



THE OHIO STATE UNIVERSITY

COLLEGE OF FOOD, AGRICULTURE, AND
ENVIRONMENTAL SCIENCES

Standard Operating Procedure

EPA Method 6010 Inductively Coupled Plasma (ICP) Spectrometry Analysis, Version 9
Soil Environmental Chemistry Program, The Ohio State University

ICP MANUAL



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1.0 Scope

1.1 Inductively coupled plasma-atomic emission spectrometry may be used to determine the following trace elements in solution; Aluminum (Al), Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Boron (B), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Potassium (K), Selenium (Se), Silver (Ag), Sodium (Na), Sulfur (S) Strontium (Sr), Thallium (Tl), Vanadium (V), Zinc (Zn).

2.0 Definitions

- 2.1** Matrix Spike: A duplicate sample is spiked in order to provide information about the effect of the sample matrix on the sample preparation and/or measurement methodology.
- 2.2** Serial Dilution: A serial dilution consists of a comparison of the results of a sample and another aliquot diluted by a known factor.
- 2.3** Laboratory Control Sample: The laboratory control samples is a certified QC standard (or dilution) for ICP analysis. The laboratory control sample is SPEX CertiPrep Group LPC standard 1, Fisher Cat. No. LPC-1-100N.
- 2.4** ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry.

3.0 Instrumentation and Facilities

3.1 ICP-AES and ICP-HG-AES analysis are carried out on an Agilent Technologies 720 ICP-OES (Agilent Technologies Inc., Santa Clara, CA) at the Soil Environmental Chemistry Lab, The Ohio State University, Dr. Nick Basta, Director.

4.0 Materials and Supplies

- 4.1** Single element ICP grade standards (SPEX CertiPrep Group, Metuchen, NJ, Assurance ICP Standards).
- 4.2** Laboratory control sample, SPEX CertiPrep Group LPC standard 1, Fisher Cat. No. LPC-1-100N.
- 4.3** Periodic table mix 1 for ICP (TraceCert, Sigma-Aldrich 3050 Spruce Street SAINT LOUIS MO 63103 USA)
- 4.4** Varian/Agilent tuning solution, Varian part no. 190005800.
- 4.5** Agilent ICP-OES Wavecal solution (Agilent part no. 6610030100)
- 4.6** Trace metal grade HCl.
- 4.7** Hamilton Autodiluter.
- 4.8** 15ml Falcon tubes

5.0 ICP-OES Procedure

5.1 Creating a Runlist

5.1.1 Create excel run list of ICP samples with similar matrix. Create from analysis sheet or sample list.

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- 5.1.2** Include analysis ID, ICP run name (Year-# run of that year i.e. 18-1), and ICP sample number. Also include operator, nebulizer (seaspray or slurry), ICP tubing configuration (aka pump tubing colors. Usually blk-blk and blu-blu), elements of interest and associated QC checks to be activated in the method.
- 5.1.3** A template like the one below that contains this information can be found in the “Runlist Template” spreadsheet on the desktop. This will go in the columns to the right of the sample analysis IDs.

ICP #	ICP Run				
18-1	1				
18-1	2				
		Operator:	Alyssa		
		Instrument	Agilent		
		sample	blk blk		
		waste	blu blu		
		nebulizer	Seaspray		
		matrix	3%		
		Run date:			
		QC			
		CRI	0.04 Ba	Ran did not flag	
		ICV	4 Ba		
		CCV	1 Ba		
		Spike			
		0.25 mL LCP/ 5 mL comp			

- 5.1.4** Save run list as “ICPyear - #” on the W drive>SECLab>ICP>year>runlist.

5.2 Turning on the ICP

- 5.2.1** Allow 45 minutes for the ICP to warm up before beginning a run
- 5.2.2** Ensure that the regulator pressure is 100 PSI and the gas tank pressure is >150 PSI. If the tank pressure falls below 150 PSI at any point in the run, turn on the pressure builder. The speed at which this builds pressure varies greatly between tanks (between 3 and 30 minutes). The pressure builder speed can be increased by opening the valve more and vice versa.
- 5.2.3** Turn on the water cooler and allow 2 minutes before attempting to turn on the ICP. The ICP will give a failure message if the cooler is off or if insufficient cooldown time has passed.





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- 5.2.4** Hook up all tubing: the yellow tube (gray-gray) for the autodilutor rinse, the blk-blk tubing for the sample, and the blu-blu tubing for the waste line. Ensure the tubing is flowing in the proper direction; both pumps rotate clockwise. Check the waste carboy and replace if full. Refill the rinse solution with 3% HCl (square dispenser by the reagent-grade DI. Use another bottle (behind computer) and funnel to transfer 3% into the container, rather than removing the rinse container. This will prevent flow problems.
- 5.2.5** Ensure that the nebulizer installed on the instrument is appropriate for your run. A seaspray nebulizer is used for most sample types. A slurry nebulizer is needed for high solids samples. A SWEL staff member can change the nebulizer if needed.
- 5.2.6** Visually inspect the torch for buildup inside of the torch. Buildup at the end of the torch will not impact the run. A flashlight is useful for this. A SWEL staff member can change the torch if needed.



These icons control the pump flow. The leftmost icon turns off the pump, the rightmost pump is high speed, and the middle icon is normal speed. Turn the pump on normal or high speed and that the flow is in the right direction, that there are no blockages in the line, and that there are no leaks at the junctions.

- 5.2.7**  Select this icon to turn on the torch.  Select this icon to turn off the torch.
- 5.2.8** As you turn on the torch, watch the flame. The flame will initially flicker or may turn orange. This is normal. However, if this continues, or the torch fails to ignite, let a SWEL lab member know.
- 5.2.9** After the torch ignites, check the lines for good flow. First, ensure that the spray chamber of the nebulizer is filled with mist, rather than clear. This may take several seconds when the ICP is first started if the lines were cleared in the previous run. The mist may be difficult to see, but turning the pump to fast can make it more visible. Ensure that there is no water building up in the spray chamber- this may be caused by a blocked waste line or backwards tubes. Ensure there is no liquid traveling up into the torch- this may be caused by backwards lines and will cause the torch to flicker or go out. The torch must be replaced if wet.
- 5.2.10** After the flame and lines have been checked allow the instrument 45 minutes to warm up before beginning a run

5.3 Making Standards and QC checks



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- 5.3.1** Calibration standards are prepared for each method run by serial dilution of a stock standard prepared from a certified mix or certified individual element standards. The dilutions should be done into a matrix comparable to the samples. Preparing 10mL of standard allows for 3 calibrations. Label tubes with matrix, concentration, operator initials, and the date. Discard after 1 week.
- 5.3.2** QC checks are run to ensure the calibration is still valid, that the standard matrix is appropriate for the sample matrix, and that there are no significant matrix effects. Label tubes with matrix, concentration, operator initials, and the date. Discard after 1 week. They are created and run as follows:

 - 5.3.2.1** Initial calibration verification (ICV) is performed using a certified mix or dilution of a certified mix and run immediately after instrument calibration. Standards must fall within $\pm 10\%$ for ICP-OES ($\pm 15\%$ for Al and Fe).
 - 5.3.2.2** CRI is performed using dilution of a certified mix to achieve approximately 50ppb concentrations and run immediately after instrument calibration. Standards must fall within $\pm 20\%$ for ICP-OES
 - 5.3.2.3** Continuing calibration verification (CCV) is performed by dilution of the calibration standard. One CCV is run after every ten samples. Standards must fall within $\pm 10\%$ for ICP-AES ($\pm 15\%$ for Al and Fe).
 - 5.3.2.4** Continuing calibration blank (CCB) is a calibration blank run after every ten samples with the CCV. The calibration blank must fall below the MDL. If a calibration blank is above the detection limit, the instrument must be recalibrated and the previous samples to the last CCB re-run.
- 5.4 Making Standards and QC checks**

 - 5.4.1** A matrix spike and serial dilution is run with a composite sample to ensure the standard matrix is appropriate for the sample matrix and to ensure that there are no matrix effects. These should be analyzed at the very beginning of a run. If the spike or dilution recoveries fall outside acceptable limits, then the samples should be diluted. A comp set should be run for each matrix included in the run.
 - 5.4.2** Make a composite sample (Comp) by pouring into a separate tube 1-2 mL of a number of samples until approximately 14 mL has been obtained. Cap and invert to fully mix. Because the comp may be used to get an estimate of element concentration in relatively homogenous sample sets (and can predict if dilution is needed), it



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is best to not include blanks or sample spikes when making the comp.

5.4.3 Matrix Spike (Comp Spike): Use 5mL comp to prepare the comp spk. For elements of interest, the spike should be 1ppm if the concentration in the comp is 0-2 ppm. This can be achieved by spiking 5mL comp with 0.250mL LPC.

5.4.3.1 If the element concentration is greater than 2ppm, the sample should be spiked with a concentration 50-100% of the comp concentration. This can be done using the element standards on the autodilutor cart. The "Spike Calculator" spreadsheet (on desktop) can be used to easily calculate spikes.

5.4.3.2 The matrix spike should not consist of more than 10% of the sample volume.

5.4.3.3 Spike recoveries must fall within the limits of 75-125%.

5.4.3.4 Record matrix spike preparations in ICP run list.

$$\%Difference = 100 * \frac{(\text{comp spike conc.} - \text{initial conc.})}{\text{Spike added}}$$

5.4.4 Serial Dilution (Comp x5): Prepare dilution using an autodiluter.or pipette. A single 5x dilution is typically used.

5.4.4.1 Record dilution preparations in ICP run list. The % difference for the dilution tests must be no more than 15%

5.4.4.2 An error greater than 15% is acceptable when the dilutions are below the reporting limit.

$$\%Difference = 100 * \frac{(\text{initial} - (\text{diluted} * \text{DilutionFactor}))}{\text{Initial}}$$

5.5 Setting up the method

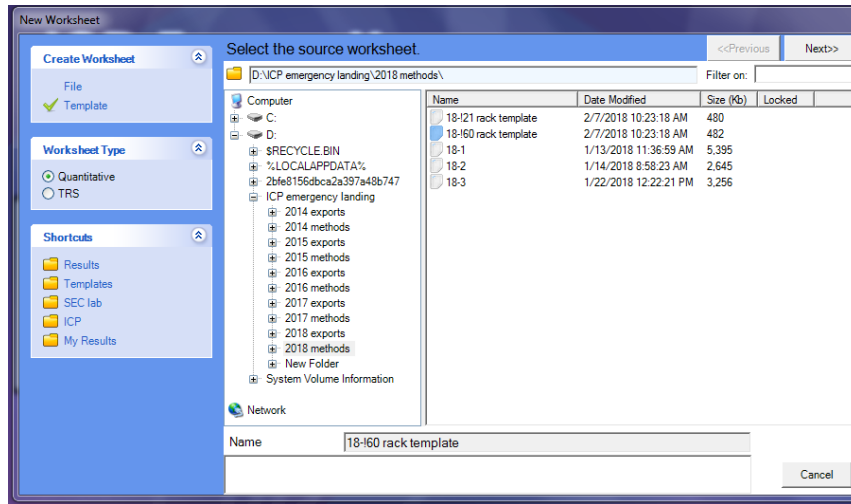
5.5.1 Load method from appropriate template

5.5.2 Agilent: Select File-New.... Under Create Worksheet, select Template.

5.5.3 Go to D:\IDP emergency landing\YYYY methods\

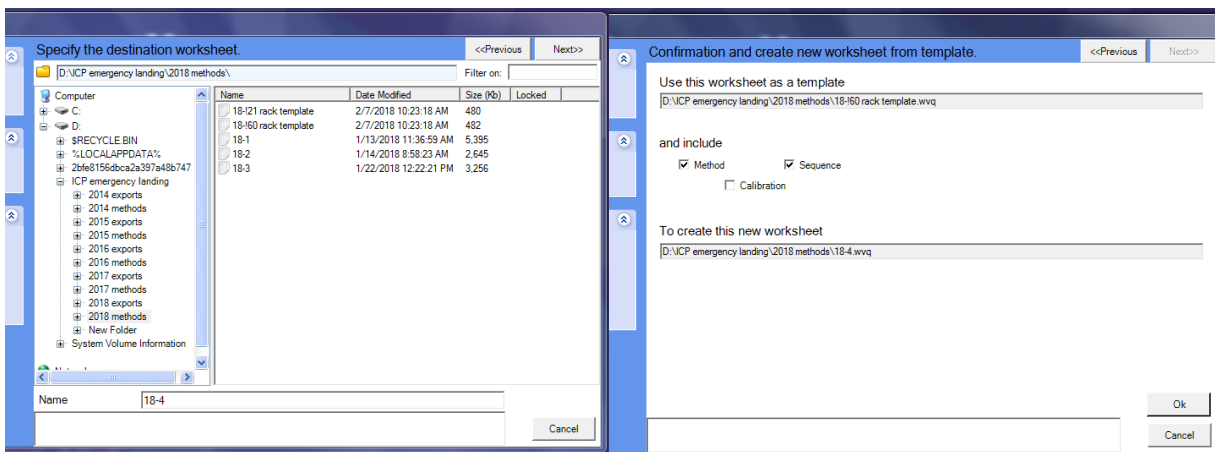
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5.5.4 A previous run can be used as a template. For a new run, select the 18-21 rack template for 50mL tubes, or the 18-60 rack template for 15mL tubes. Files can be selected in the center pane, not the right pane.



5.5.5 Select next to rename the template to the run name (YYYY-Run#). The run data will be stored in this folder.

5.5.6 When conducting a new run, select the Method and Sequence options. A new run will be created using the method and sequence of the template run. If the run is to use the same calibration as the template run, select the Calibration option as well.



5.6 Modifying the Method



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Select the Method tab>EditMethod...

- 5.6.1** Adding Elements: The template contains the most commonly run elements. Additional elements can be added in the Element Tab. Select "Add..." to add element. Choose the top two recommended lines. When adding elements, be sure to update the standards and to change the MultiCal parameters to match the other elements (the default values are different than the ones in our template). Update the QC checks and QC blanks (these will automatically be selected for QC actions).
- 5.6.2** Conditions: For most runs, the template conditions do not need to be changed. For high salt/organic samples, however, increasing the rinse time to 45-60 seconds is recommended.
- 5.6.3** Standards: The standards in the template correspond to the "Periodic table mix 1 for ICP" standards described above. Standards can be changed or added. Copy and paste are useful functions here. If more than 10 standard solutions are required, then the sequence must be modified (see below). In the template, there are 10 standards but 5 are blanks. While standards can be modified during a run, the number of standards cannot, so blank standards allow additional standards to be added during a run if needed.
- 5.6.4** QC Test: Checking the boxes turns on QC Actions for an element. Turn on QC Actions for elements of interest for CCV, CRI, and CCB.
- 5.6.5** Most method options cannot be changed once the run is started

5.7 Modifying the Sequence


Select the Sequence tab>Sequence Editor...

- 5.7.1** If a different QC set is desired than the one in the template, this can be changed under the Rate generated QC tab of the Sequence Editor.
- 5.7.2** If more than ten standards are required, go to the "Autosampler Setup..." tab to change the standard rack from the 11 rack to the third 60 rack. Under "Rack Properties", change the Type and Use.
- 5.7.3** **Sequence options cannot be changed once the run is started**

5.8 Calibration

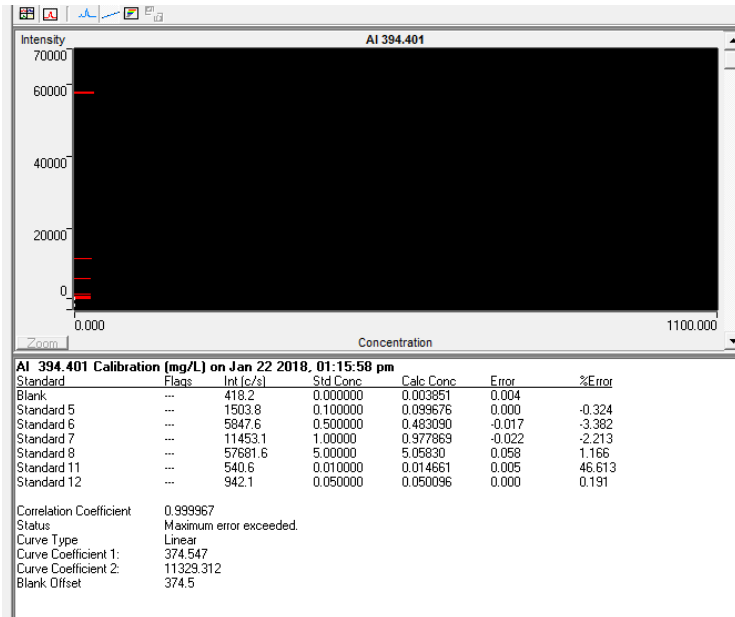
- 5.8.1** Go to the Analysis tab. Individual samples cannot be selected until after the run has started. The start arrow will turn green when samples are highlighted. Start and immediately stop the run. Now individual samples can be selected. Selected the blank and run.

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5.8.2  Under the Multiple Graphs Spectrum graphs view, inspect the spectrum graphs for each element. While most elements should show no peak, the following elements may have a peak: Ar, B, Be 313, Ca, Cu 324, Fe, K, Mg, Na, S, V, and Zn. If a line is having difficulty calibrating, looking at a previous runlist can help determine whether a blank peak is normal or not. Some elements, notably arsenic, are prone to dirty blanks. If this occurs, rinse on high speed with 24% acid for several minutes. If blank is still dirty, run the standards (highest to lowest) and rerun the blank at the end.

5.8.3 When a clean blank has been obtained, run all standards (including the blank). Once the instrument has run the calibration standards, check to ensure all lines are calibrated. Linear calibration must meet the criteria of: $r^2 = 0.995$, and calculated concentrations from the regression within 15% for each standard in the calibration. If these conditions are not met, the line will not calibrate. In this case, examine the % error for each element on the “Single Graph

Calibration Graph  screen.



5.8.4 Mask values of the calibration with high error. Start with the highest error standard (usually the lowest standard). Right click on that standard and select edit replicates. If the error is low (<20%) and/or there is a clear outlier, mask one replicate and recalculate to try to



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obtain a curve. Otherwise, mask all replicates and recalculate. This can be repeated with other standards so long as there are at least 3 standards used in the calibration. The reporting limit (RL) for a run is the lowest standard that has at least two replicates.

Reading	Net Intensity	Background	Conc	Flags
Mean	---	---	---	
Rep 1	522.697	21859.996	0.013	e
Rep 2	562.674	21806.844	0.017	e
Rep 3	536.578	21764.318	0.014	e

6.0 Running

6.1 After calibration, the run can be started. QC sets are run after the initial calibration and after every 10 samples. QC actions can pause a run if the operator will be nearby (under Sequence Parameters, select “Plasma on & pump slow”, or end a run if absent (“Plasma off & pump off”).

At end of sequence

At end of a run you can save gas by automatically switching the plasma off (to stand-by mode). The following options are available.

- Plasma on & pump slow
- Plasma off & pump slow
- Plasma off & pump off

Advanced

- Store wavelength spectrum graphics
- Subtract preparation blank

On calibration failure: Continue in emission

Poly boost off:

Audible warning: 5 cycles

Rinse time (end of worksheet): 0 s

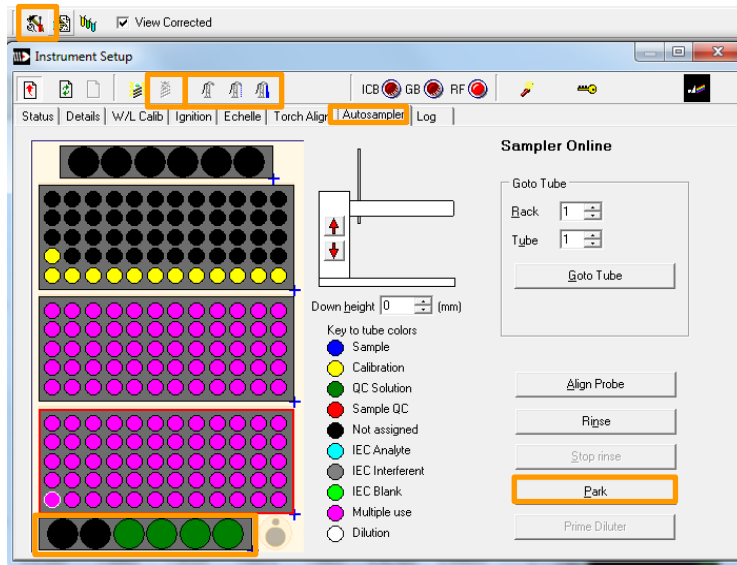
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6.2 In cases where one line is calibrated well but the other line is calibrated poorly or not calibrated, QC actions can be turned off so that the run will not be disrupted by this line. In this case, right click any sample in that line and deselect “QC Actions”.

7.0 Ending a Run

7.1 Operator present: The lines should be rinsed and dried following every run. After all samples have been run, turn the pump speed to fast and rinse with 3% for at least 5 minutes. Subsequently, rinse with DI for at least 10 minutes (fill a 50mL falcon tube with DI and place in an unused space in rack. Open Instrument Setup>Autosampler and double click on the space where the DI tube is located to place the probe there). After rinsing, park the probe and continue pumping until the spray chamber empties. Immediately turn off the ICP (running for prolonged periods without liquid can damage the torch). Pump the lines until dry. Inspect the torch for buildup. Samples high in salts or organic matter can quickly dirty a torch. Inform a SWEL staff member if there is buildup on the torch.



7.2 Operator absent- The rinse procedure after running overnight is the same as described above, but with the ICP off.

8.0 Post-Run and Data Handling

8.1 Methods are stored on D drive during analysis automatically but must be copied to W drive following analysis. (Wdrive>SECLab>ICP>ICP Expert W Drive>year>my results>year.)

8.2 Export data

8.2.1 Highlight samples to be exported (exclude the 10 samples prior to QC failure and failed QC block).



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Flag	Measurement	QA/QC	Frequency	Acceptance Criteria	Corrective Action
		Check ¹			

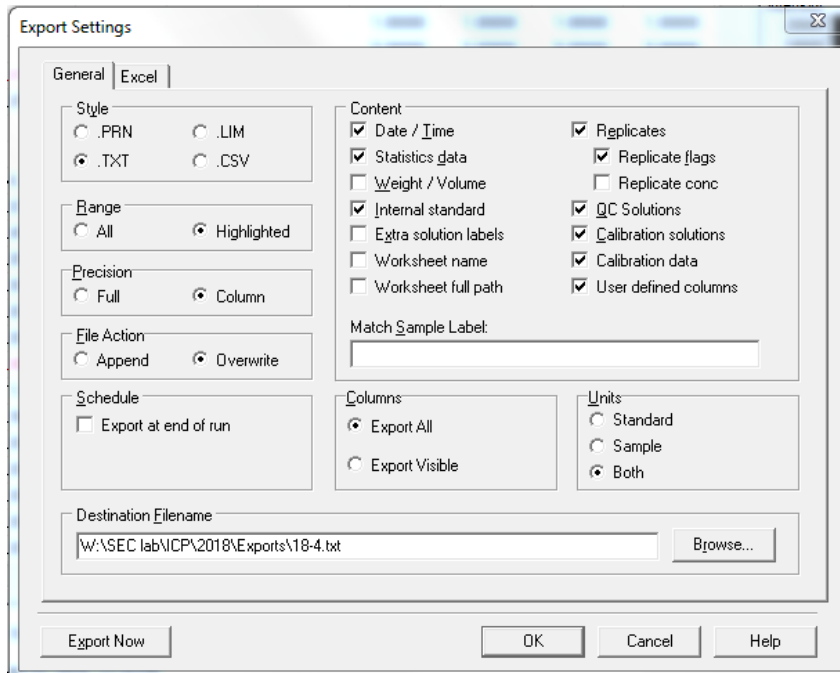
8.2.2 Bring up the Export Settings by pressing ctrl+E or File>Export Settings. The default settings are shown below.

8.2.3 Export selected samples as txt file onto W:\SEC lab\ICP\2018\Exports\YY-#.txt and D:\ICP emergency landing\2018 exports\YY-#.txt

8.2.3.1 YY is the year and # is the ICP number (i.e. 18-5 for the 5th ICP run of 2018)

8.3 Summarize data

8.3.1 See ICP Data Summary and Reporting SOP



9.0 Corrective Action

9.1 The table below details the quality control checks, frequency, and corrective action procedure for each quality control check.



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a		Calibration	r^2	Calibration	≥ 0.995 ICP-AES	Check calibration stds and recalibrate.
b		Calibration	% Dev	Calibration	$\pm 15\%$ ICP-AES	Check calibration stds and recalibrate.
c		Calibration	ICV/LCS	After calibration but before samples.	$\pm 10\%$ ICP-AES ($\pm 15\%$ for Al & Fe)	Stop analysis, determine and correct problem, and recalibrate.
d		Calibration	CCV/LCS	Every 10 samples	$\pm 10\%$ ICP-AES ($\pm 15\%$ for Al & Fe)	Stop analysis, determine and correct problem, and recalibrate. Report only values prior to the last good CCV.
e		Reporting Limit (RL)	RL	Calibration, with consideration of method blank.	The lowest calibration standard utilizing at least 2 replicates and falling within 15% of the value predicted by the regression line. If the method blank is higher than the calibration reporting	If elevated reporting limit is related to failure of low-end calibration standards, remake standards and recalibrate. If elevated reporting limit is due to method blank contamination, method / extraction may need to be



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					limit, the reporting limit shall be 10x the element concentration present in the method blank.	redone and care taken to identify contamination source.
f		MDL	LOQ check	After calibration but before samples and after last sample. The MDL is also established on an annual basis.	±20% ICP-AES	Stop analysis, determine and correct problem, and recalibrate. Report only values prior to the last good LOQ check.
g		Instrument Drift/ Sample Carryover	ICB	After calibration but before samples.	Below MDL	Stop analysis, determine and correct problem, and recalibrate.
h		Instrument Drift/ Sample Carryover	CCB	Every 10 samples.	Below MDL	Stop analysis, determine and correct problem, and recalibrate. Report only values prior to the last good CCB..
i		Linear Range	LRV	Once per analytical run if analyte concentration in the samples is more than 20% greater than highest	±10% ICP-AES	Samples with analyte concentrations above the LRV must be diluted and re-analyzed.



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				calibration standard. The LRV is also established on an annual basis.		
j		Matrix effects	Matrix spike	One per group of samples with similar matrix type.	±25% ICP-AES	If Matrix spike fails: 1 st) Dilute sample, perform matrix spike on diluted sample. If spike still fails or analyte is below MDL then, 2 nd) Use internal standard to correct for matrix affect and perform matrix spike using internal correction. If matrix spike still fails then, 3 rd) Use standard additions to analyze samples.
Flag		Measurement	QA/QC Check ¹	Frequency	Acceptance Criteria	Corrective Action
k		Matrix effects	Serial Dilution	At least one per group of samples with	% difference ± 15% if above the RL	If serial dilution fails: 1 st) Dilute



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				similar matrix type.		sample, perform serial dilution on diluted sample. If serial dilution still fails or analyte is below MDL then, 2 nd) Use internal standard to correct for matrix affect and perform serial dilution using internal correction. If serial dilution still fails then, 3 rd) Use standard additions to analyze samples.
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