

**Illinois State Water Survey
Health and Environmental Application Laboratory**

**Standard Operating Procedure
For the Determination of
Calcium, Magnesium, Sodium, Potassium
by Inductively Coupled Plasma-Optical Emission Spectroscopy
Agilent 5100 SVDV**

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NOTE THE HEALTH AND SAFETY WARNINGS IN Section 4.0

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1.0 Scope & Applicability

1.1 Method Application

The ASTM D1976-12 method, "Standard Test Method for Elements in Water by Inductively-Coupled Argon 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). Appropriate concentration ranges for each of the analytes are listed below. 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 = MDL - 10.0 mg/L
Mg = MDL - 2.0 mg/L
Na = MDL - 10.0 mg/L
K = MDL - 5.0 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 ppm and cesium at 500 ppm. 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
DI	Deionized (water)
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
FBYY####	Deionized water sample for quality control .The first two places designated by YY are for the year. The four places designated by #### are for the sample number.
FR50YY##	An in-house prepared quality control synthetic sample targeting the 50% concentration of all samples analyzed by the ICP-OES instrument for the NADP/NTN. The first two places designated by

	YY are for the year. The two places designated by ## are for the sample number.
FHYY####	An in-house prepared quality control solution targeting the high end of the calibration curve. The first two places designated by YY are for the year. The four places designated by #### are for the sample number.
FMYY####	An in-house prepared quality control solution targeting the middle of the calibration curve. The first two places designated by YY are for the year. The four places designated by #### are for the sample number.
FLYY####	An in-house prepared quality control solution targeting the low end of the calibration curve. The first two places designated by YY are for the year. The four places designated by #### are for the sample number.
FSPYY####	A QC check solution prepared by the analyst designated to check the calibration limits. The four places designated by #### are for the sample number.
LIMS	Laboratory Information Management System
MDL	Method Detection Limit (for current MDLs see operator or QA specialist)
NADP	National Atmospheric Deposition Program
NTN	National Trends Network
QA/QC	Quality Assurance/Quality Control

4.0 Health & Safety Warnings

- 4.1 Eye protection is required in the laboratory.
- 4.2 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.
- 4.3 Safety Data Sheets (SDS) applicable to this SOP are available through the **Division of Research Safety**, and can be found online at <http://www.dr.illinois.edu>.
- 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 <http://isws.illinois.edu/staffonly/resources/manuals.asp>. Procedural notes are included in test methods used (e.g. ASTM International, United States Environmental Protection Agency (USEPA), or Standard Methods for the Examination of Water and Wastewater).
- 4.5 The University of Illinois **Division of Research Safety** requirements for chemical safety can be found at <http://www.dr.illinois.edu/trainingapp/Quizzer/qdbQuizMain.aspx?hfo=10>.

4.6 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 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.

5.2 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. Follow safety precautions and proper use of regulators/gauges when operating pressurized gas tanks.

5.3 There is a 2 gallon waste container in place to collect unused sample from the spray chamber; make sure that it is not overflowing. This method does not utilize any solvents and reagents that are considered hazardous. Non-hazardous wastes 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 ppm 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 Ca²⁺ 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 the maintenance section for cleaning details.

7.0 Personnel Qualifications

Analysts should be trained either by an experienced analyst or by participation in a training course on an instrument similar to the one being used in the lab. Basic ICP-OES theory, methods of operation and the knowledge of software used is vital. Proven capability should be verified by comparison of precipitation sample values and quality control checks to known concentrations. A minimum of a Bachelor's degree in Biology, Chemistry, Environmental Studies, or another closely related field is required.

8.0 Equipment and Materials

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 Chemicals & Solutions

8.2.1 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 ppm Mn.

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

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

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

8.2.5 Optima Nitric Acid - 500 mL, Fisher Scientific, Catalog # A467-500.

8.2.6 Quality Control Standards. Simulated rain solutions prepared internally targeting the 50th percentile concentrations of the NADP/NTN precipitation values.

8.2.7 Stock Standards – SCP Science 1000 ppm calcium, Catalog # 140-051-201, 1000 ppm magnesium, Catalog # 140-051-121, 1000 ppm sodium, Catalog # 140-051-111, and 1000 ppm potassium, Catalog # 140-051-191.

8.2.8 Stock Standards - Spex CertiPrep ICP Standards 1000 ppm and 10,000 ppm calcium, magnesium, sodium and potassium.

8.2.9 Trace metal grade HCl - 500 mL, Fisher Scientific, Catalog # A508-P500.

8.2.10 Triton X-100 - 500 mL, Fisher Scientific, Catalog # 8698516.

- 8.2.11 Yttrium - Internal Standard, 1000 ppm. 500 mL, Fisher Scientific, Spex Certiprep PLY2-2X.
- 8.3 Supplies
- 8.3.1 Auto sampler probe SPS 4 (Agilent 9910111900)
- 8.3.2 Class A Volumetrics
- 8.3.3 Eppendorf adjustable pipettes and tips (Brinkman)
- 10 - 100 μ l - Fisher Scientific # 05-402-48
 - 100 - 1000 μ l - Fisher Scientific # 05-402-50
 - 1 - 5 mL – Fisher Scientific
 - tips for 100 - 1000 μ l - Fisher Scientific # 21-372
 - tips for 10 - 100 μ l - Fisher Scientific # 21-371
 - tips for 1 mL - 5 mL Fisher brand
- Rainin electronic pipettes and tips
- 20 - 200 μ l – S/N A1416739U
 - 100 - 1000 μ l – S/N A1417215U
 - 500 μ l - 5 mL – S/N A1430084U
- 8.3.4 Helix locking screw for spray chamber (Agilent G8010-80043)
- 8.3.5 Helix seal for spray chamber (Agilent G8010-80042)
- 8.3.6 Filter Paper – Whatman Quantitative Grade Paper, Grade 50; L x W: 15 cm x 23 cm (Fisher Scientific # 09-927-888)
- 8.3.6 Kimwipes® – Fisher Scientific
- 8.3.7 Narrow mouth 1000 mL high density polyethylene bottles 1000 mL for modifiers and standards - Fisher Scientific # 02-923F
- 8.3.8 Nebulizer – Inert OneNeb nebulizer (Agilent 2010126900)
- 8.3.8 Nebulizer – SeaSpray glass concentric nebulizer U-series (Agilent G8010-60255)
- 8.3.9 Parafilm® - 2" x 250' Used for sample tube and volumetric flask coverage. (Fisher Scientific # S-37441)
- 8.3.10 Safety Glasses - meet ANSI standards, Fisher Scientific.
- 8.3.11 Sample connector (UniFit) fit for U-Series glass concentric nebulizer (Agilent G8010-80035)
- 8.3.12 Sample vials - 8 mL volume, polystyrene 13 mm x 100 mm (Fisher Scientific # 14-956-8E and VWR # 60818-849)

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

8.3.14 Torch clamp (G8000-64140)

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

8.3.16 Tubing

- Black-black ID 0.76 mm (SCP Science 022-030-007)
- Blue-blue ID 1.65 mm (SCP Science 022-030-013)
- Orange-white ID 0.64 mm (SCP Science 022-030-006)
- Auto sampler pump (Agilent 3710049000)
- Drain connector UniFit (Agilent G8010-80036)
- Nebulizer capillary (Agilent 2410020500)

8.3.17 Vitex Gripping Paper, PK+6 (Glass Expansion KK711E)

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

9.0 Solutions and Standards Preparation

9.1 Solutions Preparation

9.1.1 Cesium Chloride Solution (100,000 ppm cesium).

Dissolve 126.7 g of CsCl, dried at 105°C for one hour, in DI water and dilute to 1 L. Prepare as needed and store at room temperature in a 1 Liter HDPE bottle.

9.1.2 Internal Standard Solution Yttrium (2 ppm) and Cesium Chloride (500 ppm cesium).

Add 5 mL of the 100,000 ppm cesium solution to a 1 L flask half filled with DI water. Add 2 mL of 1000 ppm yttrium to the same flask and dilute to 1 L.

9.1.3 Agilent Tuning Solution.

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

9.1.4 Triton X-100 Solution.

Triton X-100 Solution

Prepare a 1% solution. This solution is used when cleaning the spray chamber in place or in a sonicator. Fill a 1 liter 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 as much as possible with DI water and shake. The concentration for this solution does not need to be exact.

9.1.5 Acid Bath Solution.

Used for leaching dirty spray chambers. Use a ~ 5% HCl solution. 400mL DI water and 20mL of 37% (or 12M) HCl. Add 200mL of DI water to plastic beaker and then 20mL of 37% 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.

9.1.6 Aqua Regia Cleaning Solution.

Prepare a 1:3 dilution of Optima HNO₃ and trace metal grade HCl. This solution is used to clean the torch when analyzing metals. The torch can be cleaned with just deionized water for routine analysis of minerals.

9.2 Standards Preparation

9.2.1 Certified stock solutions are purchased from Spex CertiPrep through Fisher Scientific annually in 1000 ppm and 10,000 ppm concentrations. The standards prepared from the certified stock are verified using certified reference solutions and internal QC solutions. 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 are shown in Table 1. The necessary volumes added to achieve the concentration desired are shown in Table 2.

9.2.2 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 volumetric 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.

9.2.3 Standards concentrations and stock volumes are as follows:

Table 1 – Standards Concentrations

	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	.0100	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

	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
	Calcium 10.000 mg/L	Sodium 10.000 mg/L		
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		

9.3 QCs Preparation

9.3.1 Certified stock solutions are purchased from SCP Science through Fisher Scientific in 1000 ppm 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 are shown in Table 3. The necessary volumes added to achieve the concentration desired are shown in Table 4.

9.3.2 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 volumetric 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.

9.3.3 QC concentrations and stock volumes are as follows:

Table 3 – QC Concentrations

	Calcium mg/L	Sodium mg/L	Potassium mg/L	Magnesium mg/L
FSP	10.000 mL/1L	10.000 mL/1L	5.000 mL/1L	2.000 mL/1L
FH	2.500 mL/1L	2.500 mL/1L	2.000 mL/1L	1.000 mL/1L
FM	1.500 mL/1L	0.50 mL/1L	1.000 mL/1L	0.100 mL/1L
FL	0.040 mL/1L	0.040 mL/1L	0.010 mL/1L	0.010 mL/1L

Table 4 – Stock Volumes for QC Preparation

	Calcium 1000 mg/L	Sodium 1000 mg/L	Potassium 1000 mg/L	Magnesium 1000 mg/L
FSP	10.000 mL/1L	10.000 mL/1L	5.000 mL/1L	2.000 mL/1L
FH	2.500 mL/1L	2.500 mL/1L	2.000 mL/1L	1.000 mL/1L
FM	1.500 mL/1L	0.50 mL/1L	1.000 mL/1L	0.100 mL/1L
FL	0.040 mL/1L	0.040 mL/1L	0.010 mL/1L	0.010 mL/1L

10.0 Instrument Set-up

10.1 Power up equipment.

10.1.1 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.

10.1.2 Open the ICP Expert software.

10.1.3 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 three different colored lights to indicate the status of the instrument: green, yellow, and red.

- 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 sample.
- 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.

- 10.1.4 The autosampler is usually left on and no alignment is needed. If the power is off, turn on 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 then refill the DI water reservoir container with clean DI water, keeping it filled throughout analysis.
- 10.2 Connect the pump tubing.
- 10.2.1 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.
- 10.2.2 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 on the top of the pump.
- 10.2.3 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.
- 10.2.4 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 on the bottom of the pump.
- 10.2.5 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.
- 10.2.6 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.
- 10.2.7 After connecting the pump tubing, click "rinse" option in 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.

10.2.8 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.

10.3 Igniting the plasma.

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

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

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

10.3.3.1 This will bring up a picture of the instrument and all of its components. A list of the components can be found on the left hand side of the screen highlighted in green, yellow, red, or grey.

- Green - the component is functioning correctly.
- Yellow - the component is currently performing an action.
- Red - the component has a fault.
- Grey – the component is offline.

In addition to the list of components, a picture of the instrument and its components are displayed on this page. If one of the components on the list is highlighted in red, it will also be flashing in red on the picture.

10.3.3.2 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. (See section 14.0 for troubleshooting).

10.3.3.3 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.

10.3.4 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.**

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

10.4 Create a worksheet.

10.4.1 On the home screen, select **Open** and **Template-2021.esws**. This template can be found at C:\Users\Public\Public Documents\Agilent\ICP Expert 5100\Templates

- 10.4.2 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.
- 10.5 Create a run.
- 10.5.1 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.
- 10.5.2 Hand type or scan the samples into the worksheet.
- 10.5.3 An FL, FM, FH, FR50, FSP, and FB must be analyzed immediately after calibration of the instrument and at the end of the run.
- 10.5.4 A combination of any two quality control solutions (FL, FM, FH, and FR50), or one QC solution and a replicate sample should be inserted for every twelve samples analyzed. Replicate samples are run as QCs throughout the run and are randomly picked samples from the day's sample list.
- 10.5.5 Select the **Analysis** tab. On the left hand side of the worksheet, check all samples to be analyzed.

11.0 Handling and Preservation

- 11.1 Samples to be analyzed on the ICP-OES for cation metals are stored on trays in the collection area. Samples are retrieved from this area by each analyst prior to analysis and checked for proper sequence of numbers to be analyzed. Samples are kept at 4 °C ± 2°C in room 301 refrigerator.
- 11.2 All samples are to be handled with care. Avoid any direct hand/body contact with the sample or interior of bottle/lid.
- 11.3 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.
- 11.4 No form of preservation is applied to precipitation samples.

12.0 Sample Preparation and Analysis Procedures

- 12.1 Cleaning the 13 x 100 mm test tubes.
 - 12.1.1 Fill a sample rack with test tubes.
 - 12.1.2 Fill the test tubes with DI water and cover the rack with Parafilm®
 - 12.1.3 Allow the test tubes to soak overnight.
 - 12.1.4 Rinse the tubes 3 times with clean DI water and let dry completely before using.

- 12.1.5 Sample tubes are non-sterile polystyrene and used once, then disposed.
- 12.2 Sample Pouring
- 12.2.1 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 onto the SPS 4 Autosampler. After all rows of samples have been placed onto the sampler, load the quality control checks (FR50, FL, FM, FH, replicated samples) or any other special samples, dilutions, or checks. Keep samples covered with Parafilm® until you are ready to analyze.
- 12.2.2 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. Place the blank standard into position 1, standard 0 into position 2, standard 1 into position 3, standard 2 into position 4, standard 3 into position 5, standard 4 into position 6, standard 5 into position 7, standard 6 into position 8, standard 7 into position 9, standard 8 into position 10, and standard 9 into position 11.
- 12.3 Sample Analysis
- 12.3.1 After the instrument has warmed up for 45-60 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 page, and select **Read** 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.
- 12.3.2 Verify acceptable signals: Ca (315) – 2, Ca (393) – 270, K – 70, Na – 100, Y – 35 000.
- 12.3.3 Press the **Start** 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 has been predetermined and loaded into the method.
- 12.3.4 Verify that the correlation coefficients for calibration of each analyte is at least 0.999.
- 12.3.5 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 the instrument 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.
- 12.3.6 Control charts. Control limits for the quality control solutions are determined and updated annually. Control charts for all of these samples are viewed in the LIMS system, see section 13.4.1.
- 12.3.7 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.
- 12.3.8 Analysis will continue until the end of the sequence is reached.

- 12.4 Instrument shut down.
- 12.4.1 The plasma will remain on, once the analysis is complete, unless programmed otherwise. Allow the DI water to be aspirated for about 5-10 minutes on high speed pump after the run is complete.
- 12.4.2 Return pump speed to normal and turn the plasma off by selecting the **plasma off** button located at the top of the page.
- 12.4.3 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.
- 12.4.4 Release the tension for all three channels of the peristaltic pump and the autosampler pump.
- 12.4.5 Turn off the chiller.
- 12.4.6 Empty the waste container.

13.0 Data Reduction and Storage

- 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 Ca²⁺ data thoroughly for carryover. Repeat samples with suspected carryover. Samples with concentrations at or below 0.500 ppm are repeated if they follow a sample containing 1.000 ppm or greater of calcium.
 - 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 ppm 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 (mmddySYS2.csv). Export to C:\Users\Public\Public Documents\Agilent\ICP Expert 5100\Exported Data\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 ppm and the lowest calibration standard for 315.887 nm is also 1.000 ppm. 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 percent 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 from one of the following: **FBYY####**, **FHYE####**, **FMYY####**, **FLYY####**, **FR50YY##**, **FSPYY####** (where "YY" is the two-digit year and "X" is the current sequential number, usually 1). 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**.
- To view control charts, select **QC Samples**. In the pull-down box, select **FBYY####**, **FHYE####**, **FMYY####**, **FLYY####**, **FR50YY##**, **FSPYY####** (where "YY" is the two-digit year and "#" is the current sequential number, usually 1). Change the date range to view the graph.
- 13.5 Data sets are checked for completeness by the analyst and sent to the data manager each week.

14.0 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 as needed by Agilent.

14.1 Daily maintenance

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

14.1.2 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. (See section 14.5 for troubleshooting).

14.1.3 Check to see that the exhaust fan is on by looking to see that the Kimwipe is being picked up above the old ICP. DO NOT RUN if the exhaust fan is not on as this causes torches to melt. (See section 14.5 for troubleshooting).

14.2 Weekly maintenance

14.2.1 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 the black/black and orange/white tubing on one end and connect those ends to the Y-piece.

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

14.2.3 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.

14.2.4 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.

14.2.5 Clean the spray chamber. 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 has passed, wipe off tubing with a Kimwipe and place back in DI water container. Let rinse, still on fast pump, for approximately 15 minutes. Watch the drain tubing to become clear again with large bubbles.

14.3 Monthly maintenance

14.3.1 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).

14.3.2 Perform an 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.

14.3.3 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.

14.4 Troubleshooting.

14.4.1 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.

14.4.2 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.

14.4.3 Plasma won't light: check to see if the torch is wet. If it is, it will be necessary to change it out and also 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.

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

14.4.5 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.

14.4.6 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.

14.4.7 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 if necessary. Change out all pump tubing.

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

15.0 Computer Hardware and Software

15.1 HP Computer, Intel(R) Xeon(R) CPU E3-1225 v3 @ 3.20 GHz 3.20 GHz, 4 GB Ram.

15.2 Operating System: Windows 10 Professional, Version 2009 service pack 1.

16.0 Data and Records Management

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

16.2 ICP-OES standard logs containing information about standard and QC preparations, upgrades, software issues, and solutions are kept with the instrument. All log books are kept permanently.

16.3 A log sheet is maintained in a binder which provides documentation of torch alignments, dark current scans, wavelength calibrations, chiller unit water level checks, air filter checks and water filter checks.

16.4 Current SOPs and instrument manuals are maintained in each lab where the instrument is located.

16.5 Data files are kept on a PC for 1 year from the date they are sent to the Program Office, then transferred to CD ROM for archiving (see Computer Support Staff for backup and computer program assistance,).

16.6 A complete instrument and file backup procedure is performed once a week on each instrumental computer (see *Computer Backup and Recovery*, SOP #DATA-31).

17.0 Quality Control and Quality Assurance

17.1 A calibration curve is always used at the start of each run followed by a blank. A Coefficient of Determination of $\geq 99.9\%$ for Ca, Mg, K, and Na is required (see section 18.3).

17.2 One solution of internally-prepared simulated rain containing cation concentrations approximating network 50th percentile level is used for Ca, Mg, K, and Na to verify calibration curves (FR50). Control limits and warnings are established at the time of preparation by measuring new QCS standards at least 10 times and calculating the standard deviations (see section 18.3). Control limits and warnings for FLYY####,

FMYY#####, FHYY#####, and FSPYY##### are calculated the same way (see section 18.3).

- 17.3 Blind internal blanks, splits, replicates, and QCS are analyzed. Values are compiled and checked after data has been transferred to LIMS by the QA chemist.
- 17.4 As a system check, a DI water blank is analyzed after the calibration curve and at the end of each run. If Ca, Mg, K, or Na is found at or above the Method Detection Limits (MDL), another DI water blank is analyzed. If the high value still exists, DI water from a separate source is analyzed. If the DI water from the separate source shows greater than the MDL concentration, further review of the system will be conducted.
- 17.5 QC control charts are maintained by the analyst and may be checked in the LIMS upon data transfer to observe fluctuation of these samples over time. The bench analyst can observe real time data generation and make adjustments to the instrument according to the QC results.
- 17.6 Accuracy is determined on a weekly schedule by reanalyzing selected samples. Report the results of the reanalysis values to the QA chemist on the preprinted forms provided. If any major differences are determined between the original and the reanalysis values, then comments should be included to explain the reasons and suggestions for any changes. Refrigerated samples (if available) should be analyzed to compare to original value.
- 17.7 The QA chemist overlooks all QC data collected and makes suggestions for improvement or correction.
- 17.8 Participation in several interlaboratory comparison programs include: National Water Research Institute (NWRI), Norwegian Institute for Air Research (NILU), World Meteorological Organization (WMO), and USGS Blind Audit.

18.0 References

- 18.1 ASTM D1976-12, Standard Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy, ASTM International, West Conshohocken, PA, 2012, www.astm.org
- 18.2 *Method Collection and Analysis of Precipitation*, M.E. Peden, et al., Illinois State Water Survey, 1986.

Appendix A Instrument Conditions and Method

The screenshot displays the ICP Expert software interface. The top menu bar includes File, View, Save, Plasma, Pump, Run, Stop, ICP-Applet, Instrument, Autosampler, and Report. The main window is titled 'Untitled' and contains several panels:

- Summary**: Shows a table of elements and standards.
- Elements**: Lists Ca (315.887 nm), Ca (893.366 nm), K (766.491 nm), Mg (280.270 nm), Na (589.592 nm), and Y (371.029 nm).
- Conditions**: The active panel, divided into 'Common Conditions' and 'Measurement Conditions'.
- Standards**: Shows 'Internal Standard' for Y.
- QC**: Quality Control section.
- Sequence**: Sequence settings.
- Autosampler**: Autosampler settings.
- Analysis**: Analysis parameters.

Common Conditions:

- Replicates: 3
- Pump speed (rpm): 12
- Sample introduction: Manual
- Uptake delay (s): 25
- Rinse time (s): 60
- Oxygen injection:
- Fast pump: (checked)

Measurement Conditions:

- Read time (s): 10
- RF power (kW): 0.75
- Stabilization time (s): 25
- Viewing mode: Axial
- Viewing height (mm): 8
- Use multiple conditions:
- 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

Table of Elements and Standards:

Label (Wavelength nm)	Type	Background Correction	Number of Pixels
Ca (315.887 nm)	Analyte	Fitted	1
Ca (893.366 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

Graph: A plot showing Intensity versus Wavelength (nm). The x-axis is labeled 'Wavelength (nm)' and the y-axis is labeled 'Intensity'. The plot title is 'Ca (315.887 nm)'. Below the graph, there are controls for 'View Graph', 'Read', and 'Time scan'.

Appendix B Calibration Standards and Parameters

ICP Expert - Untitled1.evs

File | New | Open | Save | Run | Stop | ICP Applet | Instrument | Autosampler | Report

Help

Concentrations

Correlation coefficient limit: 0.9990

Standard additions: Enable MultiCal view

Include blank in calibration: Use reagent blank

MultiCal summary concentration:

Enable recipe:

Number of standards: 10

Solution Label	Peak Tube	Ca (315.837 nm)	Ca (393.366 nm)	K (766.491 nm)	Mg (280.270 nm)	Na (588.952 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	0.0650	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	0.1000	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 Through Blank	Minimum Concentration	Maximum Concentration	Calibration Error
Ca (315.837 nm)	ppm	Linear	<input checked="" type="checkbox"/>	2.0000	11.0000	10 %
Ca (393.366 nm)	ppm	Linear	<input checked="" type="checkbox"/>	0.0000	2.0000	15 %
K (766.491 nm)	ppm	Linear	<input checked="" type="checkbox"/>	0.0000	2.2000	15 %
Mg (280.270 nm)	ppm	Linear	<input checked="" type="checkbox"/>	0.0000	2.2000	15 %
Na (588.952 nm)	ppm	Linear	<input checked="" type="checkbox"/>	0.0000	11.0000	15 %

Summary

Elements

Conditions

Standards

QC

Sequence

Autosampler

Analysis

Online












AN.HEAL.IN.ICP-cations.5.0 (AN-0082.4)

Final Audit Report

2021-07-27

Created:	2021-07-22
By:	Evan Rea (erea@illinois.edu)
Status:	Signed
Transaction ID:	CBJCHBCAABAANKHp3lqjVsBta4kyxV-Tamzm8fMW_WGj

"AN.HEAL.IN.ICP-cations.5.0 (AN-0082.4)" History

-  Document created by Evan Rea (erea@illinois.edu)
2021-07-22 - 4:33:41 PM GMT- IP address: 130.126.104.63
-  Document emailed to Margarita Bargon (rbargon@illinois.edu) for signature
2021-07-22 - 4:37:11 PM GMT
-  Email viewed by Margarita Bargon (rbargon@illinois.edu)
2021-07-22 - 4:42:10 PM GMT- IP address: 130.126.105.203
-  Margarita Bargon (rbargon@illinois.edu) verified identity with Adobe Sign authentication
2021-07-22 - 4:43:01 PM GMT
-  Document e-signed by Margarita Bargon (rbargon@illinois.edu)
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-  Nina Gartman (ngartman@illinois.edu) verified identity with Adobe Sign authentication
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Signature Date: 2021-07-26 - 5:41:32 PM GMT - Time Source: server- IP address: 130.126.104.71
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2021-07-26 - 5:41:34 PM GMT
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2021-07-26 - 6:23:29 PM GMT

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✔ Agreement completed.

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