ESI SC/FAST Software Main Screen

- 11.4.6.5 **Prime the Syringes:** In the **ESI SC/FAST Main Screen**, click on the drop down next to the Stop and Play icons. Select one of the “Prime\_Syringe” programs from the drop-down list and then click on the blue Play button. The prime programs may be repeated, as needed. If the reagent bottles were run dry or air was introduced into the lines due to refilling or replacing of the solutions, then a longer prime program is needed. If the ICP instrument was run the day before and no air was introduced, then a shorter prime program is allowed. As the user becomes more familiar with the instrument, the required flushing and priming time per circumstance becomes more obvious.



**Figure 2. Syringe Prime Options**

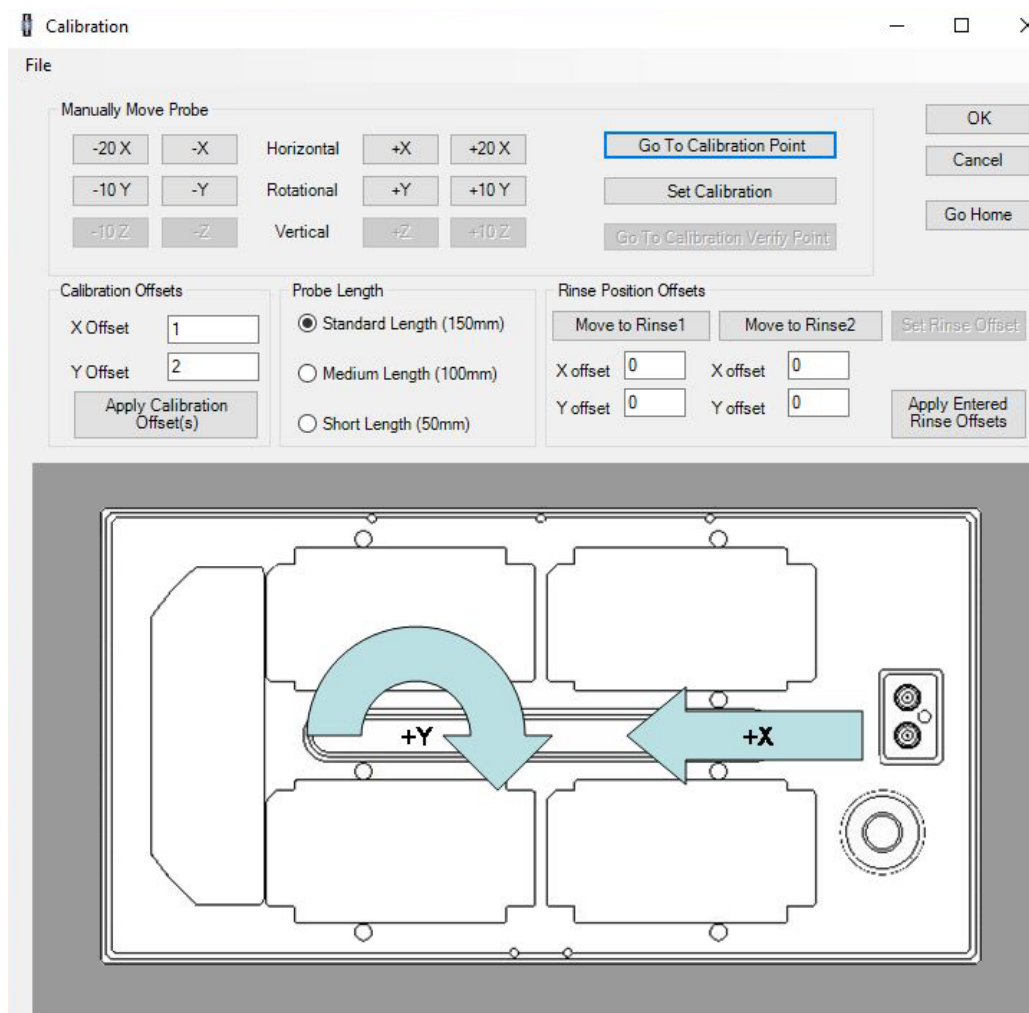


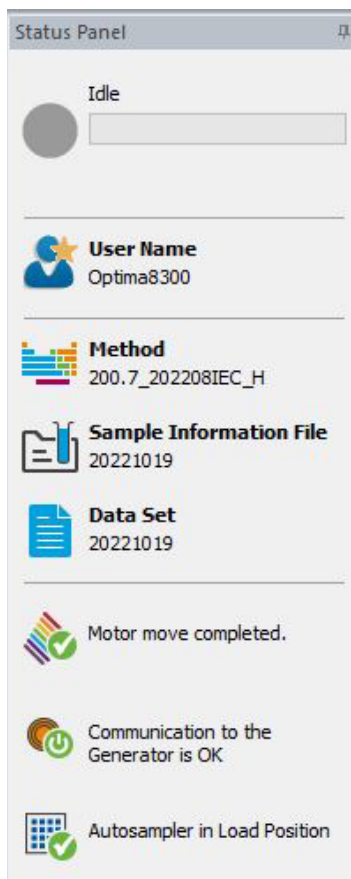
Figure 3. Sample Probe Calibration

- 11.4.6.8 **Peristaltic Pump:** Before every analytical run, change the peristaltic pump tubing – one Black/Black carrier and two Gray/Gray waste lines. All lines should be changed before beginning analysis. The carrier solution tubing is placed on the outermost (left) slot on the pump and the two waste lines are placed on the second and third slots. The right most slot closest to the instrument remains empty. Align pump tubing on the rollers to be in the middle under each magazine arm fitting. If the tubing is not centered in the channel,



then it can disturb the tubing adjacent to it. The peristaltic pump runs **CLOCKWISE**. Make sure to install the tubing on the pump so that the waste liquid is pumped **out** of the spray chamber. If the tubing is installed in the wrong direction, the spray chamber will flood. Place the clamp around the tubing and swing back the cam lever.

- 11.4.6.9 Make sure all 2% HNO<sub>3</sub> rinse bottles on the prepFAST autosampler are filled and place the carrier probe in the 2% HNO<sub>3</sub> bottle by the ICP.
- 11.4.7 Waste Container – Check that the hazardous waste container (under the instrument) is empty or ensure adequate volume remains for the intended sequence.
- 11.4.8 Inspect Sample Introduction System – inspect that all tubing appears to be clean and free of kinks or slits. Examine the nebulizer and the spray chamber for evidence of build-up or other contamination. Inspect the probes and attached tubing and all tubing to/from the prepFAST valves and syringe pump. If any of the tubing appear to be dirty, discolored, blocked, or damaged, remove and clean it or replace it before continuing on.
- 11.4.9 Start Syngistix Software: Double click on the **Syngistix for ICP** icon. The Status Panel will be on the right of the screen. Check for startup errors and address as needed, ensure all devices are connected and check that the software is in the Online mode – not Offline mode. If all is correct, all components of the status panel will have a green check mark indicating the ICP is communicating correctly with the different accessories.





## 11.5 Instrument Operating Procedure: Ignition

11.5.1 Igniting the Plasma: In the **Instrument** tab, click on **Plasma Control** and the **Plasma Control** dialog opens. Click the blue power button to ignite plasma. The ignition of the plasma takes a minute or so. Torch and nebulizer gases are now activated. Confirm there is carrier flow into the nebulizer and waste flow out of the spray chamber. If there is no flow, make sure tubing is clamped to the pump correctly, ensure tubing was placed in the correct direction of flow, check peristaltic tension, and look for kinks or slits in the tubing. The flow pattern of the spray chamber waste line should be smooth and steady. If the flow is not steady, adjust the tension on the control screws. Make sure that there is no leakage at any of the tubing connections. During usual operation, the plasma should be smooth inside the torch, gradually tailing as the plasma moves away from the torch and the plasma should appear bluish-white in color. Remember to allow 30-60 minutes for the plasma and torch box to achieve thermal equilibrium before beginning analysis. If this is not done, a significant amount of signal drift may be evident during analysis.

11.5.1.1 If there is a problem with ignition, the plasma will not light, and the power button will be grayed out. Plasma ignition should occur on demand. Occasionally, two or three attempts are necessary to light the plasma, especially if room air has entered the gas lines or water is in the compressed air lines. Check the sample introduction system to ensure all connections are made and air is not leaking into the system. Click on the **Instrument** tab and in the **Utilities** group, select **Diagnostics** to look at the instrument message history. Any problems with the spectrometer, plasma, and autosampler are contained in this log.

11.5.1.2 It is not recommended to begin troubleshooting ignition problems by changing the plasma conditions or torch parameters, as doing so will alter IEC factors and require a new table.

11.5.1.3 Once the plasma is lit, allow the instrument to stabilize for 60 minutes before starting any analysis.

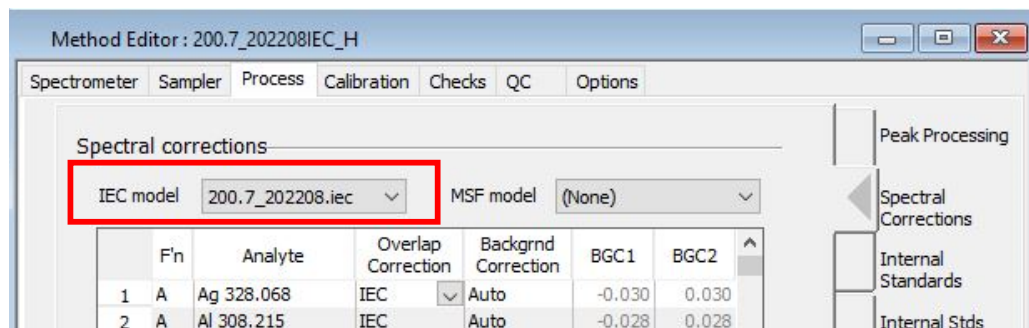
## 11.6 Instrument Operating Procedure: Set Up Analysis – Instrument Method

***Syngistix for ICP Software Guide (8) gives step-by-step instructions for setting up a new Instrument Method in the Method Editor Chapter, pages 43 to 105.***

11.6.1 Open the existing instrument method by clicking on the **Analysis** tab and pressing **Open** in the **Method** group.

11.6.1.1 If performing an analytical run to generate an IEC table, then the instrument method must have IEC off. **If analyzing samples, the instrument method must have the most current IEC routine loaded.**





11.6.2 Changes to the analytical parameters like background points, points per peak, viewing mode and internal standard selection are not allowed on a day-to-day basis and should only be made if a new instrument method is being created. The instrument method with the IEC table engaged for sample analysis must, at its core, remain the same as the instrument method used to generate the IEC table. Otherwise, the correction routine may not work properly.

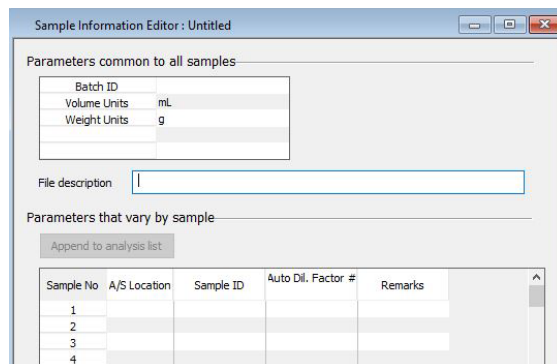
11.6.2.1 Changes to the instrument method that do not affect analytical parameters, like autosampler location of calibration standards, updating QC control limits, adding or removing QC elements, etc. are allowed.

## 11.7 Instrument Operating Procedure: Set Up Analysis – Sample Information List

***Syngistix for ICP Software Guide (8) gives step-by-step instructions for setting up the Sample Information File in the Sample Information Editor Chapter, pages 107 to 135.***

11.7.1 The sample information file is used to store information about the samples. Enter IDs for samples in the sample information file. Enter IDs for the blanks, standards, and QC samples in the Method Editor. If you enter IDs for blanks, standards, or QC samples in the Sample Information Editor, these solutions are analyzed as samples. This may be necessary if there are more than 20 QC samples because the Method Editor only allows for 20 QC Samples.

11.7.2 To display the Sample Information Editor, go to the On the **Analysis** tab, in the Sample Information group, click the **New** button. Select the "ESI-prepFAST.sidx" and click **OK**. Alternatively, an existing Sample Information File may be opened and edited for the intended analysis. Do make certain to not overwrite the existing file and instead save as a new file.





- 11.7.3 The <Batch ID> shall be set as the date of the run, using four integers for the year, two for the month and two for the day, i.e., YYYYMMDD or 20221015.
- 11.7.4 In the <File Description> field list the sample login batch.
- 11.7.5 In the <A/S Loc> column, enter the locations of the samples using “401” for the front left position on the front right autosampler rack (Rack 4). Racks 1 and 3 are typically used for calibration standards and QC samples. However, the autosampler trays can be swapped as the user sees fit to maximize sample throughput and to better suit the analysis being conducted. Do make certain not to use the same autosampler location for two different samples, see Section 11.8.1.1 on how to check autosampler locations prior to beginning analysis.
- 11.7.6 In the <Sample ID> column, enter the sample ID, any manual dilution factor and other pertinent information (e.g., 2202405 (1.06) LFM). The number in the parenthesis is the manual dilution factor. There is a 25 characters limit for this field.
- 11.7.7 Entering 1 in the <Auto Dil Factor #> column will result in no automatic dilution. This auto dilution feature is rarely used because the values produced by the analysis will automatically be corrected for the dilution, i.e., only final results will be produced, and raw results are omitted. The raw results are needed for data entry into the LIMS. The raw results can be back calculated from the final results, but it is not customary for our program to do this.
- 11.7.8 In the <Remarks> column, enter any relevant information concerning the sample's analysis or sample conditions.
- 11.7.9 For samples digested from solid material: enter the mass of the original solid in grams (g) in the <Initial Sample Wt.> column and enter the final volume at the end of digestion in milliliters (mL) in the <Sample Prep. Vol.> column.
- 11.7.9.1 These columns or parameters are not defaulted into the Sample Information File Editor since they are not commonly used. Click on **Parameter List** in the **Sample Information** group of the **Analysis** tab. The **Sample Information Parameters** dialog appears, and the desired fields can then be selected. Click **OK** when all appropriate fields have been selected. The Sample Information File Editor will automatically update to contain the added fields.

Sample Information Parameters ? X

Common Parameters	Available Parameters	Variable Parameters
Batch ID Volume Units Weight Units	Aliquot Volume Analyst Name Analyze QCs Before * Diluted To Vol. Initial Sample Vol. Initial Sample Wt. Matrix Check Samples Nominal Sample Wt. Read Delay * Reagent Blanks Used Recalibrate Before * Sample Limits * Sample Prep. Vol.	A/S Location Sample ID Auto Dil. Factor # Remarks

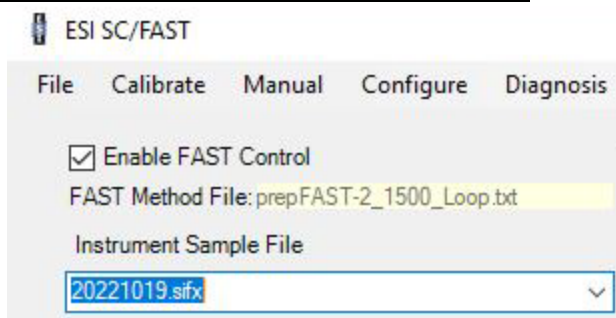
\* Overrides settings in the method # Pertains to prepFAST

OK Cancel





- 11.7.10 Once all changes have been made, save the Sample Information List with the Batch ID from Section 11.7.3 by clicking **Save** in the **Sample Information** group of the **Analysis** tab.
- 11.7.11 Open the ESI SC/FAST Software and select the current Sample Information File from the drop-down list. It is **CRITICAL** for accurate sample analysis that the correct Sample Information File be loaded in the ESI SC/FAST software.



## 11.8 Instrument Operating Procedure: Sample Analysis

- 11.8.1 Prepare the calibration standards, samples, and QC samples for analysis, including any necessary dilutions or spikes. Place the prepared samples in the appropriate autosampler rack.
- 11.8.1.1 Generate the autosampler loading list by clicking on **Autosampler Load List** in the **Analyze** group of the **Analysis** tab. Print the loading list by clicking on the **Syngistix** icon button in the upper left corner of the application and then select **Print Active Window**. The autosampler loading list is used to ensure the correct sample vial is placed in the autosampler position indicated in the Sample Information File.
- 11.8.2 In the Syngistix software, click on **Analysis** in the **Analyze** group of the **Analysis** tab. The **Analysis** dialog window opens. Select the **Manual** tab in the Analysis window.
- 11.8.2.1 Analyze at least three Calibration Blanks by clicking the **Analyze Blank** button. This should be done before beginning sample analysis to rinse out the sample introduction system and to ready the instrument for analysis. It not necessary to save these determinations to a dataset.
- 11.8.3 In the Syngistix software, click on **Analysis** in the **Analyze** group of the **Analysis** tab. The **Analysis** dialog window opens. Select the **Automated** tab in the Analysis window.
- 11.8.3.1 Verify the appropriate method is selected in the queue. If not, double-click the first cell under "Method" and select the appropriate method. Make sure "All Defined" is selected on the Define Samples column.
- 11.8.3.2 Look at the file name listed below "Use Sample Info". If it is not the same as the desired sample information file, click on the **Open** button (it looks like a folder within the field) and select the desire file name. Ensure the box for "Use Sample Info" is checked.



- 11.8.3.3 Click on the **Open** button below the “Save data to Results Data Set”. Enter a name identical to the batch ID used in the Sample Information File in Section 11.7.10, list the login batch numbers in the “Description” field and click **OK**. If multiple analytical runs are performed in one day, then add the suffix “A” to the name the second run of the day, and “B” to the third run of the day, and so on. Ensure the box for Save data to Results Data Set” is checked.

The screenshot shows the 'Analysis' software window with the 'Automated' tab selected. The 'Method source' section has 'Use the active method for your analysis' selected. The 'Define Samples' table is visible, and the 'Save data to Results Data Set' checkbox is checked. The 'Run list' table on the right contains the following data:

Seq.	Loc.	Type	Sample ID	Status
1	1		Cal Blank	
2	101		Group 1A S1	
3	102		Group 1A S2	
4	103		Group 1A S3	
5	104		Group 1B S1	
6	105		Group 1B S2	
7	107		Group 2 S1	
8	108		Group 2 S2	
9	109		Group 2 S3	
10	110		Group 3 S1	
11	111		Group 3 S2	
12	112		Group 3 S3	
13	113		Group 4A S1	
14	114		Group 4A S2	
15	116		Group 4B S1	
16	117		Group 4B S2	
17	118		Group 4B S3	
18	119		Group 5 S1	
19	120		Group 5 S2	
20	121		Group 5 S3	
21	102		G1A IPC-ICV	
22	105		G1B IPC-ICV	
23	108		G2 IPC-ICV	
24	111		G3 IPC-ICV	
25	114		G4A IPC-ICV	
26	117		G4B IPC-ICV	

- 11.8.3.4 Make sure all samples and QC appear in the sample list in the order desired. If they do not, edit the Sample Information File as needed and click the **Rebuild list** button. Once the sample list is updated and confirmed, click on **Print list**. This is the planned analytical sequence and **must** be included in the data packet.
- 11.8.3.5 Click on **Analyze All** to begin the analytical run. Ensure the plasma has been on and the instrument has equilibrated for at least 60 minutes before starting.
- 11.8.3.6 An interrupted calibration and sample analysis cycle can be activated by first clicking **Calibrate** and once the calibration curve is acquired, then clicking **Analyze Samples**. This allows for a pause between the calibration and sample analysis. It is up to the analyst's discretion which feature they prefer to use.



### Typical Analytical Sequence

Sequence	Sample ID
1	Calibration Blank
2	Calibration Standard Solutions
3	IPC-ICV(s), $\pm 5\%$ of TV
4	ICB, $< \frac{3}{4}$  MRL
5	QCS(s), $\pm 5\%$ of TV
6	LRB, $< \frac{3}{4}$  MRL
7	LFB(s), $\pm 15\%$ of TV
8	MRL Checks, $\pm 20\%$ of TV
9	IPC-CCV(s), $\pm 10\%$ of TV
10	CCB, $< \frac{3}{4}$  MRL
11	Sample 1
12	Sample 2
13	Sample 3
14	Sample 4
15	Sample 5
16	Sample 6
17	Sample 7
18	Sample 8
19	Sample 8 Duplicate, RPD $< 20\%$
19	Sample 8 LFM, % Recovery of $\pm 30\%$
20	IPC-CCV(s), $\pm 10\%$ of TV
21	CCB, $< \frac{3}{4}$  MRL
22	Additional sets of $\leq 10$ samples which may include LFB(s) ( $\pm 15\%$ of TV), LRB(s) Sample Duplicate(s), and LFM(s) as necessary
22	IPC-CCV(s), $\pm 10\%$ of TV
23	CCB, $< \frac{3}{4}$  MRL
24	$\leq 10$ SIC standards, $\pm 10\%$ of TV for interferent and all un-spike analytes $<  MRL $
25	IPC-CCV(s), $\pm 10\%$ of TV
26	CCB, $< \frac{3}{4}$  MRL
27	Additional sets of $\leq 10$ SIC standards
28	IPC-CCV(s), $\pm 10\%$ of TV
29	CCB, $< \frac{3}{4}$  MRL
30	$\leq 10$ LDR Checks, $\pm 10\%$ of TV
31	IPC-CCV(s), $\pm 10\%$ of TV
32	CCB, $< \frac{3}{4}$  MRL



- 11.8.4 Once the calibration blank has been acquired, document the yttrium internal standard counts in both axial and radial mode in the ICP maintenance logbook, Section 11.10. The purpose of this is track the intensity of an analyte (Y in this case) to check the instrument's sensitivity trends.
- 11.8.5 In the **Results** tab, in the **Results** group click on **Data Viewer**. Use this screen to Monitor the results of the QC samples and field samples as the analytical run is in progress. If recoveries are not within specifications, stop the run and troubleshoot.
- 11.8.6 Monitor the volume of the rinse bottles, blank bottle, and standards vials. If bottles need to be replenished, do so before levels get too low as possible air bubbles could be introduced into the various lines if levels are low. Make sure the waste jug does not get too full, otherwise, backpressure could occur.
- 11.8.7 The sample probe moves quickly during the run. If the sample probe arm gets hit and interrupted, then the sample probe will be out of alignment. Stop the run, align the probe, and restart the run. It is best to put all standards and sample vials into the trays before beginning analysis.
- 11.8.8 Once the run has finished, in the Analysis window click on **Print list** to print the actual analytical sequence with the status of each determination. This is the actual analytical sequence and **must** be included in the data packet.
- 11.8.9 Once all determinations have been finished for the day, perform the following:
- 11.8.9.1 Rinse the system.
  - 11.8.9.2 Turn off the plasma.
  - 11.8.9.3 Release peristaltic pump tubing from the clamp and rollers.
  - 11.8.9.4 Cover and store all solutions.
  - 11.8.9.5 Bring hazardous waste container to the Hazardous Waste Storage Room and empty container contents into the appropriate Inorganic Waste Drum.
- 11.9 **Reprocessing** – A sample dataset can be reprocessed to generate reports, to reload the data, to edit typos in the Sample ID, to change the sample type of Sample (i.e., a standard was analyzed as a sample), to change the concentration or limits of a QC sample, etc. Edits that drastically change the method or analytical parameters are not allowed since it will affect the correction factors, see Section 11.6.2.
- 11.9.1 Confirm that the method loaded in the Method Editor is the appropriate one and that it contains the correct settings for the results data set that is to be reprocessed.
  - 11.9.2 In the **Results** tab, in the **Results** group, click **Reprocess**. The **Data Reprocessing** window appears. Reprocessing cannot be accessed if the Analysis Control Window is open.
  - 11.9.3 In the **Data Reprocessing** window, the “Data set to reprocess” defaults to the dataset from the most recent analysis. To change to a different dataset, click the browse icon in the field and in the **Select Results Data Set** dialog that appears, select the results data set that contains the data desired for reprocessing.



- 11.9.4 Click the **Save reprocessed data** check-box to activate the **Save reprocessed data to** field. Click on the browse icon in this field and type a new data set name or select an existing one. If an existing dataset is selected, the existing dataset will not get overwritten instead the reprocessed data will be appended to the end of the dataset.
- 11.9.5 In the **Data Reprocessing** dialog table, review the information. The Sample IDs and all other sample information listed in the table come from the original dataset file. To edit this information, type the new information into the fields as desired. To access a pop-up menu containing commands for editing the table, right click anywhere in the table. To hide columns that do not contain data, select the **Hide Empty Columns** check box.
- 11.9.6 To select items of interest for reprocessing, select the associated row numbers in the table. To select a series of rows, click on the first-row number of interest, hold down the **Shift** key, and click on the last-row number of interest. You can also drag over the row numbers column using the mouse cursor. The order in which samples are selected is the order in which reprocessing occurs. As you select each row, the reprocessing sequence appears in the Sequence column.
- 11.9.7 Click on **Reprocess**.

Seq.	Sample ID	Sample Type	Omit Replicates	Matrix Check Samples	Date Time	Initial Sample Wt.	S
1	Cal Blank	Calib Blank 1			10/19/2022 9:58:13 AM		
2	Group 1A S1	Calib Std. 1			10/19/2022 10:00:42 AM		
3	Group 1A S2	Calib Std. 2			10/19/2022 10:02:47 AM		
4	Group 1A S3	Calib Std. 3			10/19/2022 10:04:53 AM		
5	Group 1B S1	Calib Std. 4			10/19/2022 10:07:06 AM		
6	Group 1B S2	Calib Std. 5			10/19/2022 10:09:03 AM		
7	Group 2 S1	Calib Std. 6			10/19/2022 10:10:56 AM		
8	Group 2 S2	Calib Std. 7			10/19/2022 10:12:27 AM		
9	Group 2 S3	Calib Std. 8			10/19/2022 10:13:57 AM		
10	Group 3 S1	Calib Std. 9			10/19/2022 10:15:36 AM		
11	Group 3 S2	Calib Std. 10			10/19/2022 10:17:24 AM		
12	Group 3 S3	Calib Std. 11			10/19/2022 10:19:11 AM		
13	Group 4A S1	Calib Std. 12			10/19/2022 10:21:10 AM		
14	Group 4A S2	Calib Std. 13			10/19/2022 10:22:38 AM		
15	Group 4B S1	Calib Std. 14			10/19/2022 10:24:05 AM		
16	Group 4B S2	Calib Std. 15			10/19/2022 10:25:54 AM		
17	Group 4B S3	Calib Std. 16			10/19/2022 10:27:43 AM		
18	Group 5 S1	Calib Std. 17			10/19/2022 10:29:23 AM		
19	Group 5 S2	Calib Std. 18			10/19/2022 10:31:13 AM		

\* Overrides settings in the method      > Samples contain Universal Data Acquisition

Figure 10. Data Reprocessing Window





## 11.10 Maintenance

The following actions are performed on days the instrument is used. All maintenance performed is logged in the ICP maintenance logbook. In the Customer Hardware and Service Guide (7), Chapter 5 provides the needed information on Maintenance and Chapter 6 gives information on Troubleshooting. The prepFAST Method Guide-Optima Syngistix ICP pamphlet (12) gives step-by-step instructions on how to configure, prime, and set up a method for the autosampler.

### 11.10.1 Logbook – Record the following when conducting analysis or any maintenance on the ICP-OES.

11.10.1.1 Write a description of any issues that arise, such as frequent QC failures, plasma related issues, problems with the software, etc.

11.10.1.2 Record when maintenance is performed and note which parts are replaced.

11.10.1.3 Document service calls and the resolutions to the problem(s).

11.10.1.4 When performing an analytical run, document the yttrium intensity of the calibration blank. Record yttrium intensities in both axial and radial mode and their RDSs. Date and initial each entry.

## 11.11 Printing Reports

### 11.11.1 Generate detailed results report using Data Manager:

11.11.1.1 Double-click on the **Data Manager** icon to load the application. See the Syngistix Data Management Software Guide (9) for detailed steps on how to manage data, prepare reports, and create exports of the data.

11.11.1.2 In the Data Manager application, ensure the **Results** library is loaded. A list of the result dataset files in the library will appear on the left of the screen.

11.11.1.3 Highlight the datafile to be reported and click on the **Report** icon in the **Reporting** group. The **Data Reporting Wizard** appears and the first step is to choose whether to “Create new design” or “Use existing design”.

11.11.1.3.1 If the radio button for “Use existing design” is chosen then the **Open** button (looks like a folder) must be clicked to select the existing report design. Pick the desired design and click **Open**. The report design is now loaded into the **Data Reporting Wizard**. Click Preview to see a snapshot of the report. If the report looks good, then click on the **Printer** icon. Normally, the report is also saved as a PDF file to keep a soft copy record of the reports.

11.11.1.3.2 If the radio button for “Create new design” is selected then follow the prompts of the **Data Reporting Wizard** to create a report format with the desired analyte wavelengths, samples, and layout desired. Preview may be chosen on any page at any time to see the current report format.

11.11.1.4 This is the Optima Report and **must** be included in the data packet.





11.11.2 Generate detailed calibration curve report using Reprocessing:

11.11.2.1 Click on **Clear** in the **Results** group of the **Results** tab to delete the results log.

11.11.2.2 Click on **Reprocess** in the **Results** group of the **Results** tab to open the Data Reprocessing window, see Section 11.9. Load the desired dataset and only select the calibration standards. Click **Reprocess**.

**Note:** For this report to work, the detailed calibration summary must be checked in the Options tab of the Method Editor.

11.11.2.3 Click on the **Results** icon in the **Results** group of the **Results** tab. The Results window appears with the detailed calibration summary. Print the Results log with the calibration summary by clicking on the **Syngistix** icon button in the upper left corner of the application and then select **Print Active Window**.

11.12 **Library Manager:** It is very important to maintain the Library Manager. Maintenance of the Library is performed semi-annually or as needed. See the Syngistix Data Management Software Guide (9) for detailed steps on how to archive, delete, and pack the libraries.

11.12.1 It is best to perform management of the Results library when the Syngistix for ICP software is not in use. Otherwise, some functions of the Data Manager application will not function correctly.

11.12.2 Double-click on the **Data Manager** icon to load the application. Ensure the **Results** library is loaded. A list of the result dataset files in the library will appear on the left of the screen. Highlight all desired dataset files. Multiple dataset files may be selected by holding down the CTRL key.

11.12.3 Click on **Check** icon in the **Maintenance** group to check the dataset files for errors.

11.12.4 Click on **Archive** icon in the **Maintenance** group. The **Archive Data Sets** dialog window appears. Ensure the box for "Remove data after archive" is selected. The file path for Archive has a default location, but an alternate file path may be used if needed. Click on **Archive**. The archiving process may take several minutes depending upon the size and number of files being archived. Dataset files may be restored from archive at any time.

11.12.4.1 The Methods library could also be archived, if desired. Switch to the Methods library by clicking on the dropdown list next to Library Category. Archiving of the methods library not typically done since the method files are much smaller than the dataset files.

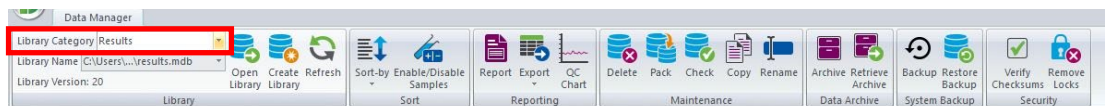


Figure 11. Data Manager Ribbon- Library Selection

11.12.5 After the dataset files have been archived and deleted from the active library. The library must be packed to reduce its size and thus reduce the space it occupies on the computer's hard drive. The library size does not reduce automatically when data sets are deleted. Click on **Pack** icon in the **Maintenance** group. The **Pack Library** dialog window



appears with the link to the library being packed. Click on **Pack**. This will not work if the Syngistix for ICP software application is open.

- 11.12.6 The archived dataset files are then backed-up to the WES SharePoint server by saving the files to a thumb drive and transferring to a computer connected to the network server.

## 12.0 DATA ANALYSIS AND CALCULATIONS

- 12.1 Sample data are reported in units of mg/L for aqueous samples and mg/kg dry weight for solid samples.
- 12.2 For all analytes, report the data generated directly from the instrument with allowance for sample dilution. All raw results are recorded in the MassDEP/WES LIMS, WinLIMS, as reported by Syngistix. WinLIMS is configured to report all values less than the MRL as < MRL, with the MRL concentration stated.
- 12.3 If the MRL or blank(s) fail for an analyte, raise the MRL to the next highest level if the end users' data quality objectives are still met.
- 12.4 For total recoverable analytes in solid samples, the (C) concentration in mg/kg is calculated as follows:

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

where:

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

- 12.5 To report percent solids in solid samples (Section 11.3) calculate as follows:

$$\% \text{ Solids (S)} = \frac{DW}{WW} \times 100$$

where:

- DW = Sample weight (g) dried at 60°C  
WW = Sample weight (g) before drying

**Note:** If the data user or program requires that the reported percent solids be determined by drying at 105°C, repeat the procedure referenced in Section 11.3 using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

## 13.0 METHOD PERFORMANCE

- 13.1 MDL studies are performed for direct analysis and total recoverable metals determined for the wavelengths used in this method. The MDLs were determined in reagent water matrix acidified to 2% HNO<sub>3</sub>. MRLs are then determined from the MDL studies. The results are electronically stored.



## 14.0 MAINTENANCE

- 14.1 Maintenance on the Optima 8300 DV ICP-OES is performed by the lead analyst before starting analyses, See Section 11.4. Major maintenance operations are performed by a PerkinElmer Customer Service Engineer. Service calls are placed to the company when the lead analyst is not capable of performing the required maintenance. Service call reports are kept on file.

## 15.0 POLLUTION PREVENTION

- 15.1 Refer to the WES Environmental Management System (EMS) policy and SOPs regarding pollution prevention.
- 15.2 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.

## 16.0 WASTE MANAGEMENT

- 16.1 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.
- 16.2 All chemical waste is collected in sealed waste containers. Once the waste containers reach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste drum (organic or inorganic). Within 180-days of waste accumulation, the waste drum is transported off the premises by a licensed hazardous waste management contractor. Under the WES EMS, a chemical inventory database has been developed to track purchases and use of chemicals and other hazardous materials, and the waste generated using these chemicals.

## 17.0 REFERENCES

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7. Perkin-Elmer, Inc. 2014. *Optima 8300 – Customer Hardware and Service Guide*, 330 pp. Part # 0991132.
8. Perkin-Elmer, Inc. 2014. *Syngistix Software Guide*, Revision 1.0, 264 pp. Part # 09931145.
9. Perkin-Elmer, Inc. 2014. *Syngistix Data Management Software*, Revision 1.0, 108 pp. Part # 09931146.
10. Elemental Scientific, M-14115 prepFAST S400V Basic Operation Manual, 8 pp.
11. U.S. Environmental Protection Agency. 2016. Revision 2 Text – *Definition and Procedure for the Determination of the Method Detection Limit from 40 CFR 136, Appendix B*, December 2016.
12. Elemental Scientific, M-14025 prepFAST Method Guide-Optima Syngistix ICP, 16pp



## 18.0 TABLES

**TABLE 1. Quality Control Elements and Acceptance Criteria for EPA Method 200.7 – Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry**

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Every run.	$r^2 > 0.995$	Determine the cause and recalibrate with new standards.
Internal Standard	Every run. Yttrium is added to all standards and sample solutions.	Internal Standard Recoveries: 80-120% of response found in Calibration Blank. RSDs should be less than 3%.	Check Yttrium flow rate. Suspect a sample introduction issue if RSDs are high. Responses outside 80-120% may indicate matrix effect; dilute sample and reanalyze.
Instrument Performance Check (IPC-ICV, IPC-CCV)	Immediately following each calibration (IPC-ICV), after every tenth sample (IPC-CCV) and at the end of the run (IPC-CCV).	IPC-ICV ( $\pm 5\%$ ) Concentration = the midpoint calibration standard. IPC-CCV ( $\pm 10\%$ ) Concentration = 2 mg/L for all analytes, except Ag is 0.25 mg/L; K, P and SiO <sub>2</sub> are at 10 mg/L.	Reanalyze IPC. If outside range, recalibrate, and re-analyze sample(s) since last successful IPC-CCV, or discontinue & recalibrate instrument if necessary.
Calibration Blank (ICB, CCB)	Immediately following each IPC-ICV (ICB) and after every IPC-CCV (CCB).	$< 2.2$ times the analyte MDL ( $< 3/4$  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)	After calibration.	95-105% recovery from triplicate determinations.	Acceptable range must be met before continuing with sample analysis. Recalibrate and repeat.
Laboratory Reagent Blank (LRB)	One with each batch of 20 or fewer samples.	$< 2.2$ times the analyte MDL ( $< 3/4$  MRL ) or $< 10\%$ of the analyte level measured in the sample.	Determine and eliminate the source of contamination and then repeat sample analysis. 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.



**TABLE 1. Quality Control Elements and Acceptance Criteria for EPA Method 200.7 – Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry**

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Laboratory Fortified Blank (LFB)	One with each batch of 20 or fewer samples.	Recovery: 85 – 115%	The source of the problem must be identified and resolved before continuing analysis. If reanalysis is not possible, the data are qualified.
Minimum Reporting Level (MRL) Check Standard	With every analytical run and before sample analysis.	Recovery: 80 – 120% ( $\pm 20\%$ ) 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 analytical run, raise the MRL to the lowest standard which meets the MRL check criteria. If the problem persists, suspect that the MDL and MRL are too low for the analytical conditions.
Laboratory Duplicate	One with every 10 or fewer samples.	Relative percent difference among duplicates (RPD) $\leq 20\%$ .	Repeat analysis with new aliquots if suspect result in error or qualify the data. If the sample is non-homogenous, note this with the duplicate's result in the LIMS report. If reanalysis is not possible, the data may be qualified.
Laboratory Fortified Matrix (LFM)	One with every 10 or fewer samples.	Recovery: 70 – 130% Note: Recovery calculations are not reported 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.
Spectral Interference Check (SIC)	For analytes with documented interferences (see Tables 2A and 2B), the appropriate single element SIC standard(s) are analyzed with every analytical batch. Analyzed at the end of the run after sample analysis.	Recovery of 90-110% for the single element in the SIC standard. The analyte of interest (not spiked into SIC standard) should have concentration values $< [MRL]$ .	The interferent concentration should be below the upper limit of the LDR and 90-100% recovery must be met. If un-spiked analyte is $> [MRL]$ and contamination or error in the standard prep is suspected, re-prepare the standard and analyze. If the fresh standard still fails, a new IEC table may be needed.





**TABLE 1. Quality Control Elements and Acceptance Criteria for EPA Method 200.7 – Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry**

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Linear Dynamic Range (LDR) Check	Included with every analytical batch with samples that have results exceeding the calibration curve. Analyzed at the end of the run after sample analysis.	Recovery: 90 – 110%	If contamination or error in the standard prep is suspected, re-prepare the standard and analyze. If the fresh standard still fails, samples with analyte results over the calibration curve must be diluted to fall within the curve.
Method Detection Limit (MDL) Determination (Revision 2)	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 (ideally 1 to 5x) the experimentally determined MDL.	Repeat MDL study spiking the blank matrix with lower concentration of the target analyte
Linear Dynamic Range (LDR)	Every year or whenever there is a change in instrument hardware or operating conditions, by judgment of the analyst.	Recovery: 90 – 110%	If change in instrument, change upper limit of LDR to new values. If no change in instrument, check/service instrument. If instrument functioning correctly, change LDR.



**TABLE 2A. On-Line Method Interelement Spectral Interferences for Recommended Analytes in Reagent Water from Analytical Run on 01/26/2022**

Analyte	Wavelength (nm)	Minimum Analyte Concentration for Interference Correction (mg/L)	Interferent(s)*
Silver (Ag)	328.068	0.010	Mo, Mn, Ca
Aluminum (Al)	308.215	0.25	V, Ce, Mo
Arsenic (As)	193.696	0.125	V
Boron (B)	249.677	0.010	Co, Ti, Cr, Ba, Mn, Fe
Barium (Ba)	493.408	0.0025	Sr, Ce
Beryllium (Be)	313.042	0.0025	V, Ce
Calcium (Ca)	315.887	0.10	Co, Mo, Ce
Cadmium (Cd)	226.502	0.020	Fe
Cerium (Ce)	413.764	0.0050	Mo, Ca
Cobalt (Co)	228.616	0.010	Ti
Chromium (Cr)	205.560	0.010	Ni, Mo, V, Ce
Copper (Cu)	324.752	0.0025	Mo, Ba, Ti, Mn, Sr, Se, Ce, Mg, Co, Fe
Iron (Fe)	259.939	0.010	Mo, V, Mn
Potassium (K)	766.490	0.25	None
Lithium (Li)	670.784	0.010	Sn
Magnesium (Mg)	279.077	0.10	Fe, Mn
Manganese (Mn)	257.610	0.0025	Ce
Molybdenum (Mo)	203.845	0.020	Ti, Ce
Sodium (Na)	588.995	0.10	Ce
Nickel (Ni)	231.604	0.020	Co, Ti, Ce
Phosphorus (P)	214.914	0.125	Cu, Li, Mo, Fe
Lead (Pb)	220.353	0.020	Cu, Ce, Ti, Ca
Antimony (Sb)	206.836	0.050	Cr, Ti, Ca
Selenium (Se)	196.026	0.050	Be, Ce, Mn
Silicon (Si)	251.611	0.050	Mo, Ti, Fe
Tin (Sn)	189.927	0.10	Mg
Strontium (Sr)	421.552	0.0005	Ca, Ba, Ce, Al, Fe
Titanium (Ti)	334.940	0.0005	Cr, Cu, Ce, Co, V, Ca
Thallium (Tl)	190.801	0.10	Mo, Co, Ce, V
Vanadium (V)	292.402	0.020	Mo
Zinc (Zn)	213.857	0.020	Ni, Cu, Fe

\*Observed interferents depend on the minimum analyte concentration for interference correction and on the concentration of the interference standard analyzed. Interferents are ranked by magnitude of intensity with the most severe interferent listed first in the row.



**TABLE 2B. On-Line Method Interelement Spectral Interferences for Secondary Analytes in Reagent Water from Analytical Run on 01/26/2022**

Analyte	Wavelength (nm)	Minimum Analyte Concentration for Interference Correction (mg/L)	Interferent(s)*
Aluminum (Al)	396.153	0.10	Mo, Ce, Ca
Arsenic (As)	188.979	0.125	Mo, Cr, Ca
Barium (Ba)	233.527	0.0050	V, Fe
Beryllium (Be)	313.107	0.0050	Ce
Calcium (Ca)	317.933	0.10	None
Copper (Cu)	327.393	0.0050	Co, Ti, Ce, Ba, Mn, Se
Iron (Fe)	238.204	0.0050	Co, V, Sb
Magnesium (Mg)	285.213	0.0050	Cr
Manganese (Mn)	259.372	0.010	Mo, Fe
Molybdenum (Mo)	202.031	0.010	None
Sodium (Na)	589.592	0.050	Mo, Ce
Nickel (Ni)	221.648	0.010	Si, Co, Ce
Lead (Pb)	217.000	0.25	Sb, Mo, P, Al, Fe
Antimony (Sb)	217.582	0.10	V, Pb
Vanadium (V)	290.880	0.050	Mo, Mg

\*Observed interferents depend on the minimum analyte concentration for interference correction and on the concentration of the interference standard analyzed. Interferents are ranked by magnitude of intensity with the most severe interferent listed first in the row.

**TABLE 3. Mixed Calibration Standard Solutions**

Solution Name	Analytes
Group 1A	Ag, As, B, Ba, Ca, Cd, Cu, Mn, Se, and Sr
Group 1B	Sb
Group 2	K, Li, Mo, Na, and Ti
Group 3	Ce, Co, P, and V
Group 4A	Al, Cr, Hg, and Zn
Group 4B	SiO <sub>2</sub> and Sn
Group 5	Be, Fe, Mg, Ni, Pb, and Tl