1.0 TITLE

Determination of Alkalinity, pH, and Conductivity by Man-Tech Auto Titrator

2.0 LOCATION

Wet Chemistry Manual Lab

3.0 SCOPE & APPLICATION

3.1 The following procedure is applicable to the operation of the Man-Tech autotitrator and conductometer.

3.2 pH: At a given temperature the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment is pH-dependent (acid-base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control). This procedure is applicable to drinking, surface, and saline waters, domestic and industrial waste waters, and acid rain. The range is from 0 to 14 pH units. Buffer capacity is the amount of strong acid or base needed to change the pH value of a 1-L sample by 1 unit. Natural waters usually have pH values in the range of 4 – 9, and most are slightly basic because of the presence of bicarbonates and carbonates of the alkali and alkaline earth metals. Temperature effects the electrometric measurement of pH. At 25 ºC, pH 7.0 is neutral. The neutral point is temperature dependent and is pH 7.5 at 0 ºC and pH 6.5 at 60 ºC.

3.3 Alkalinity: Alkalinity of a water is its acid-neutralizing capacity and is the sum of all the titratable bases. Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Alkalinity in excess of alkaline earth metal concentration is significant in determining the suitability of a water for irrigation. Measurements are also used in the interpretation and control of water and wastewater treatment processes. This method is applicable to drinking water, surface and saline waters, and domestic and industrial wastes and is suitable for all concentration ranges of alkalinity.

3.4 Conductivity, *k*, is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors, while molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

Laboratory conductivity measurements are used to: establish the degree of mineralization to assess the effect of the total concentration of ions on chemical equilibria, physiological effect on plants or animals, corrosion rates, etc.; assess the degree of mineralization of distilled and deionized water; evaluate variations in dissolved mineral concentration of raw water or wastewater (minor seasonal variations found in reservoir waters contrast sharply with the daily fluctuations in some polluted river waters); estimate total dissolved solids in a sample; and approximate the cations or anions in some waters.

4.0 SUMMARY

4.1 A known volume of sample is automatically drawn and dispensed into a vessel for analysis and/or analyzed in sampler tube. The data results are stored in a file and uploaded into the LIMS database. The analysis and lab number are controlled via the PC-Titrate software.

4.2 PH: pH is determined in replicate using a combination glass/reference temperature compensating electrode. The replicate analysis is performed to condition the probe and the difference between the replicates must agree within 0.1 pH unit, in which case the first value will be reported. The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a specific pressure. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, a glass electrode is used instead

4.3 ALKALINITY: Hydroxyl ions present in the sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. To quantitatively measure alkalinity, a known volume of sample is titrated in a vessel with a standard H_2SO_4 acid solution to electrometrically determined endpoints of pH 8.3, 4.5, & 4.2. The volume of acid consumed is used to calculate the total alkalinity including bicarbonate, carbonate, and hydroxide concentrations in the water sample. Use of the appropriate titrant is important in order to provide accurate results. For samples of low alkalinity, less then 20 mg/L, the use of an extrapolation technique based on the near proportionality of concentrated hydrogen ions to excess of titrant beyond the equivalance point is used. See 13.1.2.

4.4 CONDUCTIVITY is measured in the auto sampler tube using a temperature compensating conductivity meter.

5.0 REFERENCES

5.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500-H^+ B, (1996).

5.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2320B, (1997).

5.3 Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2510B, (1997).

5.4 PC-Titrate Windows Software (version 2.5) Manual, Man-Tech Associates Inc., PC-Titration Plus, 2 Admiral Place, Guelph, ON, N1G 4N4, Canada.

5.5 Model 4310 Conductivity Meter Operating Manual, Jenway Limited, CM6 3LB, England.

5.6 Standard Methods for the Examination of Water and Wastewater, Online Edition, Method 4500-H^+B, (2000)

6.0 SAMPLE COLLECTION, HANDLING & PRESERVATION

6.1 Samples for all parameters are stored at 0-6.0ºC. Use “RAW” (unpreserved and unfiltered).

6.2 Hold Times:

Parameter Description	Matrix	Hold Time Starts – Ends With
Alkalinity	Liquid	14 days from sample collection to analysis
	Soils with Extraction	180 form sample collection start of sample extraction; 14 days from end of sample extraction to analysis.
Conductivity (EC)	Liquid	28 days from sample collection to analysis
	Soils with Extraction	180 form sample collection start of sample extraction; 28 days from end of sample extraction to analysis
pH	Liquid	1 days from sample collection to analysis

7.0 APPARATUS & SUPPLIES

7.1 Man-Tech auto sampler unit
7.2 PC-Titrate interface module
7.3 TitraSip Module
7.4 100 mL Titration vessel with holder
7.5 Jenway 4310 Conductometer
7.6 HM Digital Conductivity/TDS Meter Model 4510
7.7 pH Electrode
7.8 Conductivity Electrode
7.9 Thermometer, verified before use (refer to Control of Measuring and Test Equipment ID1522)
7.10 85ºC Oven
7.11 Sample tubes
7.12 Class A volumetric glassware.
7.13 Analytical balance, calibration verified before use (refer to Control of Measuring and Test Equipment ID1522)
7.14 Mechanical pipettes, accurate delivery verified before use (Control of Measuring and Test Equipment ID1522)

8.0 REAGENTS & STANDARDS

NOTE: All reagents and standards are prepared using Class A volumetric glassware. Store each prepared solution, except as noted, in a labeled plastic bottle at room temperature. Solutions expire after one year or PCN expiration date, whichever is sooner. Standardized reagents used for titrations expire **one month after opening**, but can be extended by verifying standardization, refer to Acidity ID 1475. (refer to CAR1412).

NOTE: When opening a new bottle of pre-made certified solution from a vendor, the true value must be obtained by looking up the lot number in the “Search” field under “Certificate of Analysis” at www.fishersci.com, or by looking up the PCN report to view the COA. The true value must be entered into the Mantech software before running a workgroup with the new acid. See §11.9.7.

8.1 2 N Stock Sulfuric Acid (H_2SO_4): Refer to Acidity ID 1475 or purchase pre-made certified 2 N stock.

8.2 1 N Stock Sulfuric Acid (H_2SO_4): Refer to Acidity ID 1475 or purchase pre-made certified 1 N stock.

8.3 0.2 N Sulfuric Acid (H_2SO_4): Refer to Acidity ID 1475 or purchase pre-made certified 0.2 N stock.

8.4 0.02 N Sulfuric Acid (H_2SO_4): Refer to Acidity ID 1475 or purchase pre-made certified 0.02 N stock.

8.5 0.01 M Potassium Chloride (KCl): In a 1 L volumetric flask, dissolve 0.7456 g of dried KCl in ~ 500 mL Type I water. QS with Type I water and mix thoroughly. Store this solution in the dark either in the cabinet or in a dark bottle. The true value = 1413 µS/cm. Or purchase pre-made. Vendor's expiration dates apply.

NOTE: Solid KCl is stored in the desiccator in the balance room. Whenever a new container is opened, the solid must be dried at 105 ºC for 2 hours and then cooled in the desiccator before preparing the reagent solution.

8.6 pH Buffers: 2, 4, 7, 10, 13 are purchased pre-made from the vendor and are used to calibrate the pH probe. Store at room temperature. Manufacturer's expiration date applies.

8.7 LCSW:

8.7.1. Alkalinity: Prepare the solution from a separate source (different vendor or different lot number than stock used for the alkalinity acid standardization solution).

8.7.1.1. For use with 1 N or 2 N acid: Weigh 55.072 g of $NaHCO_3$ into a 1 L Class A volumetric flask with ~ 500mL Type I water to dissolve the solid. QS to 1 L with Type I water and mix. TV = 32,800 mg/L.

8.7.1.2. For use with 0.2 N acid: Weigh 13.768 g of $NaHCO_3$ into a 1 L class A volumetric flask. Add ~ 500 mL Type I water to dissolve the solid. QS to 1 L with Type I water and mix. TV = 8200 mg/L.

8.7.1.3. For use with 0.02 N acid: Weigh 1.3768 g of $NaHCO_3$ or pour 25mL of the 32,800 mg/L LCSW into a 1L class A volumetric flask with ~ 500 mL Type I water to dissolve the solid. QS to 1L with Type I water and mix. TV = 820 mg/L.

8.7.2. pH: A QC standard or buffer obtained from a different source than the buffers used for calibration. If the same vendor supplies both the LCSW and calibration buffer solutions, then the LCSW must be from a different lot. True Value = 6

8.7.3. Conductivity: A conductivity standard is purchased premade from a vendor; must be obtained from a different source (different vendor or different lot number than the standard used for calibration. True Value = See PCN COA.

8.8 4 M KCl fill Solution for pH probes: In a 1 L volumetric flask, dissolve 300 g of dried KCl in ~ 500 mL Type I water. QS to 1 L with Type I water and mix thoroughly. Or purchase pre-made. Vendor's expiration dates apply.

8.9 Alkalinity PQV: Weigh 0.0672g of $NaHCO_3$ into a 2L class A volumetric flask with ~500 mL Type 1 H_2O to dissolve the solid. QS to 2L with Type 1 H_2O and mix. Solution may also be purchased pre-made. Vendor's expiration dates apply. True Value = 20 mg/L.

8.10 Conductivity PQV: In a 2L volumetric flask, dissolve 0.0106g of dried KCl in ~1L of Type 1 H_2O. QS to 2L with type 1 H_2O. Solution may also be purchased pre-made. Vendor's expirations dates apply. True Value = 10 µS/cm

9.0 SAFETY

9.1 HAZARDS

9.1.1 This procedure does not propose to address all safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous.

9.2 SAFETY TECHNIQUE

9.2.1 Safety glasses are required and the use of gloves and lab coat is strongly recommended. Shorts and open-toed shoes are not allowed in the lab.

9.2.2 Use care when pouring and pipetting reagents. Always add acid to water. Use the proper method when washing glassware.

9.2.3 Do not eat or use tobacco products in the lab.

9.2.4 Wipe up ALL spills immediately. Implement the Emergency Response Plan if necessary.

9.2.5 Do not wear gloves or lab coat outside of the laboratory. Remove gloves before using a computer, telephone, etc.

9.2.6 Do not conduct “experiments” unrelated to the analysis.

9.3 PROTECTIVE EQUIPMENT

9.3.1 Use a fume hood when there is a potential for strong fumes.

9.3.2 A fire extinguisher is located in each analytical laboratory.

9.3.3 Emergency shower and eye wash stations are located in the metals prep lab.

10.0 INTERFERENCES

10.1. Do not analyze samples with visible oil on the surface, as this may coat the electrodes and syringe of the auto sampler. Obtain an oil free sample with a pipette from the bottle or run the analysis by Manual Alkalinity Qualtrax ID 1472 and Manual pH Qualtrax ID 1474. EC needs to be run on the instrument.

10.2. Oily material and suspended solids may coat the electrode and cause a slower response. Gently wipe probe or wash with detergent wash and then rinse with distilled water. Follow cleaning procedures supplied with electrode as needed.

10.3. Do not filter, dilute or alter the sample when “Raw” samples are stated to be used. If there is insufficient “Raw” sample volume to run the analysis on the instrument, it may be run by Manual Alkalinity Qualtrax ID 1472 and Manual pH Qualtrax ID 1474 using a smaller sample volume, or "White" sample can be used to run the analysis on the instrument.

10.4. Regularly clean and rinse the system to avoid contamination.

10.5. Samples with a high concentrations of suspended sediment will cause the alkalinity value to be higher than if analyzed on a filtered sample. This will affect the cation/anion balance. Suspended sediment can interfere with instrument function if the sediment is drawn up into the mechanism and titration vessel. Be aware of excess sediment in the bottom of sample tubes, especially after centrifuging.

10.6. Weak organic salts and inorganic acids are sources of interference for alkalinity.

10.7. Make sure that the dispensing tips are is inserted far enough into the cup, so as to be touching the liquid when dispensing. Reference CAR Qualtrax ID 8718.

11.0 PROCEDURE

11.1. Turn on the meter, computer and all instrument components. Log on to the computer (user "Wetchem" and current password).

11.2. Open PC-Titrate software.

11.3. Fill the carboy with Type I water, and clean the pH probe with KCl fill solution and fresh Type I water. To clean, drain the pH electrode, flush with Type I water, drain, fill with fresh KCl, drain, and fill with fresh KCl.

11.4. Create a workgroup in LIMS. Up to 40 samples can be analyzed on Mantech (manip) 1. Up to 80 samples can be analyzed on Mantech (manip) 2.

11.5. Gather samples from the walk-in cooler. Pour off 40 mL of each sample. Bring sample aliquots and standards to room temperature. To expedite the warming process, place aliquots in the 85 ºC oven for about 5 minutes. The use of a timer is recommended to ensure samples are not overheated.

NOTE: For each client sample, verify that the log-in number on the workgroup matches the sample number on the bottle. This ensures that samples are not inadvertently switched when they are poured off.

DO NOT dilute any sample for pH, EC, and Alkalinity For a sample with high concentration of suspended sediment, either perform the analysis manually or centrifuge the sample, high amounts of sediment may need to be decanted, note this on the bench sheet

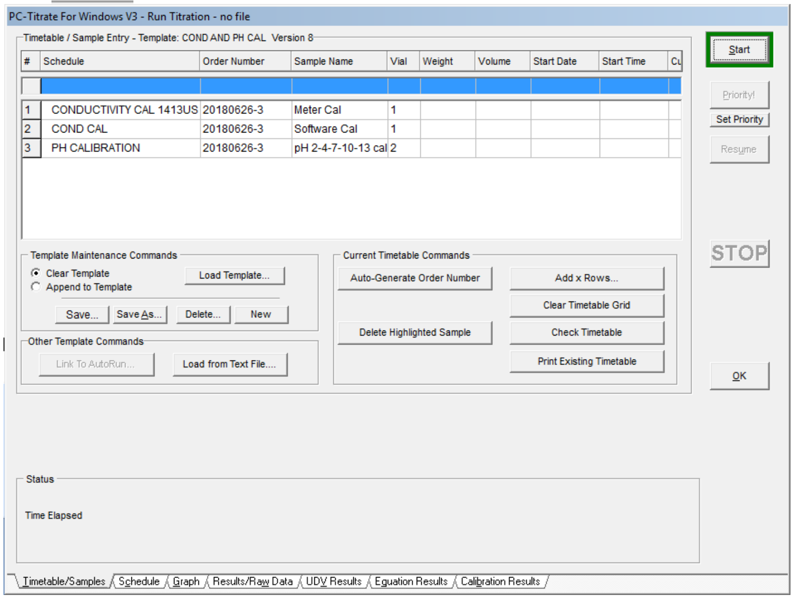
11.6. CALIBRATION: Calibrate the instrument at least once each day it is used.

NOTE: The calibration standard values are entered in the software. If the true value changes for any calibration standard then this must be reflected in the software. Verify with the department supervisor or QA/QC that the change is acceptable and refer to the Man-Tech PC-Titrate manual to update the value in the software.

11.6.1. For EC and pH load the auto sampler tray in the following order: EC calibration standard, pH 2 buffer, pH 4 buffer, pH 7 buffer, pH 10 buffer and pH 13 buffer, at least 40 mL each.

11.6.2. Fill a centrifuge tube with ~ 40 mL of pH 4 buffer Place the tube in position 55 for ManTech 1 and position 122 for Mantech 2. After calibrating, the instrument will automatically use the tube as a system purge and will fill the vessel for storage. This must be done for all runs and calibrations.

11.6.3. Click on the “pH calibration” icon and click “Start” to start EC/pH calibration run.



#	Schedule	Order Number	Sample Name	Vial	Weight	Volume	Start Date	Start Time	Cu
1	CONDUCTIVITY CAL 1413US	20180626-3	Meter Cal	1					
2	COND CAL	20180626-3	Software Cal	1					
3	PH CALIBRATION	20180626-3	pH 2-4-7-10-13 cal	2					

1) After the auto-sampler moves the probe into the EC standard, allow it to stabilize in the solution and to be prompted on the computer screen. Record the EC probe ID in the EC Calibration Log Book. Record the True Valuse (TV) and PCN of the calibration standard in the EC Log Book. Once stabilized, recod the Observed Value (OV) and temperature off the EC meter before proceding.

   - For ManTech 1 Jenway 4310 Conductometer push the right arrow to access the EC meter, “ENTER,” and click “OK” on the computer screen.

   - For ManTech 2 HM Digital Conductivity/TDS Meter Model 4510 press the Cal button 2 times, until the meter reads “cal OK,” and then click “OK” on the computer screen.

2) When the EC calibration and pH calibrations are complete, the results generate to a PDF merge file automatically. Merge the pHcalibration and updated reagent sheet together then name the file WG######-rgtcal.pdf. Verify that the calibration is correct and enter into the ManTech calibration notebook. If samples are analyzed for Alkalinity then record the normality and PCN of the H_2SO_4 solution in the logbook and on the data review checklist.

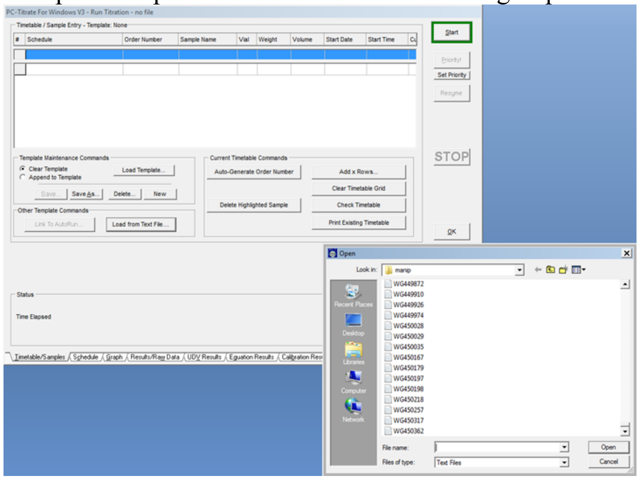
3) The pH calibration is acceptable if the result for the slopeis within the Minimum and Maximum values noted on the printout. Calibration Validity = “True” if passing or “False” if failing.

4) The EC calibration is acceptable if the reading result is withing 91%-109% recovery of the calibration standard 1413 value. Record a TV/OV of a secondary source EC standard in the EC Calibration Log Book, along with te percent recovery and probe ID.

NOTE: If the EC calibration does not pass, verify the K value is correct. The K value is on the white tag on the cord of the EC probe (i.e. K = 1.12). On the EC meter move the arrow to under the K by pushing the left or right arrow keys. Adjust the K value up or down using arrow buttons to the K value on the tag. <u>Recalibrate the EC probe</u>. Restandardiztion may be done without recalibrating pH by deleting pH from the calibration run. Contact ManTech tech support if attempts to obtain a passing standardization are not successful.

11.7. SAMPLE ANALYSIS

11.7.1. To start the analysis, open “Titrator” and go to “Run Titration.” Load the workgroup by selecting “Load from Text File” from the “Other template commands.” Browse in U:\Input\Manip and select the number of workgroup to be analyzed and then click “OK.”



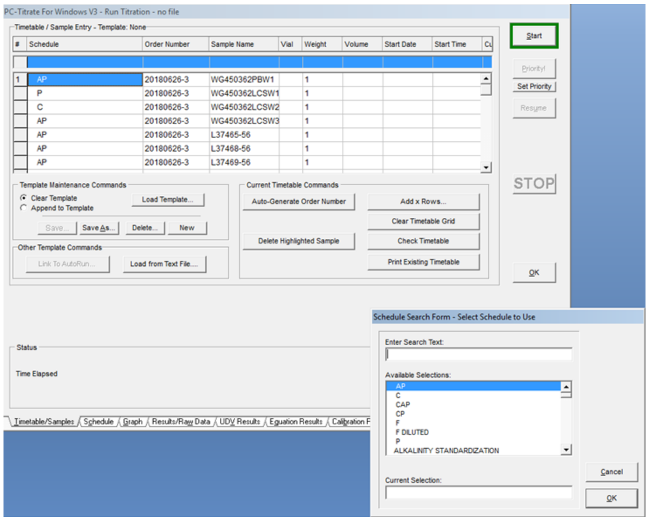
11.7.2. Verify the appropriate analysis or analyses for each sample are in the “Schedule” field. Correct the schedule if necessary, and delete the new volume amount in the “Volume” column and add a 1 to the “Weight” column.

11.7.2.1. For Alkalinity the schedules are “AP” or “ PH AND ALKALINITY”

11.7.2.2. For EC the schedules are “C” or “ COND ONLY”

11.7.2.3. For pH the schedules are “PH” or “ PH ONLY”

11.7.2.4. For EC, pH, and alkalinity the schedule name is “CAP” or “ COND PH ALKALINITY”



#	Schedule	Order Number	Sample Name	Vial	Weight	Volume	Start Date	Start Time	Cu
1	AP	20180626-3	WG450362PBW1		1				
	P	20180626-3	WG450362LCSW1		1				
	C	20180626-3	WG450362LCSW2		1				
	AP	20180626-3	WG450362LCSW3		1				
	AP	20180626-3	L37465-56		1				
	AP	20180626-3	L37468-56		1				
	AP	20180626-3	L37469-56		1				

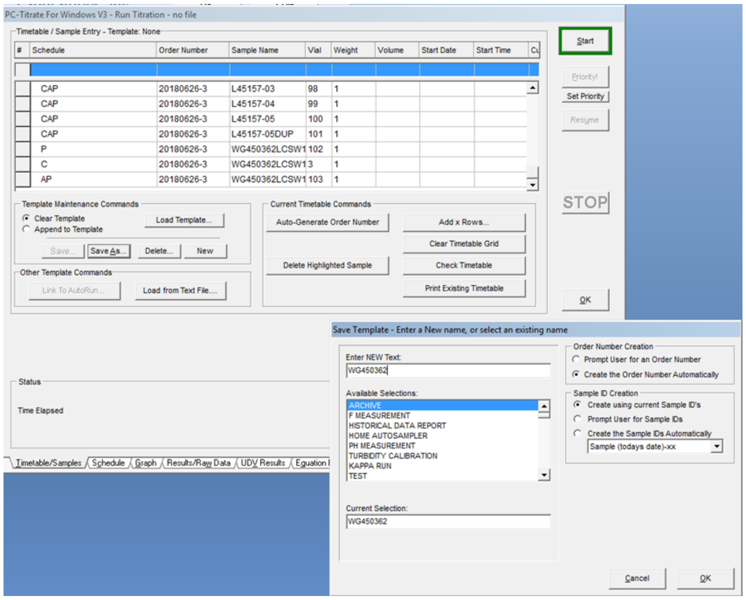
11.7.3. Enter the order numbers by clicking the top order numbers box, next click “Auto Generate Order Numbers” to enter the order numbers in that box. To populate all order numbers boxes, click away, then click the top order number field, while holding down the shift key, drag the mouse to the last order number box in the column, and then release the mouse button.

11.7.4. Enter the vial position1 for the first QC to be run. Click away and then drag down from the first line, and the software will auto increment each entry.

NOTE: EC is done prior to any other analysis. Multiple analysis for EC may be run off the same tube. ~ 30 mL of sample are sufficient for the probe to be submerged in the sample. If the probe is moved up or knocked then verify that sufficient sample is added to each tube to completely submerge the tip of the probe.

11.7.5. If more spaces are needed for additional samples, QC or retests then add rows to the template. Click on “Add x Rows…” Enter the number of rows needed and click “OK.” The extra rows will appear at the bottom of the template and can be moved if needed by highlighting the row and dragging it. Remove unneeded rows by highlighting the extra row(s) and clicking on “Delete Highlighted Sample.”

11.7.6. Save the template after all changes have been made. Use the “Check Timetable” button to verify the template is free from errors; otherwise, if a mistake was made there will be an error messages when the run is started. Load sample tubes into auto-sampler and <u>make sure all samples are in the correct position</u>.



Timetable / Sample Entry - Template: None

#	Schedule	Order Number	Sample Name	Vial	Weight	Volume	Start Date	Start Time	Cu
	CAP	20180626-3	L45157-03	98	1				
	CAP	20180626-3	L45157-04	99	1				
	CAP	20180626-3	L45157-05	100	1				
	CAP	20180626-3	L45157-05DUP	101	1				
	P	20180626-3	WG450362LCSW1	102	1				
	C	20180626-3	WG450362LCSW1	3	1				
	AP	20180626-3	WG450362LCSW1	103	1				

Enter NEW Text: WG450362

Current Selection: WG450362

Order Number Creation
○ Prompt User for an Order Number
● Create the Order Number Automatically

Sample ID Creation
● Create using current Sample ID's
○ Prompt User for Sample IDs
○ Create the Sample IDs Automatically
Sample (todays date)-xx

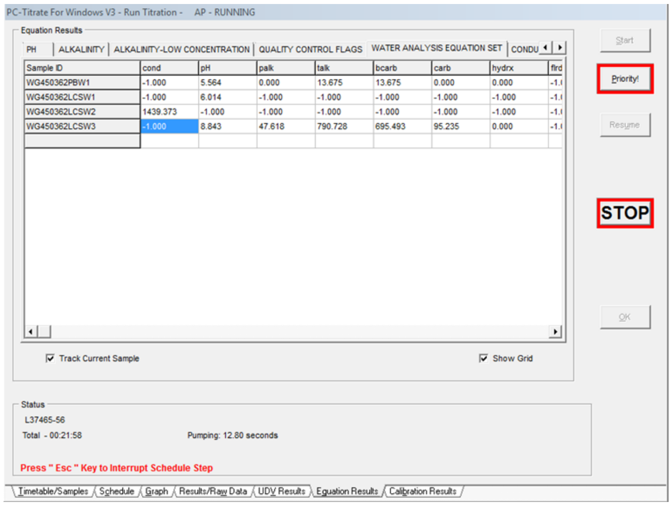
11.7.7. If a sample has insufficient sample to run a duplicate or needs to be run manuallythe dup needs to be changed.

11.7.7.1. Cross out and change on the bench sheet.
11.7.7.2. Change and save in template in PC Titrate.
11.7.7.3. Change to correct DUP in "WG Modify" in LIMS before the workgroup is exported.
11.7.7.4. Make sure both SX & DUP are being run for CAP. See 11.7.2

11.7.8. Click "Start" to begin the analysis. After the run has been started the template may still be changed or corrected for by clicking the "Priority" button. This will stop the run after analysis of the current sample is completed. The user may then make changes to the template. Save changes and click "Resume" to continue the analysis.

NOTE: If the "STOP" button is used then the template must be reloaded and edited to delete previous analysis before continuing the analysis. If the template is not edited, then the analysis will start over from the beginning.

11.7.9. The results may be viewed while the instrument is running by clicking on the "Equation Results" tab at the bottom of the screen. More tabs will appear at the top of the screen for each different analysis. Select "Water Analysis Equation Set" to view results. Verify that opening QC is within limits before allowing workgroup to continue on.



Sample ID	cond	pH	palk	talk	bcarb	carb	hydrx	flrd
WG450362PBW1	-1.000	5.564	0.000	13.675	13.675	0.000	0.000	-1.
WG450362LCSW1	-1.000	6.014	-1.000	-1.000	-1.000	-1.000	-1.000	-1.
WG450362LCSW2	1439.373	-1.000	-1.000	-1.000	-1.000	-1.000	-1.000	-1.
WG450362LCSW3	-1.000	8.843	47.618	790.728	695.493	95.235	0.000	-1.

☑ Track Current Sample
☑ Show Grid

Status
L37465-56
Total - 00:21:58
Pumping: 12.80 seconds
Press " Esc " Key to Interrupt Schedule Step

11.8. Common QC/Instrument Failures:

QC Failure-Calibration, incorrect standard, sample interferences(oily/high content carry over), inconsistent sampling, sampler not sampling, mistake in template, defect in electrode, flow rate, titrant flow rate, bubbles in syringe.
Sampler Not or Inconsistantly Sampling-clogged lines, cog band broken, cog band tightening, build up in sampler mechanism, flow rate, oil Z arm.
Error Messages-power outage occurred, system needs to be archived, program needs to be repaired in Paradox Utility, program needs to closed and reopened.
Refer to PC-Titrate Windows Software (version 2.5) Manual for instructions, consult supervisor, or contact Man-Sci Inc for technical support.

11.8.1. Bubbles trapped in the acid buret can cause interferences with readings. Ensure there are no bubbles before running a WG and clear them when necessary. To clear bubbles select "Titrator" then "Manual Control." "Clear Bubbles" will prompt you remove the lines connected to syringe. Dispense small amounts of titrant until no or few bubbles remain. Reatach titrant lines to syringe.

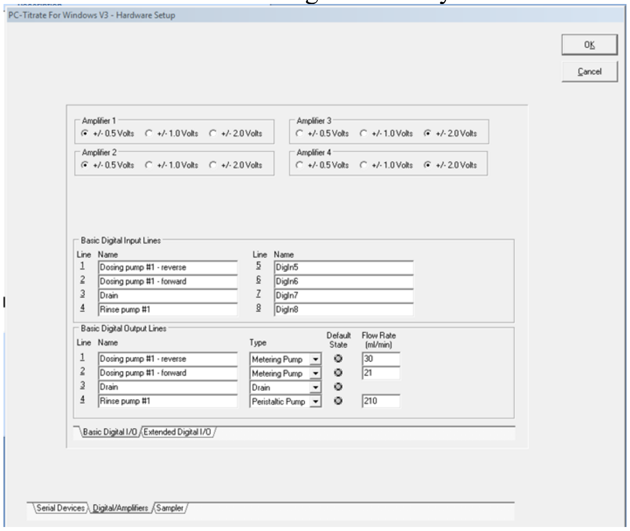
11.8.2. Monitoring the Flow Rate of the Instrument: It is necessary to monitor that the flow rates match the values entered into the program. Check the flow rates quarterly and record them, and any changes made to the program in the logbook. Reference CAR Qualtrax ID 8718.

11.8.2.1. To check the flow rate of the Sample Pump:
  11.8.2.1.1. Place the sampler needle in a beaker of Type 1 water and remove the tip from the titrasip cell.
  11.8.2.1.2. Manually turn on the sample pump until the line is fully primed with water.
  11.8.2.1.3. Place the output tip into a beaker who's weight has been recorded, and turn on the pump for exactly 1 minute.
  11.8.2.1.4. Record the weight of the beaker and water volume pumped as a final weight. Subtract the beaker's weight from the final weight to get a result.
  11.8.2.1.5. Repeat 2 more times and average the results.
11.8.2.2. To change the flow rate in the software:
  11.8.2.2.1. Go into **Interface, Hardware Setup**

11.8.2.2.2. Click on the **digital/Amplifiers** tab and then on the **basic digital I/0** tab.

11.8.2.2.3. In line 2 ("dosing pump forward"), there is a location for the flow rate.

11.8.2.2.4. Enter the average flow rate you obtained above and click on "**OK**."



Amplifier 1: ● +/- 0.5 Volts ○ +/- 1.0 Volts ○ +/- 2.0 Volts
Amplifier 2: ● +/- 0.5 Volts ○ +/- 1.0 Volts ○ +/- 2.0 Volts
Amplifier 3: ○ +/- 0.5 Volts ○ +/- 1.0 Volts ● +/- 2.0 Volts
Amplifier 4: ○ +/- 0.5 Volts ○ +/- 1.0 Volts ● +/- 2.0 Volts

Basic Digital Input Lines

Line	Name	Line	Name
1	Dosing pump #1 - reverse	5	DigIn5
2	Dosing pump #1 - forward	6	DigIn6
3	Drain	7	DigIn7
4	Rinse pump #1	8	DigIn8

Basic Digital Output Lines

Line	Name	Type	Default State	Flow Rate (ml/min)
1	Dosing pump #1 - reverse	Metering Pump	○	30
2	Dosing pump #1 - forward	Metering Pump	○	21
3	Drain	Drain	○	
4	Rinse pump #1	Peristaltic Pump	○	210

11.9. DATA EXPORT

11.9.1. Close the report on the screen and click the "Historical Report" button. Click on "Start" and this will show the "Preview Report" page.

11.9.2. Switch to "Define Search" to query the workgroup data. Filter the data by run number by double clicking on the RunNumber column, filter 1 row and then enter the Run Number from the printed raw data report in the blank space below "Filter 1 of 5, Is Equal To" and click "OK." Then go back to the Preview Report tab. Verify the correct workgroup was selected.

11.9.3. If the run number is not known, the run date can also be used as a filter. Keep in mind that multiple runs may be done on the same day and samples may have run past midnight through to the next day. Find the workgroup and note the run number. Then go back and filter the data using the run number. The Order Number may also be used to run the query.

11.9.4. Export the data using the Historical Data function: Go to "File" and "Export." Change the file type to ASCII Delimited (*.txt). Click on the browse button. Select "U" drive, double-click "Autoload," double-click "Manip1"or "Manip 2" for whatever one was used.

11.9.5. Enter the workgroup number, "OPEN," "SAVE." If samples need to be put to be run manually, change the sample status for that analysis to "PREP" after the workgroup has been exported. Change DUPs that have been changed before workgroup is exported.

11.9.6. Generate a PDF file of the raw data by clicking print and selecting the printer as PDF Merge. Name the file WG######-data.pdf. Or select a desired printer and attached the raw data print out to the workgroup.

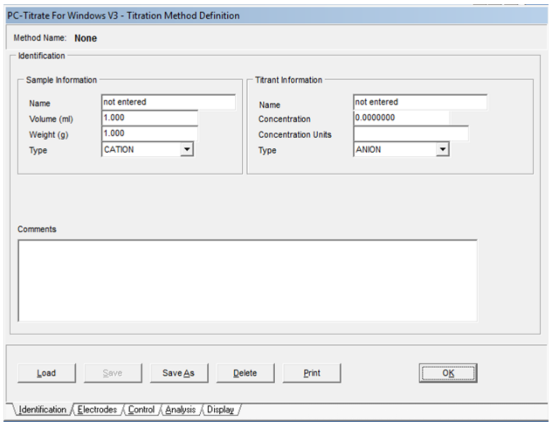
11.9.7. Print an Autotitrator Data Review Checklist Qualtrax ID 1658. Document whether ManTech (Manip) 1 or ManTech (Manip) 2 was used. Review (AREV) the data in LIMS, completing the Autotitrator data review checklist, verifying calibrations are correct or that there is an initial calibration workgroup number, correct reagent sheet, and raw data page. These pages may be as PDFs, to be merged at SREV, or hard copies.

11.9.8. If the endpoint of pH = 4.5 is not reached for Alkalinity, the "Talk" value on the raw data print out will read 0.00 and the pH will be > 6.

1) Change the sample status to STPV (stop volume) in LIMS after review.

2) Create a new workgroup for the sample(s) requiring a stronger normality of acid.

3) Analyze the sample(s) manually or on the auto titrator. If using the auto titrator, first replace the 0.02 N H_2SO_4 bottle with a bottle containing a higher normality H_2SO_4. Purge the burette manually a few times to rinse out the weaker acid and change the normality of the acid in the software. To do this select "Setup", "Titration Method", Load", highlight Alkalinity and press "OK", change the acid true value and select "Save". Repeat this process for "Alkalinity Low."


PC-Titrate For Windows V3 - Titration Method Definition

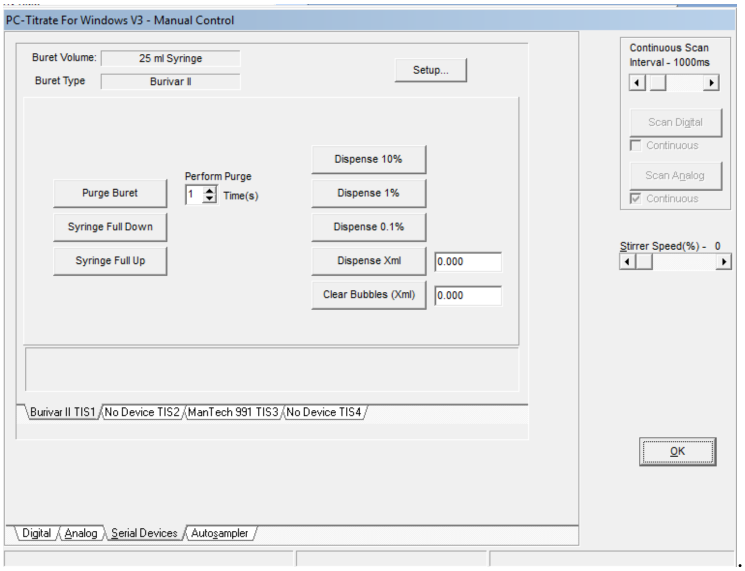
Method Name: None

Sample Information
Name: not entered
Volume (ml): 1.000
Weight (g): 1.000
Type: CATION

Titrant Information
Name: not entered
Concentration: 0.0000000
Concentration Units:
Type: ANION

Comments:

4) To purge the buret, select "Titrator" followed by "Manual Control" and choose how many times you would like to purge, 3 purges.



PC-Titrate For Windows V3 - Manual Control

Buret Volume: 25 ml Syringe
Buret Type Burivar II
Perform Purge 1 Time(s)
Dispense Xml 0.000
Clear Bubbles (Xml) 0.000
Continuous Scan Interval - 1000ms
☐ Continuous
☑ Continuous
Stirrer Speed(%) - 0

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5) When using 2 N, 1 N, or 0.2 N acids at least 1 mL of acid must be used, otherwise redo the analysis with a lower normality acid.

11.9.9. Attach all raw data, printed data, data review checklist, calibrations/calibration workgroup, and a current standard/reagent form to the workgroup bench sheet and turn in the data package for SREV.

11.9.10. Store the vessel and probes in pH 4 buffer.

12.0 QUALITY CONTROL

To ensure data validity and quality, a series of QC samples are analyzed with each workgroup. These are required by the method or by additional regulatory agencies. QC types and the associated acceptance limits are outlined in Table 12.1 along with the required corrective action if the QC is outside of the limits.

12.1 Alkalinity, pH, EC: Analyze one LCSW for each parameter for every 20 or less client samples. Also analyze a closing LCSW for each parameter at the end of the analysis.

12.2 Analyze 1 PBW for all Alkalinity per 20 or less client samples.

NOTE: If the samples are prepped by Soils run the PBS associated with the workgroup for alkalinity if the sample volume allows for it.

12.3 Alkalinity, EC, pH: Method allows for one sample duplicate (DUP) for every 20 or less client samples. Analyze one sample duplicate for every 10 or less client samples in case of stop volumes or other qualifying factors. For samples prepared by the Soils department, analysis of the prepped DUP is sufficient. If there is no prepped DUP choose a DUP only if samle volume allows it.

12.4 EC / pH Calibration acceptance criteria:

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12.4.1 pH Calibration Slope min/max are –65.00 and –53.00.

12.4.2 EC Calibration 91%-109% recovery reading from Calibration standard true value.

Table 12.1 QC types, acceptance limits and required corrective action if QC fails [1]

Quality Control	Frequency	Limits	Corrective Action
Calibration (EC & pH)	Daily	Refer to §12.4	Re calibrate if any criteria is out of limits.
PBW (ALK)	5% (by sample)	< PQL	Qualify samples > 10X PBW with B7. Qualify samples < MDL with BF. Otherwise, qualify with B4.
LCSW (ALK, EC)	5% (by sample) & end of run	90-110%	Redo all associated samples. Qualify data only with supervisor approval.
LCSW (pH)	5% (by sample) & end of run	+/- 0.1 pH unit	Redo all associated samples. Qualify data only with supervisor approval.
DUP	10% (by sample)	RPD ≤ 20 (if [sample] >10x MDL	Redo associated water samples. Qualify soil extracts.
pH replicate analysis	every pH sample	±0.1 pH units	Redo sample for pH.
PQV (EC/ALK[2])	1 per WG [if DW]	+/- 50%	Redo associated DW sxs.

12.5 Samples analyzed for pH must be qualified EB if the value is < 2 or > 13. Values outside of the calibration range are not certifiable. LIMS will automatically qualify these samples with EB.

12.6 Qualify data ZW if the sample was centrifuged and/or decanted due to high concentration of suspended sediment and Q12 if a White sample was used for analysis. Note sample treatment on the bench sheet or review checklist so the PM can write a case narrative explaining the deviation from the method.

12.7 For Alkalinity, the method states to analyze one duplicate for every 20 samples. If a DUP is a "STPV" then the DUP associated with the other 10 samples between the bracketing LCSWs may be used. Appropriately qualify all samples associated with the "STPV" DUP with RP. Note on the bench sheet, fail the "STPV" QC and send the "STPV" sample to REDO at review. If both duplicate samples are "STPV" or if the other duplicate sample fails then all 20 samples must be reanalyzed.

13.0 DATA CALCULATIONS, DATA REPORTING & ARCHIVING

13.1 ALKALINITY

13.1.1 Calculate the Normality of the H_2SO_4 using the following equation:

$$N = (A \times B) / (53 \times C)$$

Where:
A = Conc Na_2CO_3 used in reagent (**g/L**)
B = mL Na_2CO_3 used in titration
C= mL acid used in titration

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[1] Acceptance limits for ICV (pH), CCV, LFB, LCSW, AS, and DUP are based on Arizona DHS Information Update #87.

[2] Due to the low TV of the PQV, it must be run at 0.02N. DW samples that require the use of a higher Normality H_2SO_4 must have an additional PQV run at 0.02N H_2SO_4.

13.1.2 The formula for calculating alkalinity (in mg/L) is:

Potentiometric Titration to End-Point pH:

$$\text{Alkalinity} = \frac{(N) \times (B) \times 50{,}000}{\text{mL sample used}}$$

When this value yields less than 20 mg/L use:

Potentiometric Titration of Low Alkalinity:

$$\text{Alkalinity} = \frac{(2B - C) \times N \times 50\,000}{\text{mL sample}}$$

where:
B = mL titrant to first recorded pH of 4.5
C = total mL titrant to reach pH 0.3 unit lower, 4.2
N =normality of acid

13.2 The Method Detection Limit (MDL) and Practical Quantitation Limit (PQL) are as follows:

- Alkalinity:	MDL= 2 mg/L	PQL= 20 mg/L
- Conductivity:	MDL= 1 µS /cm	PQL= 10 µS /cm
- pH:	MDL = 0.1	PQL = 0.1

13.3 A replicate analysis is performed on each client sample for pH to condition the probe. If the difference between the two readings is within 0.1 pH units then the first value will be reported.

13.4 The calibration equation results can be accessed in “Run Titration.” Click on the Equation Results tab. The equation used for calibration is y = (Slope) (x) + (Intercept). Refer to the calibration information supplied by the manufacturer for additional details.

13.5 Calculate Percent Recovery of the spike using the following equation:

$$\text{Spike }\%\text{Rec} = \frac{[AS]-[Sx]}{AS_{tv}} \times 100$$

Where: AS = measured concentration of the spiked sample
Sx = measured concentration of the sample
AS_{tv} = true value of the spike

13.6 For the LCSW, & PQV:

$$\%\text{Recovery} = \frac{\text{measured value}}{\text{true value}} \times 100$$

13.7 Calculate Relative Percent Difference using the following equation:

$$\text{RPD} = \frac{[sx]-[dup]}{\left(\frac{[sx]+[dup]}{2}\right)} \times 100$$

Where: sx = measured sample value
dup = measured duplicate value

13.8 Archive the Mantech software monthly: Create an empty folder in C:\Program Files\Hinderland\Archive and name folder "Archive mm-dd-yy" In software, go to "Utilities," "Database Records," "Archive/Retrieve." Click "Next," select"Archive", "Next". Using the drop down arrow, select the Friday before the date of the archive. Select "Next, "Browse", double click on empty folder newly created in C drive, click "OK", "Next" and archive 1 month's worth of data. If the database has not been archived in while it may be necessary to perform the V3big Archive System.exe. This is much quicker for large databases; however it will take all files out of the current database. Close the software and then double-click the V3Big Archive shortcut on the desktop. The process takes 5 – 10 minutes.

13.9 Refer to Backup and Archive of Instrument Data Files ID 1533 for details of instrument data backup and archiving. Verify IDBA monthly and document the check in the instrument logbook.

13.10 To perform the quarterly restoration and restore archived data back to instrument PC: Go to:

13.10.1
\\Network\saloon\instrument\MANIP2\Program Files\Hinterland\Archive

13.10.2 Save the desired archived folder, from the previous quarter, to the Instrument PC. Right click the desired folder, select "Copy" and paste in C:\ProgramFiles\Hinterland|Archive.

13.10.3 To view archived data: Open PC-titrate software and go to "Utilities." Go to "Database records" and select "Archive/Retrieve." This opens the Database Archive Wizard. Select "Next", "Retrieve a previously archived database", "Next", and "Browse." Go to C:\ProgramFiles\Hinterland\Archive and select the "Archive mm-dd-yy" folder that was just saved to the folder. Select "OK", "Next", "Next", and "Finish". You will now only be able to perform certain functions in the software and will not be able to run new data until the software is closed and re-opened.

To view archived data: Go to: "Reporting" and select "Prepare and/or print Shazam report." Then click "File," "Open Report" and select "Water analysis historical data report archive.SRW." All archived data will now show up in "Preview Report." Data can be narrowed by using filters in the "Define Search" tab by entering the "Run Date".

Record restoration information in the log book and the P:\QAQC\Sup-editiable\Instrumet List, under the "IDBA Restore" tab. Include the date of restoration and the WG restored from the previous quarter.

13.11 EXTERNAL STANDARD LINEAR CALIBRATION FOR PH PROBE

NOTE: Calibration 1st Order ID 2318 (https://acz.qualtraxcloud.com/Default.aspx?ID=2318) may be used to calculate the slope, intercept, COD and concentrations. Use the worksheet titled "1st Order." The mantech autotitrator plots points on a graph that goes from pH 0 to pH 14 on the x-axis. The y-axis crossed the x-axis at pH 7. To get the correct y intercept the user must subtract 7 from the concentration values. To do this, add "-7" to the intercept equation following "B16." See example in Appendix B.

NOTE: There is no raw data provided by the instrument to reproduce sample results.

y=mx+b

Where: y = instrument response (A_x)
m = slope
x = concentration (C_x)
b = intercept

13.11.1 Slope (m) =
$$= \frac{\left(\sum_i^n x_i y_i \times \sum_i^n w_i\right) - \left(\sum_i^n x_i \times \sum_i^n y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n x_i^{\,2}\right) - \left(\sum_i^n x_i\right)^2}$$

Where: w_i = weighting factor for the ith calibration standard (1)
x_i= concentration for the ith calibration standard
y_i=instrument response for the ith calibration standard
i→n = calibration points in order of increasing concentration

13.11.2 Intercept (b) =
$$= \frac{\left(\sum_i^n x_i^{\,2} \times \sum_i^n y_i\right) - \left(\sum_i^n x_i \times \sum_i^n x_i y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n x_i^{\,2}\right) - \left(\sum_i^n x_i\right)^2} - 7$$

13.11.3 Calibration Coefficient (R) =
$$\frac{\left(\sum_i^n w_i \times \sum_i^n x_i y_i\right) - \left(\sum_i^n x_i \times \sum_i^n y_i\right)}{\sqrt{\left(\left(\sum_i^n w_i \times \sum_i^n x_i^{\,2}\right) - \left(\sum_i^n x_i\right)^2\right) \times \left(\left(\sum_i^n w_i \times \sum_i^n y_i^{\,2}\right) - \left(\sum_i^n y_i\right)^2\right)}}$$

13.11.4 Coefficient of Determination = R^2
Where: R = Calibration Coefficient

13.11.5 Calculated Concentration (C_x) = $\frac{(A_x - b)}{m}$
Where: m = slope corresponding to response (A_x) bias.
b = intercept corresponding to reponse (A_x) bias

13.12 The Jenway conductivity meter allows for a single point calibration only. The calibration adjustment provided is an offset of the output curve. There is no slope adjustment available in this unit. All calibration functions are done via the meter. There is no facility with this unit to carry out a calibration via the PC-titrate software.[2]

13.13 The conductance of a solution is directly proportional to the electrode surface area (cm^2) and inversely proportional to the distance between the electrodes (cm). Conductivity is typically

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[2] Conductivity cells purchased from the manufacturer are pre-calibrated and come with a specified "K" value. The K value for the cell in use is entered into the conductivity meter. The conductivity meter is then calibrated at 1413uS/cm.

reported in micromhos per centimeter (µmho/cm). In the International System of Units (SI) the reciprocal of the ohm is the Siemens (S) and conductivity is reported as milisiemens per meter (mS/m); 1 mS/m = 10 µmhos/cm and 1 µS/cm = 1 µmho/cm. To report results in SI units of mS/m divide µmhos/cm by 10.

14.0 METHOD PERFORMANCE/DETECTION LIMITS

14.1

An MDL study is not required for EC, pH or Alkalinity.

14.2 Initial Demonstration of Capability (IDOC): Analyze four replicates of the LCSW or ICV as specified in § 14.2.1. Include passing calibrations, LCSW/ICV/ICB and CCV/CCB (as pertinent to the procedure). Enter the results on the DOC Calculator ID 2268. The average percent recovery of the DOC replicates must be within ± 10%. Print and sign the form. Attach all raw data and supporting documentation, and turn in to the department supervisor for review.

On-Going Demonstration of Capability (CDOC): For CDOCs, one of the following is required:

- Analyze four replicates of the LCSW or ICV as specified in §14.2.1. Include a passing calibration, , LCSW/ICV/ICB and CCV/CCB (as pertinent to the procedure).
- 4 consecutive passing ICV/LCSWs.
- A passing PT sample

For all CDOC options, enter the results on the DOC Calculator ID 2268The average percent recovery of the DOC replicates must be within ± 10%. Print and sign the form. Attach all raw data and supporting documentation, and turn in to the department supervisor for review.

NOTE: A successful initial DOC (**IDOC**) must be completed and approved by QA/QC prior to independent generation of client data. Continued proficiency (**CDOC**) must be demonstrated and documented annually for analysts who routinely perform the procedure. Refer to Method, Instrument, & Analysis Qualification ID 1518for additional information.

14.2.1 For pH, analyze four individual replicates of the ICV. For Alkalinity and EC analyze four individual replicates of the LCSW.

15.0 DOCUMENTATION

15.1 Record the pertinent information for all prepared standards and reagents in LIMS or the Wet Chem Standards/Reagent Logbook. Include analysts' initials, prep date, expiration date, and the PCN or SCN of any stock standard or reagent used.

15.2 Record the normality of the H_2SO_4 used for Alkalinity in the logbook and on the data review checklist.

15.3 Record the appropriate information in the logbook. Include maintenance performed, problems, etc.

15.4 Label each standard or reagent stored for more than 1 day with the following information:
☐ Standard name
☐ SCN (or other unique ID)
☐ Preparer's initials
☐ Expiration date
☐ Prep date

☐ Certificate of Analysis True Value

15.5 Make sure the following information is included as part the Workgroup:
☐ Calibration data printout, if applicable.
☐ Calibration workgroup, if applicable.
☐ Acid standardization printout, if applicable.
☐ Analysis date, start time and completion time.
☐ Analyst's initials.
☐ Current standard/reagent form.
☐ Completed data review checklist.
☐ Any remarks about analysis or samples.
☐ *ANY OTHER PERTINENT INFORMATION*

15.6 Correct all errors according to ACZ protocol (single-line cross out, dated and initialed).

16.0 WASTE MANAGEMENT/POLLUTION PREVENTION

16.1 Waste may be disposed of down the drain with running water.

17.0 DEFINITIONS

17.1 Refer to ACZ's Quality Assurance Plan QualtraxID 1524
https://acz.qualtraxcloud.com/Default.aspx?ID=1524

18.0 TABLES & DIAGRAMS

Refer to Table 12.1

19.0 CORRECTIVE ACTION

19.1 For QC samples that do not meet the method acceptance criteria, refer to section 12.0. For retests that will occur past the method hold time, check first with the department supervisor to determine if the reanalysis should be conducted.

19.2 For any SOP/method deviation fill out section 1 of a Corrective Action Report ID 2296. If necessary, the department supervisor and/or project manager may provide additional information in the appropriate sections; however, QA does not need to close a minor corrective action. Attach a copy of the minor corrective action report to all workgroups affected. A minor corrective action is for documentation purposes –any SOP or method deviation may be noted on the data review checklist or on the workgroup bench sheet in lieu of using the form.

19.3 For any system failure a major corrective must be opened and the problem investigated. Any employee can initiate a major corrective action by bringing the issue to the attention of a supervisor who will in turn notify QA. Only QA can open a major corrective action. The corrective action will be assigned a unique tracking number by the QAdepartment and will be closed by QAonce the failure has been resolved. Use Corrective Action Report ID 2296.