Illinois State Water Survey
Health and Environmental Application Laboratory

Standard Operating Procedure
For the Determination of
Calcium, Magnesium, Sodium, Potassium,
Iron, Manganese, Silicon
by Inductively Coupled Plasma-Optical Emission Spectroscopy

(based on USEPA method 200.7 r4.4)

SOP Number: AN.HEAL.IN.ICP-cations

Revision 6.2 effective 8 October 2024

Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820-7495

NOTE THE HEALTH AND SAFETY WARNINGS IN Section 4.0

Prepared by:________________________ Date: 01/07/2025
Rita Bargon, Quality Assurance Officer

Approved by:________________________ Date: 01/07/2025
Evan Rea, HEAL Director

The following individuals (in addition to those listed on the cover) have reviewed this SOP:

Anthony Kilber Anthony Kilber 01/07/2025
Name (printed) Signature Date

Rachel Van Allen Rachel Van Allen 01/07/2025
Name (printed) Signature Date

Name (printed) Signature Date

Name (printed) Signature Date

Name (printed) Signature Date

Name (printed) Signature Date

Name (printed) Signature Date

Beginning Revision	Ending Revision	Revision Date	Changes
4.0	5.0	6/7/21	Revisions added throughout to clarify the procedure, updated computer directory locations
5.0	6.0	9/15/23	Changed QC scheme to align with other HEAL activities, major grammatical and formatting updates, section order changed to match other SOPs
6.0	6.1	7/17/24	Added calibration standards, combined NEON wet deposition and water chemistry projects
6.1	6.2	10/8/24	Updated title, instrument set-up, and maintenance section.

Contents

1.0 Scope & Applicability

1.1 Method Application

The USEPA 200.7 method “Determination of Method and Trace Elements in Water and Wastes by Inductively Coupled Plasma Atomic Emission Spectroscopy” is followed. This method is applicable to the determination of calcium, magnesium, sodium and potassium in precipitation samples by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Samples are analyzed at room temperature.

1.2 Scope

This method is appropriate for the analysis of ions in wet deposition samples in the following ranges:

Ca = 0.020 to 10.0 mg/L
Mg = 0.005 to 2.0 mg/L
Na = 0.010 to 10.0 mg/L
K = 0.010 to 5.0 mg/L

For the analysis of ions in water chemistry samples the ranges are:

Ca = 0.020 to 100.0 mg/L
Mg = 0.025 to 100.0 mg/L
Na = 0.01 to 100.0 mg/L
K = 0.01 to 50.0 mg/L
Fe = 0.05 to 10.0 mg/L
Mn = 0.005 to 10.0 mg/L
Si = 0.750 to 50.0 mg/L

2.0 Summary of Method

Wet deposition samples are introduced as they are received into the ICP-OES through the SPS-4 auto sampler. The samples are pumped from the auto sampler via a peristaltic pump and subsequently mixed with a solution containing yttrium at 2 mg/L and cesium at 500 mg/L. The yttrium is used as an internal standard and the cesium is used for ionization suppression. The combined sample moves into a nebulizer where it is mixed with gaseous argon to form an aerosol. This aerosol mixture moves into the spray chamber and ultimately through a plasma that is at approximately 10,000 K. At this temperature, ground state atoms in the plasma are easily excited to higher energy levels. Photons resulting from the excitation of ground state atoms are measured via a charged coupled device (CCD) detector. The detector can monitor and record data for up to 73 wavelengths of light simultaneously.

Conditions for the instrument were optimized for all analytes and are accessible in the instrument software. See Appendix A.

3.0 Definitions

ASTM International	American Society for Testing Materials International
ACS	American Chemical Society
CCB	Continuing Calibration Blank. HEAL uses deionized water as a blank, named FB.

CCV	Continuing Calibration Verification. HEAL uses several different CCVs for wet deposition analysis: • FH- an in-house prepared quality control solution targeting the high end of the calibration curve • FL- an in-house prepared quality control solution targeting the low end of the calibration curve
DI	Deionized (water) at 18.0 Mohms-cm or higher
ICV	Initial Calibration Verification. HEAL uses a simulated rain sample as an ICV: • FR50- a solution with target analyte concentrations at the 50th percentile of the NTN network results.
MDL	Method Detection Limit
HDPE	High Density Polyethylene
LIMS	Laboratory Information Management System
QA	Quality Assurance
QC	Quality Control
R^2	Coefficient of Determination reflecting the deviation of the measured data points from the calibration curve
SDS	Safety Data Sheet
SOP	Standard Operating Procedure

4.0 Health & Safety Warnings

4.1 Eye protection is required in the laboratory.

4.2 Food, drinks, and smoking are not allowed in the laboratory.

4.3 Safety Data Sheets (SDS) applicable to this SOP can be found online by using the University of Illinois Division of Research Safety (DRS) website: https://www.drs.illinois.edu/Programs/SafetyDataSheets.

4.4 The Illinois State Water Survey Chemical Hygiene Plan covers the ISWS laboratory safety program, including, but not limited to, personal protective equipment used, control equipment inventory and operations (such as vented hoods), employee training programs, medical programs, and safety. The ISWS Chemical Hygiene Plan is available at https://go.illinois.edu/ISWS-Chemical-Hygiene-Plan.

4.5 The University of Illinois DRS has a laboratory safety guide available at https://www.drs.illinois.edu/site-documents/LaboratorySafetyGuide.pdf. The ISWS has their own laboratory safety manual, available at https://go.illinois.edu/ISWS-Laboratory-Safety-Manual.

4.6 The HEAL practices pollution prevention, which encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. The quantity of chemicals purchased should be based on the expected usage during its shelf life and disposal cost of unused material.

4.7 Laboratory waste management practices must be consistent with all applicable rules and regulations. Excess reagents and samples and method process wastes should be characterized and disposed of by DRS. It is the responsibility of the user of this method to comply with relevant disposal and waste regulations.

4.8 The HEAL has listed known health and safety warnings for this SOP, but this list should not be assumed to comprise all health and safety issues.

5.0 Cautions

5.1 An efficient ventilation system should be in operation prior to igniting the plasma. A minimum uptake velocity of 200 cfm (cubic feet/minute) is required to remove the hot gases produced during instrument operation. Ensure that the exhaust fan is on and operating before analysis.

5.2 Laboratory facilities used for ICP-OES analysis should be clean. Clean glassware and clean handling techniques are necessary to minimize sample contamination. Avoid direct hand contact with precipitation samples, standards, or reagents.

5.3 Pressurized gas tanks are used for ICP-OES analysis. A large holding tank is located outside of building three. Check periodically for any cracks or leaks in valving, regulator and tubing.

5.4 There is a 2-gallon waste container in place to collect unused samples from the spray chamber; make sure that it is not overflowing. This method does not utilize any solvents or reagents that are considered hazardous. Non-hazardous waste can be disposed of down the laboratory sink with substantial amount of water.

6.0 Interferences

6.1 Ionization - Emission spectroscopy is dependent upon the presence of free neutral atoms. The high operating temperature of the plasma increases the potential for the ionization of ground state atoms. Cesium, as cesium chloride, is added in excess quantities because it is more easily ionized than the analytes thereby suppressing the ionization of any of the four analytes of interest.

6.2 Carryover - Sample carryover is a potential problem with most automated systems. To avoid sample carryover with the ICP-OES, the “smartrinse” feature in the software is utilized. This increases the wash time between samples containing higher than normal concentrations of any of the analytes. This feature has been tested with no carryover detected for each analyte up to 100 mg/L in very clean samples. In samples that are found to contain higher concentrations of calcium & magnesium, carryover of 3-4 ppb has been observed for Ca^{2+} only. Samples are repeated when carryover is suspected.

6.3 DI water contamination.

6.4 Sample uptake - A dirty nebulizer can cause uneven or decreased uptake of the samples. The nebulizer should be rinsed after each run. See section 12.2.5 for maintenance details.

7.0 Personnel Qualifications

Analysts in training must complete at least five days of training with an experienced analyst or a manufacturer’s training course, and a satisfactory demonstration of capability before analyzing routine samples.

8.0 Equipment and Supplies

8.1 Equipment

8.1.1 Spectrometer – Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES. (S/N AU14400057) Agilent Technologies, 5301 Stevens Creek Blvd., Santa Clara, CA 95051, Telephone: (877) 424-4536. All parts and supplies for the ICP-OES are supplied by Agilent Technologies. Contact Agilent Technologies with service concerns at (800) 227-9770 or at http://agilent.com.

8.1.2 Automatic Sampler - SPS.4 (Sample Preparation System) Agilent Technologies. (S/N AU17162874) Refer to Agilent operator’s manual for detailed maintenance and operating procedures and Appendix A-1 for current operating conditions.

8.1.3 Recirculating Chiller G8481A (S/N 1811-01574). Agilent Technologies. Contact Agilent Technologies with service concerns at (800) 227-9770 or at http://agilent.com

8.2 Supplies

8.2.1 Auto sampler probe SPS 4 (Agilent 9910111900)

8.2.2 Class A Volumetric glassware

8.2.3 Adjustable pipettes and tips

8.2.4 Helix locking screw for spray chamber (Agilent G8010-80043)

8.2.5 Helix seal for spray chamber (Agilent G8010-80042)

8.2.6 Filter Paper – Whatman Quantitative Grade Paper, Grade 50; L x W: 15 cm x 23 cm (Fisher Scientific # 09-927-888)

8.2.6 Kimwipes® – Fisher Scientific

8.2.7 Narrow mouth 1000 mL high density polyethylene bottles 1000 mL for QCS and standards - Fisher Scientific # 02-923F

8.2.8 Nebulizer – Inert OneNeb nebulizer (Agilent 2010126900)
Nebulizer – SeaSpray glass concentric nebulizer U-series (Agilent G8010-60255)

8.2.9 Parafilm® - 2" x 250' Used for sample tube and volumetric flask coverage. (Fisher Scientific # S-37441)

8.2.10 Safety Glasses - meet ANSI standards, Fisher Scientific.

8.2.11 Sample connector (UniFit) fit for U-Series glass concentric nebulizer (Agilent G8010-80035)

8.2.12 Sample vials - 8 mL volume, polystyrene 13 mm x 100 mm (Fisher Scientific # 14-956-8E and VWR # 60818-849)

8.2.13 Spray chamber – Double pass glass cyclonic spray chamber (Agilent G8010-60256)

8.2.14 Torch clamp (G8000-64140)

8.2.15 Torch – ICP-OES 5100 DV Easy-fit torch one piece (Agilent G8010-30228)

8.2.16 Tubing

- Black-black ID 0.76 mm (Fisher 14-190-504)
- Blue-blue ID 1.65 mm (Fisher 14-190-511)
- Orange-white ID 0.64 mm (Fisher 14-190-503)
- Three bridge grey-grey (Agilent 3710049000)
- Auto sampler pump (Agilent 3710049000)
- Drain connector UniFit (Agilent G8010-80036)
- Nebulizer capillary (Agilent 2410020500)

8.2.17 Y-piece to combine sample and internal standard (Agilent 1610132400)

8.3 Chemicals & Solutions

8.3.1 Agilent Tuning Solution - This solution is used to align the torch, calibrate wavelengths, and troubleshoot the instrument. 500 mL, Agilent, 6610030000 ICP Standard solution, 50 mg/L Mn.

8.3.2 Argon - Laboratory grade liquid argon, S.J. Smith Welding Supply, 1212 Butzow Dr., Urbana, IL 61802 , (217) 344-8044.

8.3.3 Cesium Chloride (CsCl) - Added to samples as an ionization suppressant for sodium and potassium to a final concentration of 500 mg/L cesium. 500 g, MP Biomedicals, Catalog # 02150589.

8.3.4 Deionized 18.0 Mohm-cm resistance water or better, 0.2 µm filter at point of use. ISWS Reverse Osmosis Central System.

8.3.5 Trace metals Nitric Acid - 500 mL, Fisher Scientific, Catalog # A509-P500.

8.3.6 Quality control check solution FR50 is a simulated rain solution prepared in house targeting the 50th percentile concentration of the NADP/NTN network precipitation values.

8.3.7 Stock Standards – SCP Science 1000 mg/L calcium, Catalog # 140-051-201, 1000 mg/L magnesium, Catalog # 140-051-121, 1000 mg/L sodium, Catalog # 140-051-111, and 1000 mg/L potassium, Catalog # 140-051-191. Ultra Scientific 1000 mg/L manganese, 10000 mg/L iron and silicon. Equivalent alternatives are also acceptable.

8.3.8 Stock Standards - AccuStandards ICP Standards 1000 mg/L and 10,000 mg/L calcium, magnesium, sodium, potassium, 1000 mg/L manganese, 10000 mg/L iron, magnesium, and silicon. Equivalent alternatives are also acceptable.

8.3.9 Trace metal grade HCl - 500 mL, Fisher Scientific, Catalog # A508-P500 or equivalent.

8.3.10 Triton X-100 - 500 mL, Fisher Scientific, Catalog # 8698516 or equivalent.

8.3.11 Yttrium - Internal Standard, 1000 mg/L. 500 mL, Fisher Scientific, Spex Certiprep PLY2-2X.

8.4 Reagents and Standards Preparation

8.4.1 Cesium Chloride Solution (100,000 mg/L cesium).

Weigh out 126.7 g of CsCl, dried at 105°C for one hour, then quantitatively transfer to a 1L volumetric flask containing about 800mL of DI. Dilute to the mark with DI water and mix. Prepare as needed and store at room temperature in a 1L HDPE bottle.

8.4.2 Internal Standard Solution Yttrium (2 mg/L) and Cesium Chloride (500 mg/L cesium).

Pipette 5 mL of the 100,000 mg/L cesium solution to a 1 L volumetric flask half filled with DI water. Pipette 2 mL of 1000 mg/L yttrium to the same flask and add DI water to 1 L mark.

8.4.3 Agilent Tuning Solution.

This solution must be diluted 10:1 resulting in a final concentration of 5 mg/L manganese.

8.4.4 Triton X-100 Solution.

Prepare a ~1% solution. This solution is used when cleaning the spray chamber in place. Fill a 1L HDPE bottle halfway with DI water. Using a small plastic beaker, add 10 mL of Triton X-100 to the DI water. Triton X-100 is a very thick substance. Use a squeeze bottle filled with fresh DI water to rinse the rest of the Triton X-100 out of the plastic beaker and into the HDPE bottle. The mixture will be very sudsy. Fill the HDPE bottle to the shoulder with DI water and shake. The concentration for this solution does not need to be exact.

8.4.5 Acid Bath Solution.

Used for leaching dirty spray chambers. Use a ~ 5% HCl solution. Add 200mL of DI water to plastic beaker and then 20mL of concentrated HCl. Fill the rest of the way to the 400mL line with DI water. Submerge spray chamber in solution, cover with parafilm and sonicate for 30 minutes.

8.4.6 Standards Preparation

8.4.6.1 Certified stock solutions are purchased from AccuStandard through Fisher Scientific in 1000 mg/L and 10,000 mg/L concentrations. Record the lot number, expiration date and manufacturer of the stock solutions in the ICP Standard log when preparing new standards. Standard solutions are prepared with all analytes of interest. The concentrations for the Wet Deposition samples are shown in Table 1. The necessary volumes added to achieve the concentration desired are shown in Table 2. The

concentrations for the Water Chemistry samples are shown in Table 5. The necessary volumes added to achieve the concentration desired are shown in Table 6.
The calibration curve for the wet deposition samples is split into low and high curves. The low curve incorporates standards 0.000 – 1.000 mg/L. The high curve incorporates standards 1.000 – 10.000 mg/L.

8.4.6.2 Rinse volumetric flasks three times with DI water. Fill volumetric flasks (of stated size in chart below) about half full of DI water. Add the appropriate volume of stock reagent (see tables below) to each of the flasks using a properly calibrated adjustable pipette. Dilute to the mark with DI water and mix standards well, then pour into the properly labeled HDPE storage bottles. Working standards are prepared every 6 months or as needed.

Table 1 – Standards Concentrations for the Wet Deposition Samples

	Calcium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Magnesium (mg/L)
Std. 0	0.020	0.010	0.010	0.005
Std. 1	0.025	0.025	0.025	0.025
Std. 2	0.050	0.050	0.050	0.050
Std. 3	0.100	0.100	0.100	0.100
Std. 4	0.200	0.200	0.200	0.200
Std. 5	0.500	0.500	0.500	0.500
Std. 6	1.000	1.000	1.000	1.000
Std. 7	2.000	2.000	2.000	2.000
Std. 8	5.000	5.000	5.000	
Std. 9	10.000	10.000		

Table 2 – Stock Volumes for Standards Preparation for the Wet Deposition samples

	Calcium 1000 mg/L	Sodium 1000 mg/L	Potassium 1000 mg/L	Magnesium 1000 mg/L
Std. 0	0.040 mL/2L	0.020 mL/2L	0.020 mL/2L	0.010 mL/2L
Std. 1	0.025 mL/1L	0.025 mL/1L	0.025 mL/1L	0.025 mL/1L
Std. 2	0.025 mL/0.5L	0.025 mL/0.5L	0.025 mL/0.5L	0.025 mL/0.5L
Std. 3	0.050 mL/0.5L	0.050 mL/0.5L	0.05 mL/0.5L	0.05 mL/0.5L
Std. 4	0.100 mL/0.5L	0.100 mL/0.5L	0.100 mL/0.5L	0.100 mL/0.5L
Std. 5	0.250 mL/0.5L	0.250 mL/0.5L	0.250 mL/0.5L	0.250 mL/0.5L
Std. 6	1.000 mL/1L	1.000 mL/1L	1.000 mL/1L	1.000 mL/1L
Std. 7	0.100 mL/0.5L	0.100 mL/0.5L	1.000 mL/0.5L	1.000 mL/0.5L
Std. 8	0.250 mL/0.5L	0.250 mL/0.5L	2.500 mL/0.5L	
Std. 9	0.500 mL/0.5L	0.500 mL/0.5L		

8.4.7 QCs Preparation

8.4.7.1 Certified stock solutions are purchased from Inorganic Ventures through Fisher Scientific in 1000 mg/L concentrations. Record the lot number, expiration date, and manufacturer of the stock solutions in the ICP Standard log when preparing new QCs. QC solutions are prepared with all analytes of interest. The concentrations for the Wet Deposition samples are shown in Table 3. The necessary volumes added to achieve the concentration desired are shown in Table 4. The QC concentrations for the Water Chemistry project are shown in Table 7. The necessary volumes added to achieve the concentration desired are shown in Table 8.

8.4.7.2 Rinse volumetric flasks three times with DI water. Fill volumetric flasks (of stated size in chart below) about half full with DI water. Add the appropriate volume of stock reagent (see tables below) to each of the flasks using a properly calibrated adjustable pipette. Dilute to the mark with DI water and mix standards well, then pour into the properly labeled HDPE storage bottles. Working QCs are prepared as needed.

Table 3 – QC Concentrations for the Wet Deposition samples

	Calcium mg/L	Sodium mg/L	Potassium mg/L	Magnesium mg/L
FH (CCV High)	10.000	10.000	5.000	2.000
FL (CCV Low)	0.040	0.040	0.010	0.010
FR 50 (ICV)	0.130	0.060	0.021	0.024

Table 4 – Stock Volumes for QC Preparation for the Wet Deposition samples

	Calcium 1000 mg/L	Sodium 1000 mg/L	Potassium 1000 mg/L	Magnesium 1000 mg/L
FH	10.000 mL/1L	10.000 mL/1L	5.000 mL/1L	2.000 mL/1L
FL	0.040 mL/1L	0.040 mL/1L	0.010 mL/1L	0.010 mL/1L

Table 5 -- Standards Concentrations for the Water Chemistry Samples

	Calcium (mg/L)	Sodium (mg/L)	Iron (mg/L)	Manganese (mg/L)	Silicon (mg/L)	Potassium (mg/L)	Magnesium (mg/L)
Std. 0	0.020	0.010	0.050	0.005	0.750	0.010	0.025
Std. 1	0.025	0.025	0.500	0.025	1.500	0.025	0.500
Std. 2	0.050	0.050	1.000	0.500	15.000	0.050	1.000
Std. 3	0.100	0.100	3.000	1.000	30.000	0.100	3.000
Std. 4	0.200	0.200	5.000	2.000	50.000	0.200	5.000
Std. 5	0.500	0.500	10.000	5.000		0.500	10.000
Std. 6	1.00	1.000		10.000		1.000	20.000
Std. 7	5.00	5.000				5.000	
Std. 8	10.00	10.000				10.000	
Std. 9	20.00	20.000				20.000	
Std.10	50.00	50.00				50.00	50.00
Std.11	100.00	100.00					100.00

Table 6 -- Stock Volumes for Standards Preparation for the Water Chemistry samples

	Calcium 1000 mg/L	Sodium 1000 mg/L	Iron 10000 mg/L	Manganese 1000 mg/L	Silicon 10000 mg/L	Potassium 1000 mg/L	Magnesium 1000 mg/L
Std. 0	0.040 mL/2L	0.020 mL/2L	0.010 mL/2L	0.010 mL/2L	0.150 mL/2L	0.020 mL/2L	0.050 mL/2L
Std. 1	0.025 mL/1L	0.025 mL/1L	0.050 mL/1L	0.025 mL/1L	0.150 mL/1L	0.025 mL/1L	0.500 mL/1L
Std. 2	0.025 mL/0.5L	0.025 mL/0.5L	0.050 mL/0.5L	0.250 mL/0.5L	0.750 mL/0.5L	0.025 mL/0.5L	0.500 mL/0.5L
Std. 3	0.050 mL/0.5L	0.050 mL/0.5L	0.150 mL/0.5L	0.500 mL/0.5L	1.50 mL/0.5L	0.050 mL/0.5L	1.50 mL/0.5L
Std. 4	0.100 mL/0.5L	0.100 mL/0.5L	0.250 mL/0.5L	1.000 mL/0.5L	2.50 mL/0.5L	0.100 mL/0.5L	0.250 mL/0.5L

Std. 5	0.250 mL/0.5L	0.250 mL/0.5L	0.500 mL/0.5L	2.50 mL/0.5L		0.250 mL/0.5L	0.500 mL/0.5L
Std. 6	0.500 mL/0.5L	0.500 mL/0.5L		5.00 mL/0.5L		0.500 mL/0.5L	1.000 mL/0.5L
Std. 7	0.250 mL/0.5L	0.250 mL/0.5L				0.250 mL/0.5L	
Std. 8	0.500 mL/0.5L	0.500 mL/0.5L				0.500 mL/0.5L	
Std. 9	1.00 mL/0.5L	1.00 mL/0.5L				1.00 mL/0.5L	
Std.10	2.5 mL/0.5L	2.5 mL/0.5L					2.5 mL/0.5L
Std.11	5.0 mL/0.5L	5.0 mL/0.5L					5.0 mL/0.5L

Table 7 – QC Concentrations for the Water Chemistry samples

	Calcium (mg/L)	Sodium (mg/L)	Iron (mg/L)	Manganese (mg/L)	Silicon (mg/L)	Potassium (mg/L)	Magnesium (mg/L)
ICV	3.0	2.0	3.0	1.0	1.5	2.0	3.0
CCV	10.0	10.0	10.0	10.0	10.0	10.0	10.0

Table 8 – Stock Volumes for QC Preparation for the Water Chemistry samples

	Calcium 1000 mg/L	Sodium 1000 mg/L	Iron 10000 mg/L	Manganese 1000 mg/L	Silicon 10000 mg/L	Potassium 1000 mg/L	Magnesium 1000 mg/L
ICV	1.500 mL/0.5L	1.000 mL/0.5L	0.150 mL/0.5L	0.500 mL/0.5L	0.075 mL/0.5L	1.000 mL/0.5L	1.500 mL/0.5L
CCV	5.00 mL/0.5L	5.00 mL/0.5L	0.500 mL/0.5L	5.00 mL/0.5L	0.500 mL/0.5L	5.00 mL/0.5L	5.00 mL/0.5L

9.0 Instrument Set-up

9.1 Power up equipment.

9.1.1 Turn on the chiller unit. The readings should be approximately 20°C and 54 psi. Refer to the operator’s manual for operation and troubleshooting.

9.1.2 Open the ICP Expert software.

9.1.3 The ICP-OES is always left on. Verify that the power is on by checking the indicator light in the top right-hand corner of the instrument. There are different colored lights to indicate the status of the instrument.

- Green
    - the instrument and software are connected and are ready to attempt a plasma ignition sequence, or

  - The instrument and software are connected, and the plasma ignition sequence is underway, or
  - The instrument and software are connected, the plasma is lit and running, and it is possible to run analysis of samples.
- Yellow
  - A yellow blinking light indicates the instrument and software are not connected (instrument is off-line).
  - A solid yellow light indicates that the instrument and software are connected, but the instrument is not ready to begin a plasma ignition sequence due to a tripped door or torch handle interlock, low gas pressure, low water flow or low cooling air flow.
- Red - A red light indicates an instrument firmware error causing a halt to analysis or restricting normal instrument operation.
- Grey – the component is offline.

9.1.4 The autosampler is left on and no alignment is needed. If the power is off, turn on the power to auto sampler and check the alignment of sampler probe. Check that there is no obstruction in the sampling line to impede the flow of the sample. Rinse and refill the autosampler rinse container with clean DI water, keeping it filled throughout analysis.

9.2 Connect the pump tubing.

9.2.1 The ICP-OES is equipped with a five-channel pump. At the end of the day’s analysis, the tubing is left disconnected so that it does not become flattened. Thoroughly examine the tubing to ensure that it is not flattened. If there are flat spots, replace the tubing.

9.2.2 Using the arrow indicator on the pump, connect the drain tube (blue/blue) from the bottom of the spray chamber towards the waste can on the floor. The end of the drain tube that is connected to the bottom of the spray chamber will be connected on the bottom of the pump. The end of the drain tube that is connected to the waste container will be connected to the top of the pump.

9.2.3 Connect the sample tube (black/black) to flow from the auto sampler towards the spray chamber. The end of the tubing connected to the spray chamber will be on top of the pump. The end of the tubing connected to the auto sampler will be on the bottom of the pump.

9.2.4 Next connect the internal standard cesium chloride tube (orange/white) to flow from the internal standard/cesium chloride solution towards the spray chamber. The end of the tubing connected to the spray chamber will be connected on top of the pump. The end of the tubing connected to the internal standard/cesium chloride solution will be connected to the bottom of the pump.

9.2.5 Close the tension clips on all three channels. Verify that the flow is good for all three channels, and the tension on the screws is not too tight.

9.2.6 Under **Pump** on the toolbar, select “fast” speed to start the pump. Allow air to flow through the lines, this helps you to see that the flow is moving forward and not backward. If the flow is not moving adjust the tension screw for the line you are checking. Be sure not to tighten too much. Sometimes it helps to completely loosen the tension screw and start over by very slowly tightening the screw as you watch air travel through the lines.

9.2.7 After connecting the pump tubing, click “rinse” button on the **Autosampler** tab and watch for the solution to move through both the sample and internal standard lines. The best place to observe the flow is at the Y-connector. If the solution is flowing properly then there should be a solid stream of water coming out of the nebulizer in the spray chamber.

9.2.8 When you have verified that all lines are flowing smoothly, check internal standard and rinse water levels, change the **Pump** speed to “normal” and continue to rinse.

9.3 Igniting the plasma.

9.3.1 Verify that argon is available. The pressure should be around 85 ±5 psi.

9.3.2 Verify that the torch, spray chamber, and nebulizer are connected properly. (See section 14.0 for general maintenance guidelines).

9.3.3 Check the instrument status page by selecting the **Instrument** button on the toolbar.

9.3.3.1 Check to see that all components are in green before igniting the plasma. Note: the plasma component will remain grey until the “plasma on” button is pushed.

9.3.3.2 On the bottom right-hand side of the page, verify that the polychromator is in green and reading 35.0°C, and the peltier is at -40.0°C (slightly above or below is O.K.). Close this page.

9.3.4 Before igniting the plasma, verify that all pump tubing has been connected. **Pump tubing MUST be clamped down before lighting the plasma, otherwise it will flood the torch and pre-optics.**

9.3.5 Ignite the plasma by pushing the “plasma on” button, located under **Plasma** on the toolbar.

9.3.6 If no wavelengths below 190 nm are being analyzed, neither Boost nor Snout purges are necessary. Ensure that these boxes are unchecked in the Instrument panel, under the Status tab. If Boost and Snout are necessary, ensure that the Boost box is checked immediately after plasma ignition. Check the Snout box immediately before beginning of the run. Failure to take these measures will result in unnecessarily wasting argon gas, in the case of the former, and experiencing avoidable spectral interference, in the case of the latter.

9.4 Create a worksheet.

9.4.1 On the home screen, select **Open** and **NEON_Template-2024.esws** or **WC_Template-2024.esws .** This template can be found at C:\Users\Public\Public Documents\Agilent\ICP Expert 5100\CurrentTemplates

9.4.2 Select **Save As**, C:\Users\Public\Public Documents\Agilent\ICP Expert 5100\Results\Year\Month. Type the new worksheets file name as the current date followed by SYS2 (mmddyySYS2). Click Save.

9.5 Create a run.

9.5.1 After a worksheet has been created, eight tabs will appear on the left-hand side of the screen. The **Sequence** tab should already be selected, if not select the **Sequence** tab.

9.5.2 Hand type or scan the samples into the worksheet for the wet deposition.

9.5.3 Create a Prep. Batch and Analytical Batch for the Water Chemistry samples in LIMs.

9.5.3 An FR50, FB, FL, FH, and MDL must be analyzed immediately after calibration of the instrument for the wet deposition samples and ICV, CCB, CCV and MDL must be analyzed immediately after calibration of the instrument for the Water Chemistry project.

9.5.4 After every 10 samples, analyze an FB, FL, FH and a duplicate for the wet deposition samples. After every 10 samples, analyze CCB, CCV and a duplicate sample for the Water Chemistry project.

9.5.5 Select the **Analysis** tab. On the left-hand side of the worksheet, check all samples to be analyzed.

10.0 Sample Collection, Handling and Preservation

10.1 Samples to be analyzed on the ICP-OES for cation metals are stored on trays in the room 301 refrigerator at 4°C. Samples are retrieved from this area by each analyst prior to analysis and checked for proper sequence of numbers to be analyzed.

10.2 All samples are to be handled with care. Avoid any direct contact with the sample or interior of bottle/lid.

10.3 Keep sample bottles tightly sealed when not being poured. Also keep samples and standards covered as much as possible during analysis to eliminate airborne contamination.

10.4 No chemical preservation is applied to precipitation or Water Chemistry samples.

11.0 Sample Preparation and Analysis

11.1 Cleaning the 13 x 100 mm test tubes.

11.1.1 Fill a sample rack with test tubes.

11.1.2 Fill the test tubes with DI water and cover the rack with Parafilm®

11.1.3 Allow the test tubes to soak overnight.

11.1.4 Rinse the tubes 3 times with clean DI water and let dry completely before using.

11.1.5 Sample tubes are non-sterile polystyrene and used once, then disposed.

11.2 Sample Pouring

11.2.1 Pour at least 3 mL of sample into each test tube. Label each test tube with the appropriate sample number. Pour one row at a time, then load the tubes with the precipitation or Water Chemistry samples onto the SPS 4 Autosampler. After all rows of samples have been placed onto the sampler, load the quality control checks or any other special samples, dilutions, or checks. Keep samples covered with Parafilm® until you are ready to analyze.

11.2.2 Pour a small amount (3-5 mL) of standards #0-9 and blank standard from storage bottles into “working” cups held in the standard rack.

11.3 Sample Analysis

11.3.1 After the instrument has warmed up for 20 minutes, replace DI water for the internal standard/cesium solution, condition the instrument for parameters in the sequence. Select the **Conditions** tab on the left-hand side of the worksheet and select **Read** button located on the bottom of the page above the graph. Check to see if wavelengths look normal. If not, allow the instrument to warm up longer and read the spectrum again.

11.3.2 Verify acceptable signals: Ca (315) – 2, Ca (393) – 270, K – 70, Na – 100, Y – 35 000.

11.3.3 Press the **Run** button located at the top of the page. After the instrument reads the blank sample, calibrate using all ten standards. The linear ranges for each wavelength have been predetermined and loaded into the method.

11.3.4 Verify that the correlation coefficients for calibration of each analyte is at least 0.999.

11.3.5 Monitor the quality control solutions throughout the sample analysis. If the reported value for these solutions falls outside of the control limits, repeat the failed QC solution analysis as soon as possible. If the problem persists, it will be necessary to stop and recalibrate the instrument. The samples that were analyzed prior to the quality control solution falling out of control should be reanalyzed when the system is recalibrated and determined to be back in control.

11.3.6 Continue to analyze the samples until the end of the sequence of samples, keeping an eye on the QC values and probe placement into the sample cups.

11.3.7 Analysis will continue until the end of the sequence is reached.

11.4 Instrument shut down.

11.4.1 The plasma will remain on until the analysis is complete, unless programmed otherwise. Allow the DI water to be aspirated for about 10 minutes on high-speed pump after the run is complete.

11.4.2 Return pump speed to normal and turn the plasma off by selecting the **plasma off** button located at the top of the page.

11.4.3 Move the DI water from the kitchen area to the side of the instrument, ensuring that the tubing is no longer in the water and turn the pump speed on high until the drain tube is empty.

11.4.4 Release the tension for all three channels of the peristaltic pump and the autosampler pump.

11.4.5 Turn off the chiller.

11.4.6 Empty the waste container.

12.0 Maintenance and Troubleshooting

Routine maintenance of the ICP-OES is critical to ensure accurate readings. Refer to Owner's Manual for detailed maintenance schedule. Preventative maintenance is done annually by Agilent.

12.1 Daily maintenance

12.1.1 Check the pump tubing. Verify that it is not smashed or distorted. Replace it if needed.

12.1.2 Check the flow. After connecting the pump tubing, click rinse in the autosampler tab and place the pump on fast flow. Watch for the solution to move through both the sample and internal standard lines. The best place to observe the flow is at the Y-connector. If the solution is flowing properly then there should be a solid stream of water coming out of the nebulizer in the spray chamber.

12.2 Weekly maintenance

12.2.1 Change out the pump tubing after approximately 40 hours of run time. Every week change out the sample tubing (black/black), the internal standard tubing (orange/white), and rotate the autosampler tubing. Every other week change out the drain tubing (blue/blue) and the autosampler tubing. Be sure to cut about 2 inches of black/black and orange/white tubing on one end and connect those ends to the Y-piece.

12.2.2 Check the two tubing connector pieces for dirt build-up and replace as necessary.

12.2.3 Check the torch for build-up on the inner most tube. If the torch appears to be clean, shut the door and continue. If necessary, change out the torch and clean the dirty torch by running DI water through it. The torch needs to be completely dry before using it.

12.2.4 Check the cone on the inside of the torch box for build-up. See the maintenance section in the *ICP Expert* software for detailed instructions for removing, cleaning, and repositioning the cone.

12.2.5 Clean the spray chamber and nebulizer. Once everything is hooked back up, ignite the plasma. Replace the DI rinse water with the ~1% Triton-X cleaning solution. Select "fast pump" in the software and let the solution aspirate for 15 minutes. You will see the solution in the spray chamber turn white and come down the drain tubing. When it's in the drain tubing you will see small bubbles. After 15 minutes have passed, wipe off tubing with a Kimwipe and place back in DI water container. Rinse, still on fast pump, for approximately 15 minutes. Watch the drain tubing to become clear again with large bubbles.

12.3 Monthly maintenance

12.3.1 Perform a detector calibration.

- Turn the water chiller on and let the Peltier temperature reach -40° C. DO NOT IGNITE THE PLASMA.
- Select the **Instrument** window (top of page) and go into the **Calibration** tab.

- Select **Calibrate** in the detector section (bottom of page).

12.3.2 Perform instrument calibration.

- This can only be done if a valid detector calibration has been performed previously.
- Ignite the plasma and let it stabilize for at least 20 minutes.
- Fill a test tube with diluted (1:10) tuning solution and place the autosampler probe into the tuning solution.
- Under the instrument section (on the same page as the detector section) **check the box** "use axial configuration during calibration" and press **Calibrate.**
- Record the number of wavelengths found in the maintenance binder. It is normal for the Al 167.019 line and sometimes the N 174.213 line to not calibrate.

12.3.3 Clean the instrument air filter located on top of the instrument. See the maintenance section I the *ICP Expert* software for detailed instructions for removing, cleaning, and repositioning the filter.

12.4 Troubleshooting.

12.4.1 Inconsistent or no flow through the lines: make sure the tubing is connected correctly, including the autosampler tubing. Check to see that the tubing is underneath the clamp part of the pump. Check to see if the nebulizer is clogged. Adjust the tension screws.

12.4.2 Exhaust fan not working: check that the switch is on located below the AC unit. Contact F&S to check the fan belt on the roof.

12.4.3 Plasma won't light up: check if the torch is wet. If it is, it will be necessary to change it out and to check the pre-optics lens for water droplets. Open the instrument window and be sure all the components are in green. Check to make sure argon is available and that the pressure is reading 85 ±5 psi.

12.4.4 Plasma won't stay lit: make sure lines are inside the solution and that the tubing is connected correctly. Check that the Argon pressure is reading 85 ±5 psi.

12.4.5 Gas module highlighted in red on instrument page: on the right-hand side of the page, under **Purges**, check the box in between **Boost** and the light indicator. Once the polychromator light turns green, uncheck the box. The polychromator light will turn yellow then back green.

12.4.6 Drift: the temperature of the room can cause the instrument to drift, which will be evident in the yttrium line. If the yttrium readings are drifting upwards, e.g., 1.04, 1.05, make the room warmer. If the yttrium readings are drifting downwards, e.g., 0.93, 0.92, make the room colder.

12.4.7 Inconsistent replicate readings: this may be a sign of a dirty spray chamber or sticky lines. Aspirate a 1% Triton-X solution through it for about 15 minutes and then rinse with DI water thoroughly. Check to see if the Y-piece and other connections are visibly dirty and replace them if necessary. Change out all pump tubing.

12.4.8 Failed instrument calibration: be sure that the plasma has been on for at least 20 minutes and recalibrate. Make a new tuning solution.

13.0 Data and Record Management

13.1 At the end of the run, after all samples have been analyzed, and data is stored in a temporary LIMS table to review all data.

13.1.1 Check replicates: look for signs of drift by viewing internal standards.

13.1.2 Check Ca^{2+} data thoroughly for carryover. Repeat samples with suspected carryover.

13.1.3 Check the Ca 315.887 line for background correction errors. If the background correction line is cutting off the peak adjust the line as necessary. This can be done by moving the peak marker right or left or by right clicking on the peak and changing the background correction type. Note that if one of these factors is changed for one sample it will be changed for all samples in the Ca 315.887 line. If there is a 1.000 mg/L result for both the Ca 315.887 and Ca 393.366 lines, it is acceptable to report the result in the Ca 315.887 line.

13.2 Generate a “csv” file to transport the data into the LIMS.

13.2.1 Select **File**, **LIMS**, and **Export**.

13.2.2 The file name will automatically be generated from the worksheet name (mmddyySYS2.csv). Export to C:\Users\Public\Public Documents\Agilent\ICP Expert 5100\Exported Data\NEON_2024\Year\Month. Select **Save** to export the file.

13.3 Exit the software if you have no further analysis to complete. A pop-up box will ask if you want to save the changes you made, select yes.

13.4 Importing the data into LIMS.

13.4.1 Using the instrument computer, load the Instrumental Chemistry program located in Network: \\pri-fs1\heal\HEAL-IT\Program Install Files\Lims\InstrumentalChemistry.

13.4.2 **Select Data**, **Load/Review**, **ICP**. Then select **ICP Review**, **Data IQ**, **Load Review Table** and select the file that was generated following instructions in 13.2.2.

13.4.3 The method for calcium has two wavelengths where the calibration levels overlap (393.366 nm & 315.887 nm). The highest calibration standard for 393.366 nm is 1.000 mg/L and the lowest calibration standard for 315.887 nm is also 1.000 mg/L. When a sample analysis produces a result for both wavelengths, the LIMS program will prompt the operator with a question: should the result for 393.366 nm should be replaced by the result for 315.887 nm? The operator should perform a percent difference between the two results, if the percent difference is within 10%, then select the result for 315.887 nm. If the percentage difference is greater than 10% then the sample should be reanalyzed.

13.4.4 Verify that the data and QC numbers are valid. If QC data is out of control, the sample analysis must be repeated.

13.4.5 The data can be filtered by selecting **ICP Review** then **Filter Data**.

13.4.6 Control charts of QC data may be viewed before sending the data to the LIMS. Select one of the QCs to check, then right click on all analytes, for all QCs and select **Graph**.

13.4.7 Once the data has been verified, it may be sent to the LIMS as a whole set or as separate groups. The “dilution factor” box must have a number in order for a sample to be sent to the LIMS. Type in 1 If a sample was not diluted or an appropriate dilution factor for the diluted samples. To send data select ***ICP Review, Data IO, Transfer Results to LIMS Results Table.*** The data that was showing on the screen that was marked with an X in the “OK” box has now been transferred to the LIMS.

13.4.8 To view data or control charts for samples already transferred to the LIMS, select ***LIMS, Query, LIMS Query.***

13.5 Recordkeeping

Daily logbooks are kept of instrument sample analysis, troubleshooting, repair, and maintenance. This log is shared by all ICP-OES analysts.

13.5.1 ICP-OES standard logs containing information about standard and QC preparations, upgrades, software issues, and solutions are kept with the instrument.

13.5.2 A log sheet is maintained in a binder which provides documentation of torch alignments, dark current scans, wavelength calibrations.

14.0 Quality Control and Quality Assurance

14.1 A calibration curve is always used at the start of each run followed by a blank. A Coefficient of Determination of ≥0.999 for Ca, Mg, K, and Na is required.

14.2 Each run must start with the following QC samples for the wet deposition samples: FR50, FB, FL, FH, MDL;

ICV, FB, CCV, MDL must be analyzed after the calibration for the Water Chemistry samples.

14.2.1 If any of these initial QCs are outside of the acceptance limits (see table below), then they must be immediately reanalyzed before samples can be analyzed. If the reanalyzed values are still unacceptable, then the system should be recalibrated. The QC samples should also be remade if issues persist.

14.3 After every 10 samples the following QCs must be analyzed for the wet deposition samples: FB, FL, FH and a Duplicate.

For the Water Chemistry samples FB, CCV and a Duplicate are analyzed every 10 samples.

14.3.1 If any of these ongoing QCs are outside of the acceptance limits, then they must be reanalyzed as soon as possible. If any samples are not bracketed by acceptable QCs, then those samples must be reanalyzed.

Table 14-1 - QC Criteria Summary table for the Wet Deposition Samples

QC	Type	Frequency	Criteria
FR50	ICV	Every Batch	±10%
FL	CCV	Every 10 Samples	±20%

FH	CCV	Every 10 Samples	±10%
FB	CCB	Every 10 Samples	<MDL
Duplicate	Duplicate	Every 10 Samples	±10% if > 10 x MDL

Table 14-2 - QC Criteria Summary table for the Water Chemistry project

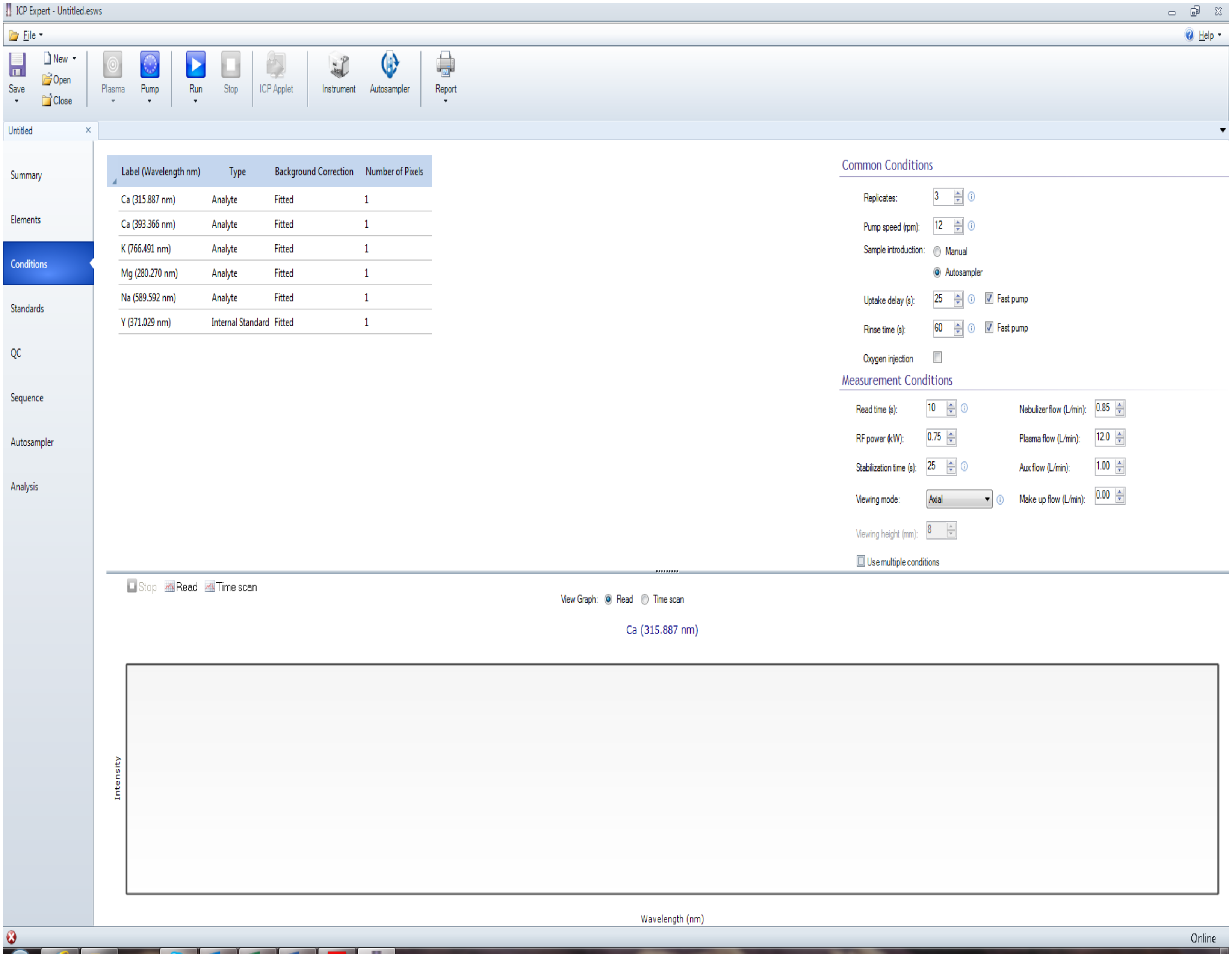
QC	Type	Frequency	Criteria
CCB	CCB	Every 10 Samples	<MDL
ICV	ICV	Every Batch	±10%
CCV	CCV	Every 10 Samples	±10%
Duplicate	Duplicate	Every 10 Samples	±10% if > 10 x MDL

15.0 References

18.1 *Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Couple Plasma – Atomic Emission Spectrometry*, Revision 4.4. Cincinnati, OH, US. EPA. 1994.

18.2 *Method Collection and Analysis of Precipitation*, M.E. Peden, et al., Illinois State Water Survey, 1986.

Appendix A Instrument Conditions and Method



Label (Wavelength nm)	Type	Background Correction	Number of Pixels
Ca (315.887 nm)	Analyte	Fitted	1
Ca (393.366 nm)	Analyte	Fitted	1
K (766.491 nm)	Analyte	Fitted	1
Mg (280.270 nm)	Analyte	Fitted	1
Na (589.592 nm)	Analyte	Fitted	1
Y (371.029 nm)	Internal Standard	Fitted	1

Common Conditions

Replicates: 3
Pump speed (rpm): 12
Sample introduction: ○ Manual ● Autosampler
Uptake delay (s): 25 ☑ Fast pump
Rinse time (s): 60 ☑ Fast pump
Oxygen injection ☐

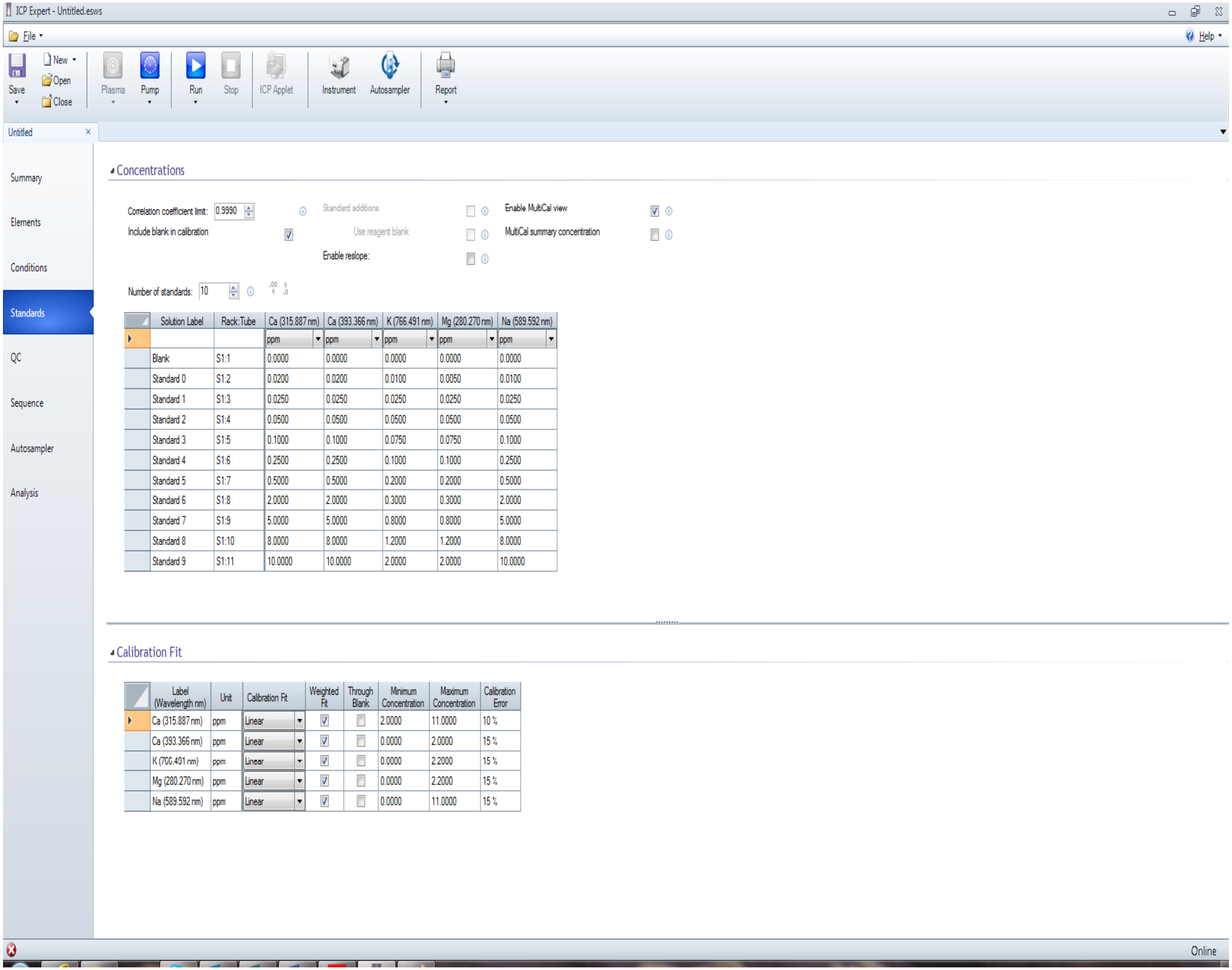
Measurement Conditions

Read time (s): 10
RF power (kW): 0.75
Stabilization time (s): 25
Viewing mode: Axial
Viewing height (mm): 8
Nebulizer flow (L/min): 0.85
Plasma flow (L/min): 12.0
Aux flow (L/min): 1.00
Make up flow (L/min): 0.00
☐ Use multiple conditions

View Graph: ● Read ○ Time scan

Ca (315.887 nm)

Appendix B Calibration Standards and Parameters



Concentrations

Correlation coefficient limit: 0.9990
Include blank in calibration ☑
Standard additions ☐
Use reagent blank ☐
Enable reslope: ☐
Enable MultiCal view ☑
MultiCal summary concentration ☐
Number of standards: 10

Solution Label	Rack:Tube	Ca (315.887 nm)	Ca (393.366 nm)	K (766.491 nm)	Mg (280.270 nm)	Na (589.592 nm)
		ppm	ppm	ppm	ppm	ppm
Blank	S1:1	0.0000	0.0000	0.0000	0.0000	0.0000
Standard 0	S1:2	0.0200	0.0200	0.0100	0.0050	0.0100
Standard 1	S1:3	0.0250	0.0250	0.0250	0.0250	0.0250
Standard 2	S1:4	0.0500	0.0500	0.0500	0.0500	0.0500
Standard 3	S1:5	0.1000	0.1000	0.0750	0.0750	0.1000
Standard 4	S1:6	0.2500	0.2500	0.1000	0.1000	0.2500
Standard 5	S1:7	0.5000	0.5000	0.2000	0.2000	0.5000
Standard 6	S1:8	2.0000	2.0000	0.3000	0.3000	2.0000
Standard 7	S1:9	5.0000	5.0000	0.8000	0.8000	5.0000
Standard 8	S1:10	8.0000	8.0000	1.2000	1.2000	8.0000
Standard 9	S1:11	10.0000	10.0000	2.0000	2.0000	10.0000

Calibration Fit

Label (Wavelength nm)	Unit	Calibration Fit	Weighted Fit	Through Blank	Minimum Concentration	Maximum Concentration	Calibration Error
Ca (315.887 nm)	ppm	Linear	☑	☐	2.0000	11.0000	10 %
Ca (393.366 nm)	ppm	Linear	☑	☐	0.0000	2.0000	15 %
K (766.491 nm)	ppm	Linear	☑	☐	0.0000	2.2000	15 %
Mg (280.270 nm)	ppm	Linear	☑	☐	0.0000	2.2000	15 %
Na (589.592 nm)	ppm	Linear	☑	☐	0.0000	11.0000	15 %

AN.HEAL.IN.ICP-cations.6.2

Final Audit Report 2025-01-07

Created:	2025-01-07 (Central Standard Time)
By:	Evan Rea (erea@illinois.edu)
Status:	Signed
Transaction ID:	CBJCHBCAABAAxuAD8VLehPz2Bku5_joOfo80x0w_hwlh
Number of Documents:	1
Document page count:	24
Number of supporting files:	0
Supporting files page count:	0

"AN.HEAL.IN.ICP-cations.6.2" History

Document created by Evan Rea (erea@illinois.edu)

2025-01-07 - 2:49:35 PM CST- IP address: 130.126.105.85

Agreement viewed by Evan Rea (erea@illinois.edu)

2025-01-07 - 2:51:15 PM CST- IP address: 130.126.105.85

✓ Evan Rea (erea@illinois.edu) authenticated with Adobe Acrobat Sign.

2025-01-07 - 2:51:23 PM CST

Document e-signed by Evan Rea (erea@illinois.edu)

Signature Date: 2025-01-07 - 2:51:23 PM CST - Time Source: server- IP address: 130.126.105.85

Document emailed to Margarita Bargon (rbargon@illinois.edu) for signature

2025-01-07 - 2:51:25 PM CST

Email viewed by Margarita Bargon (rbargon@illinois.edu)

2025-01-07 - 2:52:35 PM CST- IP address: 130.126.105.134

Agreement viewed by Margarita Bargon (rbargon@illinois.edu)

2025-01-07 - 2:52:36 PM CST- IP address: 130.126.105.134

✓ Margarita Bargon (rbargon@illinois.edu) authenticated with Adobe Acrobat Sign.

2025-01-07 - 2:52:49 PM CST

Document e-signed by Margarita Bargon (rbargon@illinois.edu)

Signature Date: 2025-01-07 - 2:52:49 PM CST - Time Source: server- IP address: 130.126.105.134

Document emailed to Anthony Kilber (awkilber@illinois.edu) for signature

2025-01-07 - 2:52:51 PM CST

Email viewed by Anthony Kilber (awkilber@illinois.edu)

2025-01-07 - 3:52:05 PM CST- IP address: 130.126.105.96

Agreement viewed by Anthony Kilber (awkilber@illinois.edu)

2025-01-07 - 3:52:24 PM CST- IP address: 130.126.105.96

Anthony Kilber (awkilber@illinois.edu) authenticated with Adobe Acrobat Sign.

2025-01-07 - 3:53:45 PM CST

Document e-signed by Anthony Kilber (awkilber@illinois.edu)

Signature Date: 2025-01-07 - 3:53:45 PM CST - Time Source: server- IP address: 130.126.105.96

Document emailed to Rachel Van Allen (vanallen@illinois.edu) for signature

2025-01-07 - 3:53:47 PM CST

Email viewed by Rachel Van Allen (vanallen@illinois.edu)

2025-01-07 - 3:54:31 PM CST- IP address: 130.126.105.137

Agreement viewed by Rachel Van Allen (vanallen@illinois.edu)

2025-01-07 - 4:28:03 PM CST- IP address: 130.126.105.137

Rachel Van Allen (vanallen@illinois.edu) authenticated with Adobe Acrobat Sign.

2025-01-07 - 4:52:08 PM CST

Document e-signed by Rachel Van Allen (vanallen@illinois.edu)

Signature Date: 2025-01-07 - 4:52:08 PM CST - Time Source: server- IP address: 130.126.105.137

Agreement completed.

2025-01-07 - 4:52:08 PM CST