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Automated PeCOD Operation Manual

For Automated PeCOD Analyzer Systems

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1.0 Getting Started

1.1 Preparing the System: Hardware

The following is a daily guide for ensuring the system will perform optimally. Use this checklist prior to starting a run. Note that some steps will not be applicable to all systems, i.e. systems running solely peCOD analysis will not have electrodes or other reagents outside of the peCOD reagents.

1. Check electrodes
    - Ensure that the electrodes are filled with the appropriate reference fill solution (4M KCl or KNO3). Daily top-ups are recommended, however electrodes should be drained and filled with fresh solution every few days for best results. Also ensure that the fill hole remains open to allow for proper flow of fill solution, if applicable.

2. Check the system set-up
    - Check that any needles used to aspirate sample, buret tips, temperature probes, electrodes and stirrers are placed in a way that they will be submerged in solution as far as they can go without hitting the bottom of the sample vessels and/or TitraSip cells. Dosing tips should be raised high enough so that they will not be submerged below the liquid level when running samples.

3. Check chemicals and reagents
    - Check that all reagent bottles are adequately full, and pump lines are primed.
    - Purge burets to fill with fresh titrant and ensure that the syringes are clear of bubbles before running titrations. See section 5.0 Manual Control– for details.

4. Check the peCOD setup
    - Check that the electrode block is properly seated inside the analyzer head, with the 3 O-rings in place, and the four thumbscrews tightened to create a good seal.
    - Ensure the sensor is seated on top of the electrode block.
    - Ensure the Port A, B, and W tubing is on securely.
    - Once the electrode block and sensor are installed properly, ensure the analyzer head is closed completely (a click should sound when closed).
    - Ensure that the peCOD is set to the correct COD range. See 7.7.3 Changing COD Ranges.

5. Check peCOD reagents
    - Check that pre-mixed peCOD solution bottles are adequately full.
    - Check that the pre-mixed blank solution is on Port B and that the Port W tubing is placed into a waste carboy.
    - Check that the pre-mixed calibrant pump tubing is submerged in the pre-mixed calibrant bottle.
    - If the system has automated electrolyte addition and/or secondary standard checks, ensure that their respective bottles are adequately full.

6. Check water / waste reservoirs
    - Check that the rinse water reservoir is adequately full so that it does not run out of rinse water during a run.
    - Check that the waste carboy is adequately empty so that it does not overflow, and that any drain lines will not become submerged in liquid. Drains are usually gravity-fed, so if lines become submerged the waste will not drain.

7. Calibrate electrode(s) and meters, as required
    - Electrodes, conductivity probes and peCODs should be calibrated at the beginning of each run of samples, or at a minimum, daily.

- Spectrophotometers can be calibrated weekly, or until QC checks fall outside of specified limits.
- Turbidity meters can be calibrated every 3 months, or until QC checks fall outside of specified limits.

1.2 Software Initialization

If the system has been shut off, power up the system and initialize the software:

Turn the power on to all instrumentation and to the computer. To start PC-Titrate, double click the PC-Titrate V3 icon found on the desktop screen. If passwords have been enabled, log on to the system with a valid user name and password.

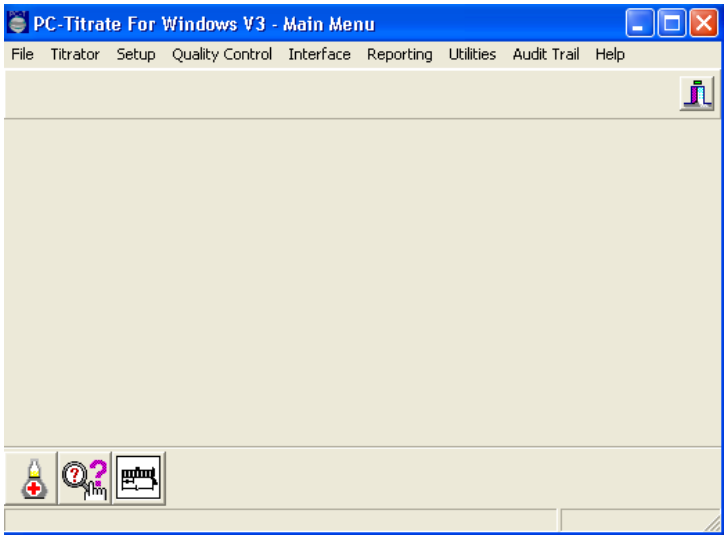
- In the "**Enter User Name**" box, enter the user name.
- In the "**Enter Password**" box, enter the password.
- Click **OK** to enter these settings and obtain access to the program main menu.

1.3. AutoRun Buttons

The below picture is an example of a main menu screen of PC-Titrate software. The icons in the bottom left corner are AutoRun buttons, which are fully customizable and used for quick access to templates containing analyses and calibrations.

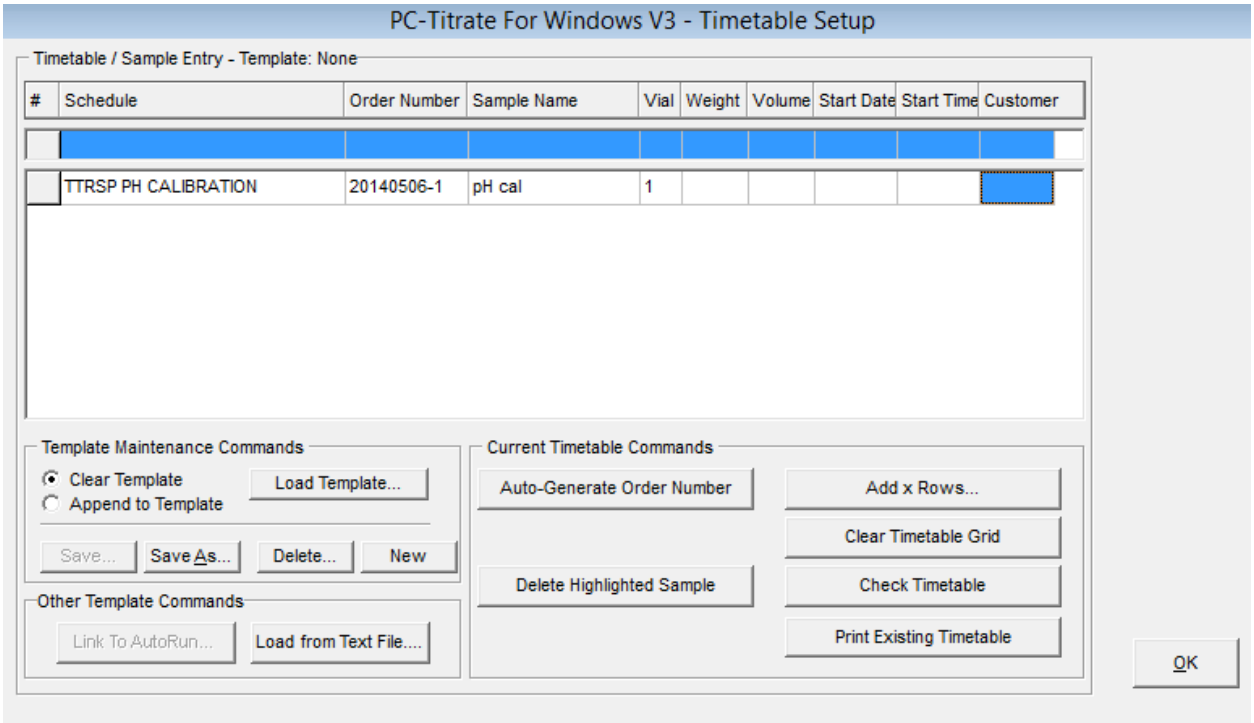
Note that your home screen may look different depending on the methods and AutoRun buttons set up for the system.

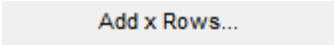
AutoRun buttons can easily be added/removed/edited as required. See 7.2. Appendix B – Creating / Editing AutoRun Buttons for details.



1.4. Running Samples

Each AutoRun button opens a timetable screen with samples and tests preloaded. Add or remove samples from the timetable by using the buttons found at the bottom of the screen. This screen may also be accessed by navigating to the **Titrator – Run Titration** tab, located in the main menu**.** This will open an empty timetable grid. Build a timetable from scratch or load an existing template by clicking the **Load Template** button.



Adding Rows 

To add samples to a timetable, click on the **Add x Rows** button. Type in the number of samples to add and click **OK**. Drag and drop the empty rows into the appropriate sample row. Be sure to fill in all necessary information required:

1. **Schedule** – Required field. Double click and select from the list. To copy the same schedule to other lines, drag and drop. Hold down the SHIFT key while dragging and dropping to populate the same schedule for all lines.
2. **Order number** – Required field. Type a number or use **Auto-Generate Order Number** button. To copy the same order number to other lines, drag and drop. Hold down the SHIFT key while dragging and dropping to populate the same order number for all lines.
3. **Sample name** – Required field. Must be unique for each line. If the same name is desired (e.g. running duplicates), drag and drop to auto-increment the name, e.g. Sample-1, Sample-2.
4. **Vial #** - if the system has an Autosampler, this is a required field.
5. **Weight** – required only if sample calculations are using weight instead of volume.
6. **Volume** – this will populate automatically from the Titration Method and must only be changed if the sample volume used is different than what is showing, for beaker and standalone systems only. This changes the volume used in the calculations, therefore this value <u>must not be changed for TitraSip systems</u> as set sample volume is programmed for automatic pumping.
7. **Start Date** – leave blank if beginning the run immediately. If the run date is not today (e.g. setting up the system to run a calibration in the morning before operator arrival), double click to select the start date. Holding down the SHIFT key, drag and drop to copy the date to additional lines.
8. **Start Time** – leave blank if beginning the run immediately. If the run time is being delayed (e.g. setting up the system to run a calibration in the morning before operator arrival), double click to select the time. If the rest of the run can begin in sequence, only fill in the first line. To schedule each remaining sample for specific times, hold down the SHIFT key and drag and drop to additional lines. This will prompt the operator to select a time increment (e.g. analyze every 1 hour, every 30 minutes, etc.)
9. **Customer** – customizable; can be left blank. Double click to see a list of options. The list is user-entered under the tab, **Utilities – Utility Databases – Edit Customer Database**. Enter the customer information, then click the + button to name the entry. Then click the checkmark button to save.

Removing Rows Delete Highlighted Sample

To remove sample rows from a timetable, click on the sample to remove then click on the **Delete Highlighted Sample** button. This will remove the sample from the list. To clear the entire timetable and start over, click the **Clear Timetable Grid** button.

Printing a Timetable Print Existing Timetable

Once the timetable of samples is complete, print a copy by clicking on the **Print Timetable** button.

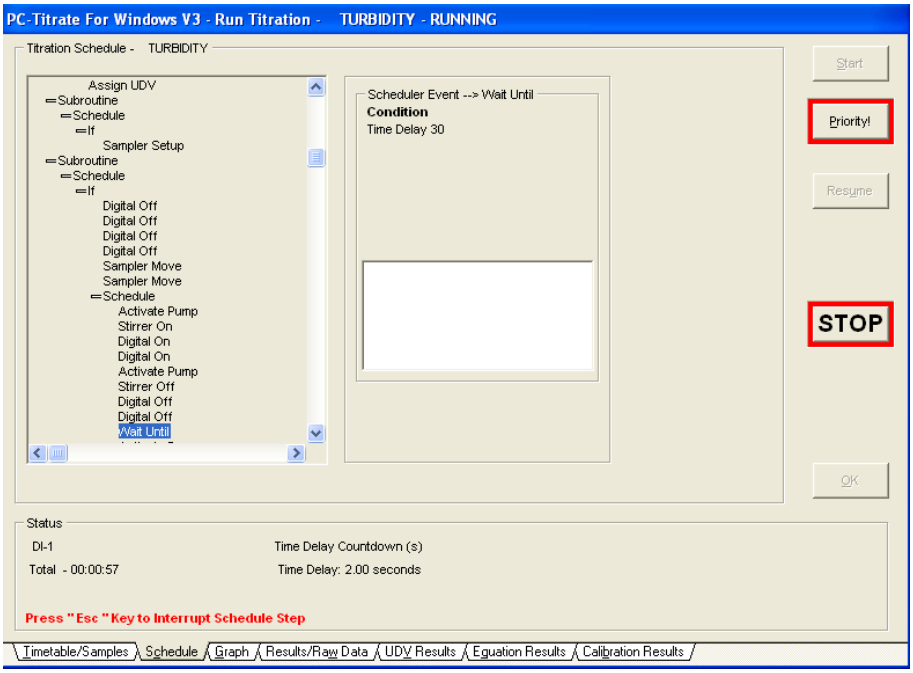
Clicking **Save** or **Save As** to save the timetable, if desired. **Save** will overwrite the original template (if loaded from an existing template or AutoRun button) and **Save As** will create a new template (prompted for a name).

NOTE: template names cannot be reused, even if the template has been deleted. It is best to just overwrite the original unless access is required at a later date. Additionally, if the original template has been linked to an autorun button, the original template remains linked to it, i.e. saving the template as a new name will require a new autorun button to be created. See **Appendix B** for details.

When the samples are ready and loaded into the Autosampler rack, begin sample analysis by clicking the **Start** button. If a message that says "Timetable contains errors" is displayed, click the **Check Timetable** button. This will indicate the cause of the error, such as missing required information.

The Schedule Tab

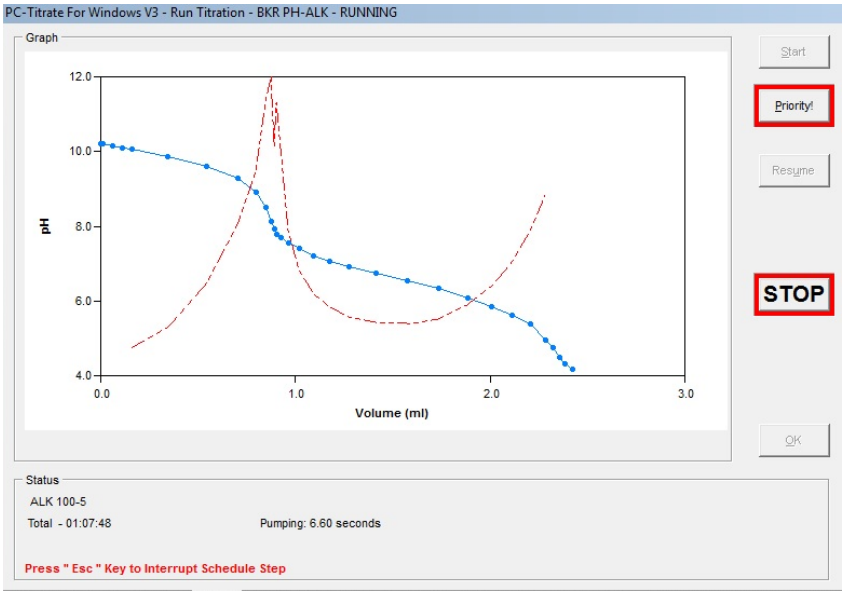
When a run is in progress, the **Schedule** tab displays a step-by-step list of actions as a sample is being analysed. Steps such as Activate Pump, Assign UDV, Titration, etc will be displayed in real time.



The Graph Tab

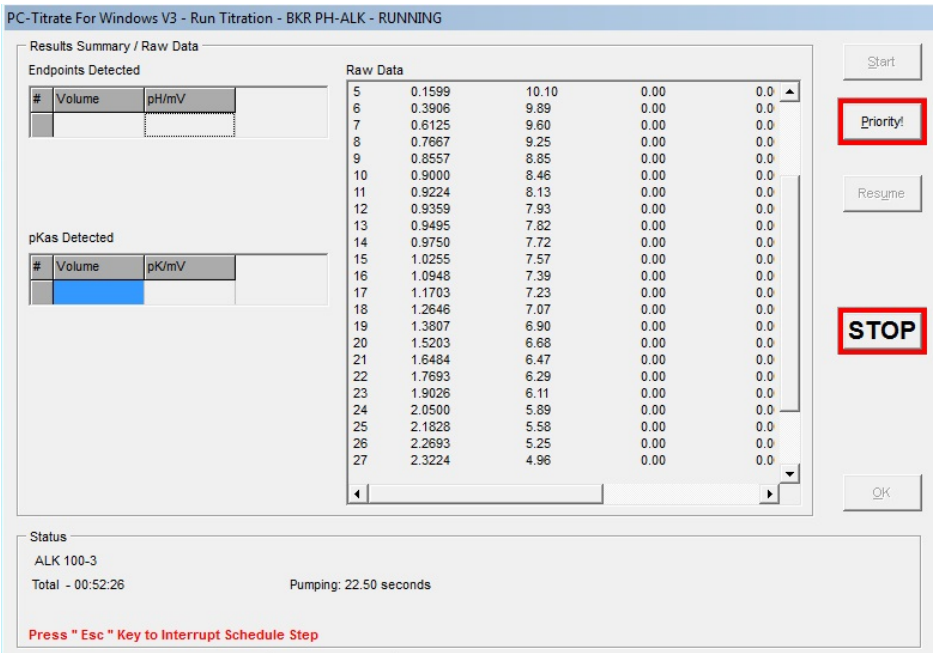
**The Graph tab is not relevant to automated systems running solely PeCOD analysis but is included for automated systems running other applications in parallel with PeCOD.*

When a run contains titrations, the **Graph** tab can be used to view titration curves in real-time as the curve is being plotted. The blue line is the titration plot, and the red line is the first derivative (when selected to appear). Any inflection endpoints found will also be indicated on the curve.



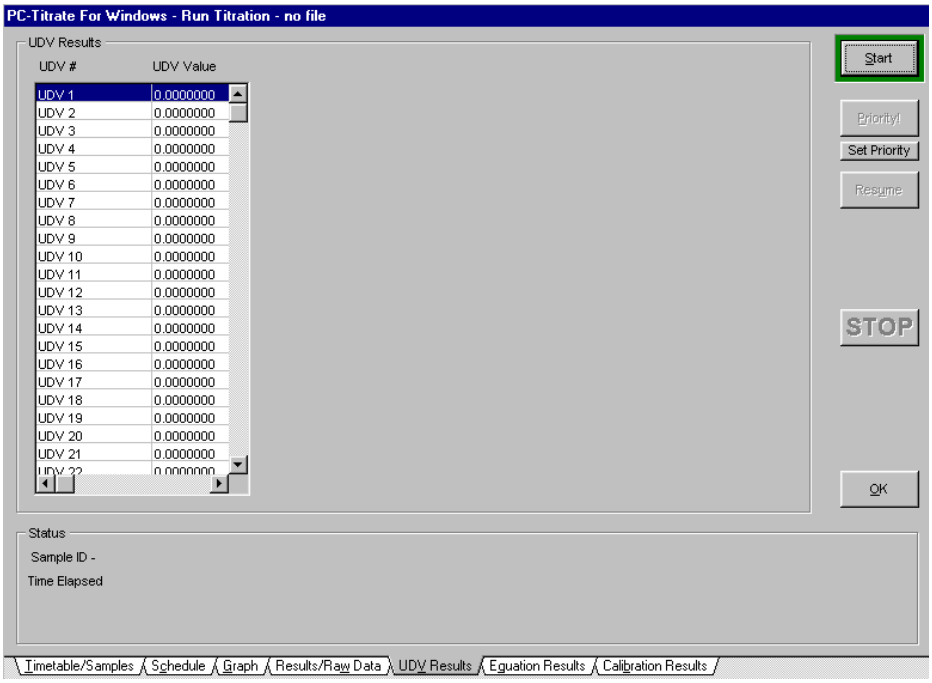
The Results / Raw Data Tab

During a titration, this tab displays the electrode reading (usually mV or pH) and the total volume of titrant added for each injection. It will also indicate any endpoints and pKas found.



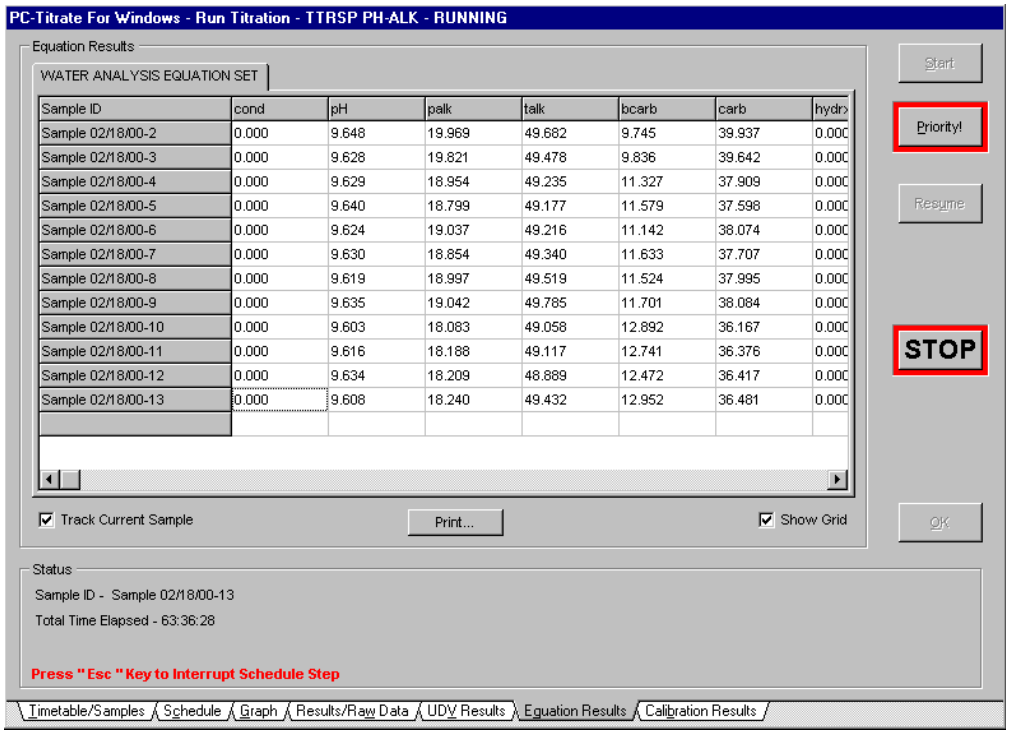
The UDV Results Tab

This screen displays the values for all UDV results, although only current sample UDVs are shown. **Appendix A** defines the standard UDVs which may be formula results, electrode readings, etc. Note that UDV definitions may vary from the standard, and some will not be applicable.



The Equation Results Tab

This tab shows the results of any formulas that are utilized within the timetable. The different formula sets will have tabs along the top of the screen and appear as they become saved. Sample data will also appear as they become available (they will be appended to the list).

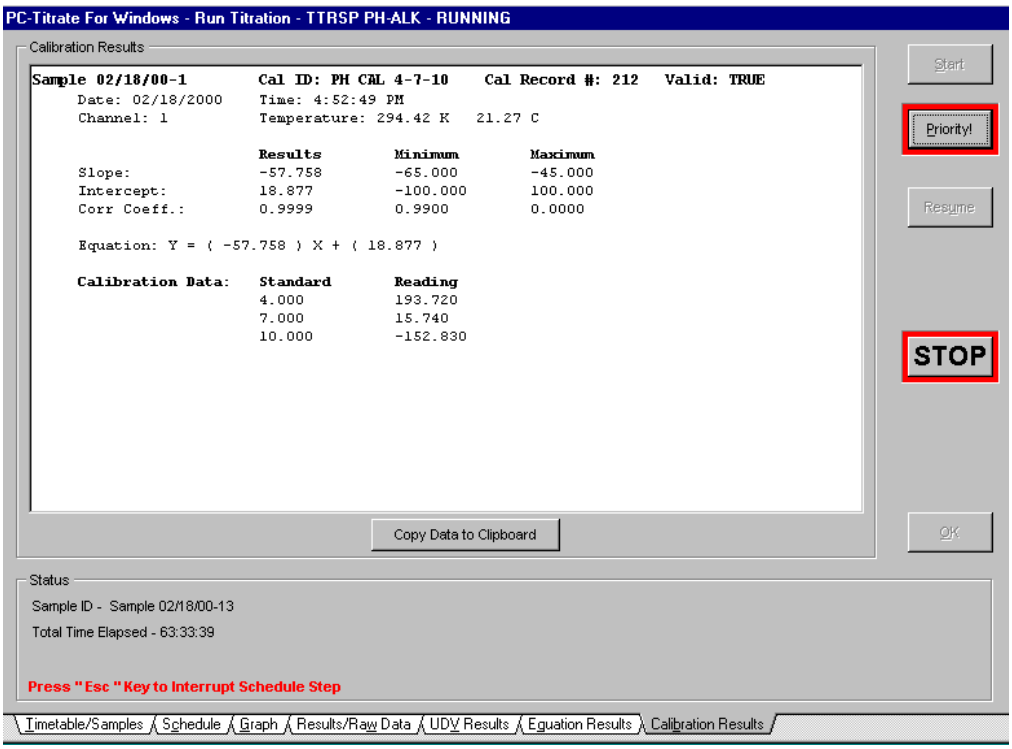


Sample ID	cond	pH	palk	talk	bcarb	carb	hydr
Sample 02/18/00-2	0.000	9.648	19.969	49.682	9.745	39.937	0.000
Sample 02/18/00-3	0.000	9.628	19.821	49.478	9.836	39.642	0.000
Sample 02/18/00-4	0.000	9.629	18.954	49.235	11.327	37.909	0.000
Sample 02/18/00-5	0.000	9.640	18.799	49.177	11.579	37.598	0.000
Sample 02/18/00-6	0.000	9.624	19.037	49.216	11.142	38.074	0.000
Sample 02/18/00-7	0.000	9.630	18.854	49.340	11.633	37.707	0.000
Sample 02/18/00-8	0.000	9.619	18.997	49.519	11.524	37.995	0.000
Sample 02/18/00-9	0.000	9.635	19.042	49.785	11.701	38.084	0.000
Sample 02/18/00-10	0.000	9.603	18.083	49.058	12.892	36.167	0.000
Sample 02/18/00-11	0.000	9.616	18.188	49.117	12.741	36.376	0.000
Sample 02/18/00-12	0.000	9.634	18.209	48.889	12.472	36.417	0.000
Sample 02/18/00-13	0.000	9.608	18.240	49.432	12.952	36.481	0.000

The Calibration Results Tab

**The Calibration Results tab is not relevant to automated systems running solely PeCOD analysis but is included for automated systems running other applications in parallel with PeCOD.*

This tab shows the resulting data for all calibrations carried out during the present run. The calibrations will appear in the order they are analyzed.



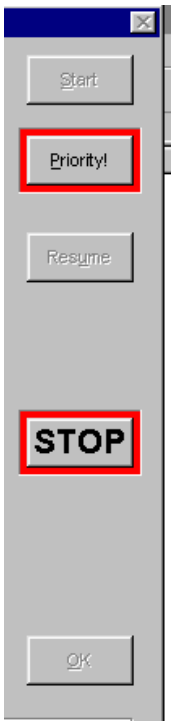
The Cal Record # shown at the top of the screen can be used to identify and find calibration results in historical calibration data.

NOTE: The Valid: TRUE result shown at the top of the screen can only be trusted for single-line fit calibrations.

2.0 Stopping / Pausing a Run

There are 3 ways to stop a run:

The STOP Button
Clicking the STOP button will stop the run in the middle of its current task and abort the timetable. Use with caution.



The Priority Button
This button is used to interrupt the timetable to allow for modifications to the timetable – e.g. insertion of a priority sample, adding additional samples, etc. Click on this button and the system will wait until the current sample is finished analyzing, then the system will pause and allow for use of the edit buttons.

From the Timetable/Samples tab, make the desired modifications. Once the system pauses, the timetable buttons will reappear to add rows. The empty rows will be added to the bottom of the timetable. Once all necessary information is entered, either leave the rows at the bottom to be analyzed at the end of the run OR drag and drop to the top of the timetable by selecting the desired row and dragging to the top of the list. Click on the Resume button to continue the run.

NOTE: if making changes to the physical position of any samples on the Autosampler, be sure to modify the vial numbers.

The Esc Key
Press the Esc key on the keyboard pauses the run. This will stop the system almost immediately, and give users the choice of continuing normally, breaking out of the current schedule step, aborting the titration, or aborting the entire run. This is useful to pause the system immediately (e.g. to obtain more rinse water, empty a waste carboy, etc.) without terminating the run.

3.0 Viewing Historical Reports

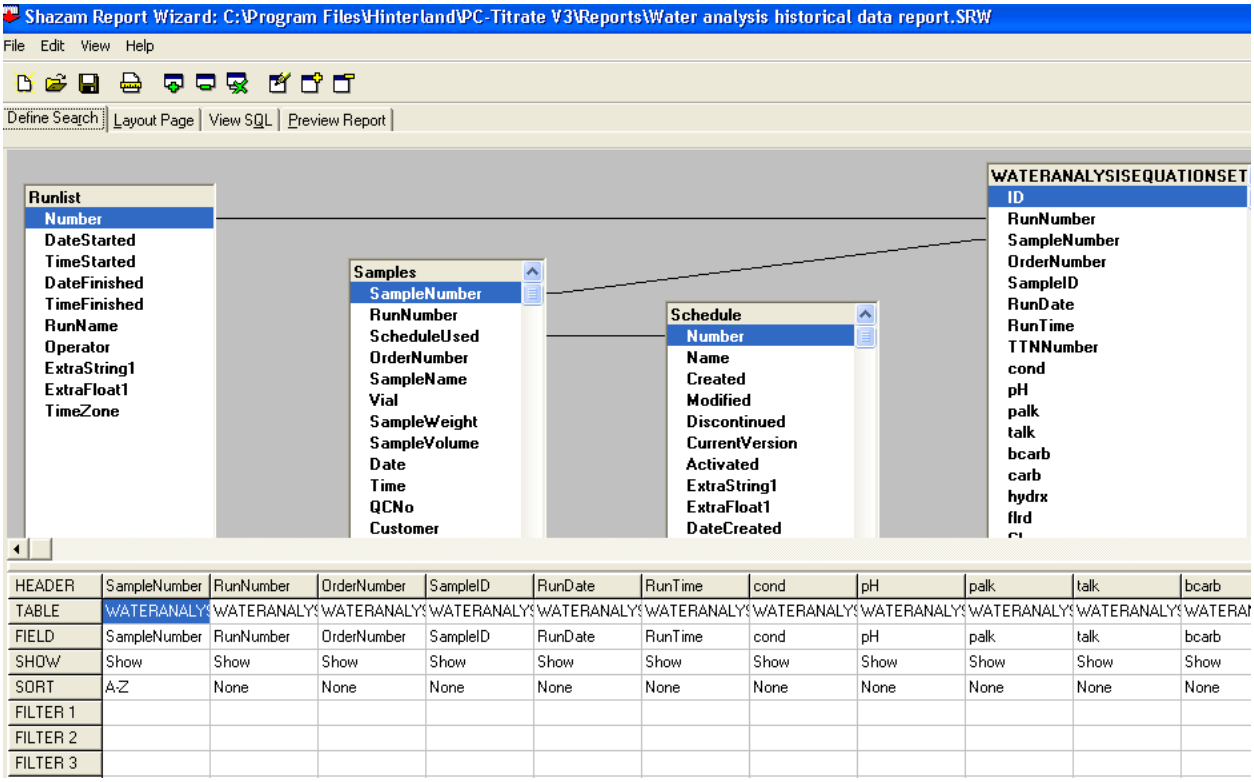
3.1. Reports

All data is saved in the database in a historical report. Once the "in-run" report is closed, that data will append to the historical report. To access the report, follow the below instructions.

1. From the main menu, click on the AutoRun button labelled "**Historical Data Report**".

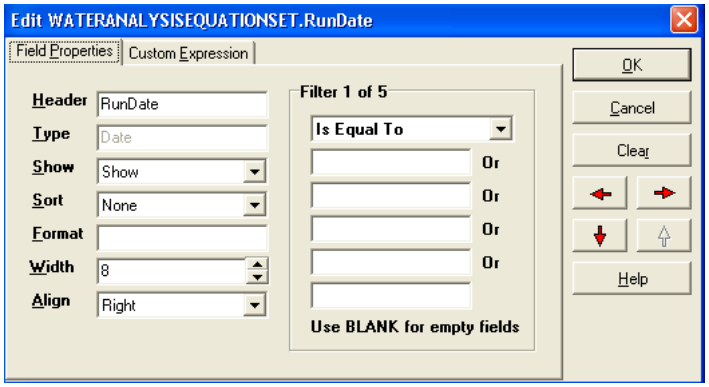
2. The "**Run Timetable"** template will appear. Click **START**.

3. After a few moments, the report will generate. This report will contain ALL historical data unless a previous filter has been specified. To filter for specific information (e.g. date, order number) click on the **Define Search** tab.



4. Note the grid on the lower half of the screen. Looking at the HEADER row, find the parameter to filter by. For example, to display only today's results use the **RunDate** column. To create a filter, double click in the **Filter 1** cell within the desired column.

5. An **Edit** window will appear. In the drop-down menu under the **Filter 1 of 5** header, select a filter parameter (e.g. Is Equal To), then type a filter value into the first empty text box. For example, to see data from April 1 2017, type 04/01/2017. The format is usually **MM/DD/YYYY** but can be verified by looking at the date format in the current report on the Preview Report tab (prior to setting filters).



6. Click **OK** and then click on the **Preview Report** tab. After a moment the report will be generated. Navigate through pages by using the arrows at the top of the screen. The arrow with the line next to it links to the last page.

7. To print this report, click on the **Print** icon or go into the **File** menu and then **Print Report**. A Print dialog box will appear. Select the printer of choice and then click OK.

8. To export a report as a text file (which can then be imported into Excel), go to **File**, **Export**. In the "File Type" drop-down menu, select ASCII Delimited File (TXT) or Fixed Field ASCII File (TXT). Click the "**…**" button next to "File Name" text box to choose a location and file name. Click OK, and a message will appear indicating that the export file has been successfully created.

9. When closing the report, a prompt to save changes to the current report before closing will appear. To save the report with the filter in place, click **Yes** (the report will remain queried as defined and will not list all data the next time it is opened), otherwise click **No.** Note that the filter can easily be changed/removed.

NOTE: reports can also be accessed "off-line" (without connection to an interface) by navigating to the **Reporting**, **Prepare and/or Print Shazam Reports** tab from the main menu. Click the "Open File" icon at the top of screen and a list of reports will appear.

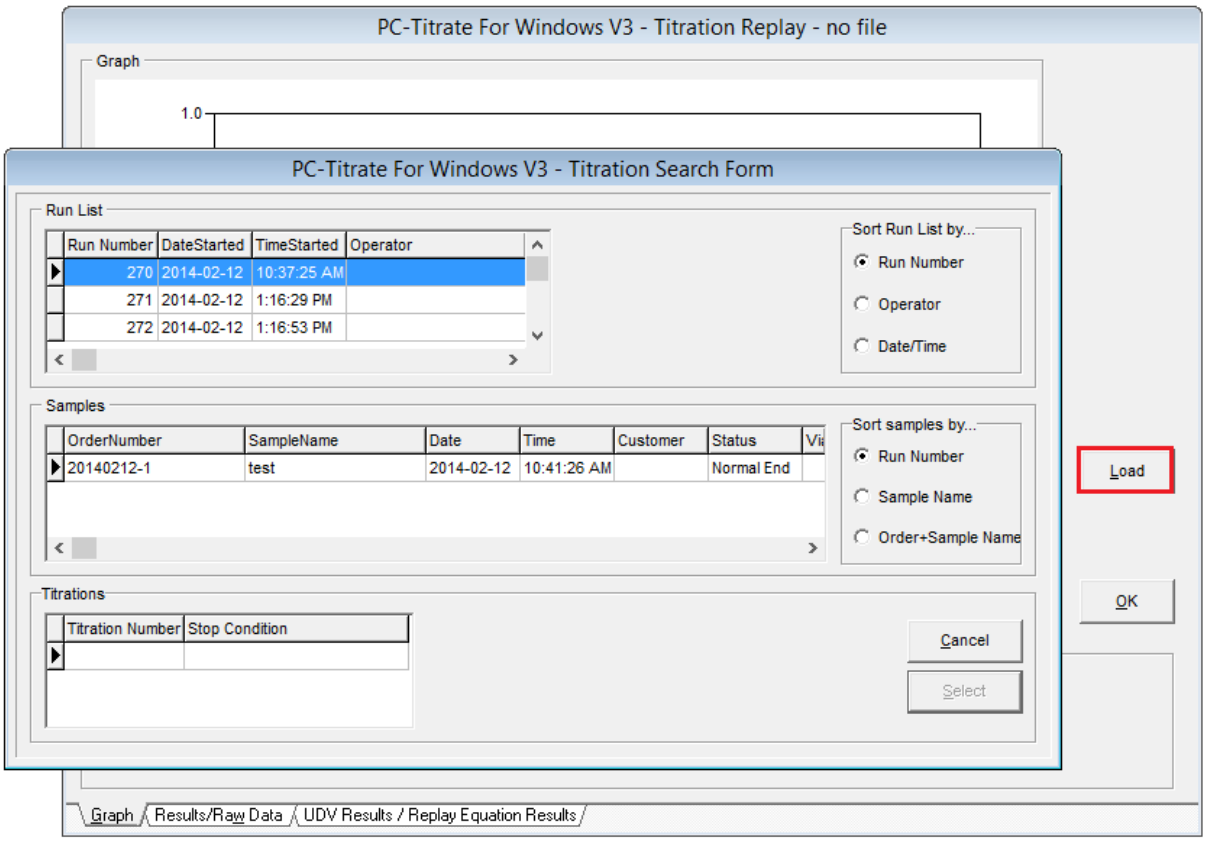
See **Appendix E** for details on how to make modifications to reports.

3.2. Replay Titration

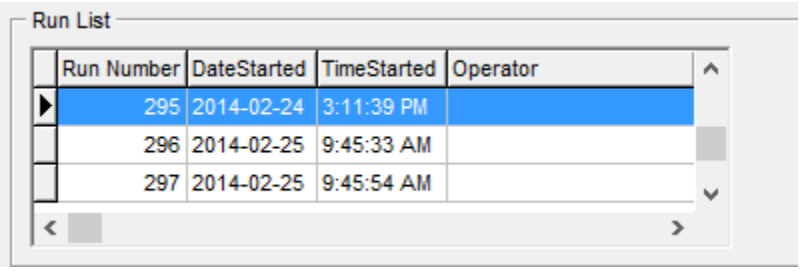
**The Replay Titration function is not relevant to automated systems running solely peCOD analysis but is included for automated systems running other applications in parallel with peCOD.*

To view previous titration information (including graphs and all equation results), open the **Replay Titration** screen located within the **Titrator** menu. This is a good place to start when troubleshooting problems with titrations.

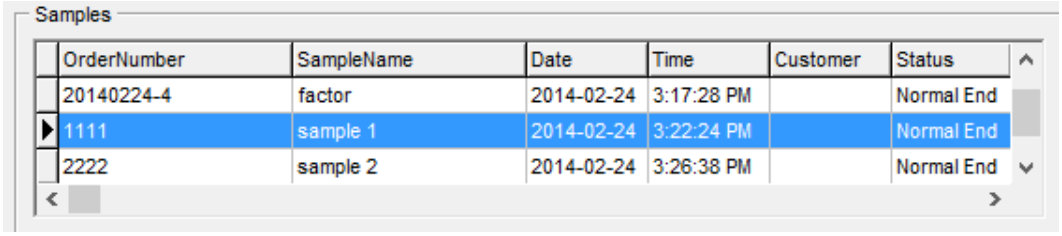
When first opening the replay screen, an empty graph will display. Click the **Load** button to open a previous run.



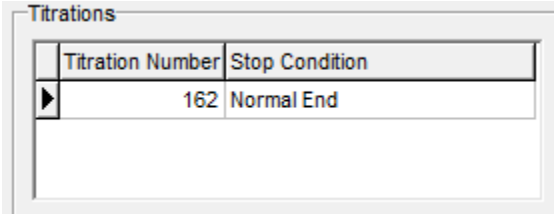
In the Run List section, select the run you wish to view. The most recent runs are at the bottom of the list. Note that only titrations run can be opened and viewed.



In the Samples section, select a sample to view.



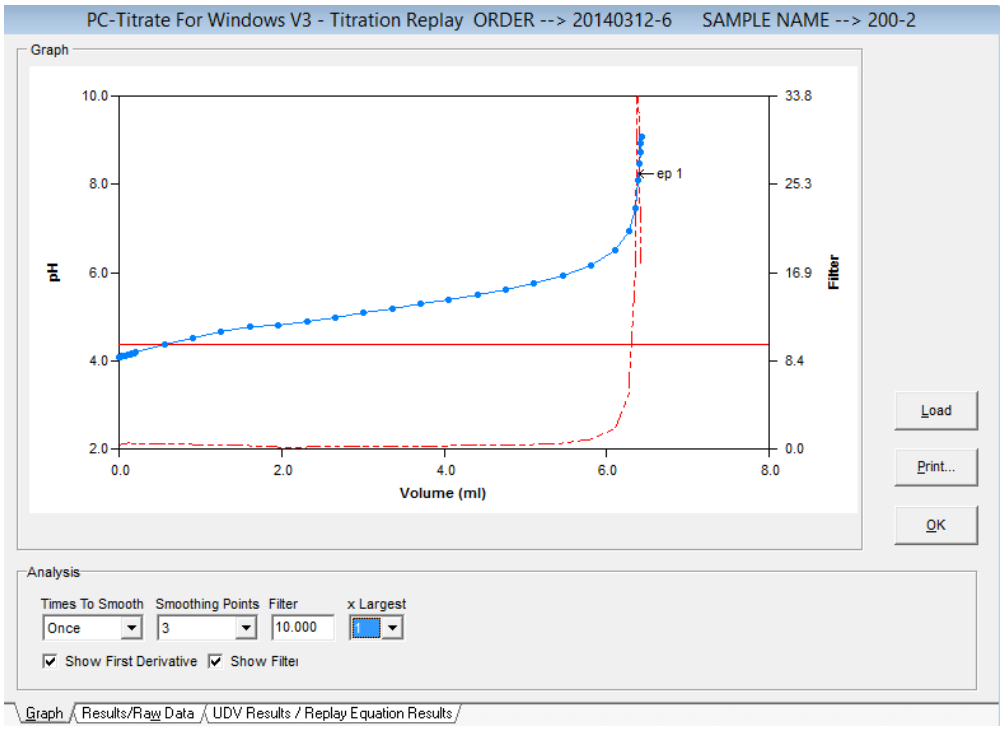
In the Titrations section, select the titration to open. Note that this step can be skipped if the sample run contained only one titration.



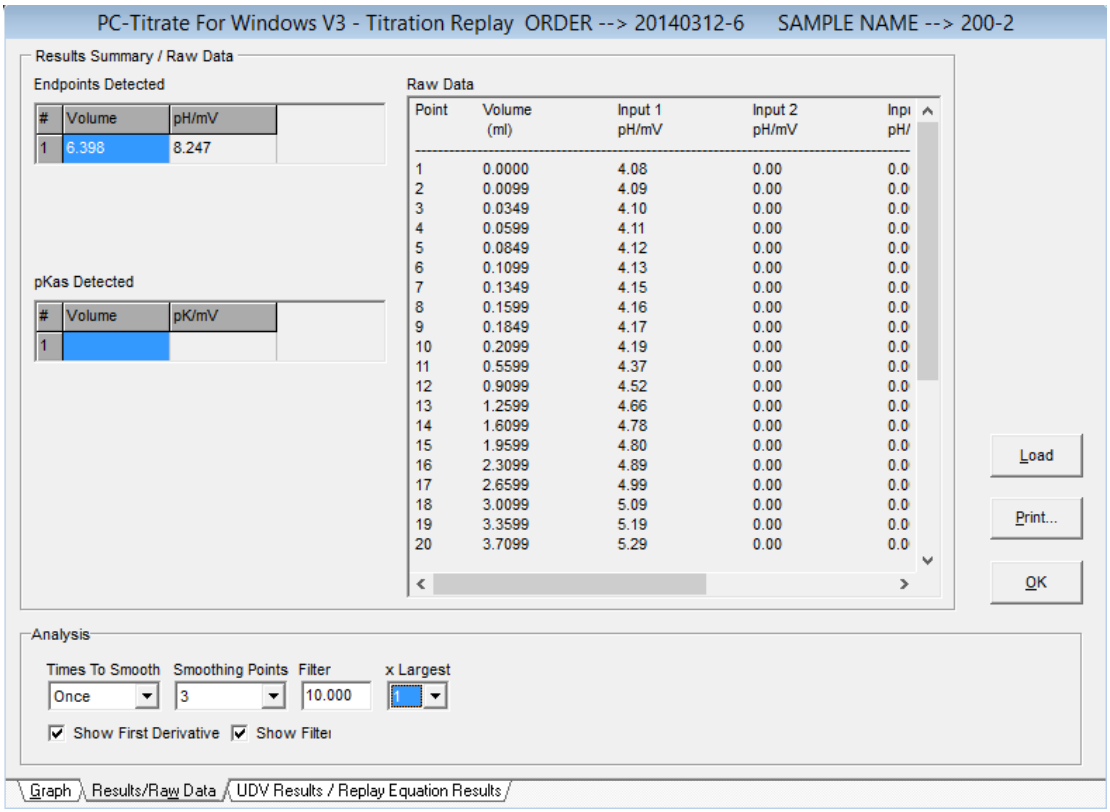
Click the **Select** button to load a sample. The first screen is the **Graph** page which displays the titration curve. The blue line is the titration plot and the red line is the first derivative (only applicable for inflection endpoints). Any inflection endpoints will be indicated on the curve.

The **Analysis** section at the bottom indicates the current smoothing and filter settings. For set endpoint methods (e.g. alkalinity) this section is not applicable. For methods relying on inflection endpoints, smoothing is used to average the slopes of the first derivative curve to prevent the selection of noise as a true endpoint. More smoothing will make endpoints harder to detect, so if the true inflection is small the smoothing should be set lower.

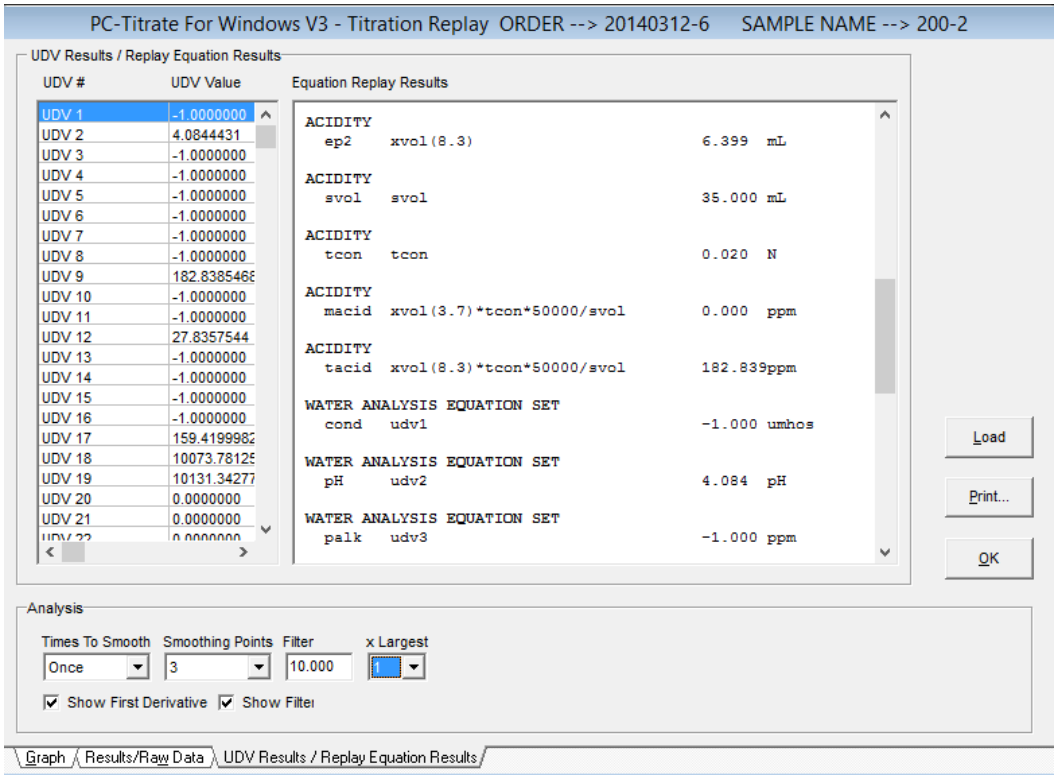
The filter setting is used to further isolate the correct inflection endpoint by filtering out noise in the first derivative curve, indicated by the solid red line. The ideal filter is set above the flat part of the first derivative and below the peak. The "x Largest" drop down menu allows the user to select how many endpoints to view on the curve, if found. Note that any changes made here are not permanent. To change settings for all future samples, see **Appendix C** for information about titration method changes.



The **Results/Raw Data** tab displays the volume and electrode reading (either pH or mV) at each injection. Any endpoints or pKas detected will also be indicated.



The **UDV Results / Replay Equation Results** tab will display the UDV values for that sample as well as all equation results, presented in the order they are saved. Note that if the titration method uses inflection endpoints, changing the smoothing settings will slightly change the results displayed as smoothing affects the location of the endpoint.



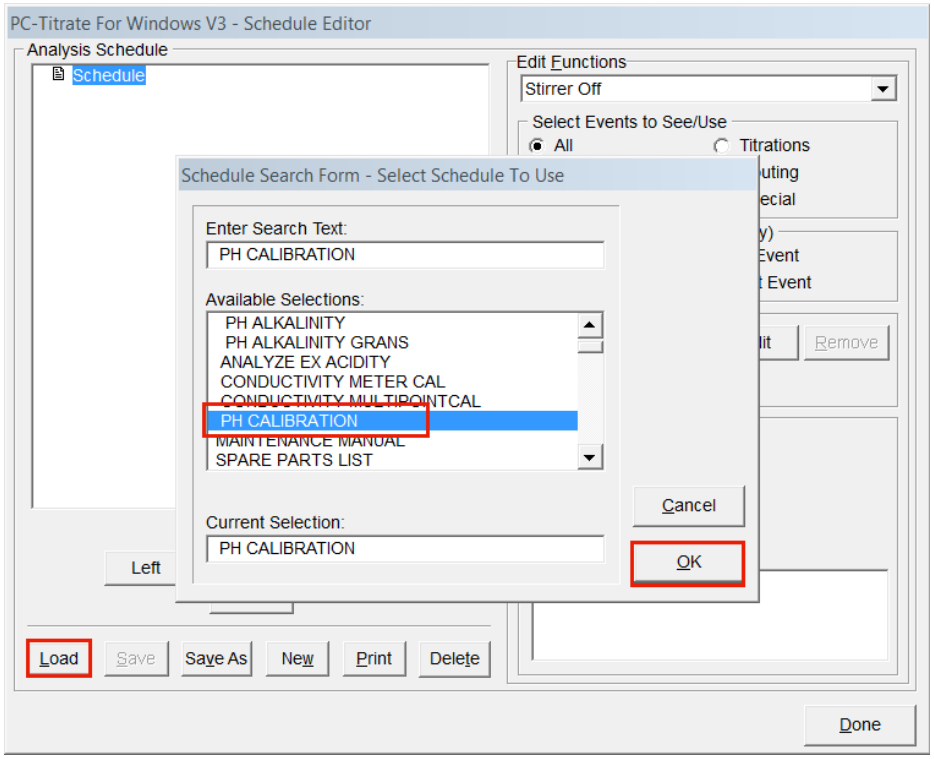
4.0 Calibrations

4.1. Calibration Templates

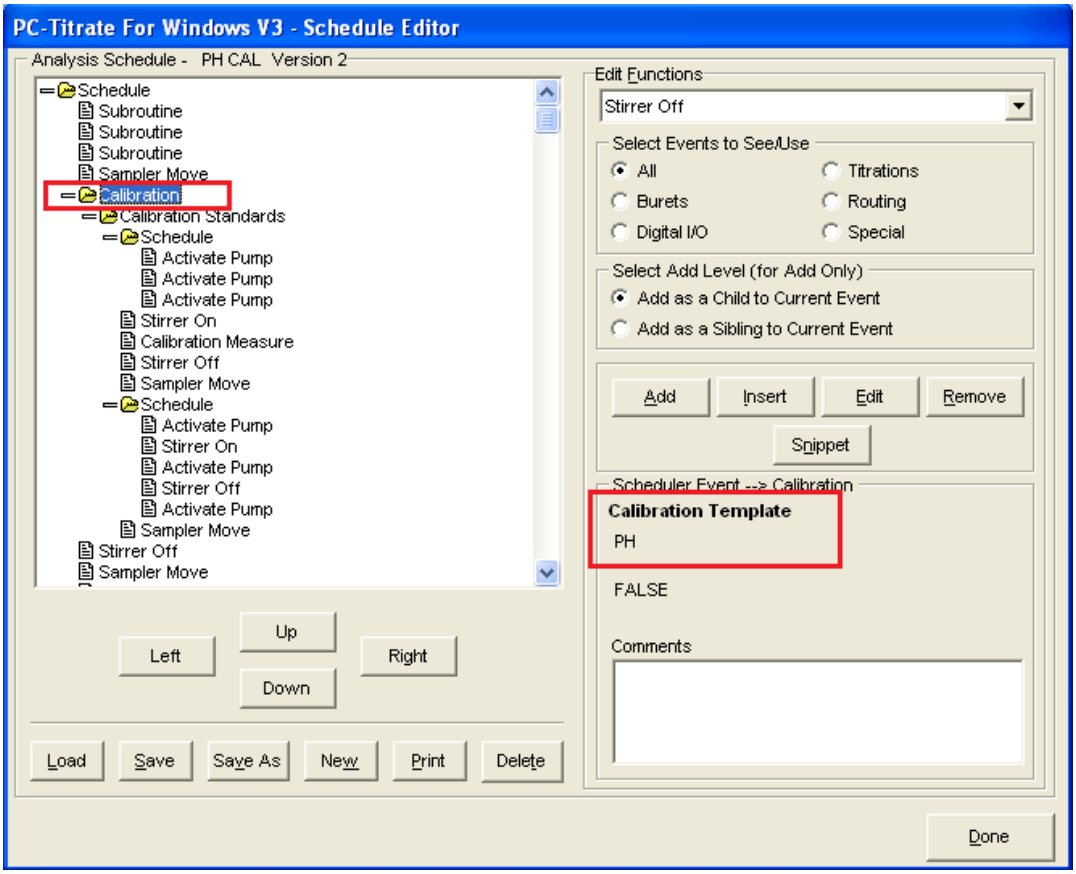
**The Calibration Templates function is not relevant to automated systems running solely PeCOD analysis but is included for automated systems running other applications in parallel with PeCOD.*

Calibration Templates define details of each calibration, including type, stability criteria and standards used.

To determine which calibration template the calibration schedule is using, go to the **Setup** tab, **Analysis Schedule**. Click the **Load** button and select the calibration schedule to view.



Click on the **Calibration** folder in the schedule steps listed on the left side of the screen. Look in the bottom right corner above the white comments box. It will indicate the name of the calibration template used. In this example the template name is PH.



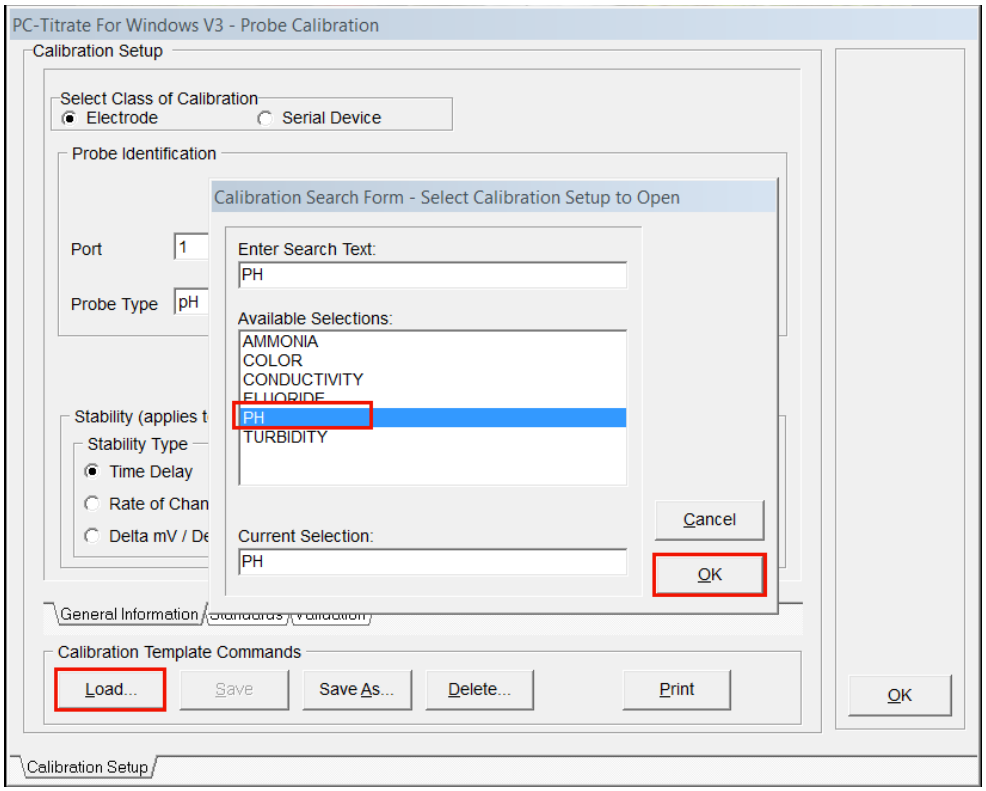
Change the calibration template in use by clicking the **Edit** button and selecting a new template.

TRUE or FALSE will appear beneath the calibration template name indicating whether the calibration report will be printed automatically after completion (TRUE means it will print). To change the current setting, click the Edit button and reselect the template currently in use. The system will then ask if the user wishes to print the calibration.

If any changes were made, be sure to SAVE your updated schedule.

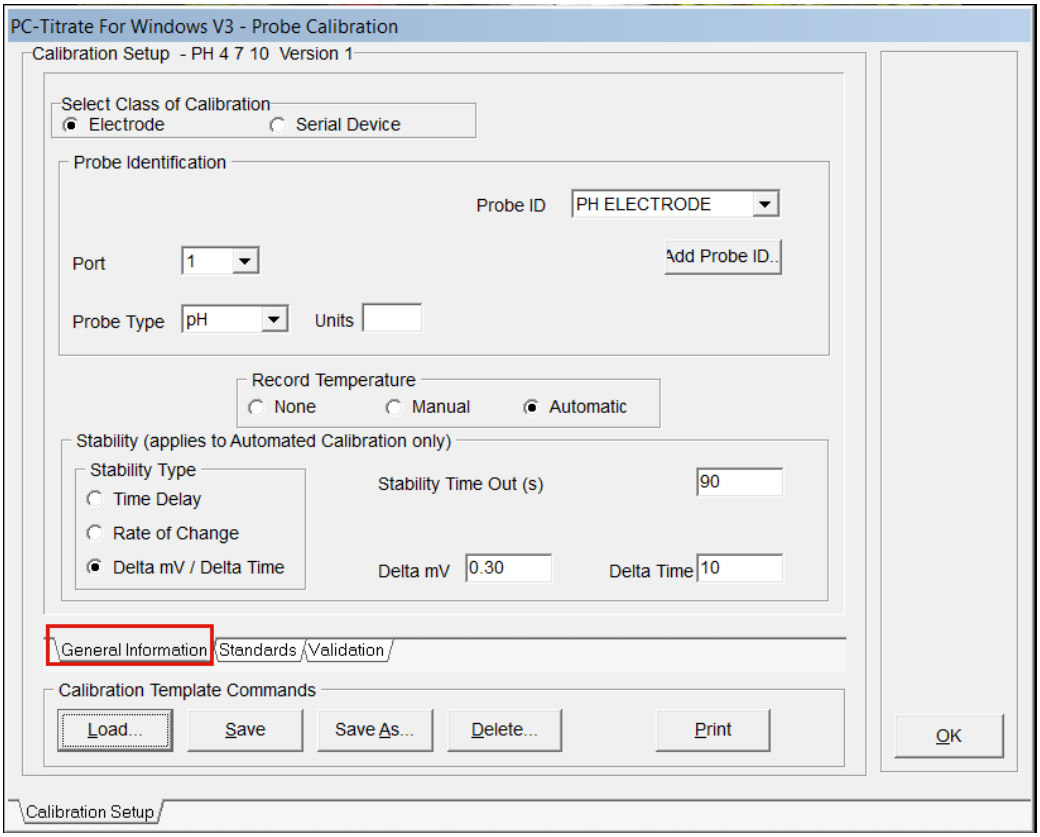
To view/edit a Calibration Template:

Go to the **Setup** tab, and select **Calibration Template**. Click the **Load** button and select the calibration to view.

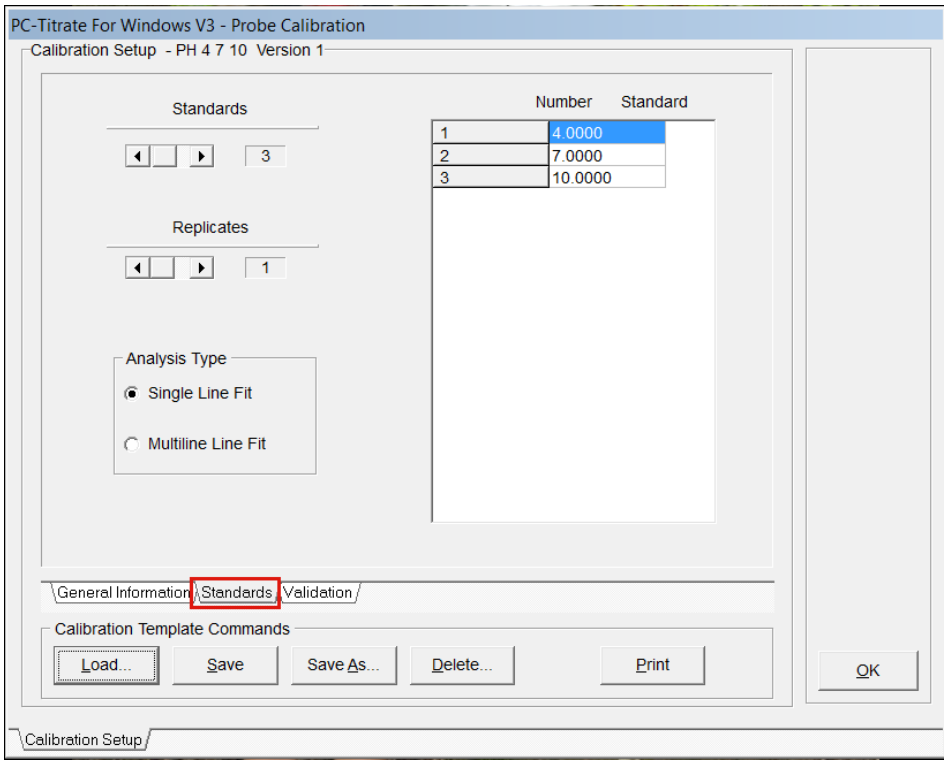


There are three tabs to choose from.

The **General Information** tab defines information such as the class of calibration (i.e. electrode or meter), the applicable electrode/meter port, probe type, temperature compensation information and stability criteria.

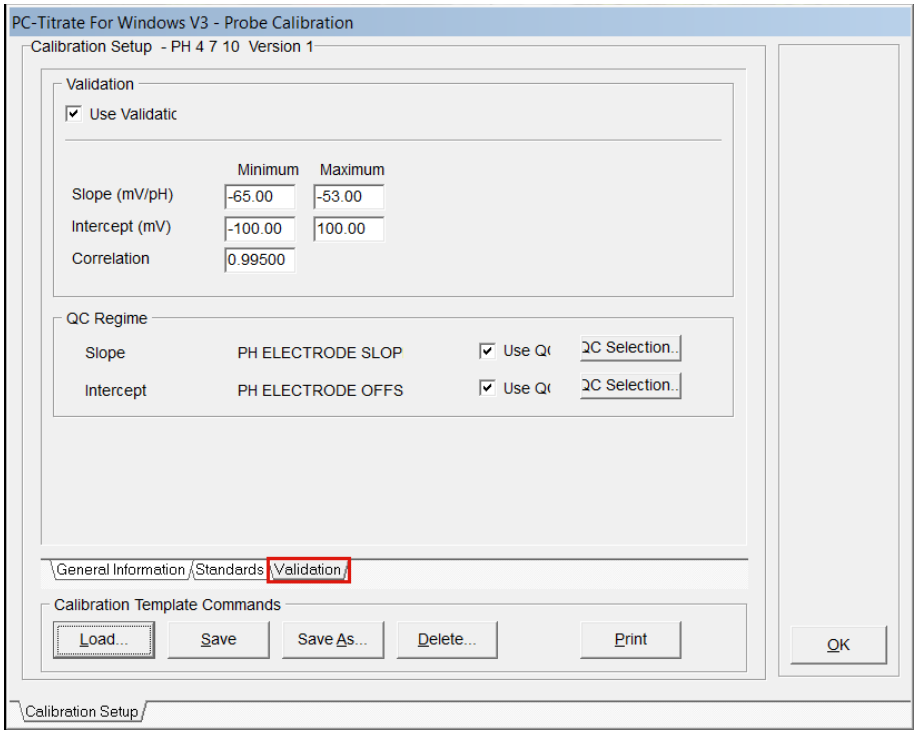


The **Standards** Tab defines which standards are being used in the calibration, and the fit type. Fit type options include Single Line fit (line of best fit) or Multi-Point (point-to-point) curve. Some calibration types also provide an option for Quadratic Fit.



Add or remove standards by clicking the arrows under Standards to the left or right. Then enter the standard value(s) in the list on the right side of the screen. You can also change the values of the current standards listed. Note that standards must be in ASCENDING order, and the minimum value to enter is 0.000000001. Keep this in mind when deleting old values as a message indicating that the value is below minimum will be displayed.

The **Validation** tab displays validation criteria (applicable for single line fit only). Define the acceptable ranges for slope, intercept and correlation coefficient.



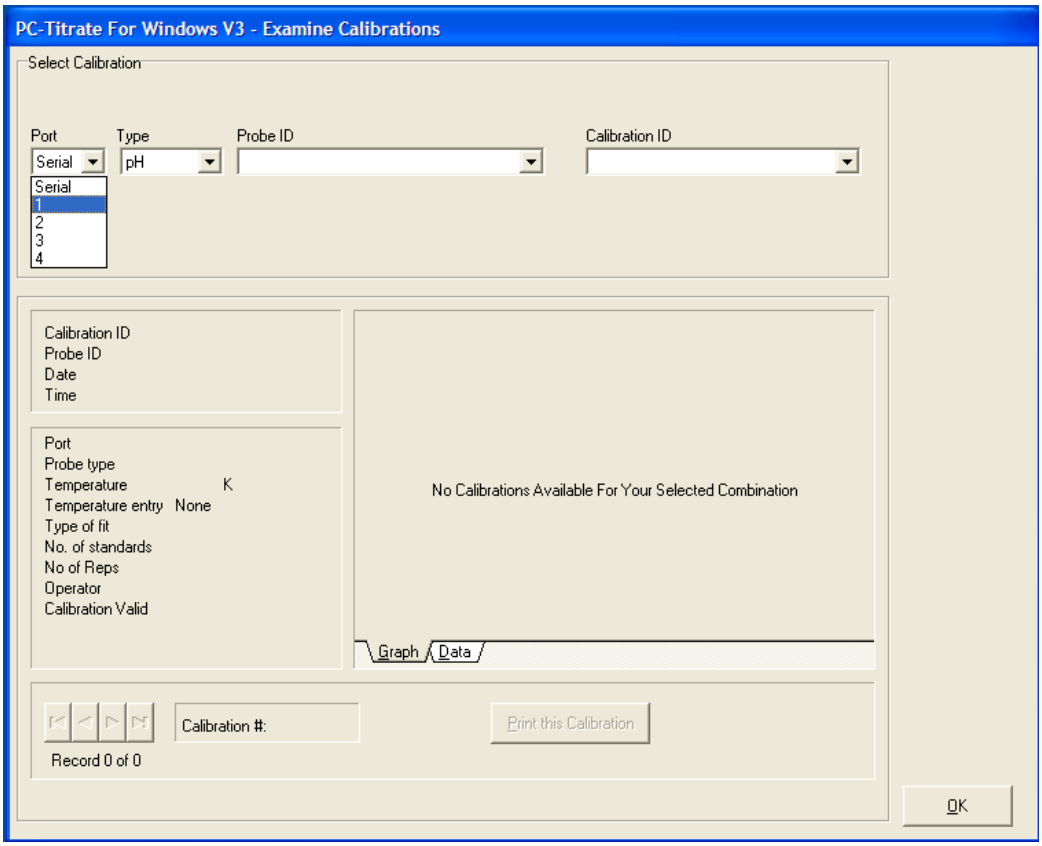
If any changes were made, be sure to SAVE the updated template. To keep both the old and new template, select SAVE AS. If choosing Save As, see **Appendix D** for instructions on how to implement the new calibration template.

4.2. Viewing / Printing Historical Calibration Data

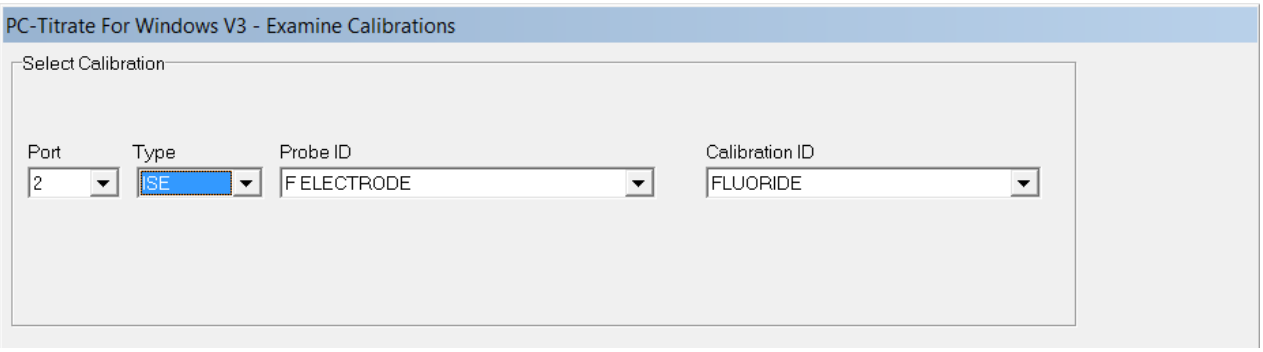
The Viewing/ Printing Historical Calibration Data function is not relevant to automated systems running solely PeCOD analysis but is included for automated systems running other applications in parallel with PeCOD. To view/print PeCOD calibration data refer to **3.0 Viewing Historical Reports or **7.2.1 Appendix B – Customized AutoRun Buttons.***

All historical calibrations are saved within the database for future viewing/printing. To view a historical calibration:

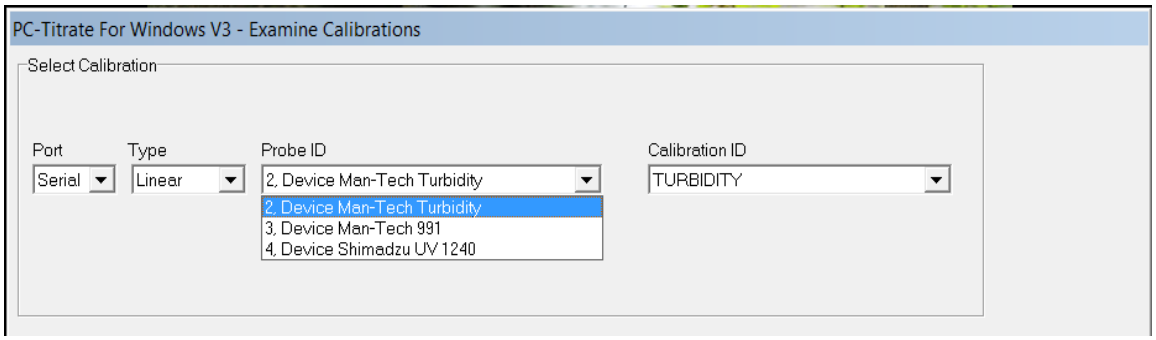
1. Go to the **Titrator** menu and select **Examine Calibrations**.
2. Using the drop-down menu, choose the port the electrode is plugged into (pH is usually on port 1, fluoride is on port 2). For serial devices (e.g. conductivity meter), select Serial.



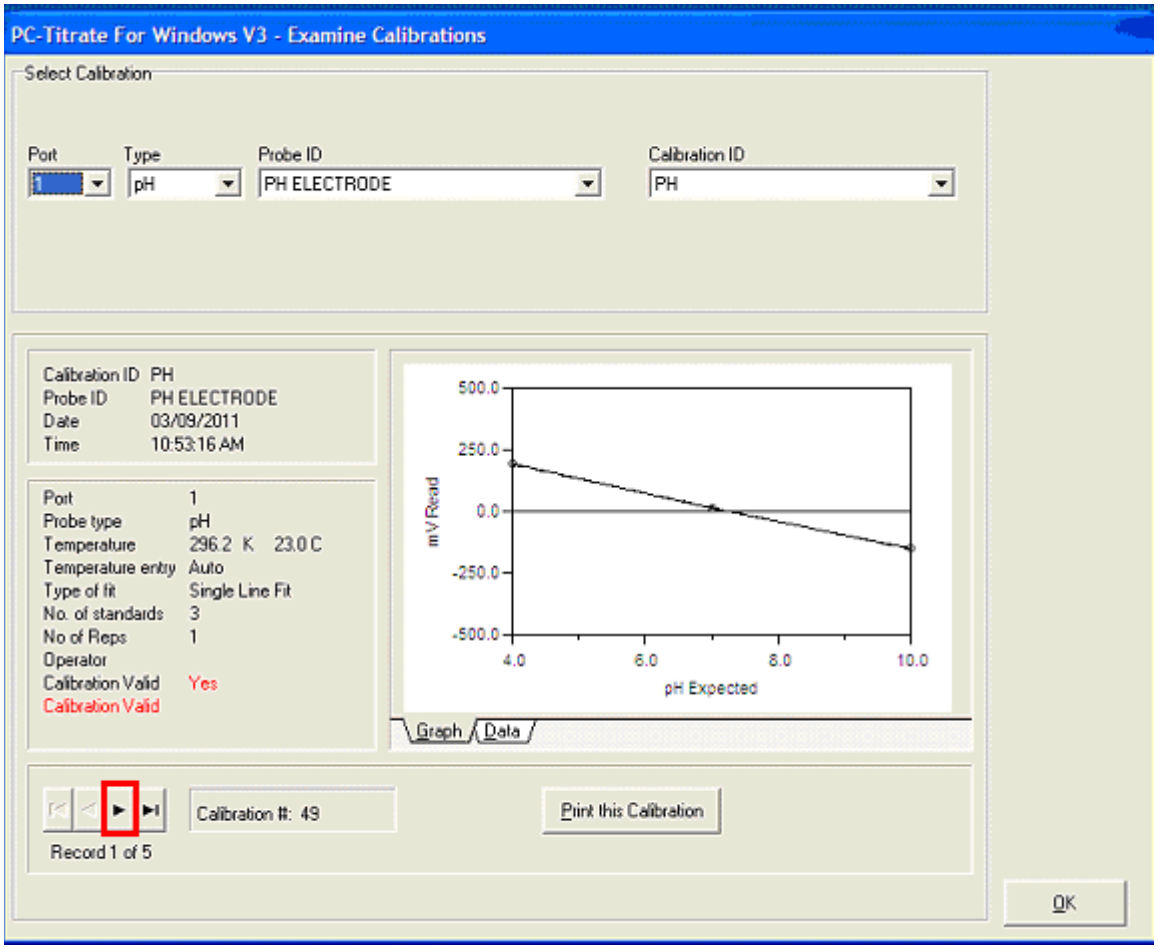
3. Choose the probe type, the Probe ID and Calibration ID using the drop-down menus.



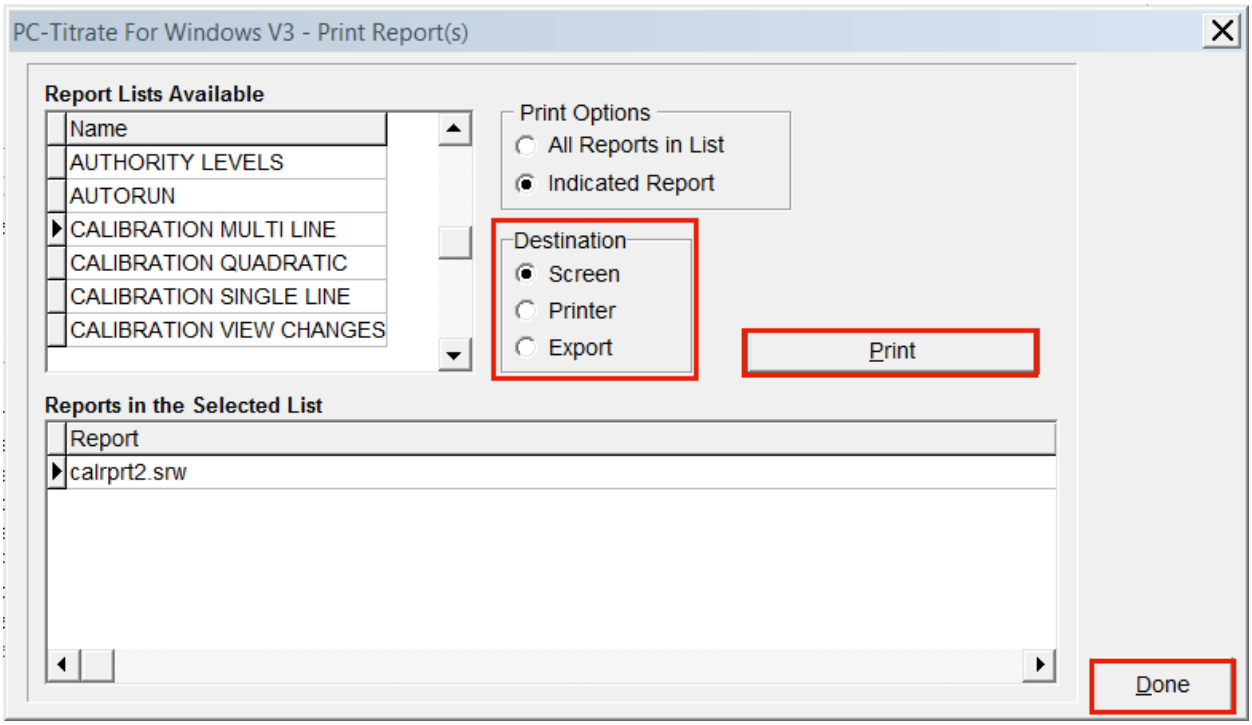
4. For a color, conductivity or turbidity calibration, the probe type should be Linear and the Probe ID drop-down menu will provide a list of all serial devices connected to the interface. Note that "Man-Tech 991" is a conductivity meter.



5. The most recent calibration will appear. Use the arrows at the bottom of the screen to scroll and view past calibrations.



6. General calibration information (e.g. date, time) will appear on the left of the screen, and the calibration record # at the bottom of the screen. On the right, the calibration graph will be displayed. View information like slope(s), intercepts(s) and readings in the **Data** tab.
7. Print the calibration report by clicking the **Print this Calibration** button and selecting the printer destination. Choose to print to the screen, printer, or export the data. Then click Print. When finished, click **Done** to exit the window, and **OK** to exit the screen and go back to the main menu.



4.3. PeCOD Calibration and QC Checks

The peCOD should complete a calibration and QC Check prior to each sample run, or at least once per day prior to sample analysis. Use the **PECOD CAL or DAILY STARTUP** Autorun button to load the calibration timetable template. Typically, this timetable will consist of a calibration followed by a QC Check. Ensure that the correct calibration is selected for the peCOD's working COD range. Once the correct COD range is setup in the peCOD and calibration schedule, input the correct tube position under the **Vial** column, if applicable. Please note, automated systems using a Titrasip won't require a **Vial** number, as the pre-mixed calibrant is pumped into the TitraSip Cell for calibrations and QC Checks. After the calibration template is complete, verify the calibration and QC Check values, from the Historical PeCOD Calibration and Results reports, according to the chart below (note, that the QC Check criteria may be adjusted to meet site-specific requirements:

COD Range	M (COD/µC)	C (µC)	Iterm (µA)	QC-Check (mg/L)
Advanced Blue	0.01 – 0.08	50 – 300	> 16	17 – 23
Green	0.02 – 0.06	150 – 700	> 16	115 – 125
Yellow	0.02 – 0.06	200 – 750	> 14	1150 – 1250
Red	0.02 – 0.06	250 – 800	> 14	11500 – 12500

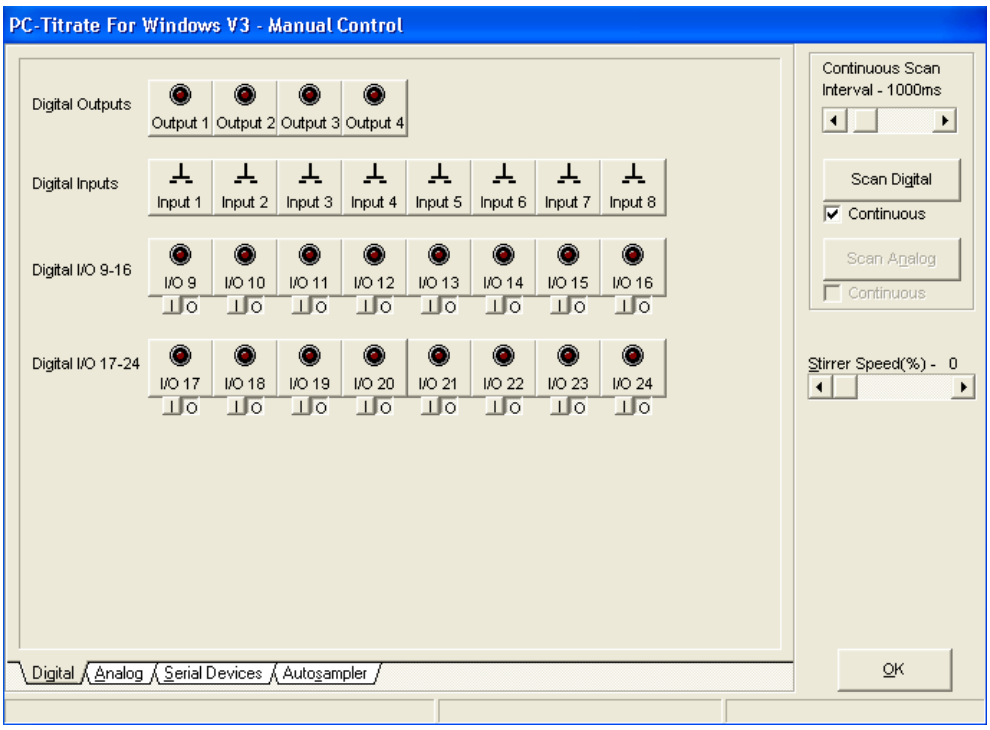
Please note, if a QC Check fails its passing criteria, the software will automatically recalibrate. If the recalibration fails, the software will attempt another calibration. If the recalibration fails a second time, the software will abort the timetable to notify the user that attention is required. If the recalibration passes, the software will continue with another QC Check. If the second QC Check fails, the software will again abort the timetable. If the second QC Check passes, then the timetable will continue, and the system is ready to analyze samples.

For troubleshooting tips for failed calibrations and QC Checks, refer to 7.6. Appendix F – Troubleshooting Guide.

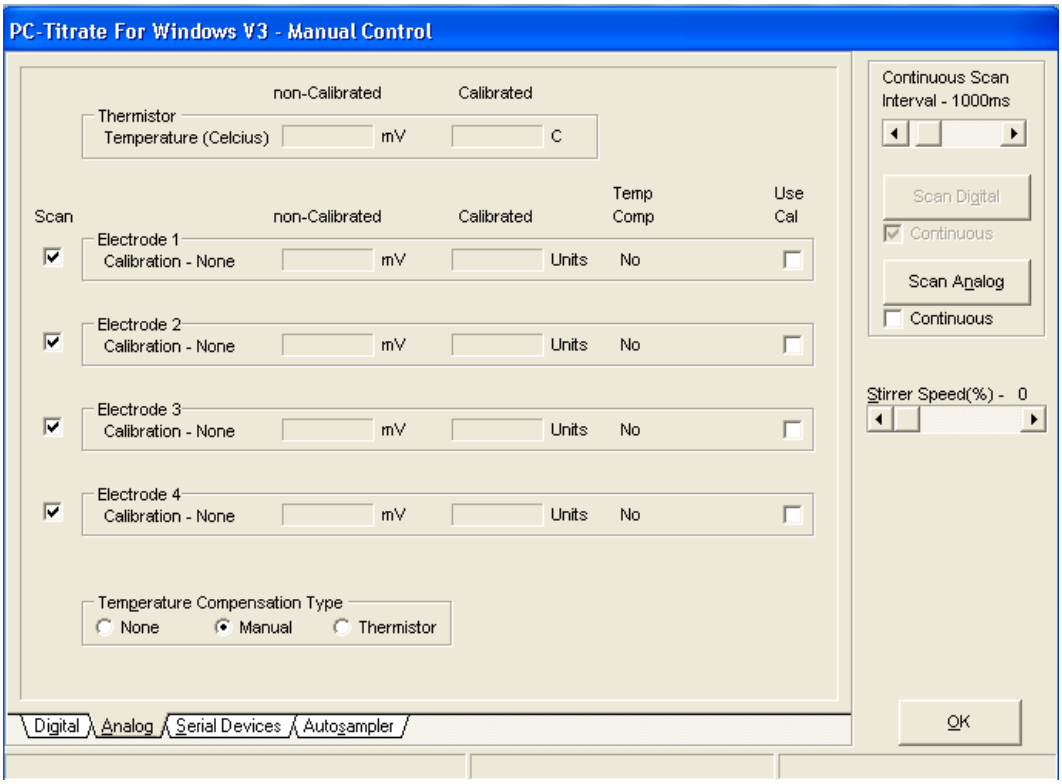
5.0 Manual Control

The user may manually control all hardware that is connected to the system through the **Manual Control** menu, located **in** the **Titrator** tab.

The **Digital** tab allows control of all digital inputs/outputs such as pumps, drains and stirrers. Identify the digital input/output number(s) by looking at the cable connected to the back of the module. Select the toggle switch for the appropriate digital number. Ensure the module switch is set to AUTO mode, where applicable.



The **Analog** tab is where manual readings of electrodes or temperature probe are displayed.

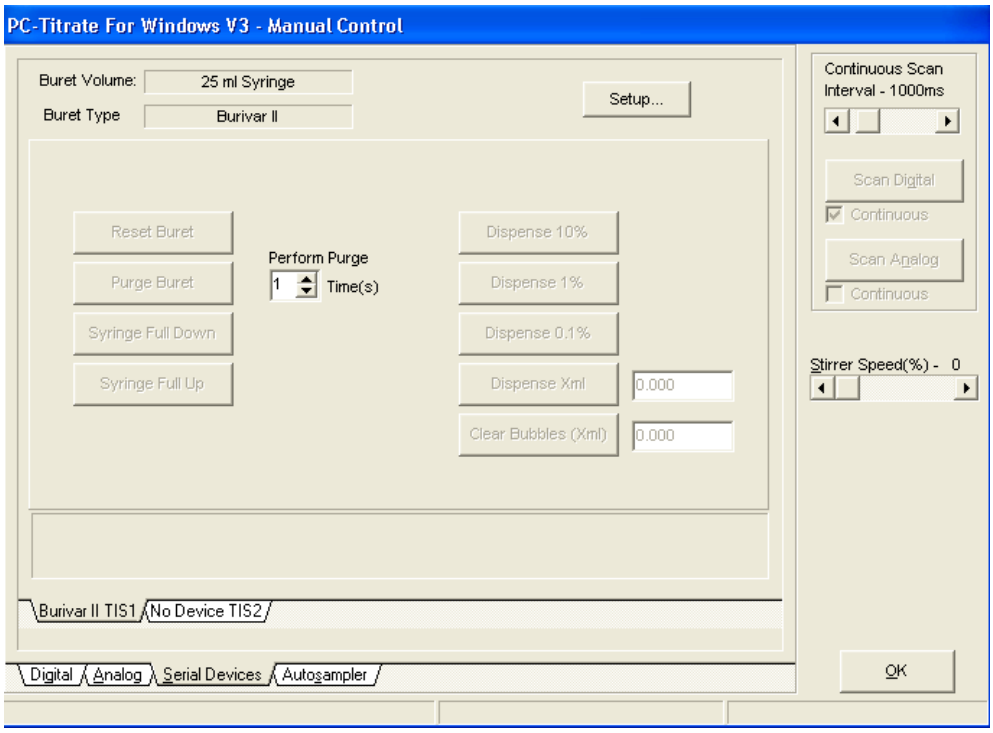


Select the "Scan" box next to the desired electrode port(s) and select the "Use Cal" box to see calibrated readings. Select which calibration to use when prompted. See section 4.2 for details.

To turn on the stirrer plugged into the back of the interface, use the scroll bar on the right side of the screen to select a speed. 20 – 30% is standard.

To take an electrode or temperature reading, click the "Continuous" box, then select **Scan Analog.**

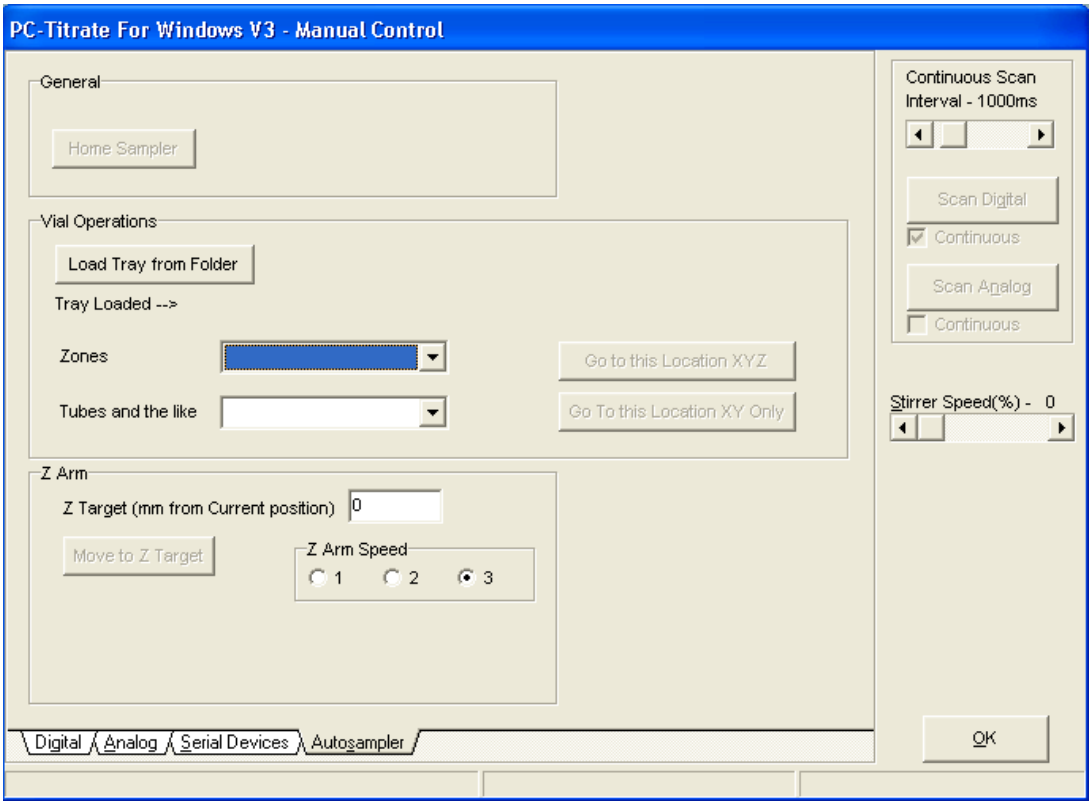
The **Serial Devices** tab controls all serial devices such as burets and meters. Each serial device has its own tab.



For meters, this screen allows the user to take a reading. Choose either Calibrated or Uncalibrated. If choosing Calibrated, select which Calibration Template to use.

For burets, this tab performs purges of the syringe (full empty/refill cycle), and injections.

The **Autosampler** tab allows the user to manually move the autosampler to various locations.



To begin, load the tray file and select "**Home Sampler**". Once the sampler moves to the home position, use the Zones and Tubes drop-down menus to select the desired location to move the sampler. Racks are labelled with position numbers.

Once a location has been selected, move the sampler XY or XYZ. Moving XY will move the arm above the position selected but it will not move down into the vessel. The Z motion can be controlled independently by entering in values for Z Target (in mm). Moving down requires a negative number and moving up positive. Change the speed of the Z-arm movement by selecting speed level 1, 2 or 3 (3 is fastest). Note that 3 is the recommended speed.

6.0 Storage and Maintenance

6.1. Backing up the Database

It is recommended that a database backup is performed on a regular basis, preferably every couple of weeks, or if any changes have been made to the database. It is recommended to save copies of the backup files to a safe location such as on a network, or memory stick in case of a hardware crash.

Since databases can become quite large, it is recommended to zip (compress) the database. This makes for easier storage and transfer (if necessary). To zip the database, locate the active Hinterland folder in **C:\Program Files.** Right click on the folder to compress and rename the folder to give it a descriptive name (i.e. date and brief description of changes made).

6.2. Restoring the Database

To restore a backed-up copy of the database, follow these instructions.

1. Close all PC-Titrate V3 software.

2. Rename the current database to ensure that a current copy of the software is available should any problems occur when unzipping. To rename the Hinterland folder:
   i. Select the **C:\Program Files\Hinterland** folder.
   ii. Right click on the Hinterland folder and select **Rename**.
   iii. Rename the folder to something that will be easily recognized, such as *Hinterland company name + date*.

3. Extract the database backup, ensuring to select the correct unzipping location (to **C:\Program Files**).

4. If the database unzipped correctly, this backup is now the active database and can be accessed by double-clicking on the PC-Titrate V3 icon on your desktop. Double-check the path of the shortcut is correct before using it by right clicking and selecting properties. It should be **C:\Program Files\Hinterland\PC-Titrate V3**.

NOTE: The working database name must match the path.

6.3. Archiving

Archiving is the process of cleaning out the database of old results and storing them elsewhere. MANTECH recommends regularly archiving the database to keep it working in top working order. How often archiving id done depends on how often the system is run and how much data has accumulated.

Archiving removes all of the data from the last time an archive was run, including recent data. All titration data and results (but not calibration data) will be removed from the database.

1. Users may wish to first print out all old reports and file them that a hard copy exists. The archived data can be retrieved electronically, when the system is not running.

2. Create a new folder entitled “Archived Data” on the computer hard drive in which to store all archived data.

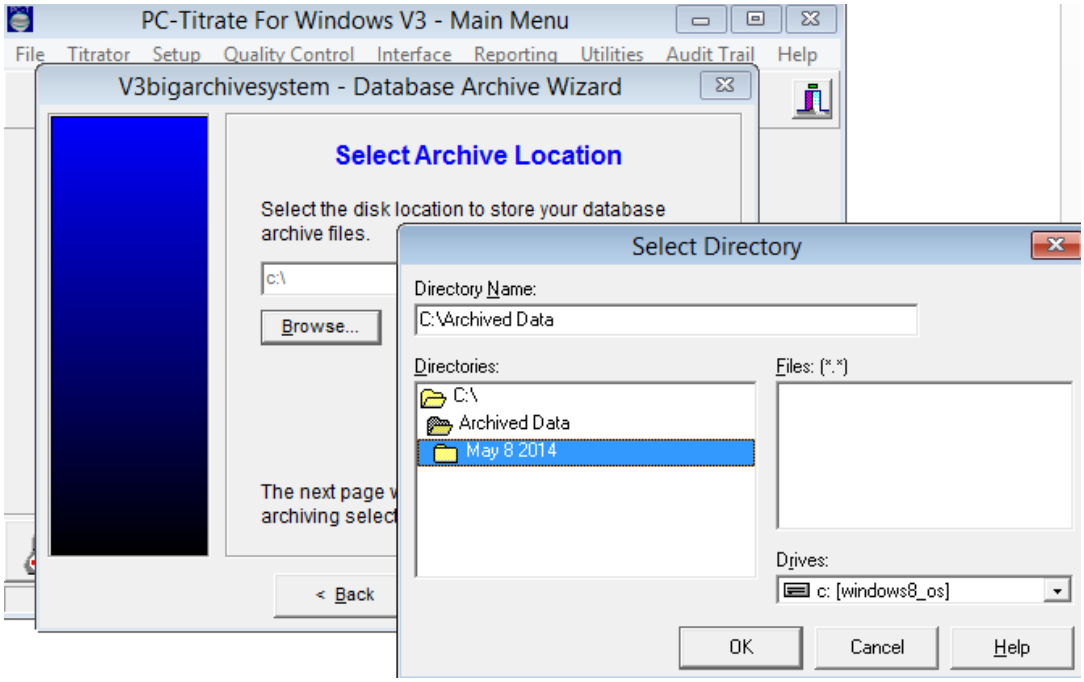
3. Within this folder, create another folder using today’s date. Note that the data must be sent to an empty folder otherwise the contents of the folder will be overwritten with the current archived data. For future archives, create another folder within the Archived Data folder, date stamp and send the new data there.

4. Create a backup of the database by following the steps detailed in section **6.1** of this document. This is recommended in case something goes wrong during the archiving process.

5. Go to **C:\Program Files\Hinterland\PC-Titrate V3** and locate the **V3bigarchivesystem** application.

6. Right click on the application and select “Run as Administrator”. When the Database Archive Wizard window opens, click **Next**.

7. Click **Browse**, select the disc location to store the archived files (use the folder just created), and click **OK**.



8. Click **Next**, and a message warning that all data will be erased from the database and stored to the disc location specified in Step 7 will be displayed.

9. Click **OK** and the data archiving process will begin. Click **Finish** when complete.

6.4. Retrieving Archived Data

When viewing retrieved data, open a special copy of the software that gives access to the archived results, including reports, titration and calibration data. Note that in this copy of the software the user will only be able to access the archived data and will not have access to any current data that has been run since the last archive nor will the system run.

To retrieve archived data:

1. Open the **Utilities** menu from the main page of PC-Titrate software.

2. Select the **Database Records** submenu, and then select **Archive/Retrieve**.

3. When the Database Archive Wizard window opens, click **Next**.

4. Select **RETRIEVE a previously archived Database** and click **Next**.

5. Click the **Browse** button and select the disc location where you have stored your archived results and Click **OK**.

6. Click **Next** twice more, and then click **Finish.**

7. Archived results may now be accessed normally through the software. Remember that certain screens will be locked. When finished, simply close the software and open it again to restore the current database.

6.5. System Storage

Overnight/Daily Storage

ELECTRODES – ensure all electrodes are placed in appropriate storage solution. If the system is running overnight, the storage vial is usually the next vial position after the last sample OR the last vial position in the rack. Use pH 4 buffer for pH electrodes and a low standard for ion selective electrodes (e.g. use ~0.1ppm Fluoride standard for storing Fluoride electrodes).

Long Term Storage

If planning to shut down the system for a long period of time (> 1-2 weeks) follow the information described below to ensure proper operation of the system upon restart.

1. ELECTRODES – drain all reference solution from the electrodes, and rinse with deionized water. For pH electrodes, refill them with fill solution, cover the fill hole with parafilm and place a bottle or protective cap over the electrode bulb. For Ion Selective Electrodes, place the protective caps over the sensing membranes and store them dry in their boxes.

2. PUMPS – Remove the aspirate line and place it in deionized water. Run the pump manually, filling the lines with DI water.

3. BURETS – Remove the aspirate line and place the line into DI water. Purge the buret three to four times to fill the line, syringe and valve with DI water.

4. DATABASE – create a backup of the database by following the instructions outlined in section **6.1**.

5. POWER – turn off all electrical power to the system.

6. PeCOD – leave the peCOD on the system with its electrode block and sensor stored inside. Ensure that DI water has been primed 6x into Port A, and either DI water or pre-mixed blank solution has been primed 3x into Port B. It's imperative that the electrode block stays hydrated.

7.0 Appendices

7.1 Appendix A – UDV Definitions

Please note that the UDV list may vary based on the system's applications. For example, systems incorporating peCOD analysis will typically reserve UDV 6 for COD.

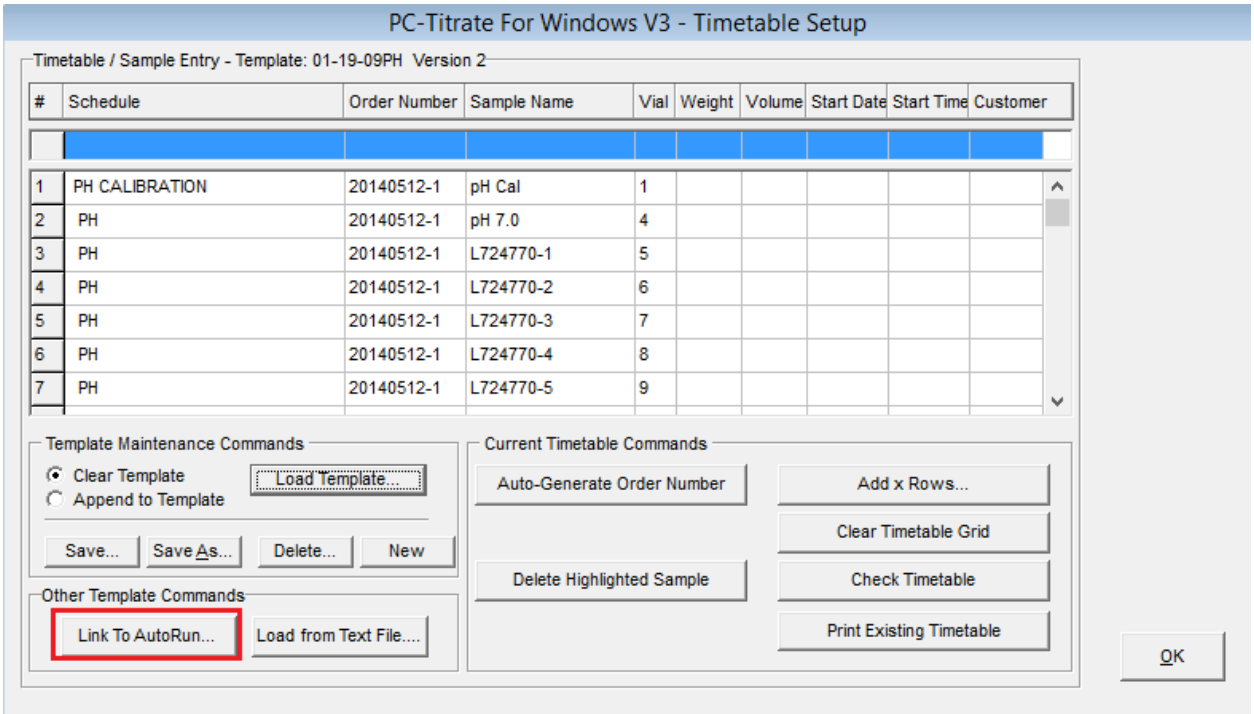
WATER ANALYSIS EQUATION SET		
UDV	**Description**	**Application**
1	cond	Conductivity
2	pH	pH
3	palk	Alkalinity
4	talk	Alkalinity
5	bcarb	Alkalinity
6	Carb/COD	Alkalinity/peCOD
7	hydrx	Alkalinity
8	flrd	Fluoride
9	Cl	Chloride
10	NH3	Ammonia
11	NTU	Turbidity
12	Temp	Temperature
13	Acid	Acidity
14	TotalHD	Total Hardness
15	Color	Color

7.2. Appendix B – Creating / Editing AutoRun Buttons

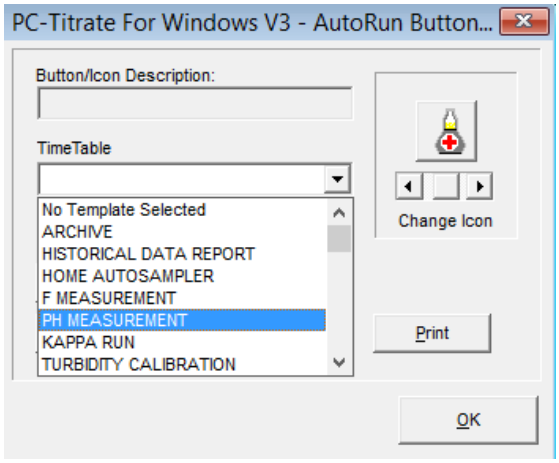
See section 1.3. AutoRun Buttons for information about AutoRun buttons and instructions for creating and saving a template.

Creating a new autorun button:

1. Create/modify a template according to the instructions in 1.4. Running Samples. Once created, save the template and click the **Link to AutoRun…** button.



2. In the window that opens, select the new template name from the time table drop-down list. New templates/timetables will appear at the bottom of the list.



3. Using the arrows, scroll through the list of available icons and make a selection.

4. Click the **Save As** button and give the new AutoRun button a name. This name will be what is displayed when hovering the mouse over the button on the home screen. Icons will appear in alphabetical order from left to right. Including spaces at the beginning of the name which will put it at the top of the list.

5. Click OK to exit the window.

To edit an existing AutoRun button:

1. From the main menu, go to **Utilities, Edit AutoRun buttons**.

2. Click the **Load** button and select the AutoRun button you wish to edit.

3. Edit the timetable/template used with this AutoRun button and/or change the icon associated with it by following the instructions above (steps 2-4 in the previous section). AutoRun buttons may be deleted by clicking the **Delete** button and choosing an AutoRun button to delete. NOTE: once an AutoRun button has been deleted, the name can never be reused as it is still saved in the history.

7.3. Appendix C – Titration Method Settings

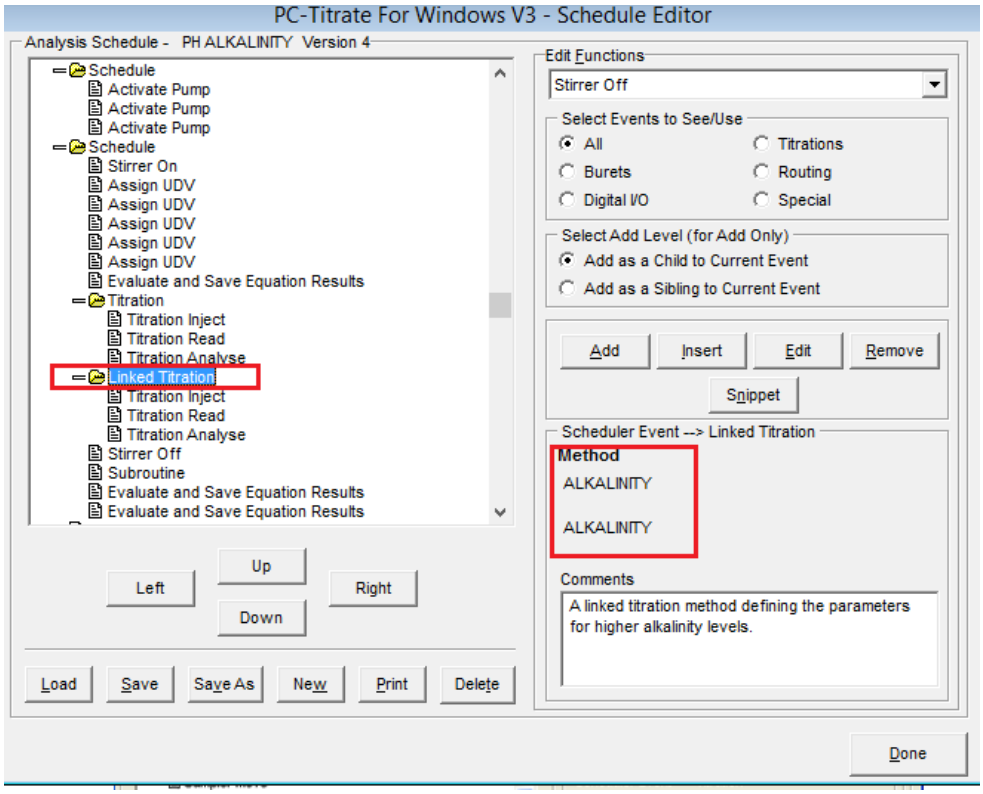
Titration Methods contain details about titrations, including titrant concentration, electrode(s) used to plot/monitor the curve, stability time, stopping criteria, etc. Before any changes are made to Titration Methods, you must first determine which methods are in use.

1. Navigate to the **Setup**, **Analysis Schedule** menu.

2. Load the desired schedule containing a titration to view/modify.

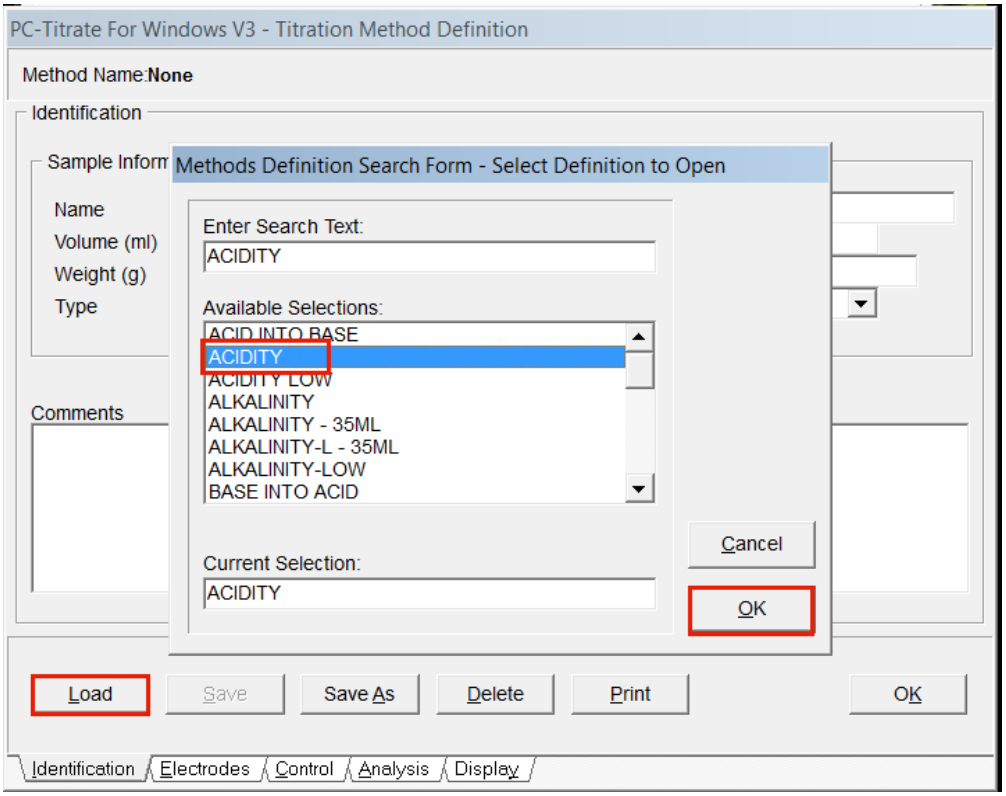
3. Locate the Titration step in the list of schedule steps on the left side of the screen. Select it, then look at the section above the white comments box in the bottom right corner of the screen. This will indicate the name of the Titration Method in use. Note this name.

4. Repeat the step above for any other Titration or Linked Titration steps found in the schedule, noting the names.

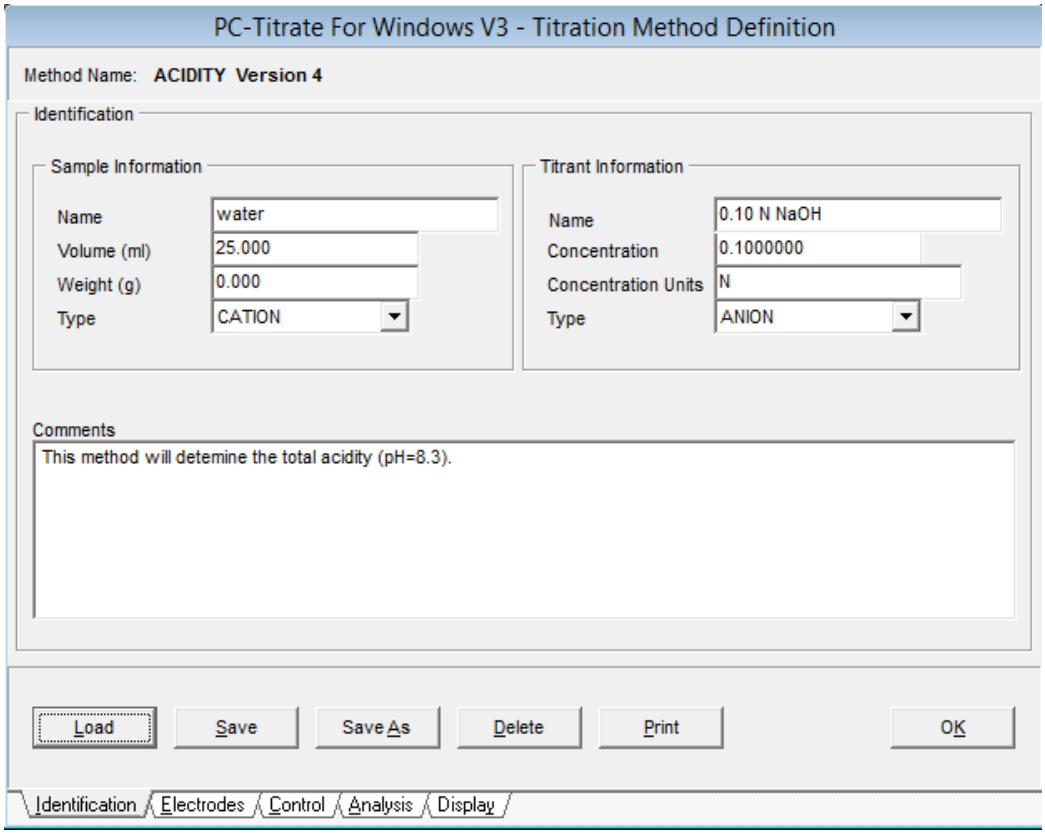


5. From the main menu, go to **Setup, Titration Method**.

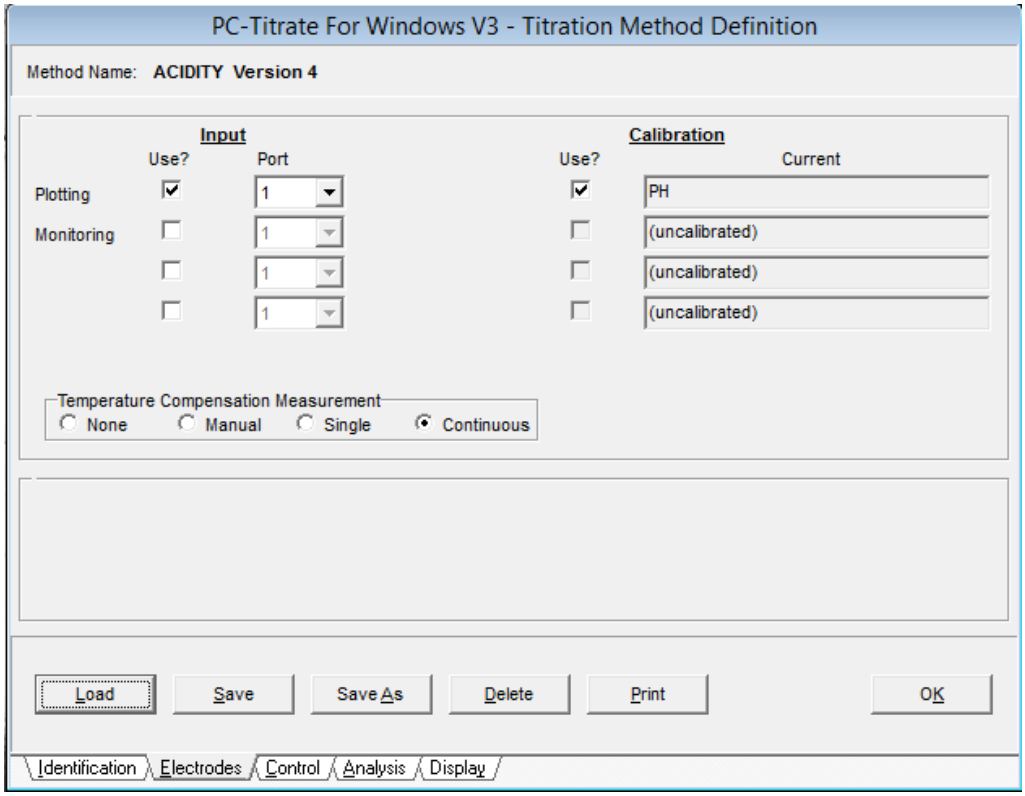
6. **Load** the titration method noted earlier and click **OK**.



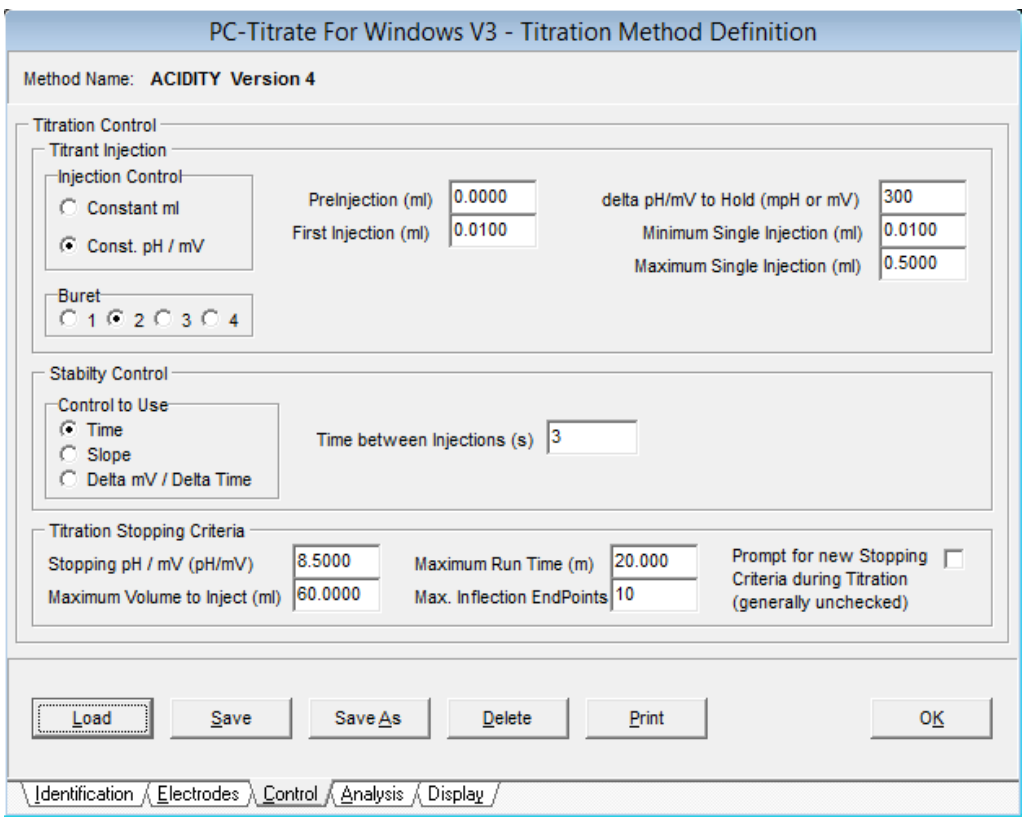
7. The first tab is the **Identification** tab. This tab defines sample and titrant information, including sample volume and titrant concentration. It also defines the sample/titrant as the cation (+) or anion (-), which indicates to the system the direction of the titration curve. Note that information on this screen must be identical for Titrations and associated Linked Titrations.



8. The **Electrodes** tab is where the active electrode is indicated. This tab is also used to define any valid calibrations, and whether temperature compensation is in use (only for pH electrodes). Note that information on this screen must be identical for Titrations and associated Linked Titrations.



9. The **Control** tab is where injection sizes, stability settings and stopping criteria are defined.

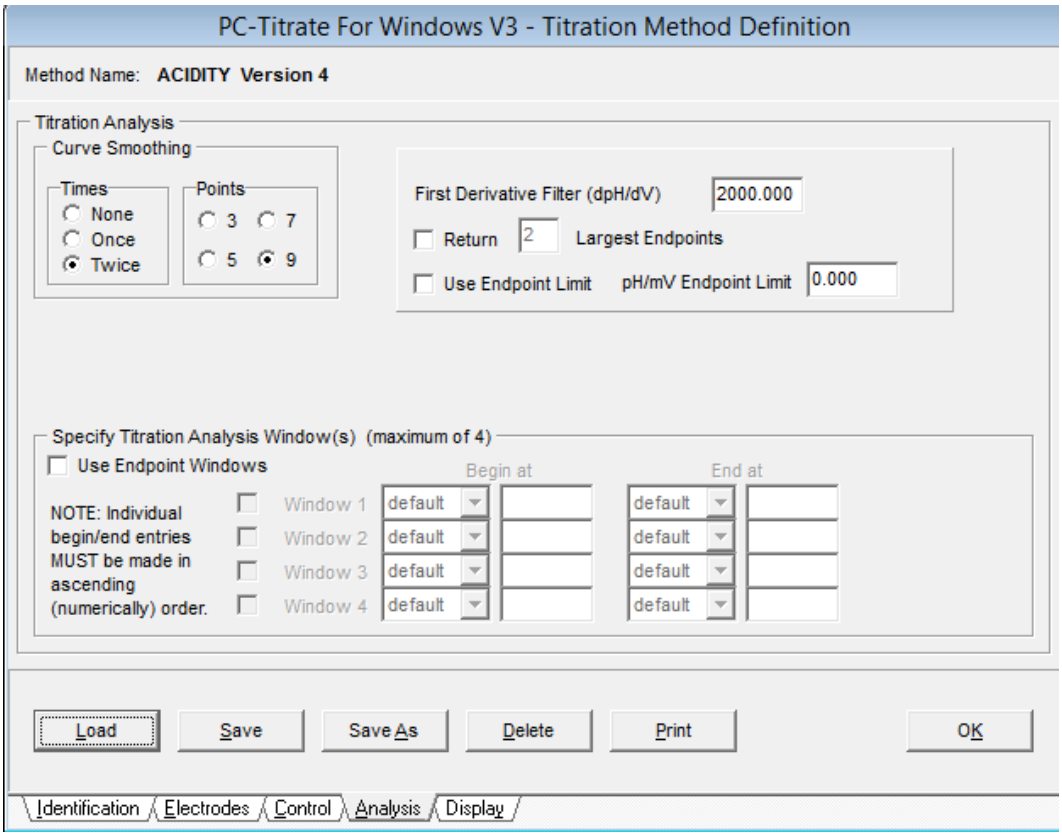


The control tab allows the user to choose a constant mL injection, or dynamic injection control in which a maximum and minimum injection size are specified, and the system determines the size of injection to use depending on the change in mV or pH from the last injection. This setting is called the “delta pH/mV to Hold” and it is specified in mpH

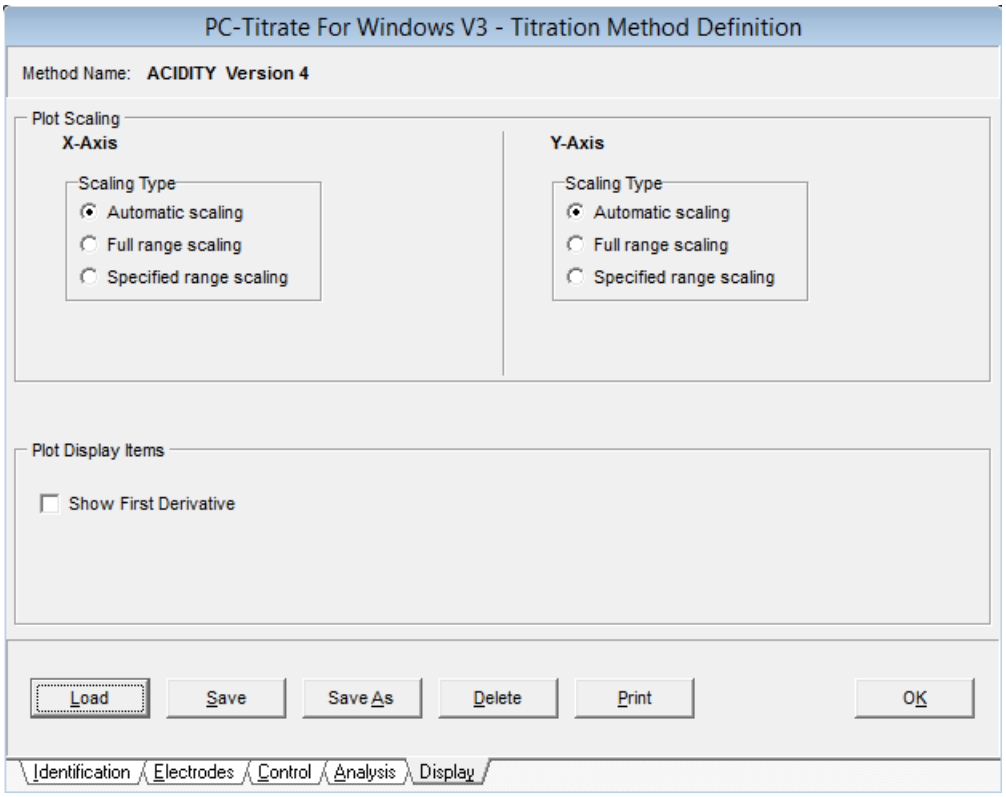
(mill-pH units) or mV, depending on the type of titration. Stability can be determined based on change in mV over time (Delta mV/Delta Time), slope (not often used), or by a simple time delay between injections.

There are various stopping criteria defined, with only one setting being the target stopping point. The others are used simply as back-ups so that titrations do not go on infinitely in case of a problem with the system. Usually the main criterion is a stopping pH or an inflection. A maximum time and maximum volume are also defined in case these criteria are not met.

10. The **Analysis** tab contains settings that help the system determine the correct endpoint. For inflection endpoint selection, the main settings used are usually curve smoothing and the first derivative filter. This is outlined in more detail in section **3.02**. Other settings in this screen are not often used. Note that information on this screen must be identical for Titrations and associated Linked Titrations.



11. The **Display** tab allows you to define the scaling of the curve, and whether the First Derivative should be plotted on the graph. Note that this is usually only used for titrations using inflection endpoints.

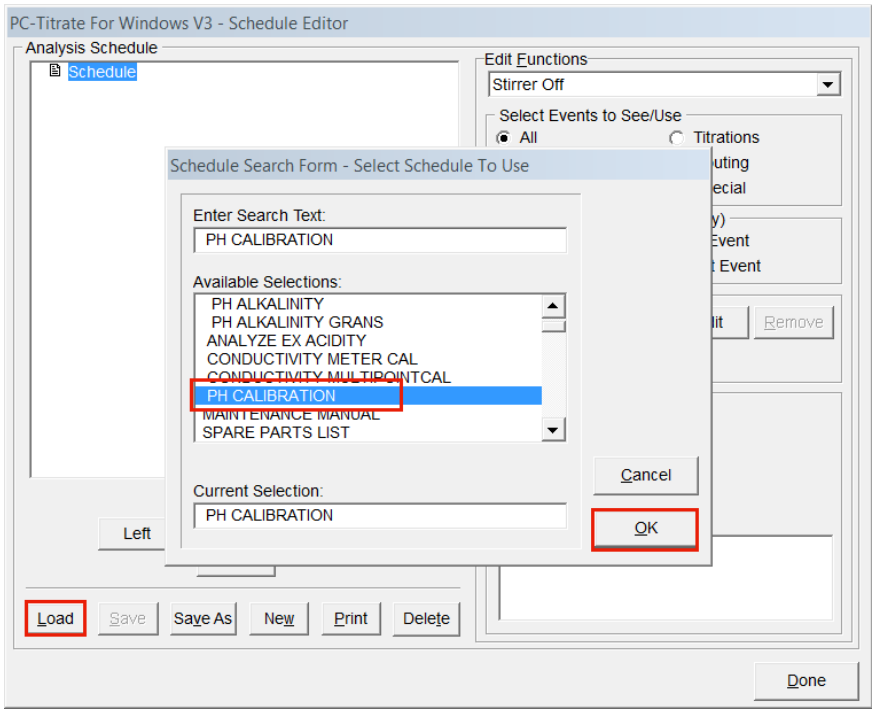


7.4. Appendix D – New Calibration Templates

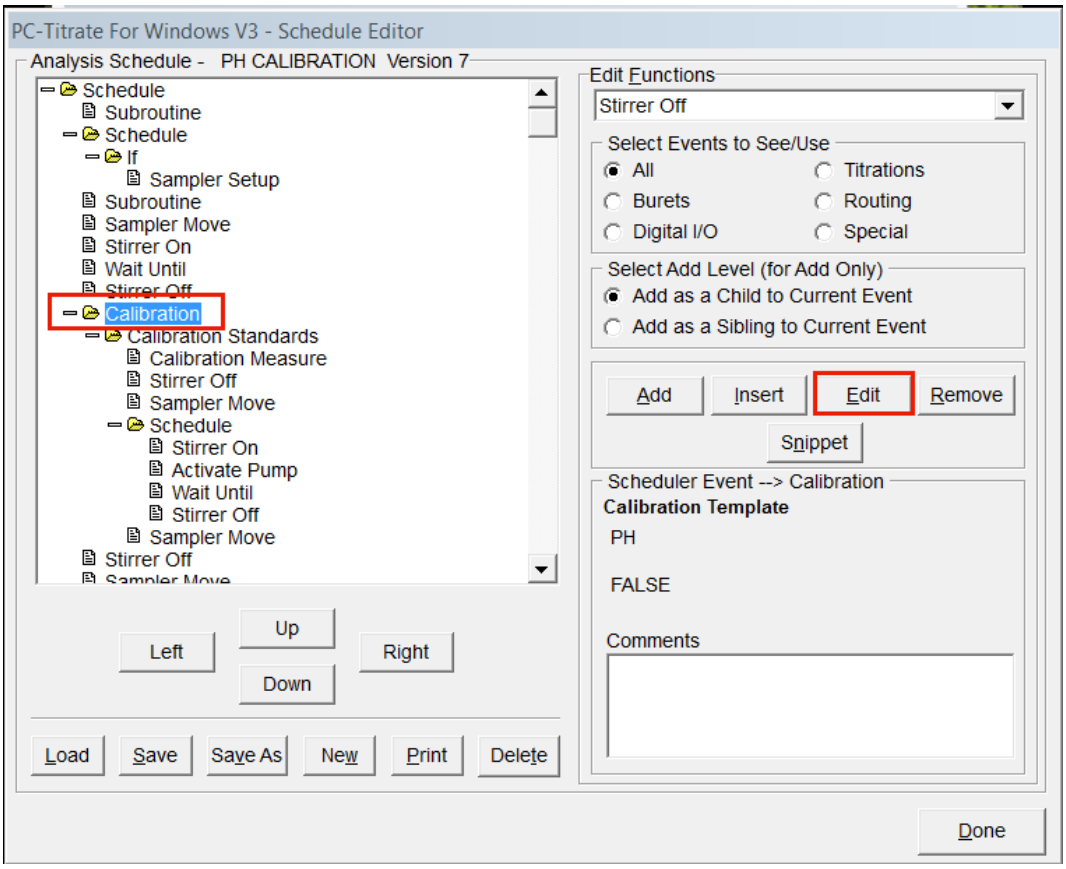
To create a new calibration template, see section 4.1. Calibration Templates.

Once the new template is created, follow the instructions below to implement it. Note – this procedure does not need to be followed when modifying an existing calibration template (i.e. when SAVING rather than SAVING AS).

1. Go to the **Setup** Menu, **Analysis Schedule**. Click the **Load** button and select the calibration schedule you wish to modify to incorporate the new calibration template.



2. Click on the **Calibration** folder in the schedule steps listed on the left side of the screen and then click the **Edit** button.



3. A list of templates will appear on the screen. Select the new calibration template, then click OK.

4. The system will then ask if you wish to print the calibration automatically after completion. Select Yes or No as desired.

5. Click SAVE to overwrite the existing schedule or SAVE AS to enter a new name and keep both the original and new schedules.

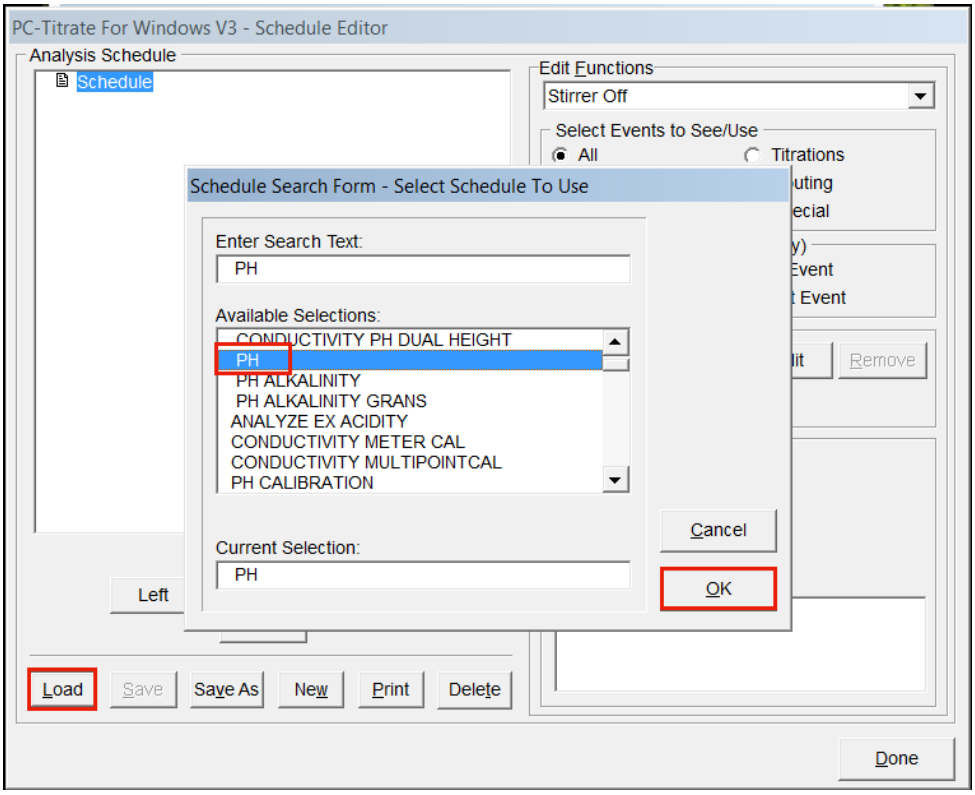
The user will need to run this calibration before the new calibration template can be implemented into sample schedules.

Once the new calibration has been run, update all schedules containing the parameter for which the calibration template has changed as well as any titration methods using that electrode. For example, if creating a new pH calibration template, any schedules containing pH will need to be modified in addition to any titration methods using the pH electrode (such as Alkalinity or Acidity). Follow the below instructions to make these modifications:

Schedule Changes:

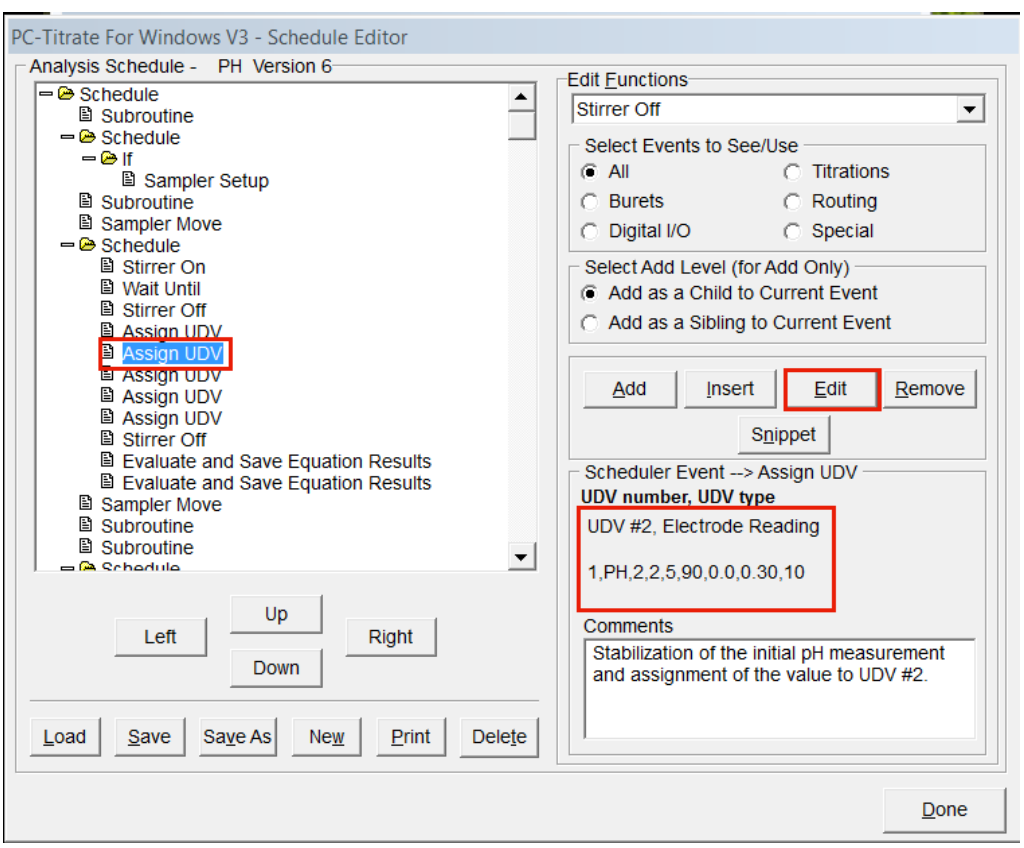
1. Go into **Setup, Analysis Schedule.**

2. Click on the **Load** button and select the schedule that you wish to modify, then click **OK**.

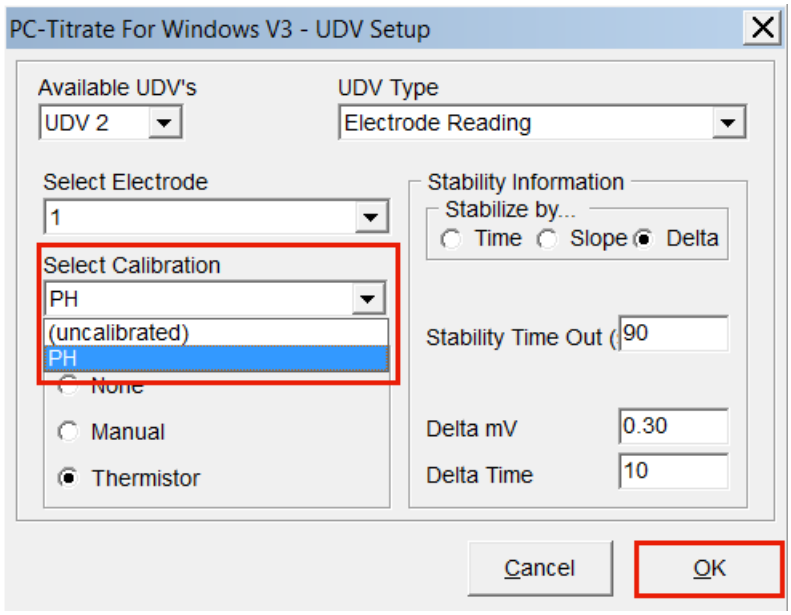


3. Look at the schedule steps on the left of the screen and locate a series of **Assign UDV** steps.

4. The second is the calibrated electrode reading. To be sure this is the correct step, look at the area in the bottom right corner above the comment box. If it indicates that it is an electrode reading, and it says something resembling a method name (in this example, it says PH) along with a series of numbers, this is the correct UDV step. Click the Edit button.



5. In the window that opens, use the dropdown menu for **Select Calibration** to choose the active calibration and click OK. Note that the new calibration template will only be available for selection after the calibration has been run.



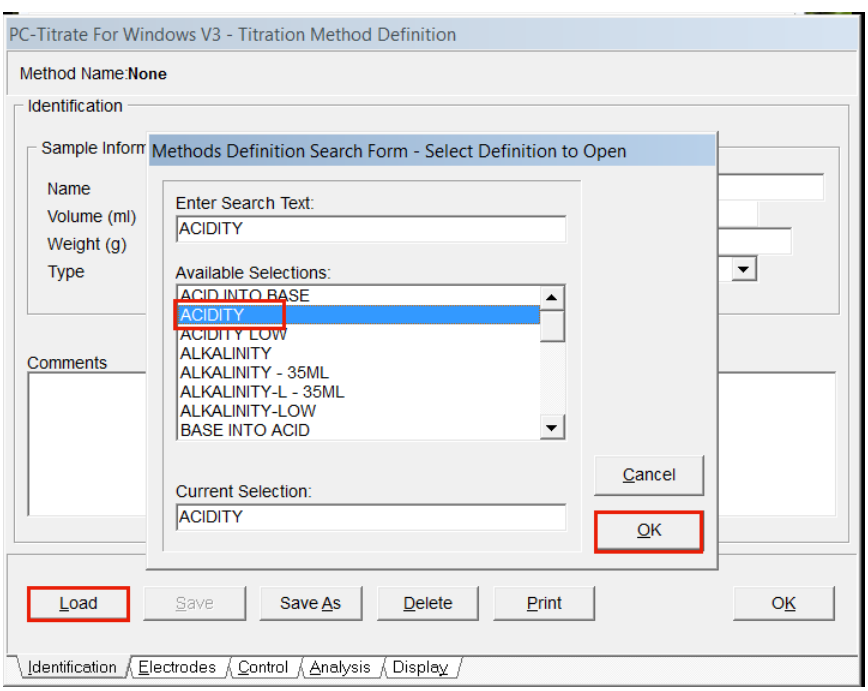
6. Click SAVE to overwrite the existing schedule or SAVE AS to enter a new name and keep both the original and new schedules. **NOTE:** The above steps must be completed for EVERY schedule containing electrode readings. Using the above example (pH), this means the PH schedule, along with the COND-PH, PH-ALK, etc will need to be modified.

Any titrations using this electrode also require modifications which occur in another menu. Please see section 7.3. Appendix C – Titration Method Settings for instructions on determining which Titration Methods are in use.

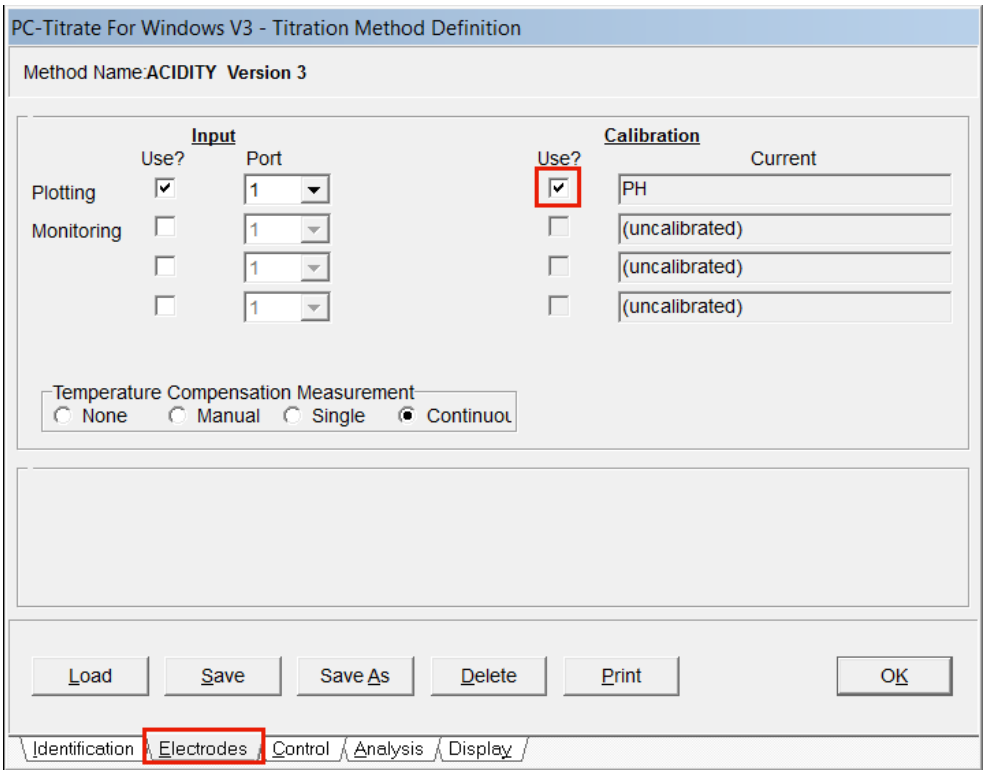
Once the Titration Method has been identified, follow the below instructions to update the calibration template selected.

1. From the main menu, go to **Setup, Titration Method**.

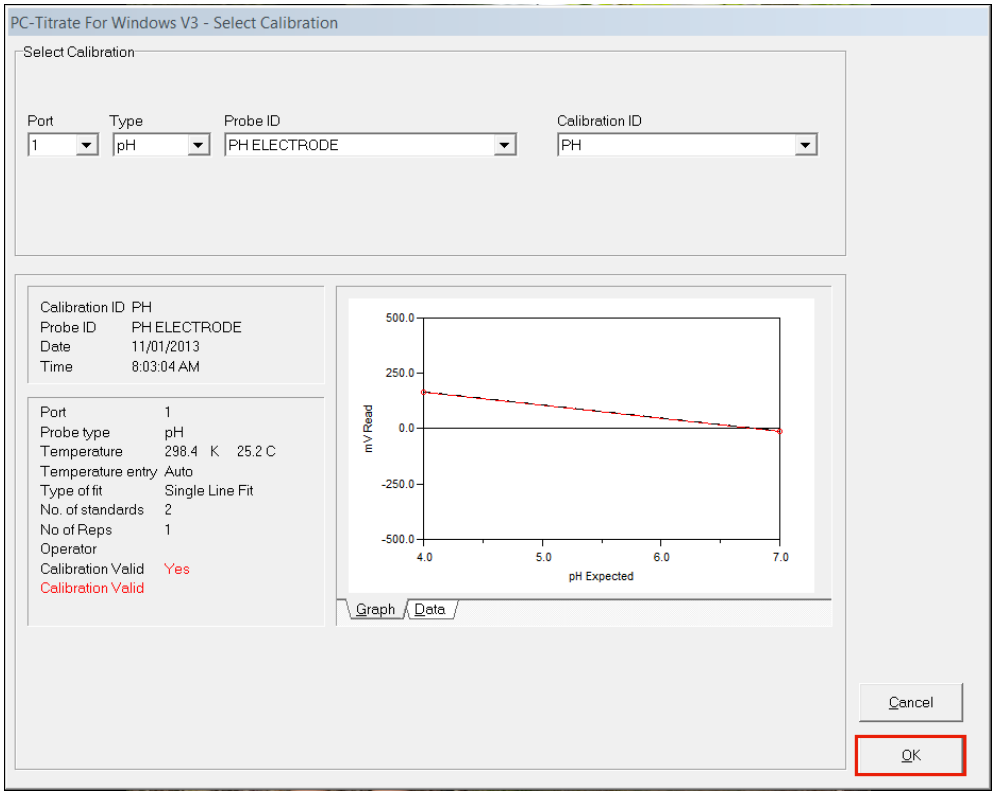
2. **Load** the first titration method noted (Acidity in this example) and click **OK**.



3. Click on the **Electrode tab** along the bottom of the window**.** Click on the **Use?** check box below the **Calibration** header.



4. In the window that opens select the electrode port, type, probe ID and calibration ID to use, click **OK**.



5. Click on the **Save** button and then **OK** to save changes and exit the screen.

7.5. Appendix E – Report Modifications

Modifying the report location:

The final report that is populated at the end of a run can be sent to the following locations:

1. Screen (i.e. the report will pop up on the screen when the run is finished)
2. Printer
3. Export location (e.g. LIMS, network location, etc.)

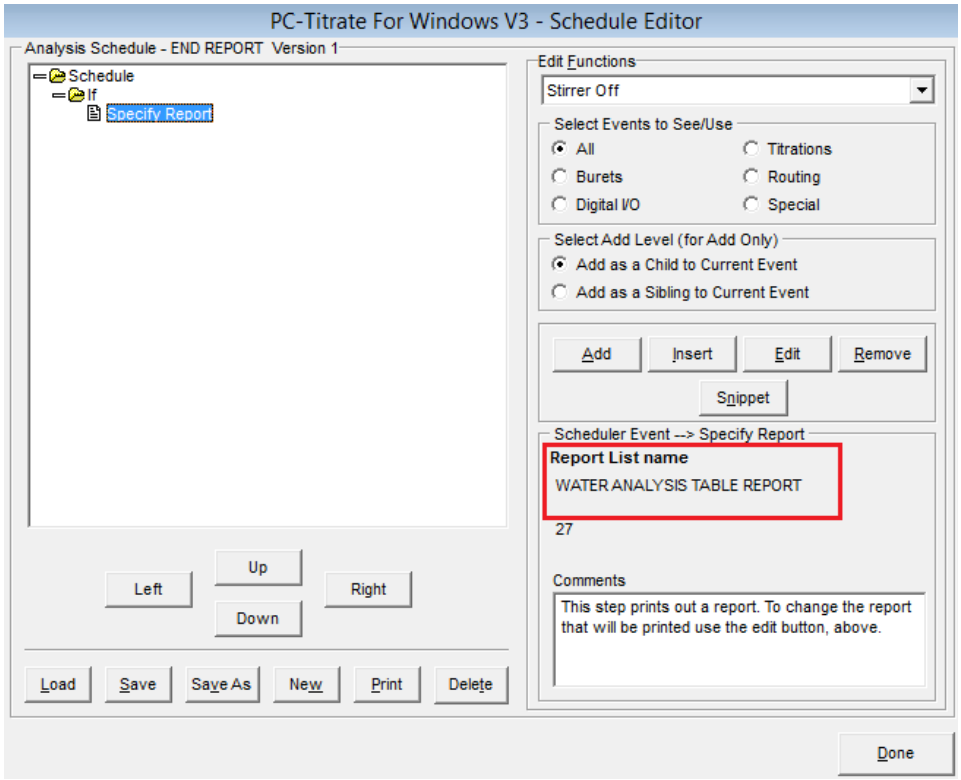
To modify the location to which the report is sent, first determine the name of the report in use.

1. From the main menu, go to **Setup**, **Analysis Schedule** option.

2. At bottom left hand corner of window, click the **LOAD** button and select one of the active sample analysis schedules (not a calibration schedule).

3. Scroll down to the bottom of the list on the left side of the screen and click on the **Specify Report** step. Note the name of the report list by looking at the bottom right hand corner, above the white comments box.

4. If there is no Specify Report step, look for a Subroutine called END REPORT. Click Load to search for this Subroutine and locate the report name by following step 3 above.

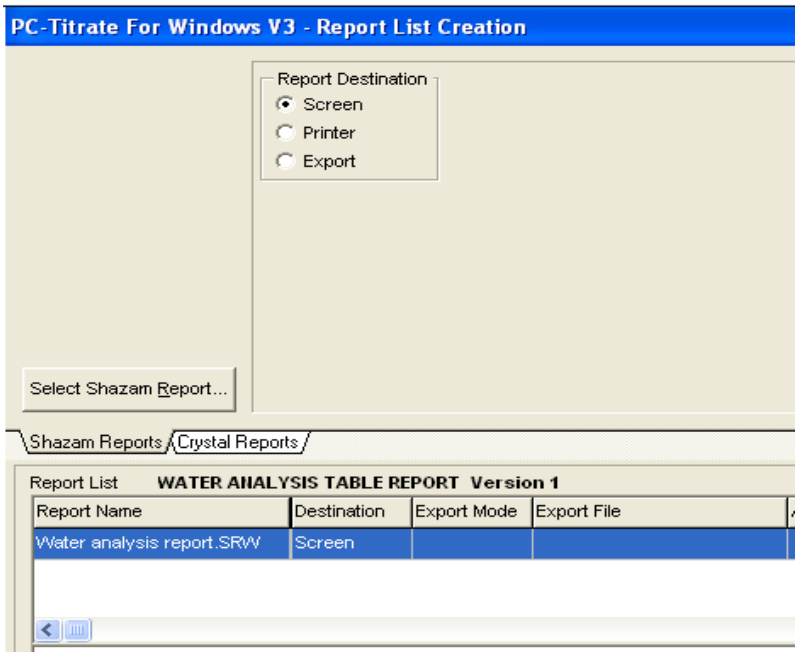


5. Click **Done** to exit.

6. From the main page of the PC-Titrate software, click the **Reporting** menu, **Create/Edit a Report List**

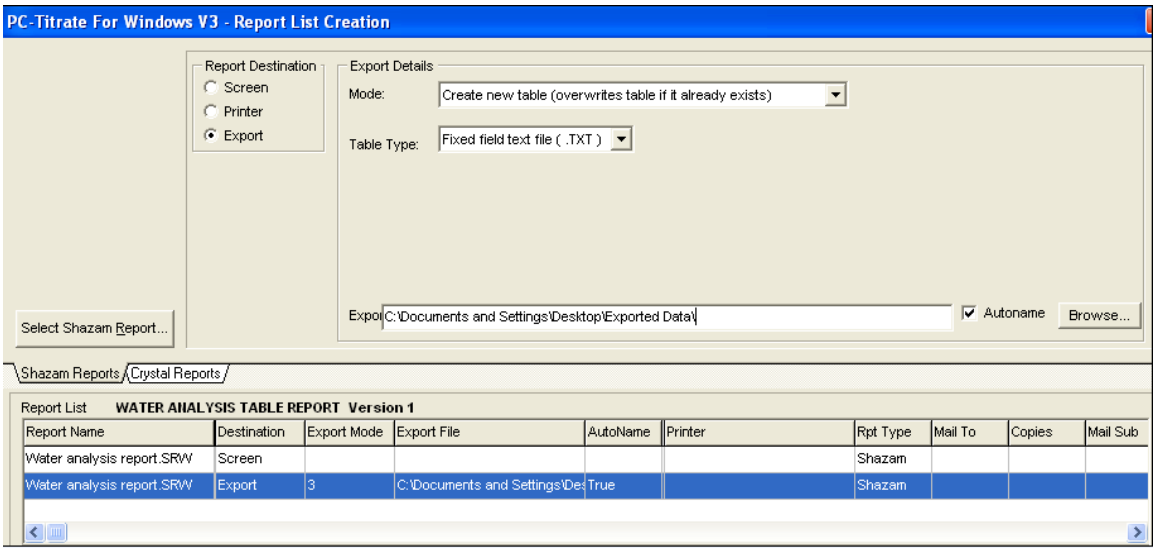
7. Click the **Load** button and select the Report List noted above, usually WATER ANALYSIS TABLE REPORT.

8. In the white area of the screen, the report name and destination of the report is displayed. Change the location by clicking one of the Report Destination radio buttons at the top of the screen.



9. To add a second or third location (e.g. to set up the report to print to the screen AND export to an external location), click on the 'Select Shazam Report' button and select the same report name that is shown in the existing report list table.

10. Once this is selected, a new line will appear in the report list table. Select the report destination to use. If selecting Printer, the report will print to the default printer selected for the computer. If Export is selected, an additional three boxes appear on the right-hand side of the screen.



If choosing Export:

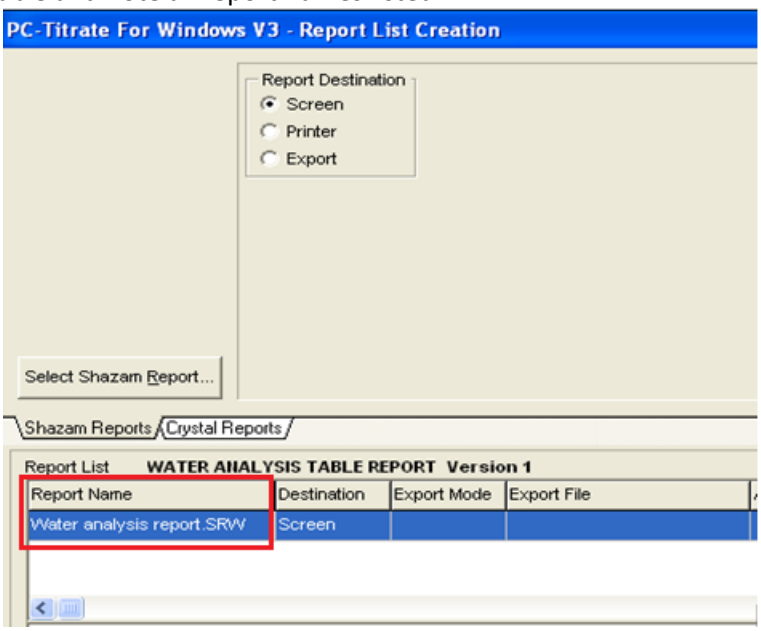
- In the mode box select "Create new table"
- In the Table Type select 'fixed field text file (.TXT)'
- Click on the browse button and select the location to send the files to. (It is best to make a folder in the location desired. Also, give the file a generic name or else the autoname function below will not work).
- Click on the autoname box so that a check mark appears. This is will create a new name each time the data is exported so the original is not overwritten.

11. Click on the Save button at the bottom on the screen.
12. Click the Done button to exit.

How to modify the report layout/formatting:

Before making modifications to the report, determine the name of the report in use. An autorun button on the main screen comes standard with most databases and will open the report (see section 3.1. Reports) but if not, follow steps 1 – 7 in 7.5. Appendix E – Report Modifications to access the Report List screen.

1. Look in the Report List Table and note all report names listed.

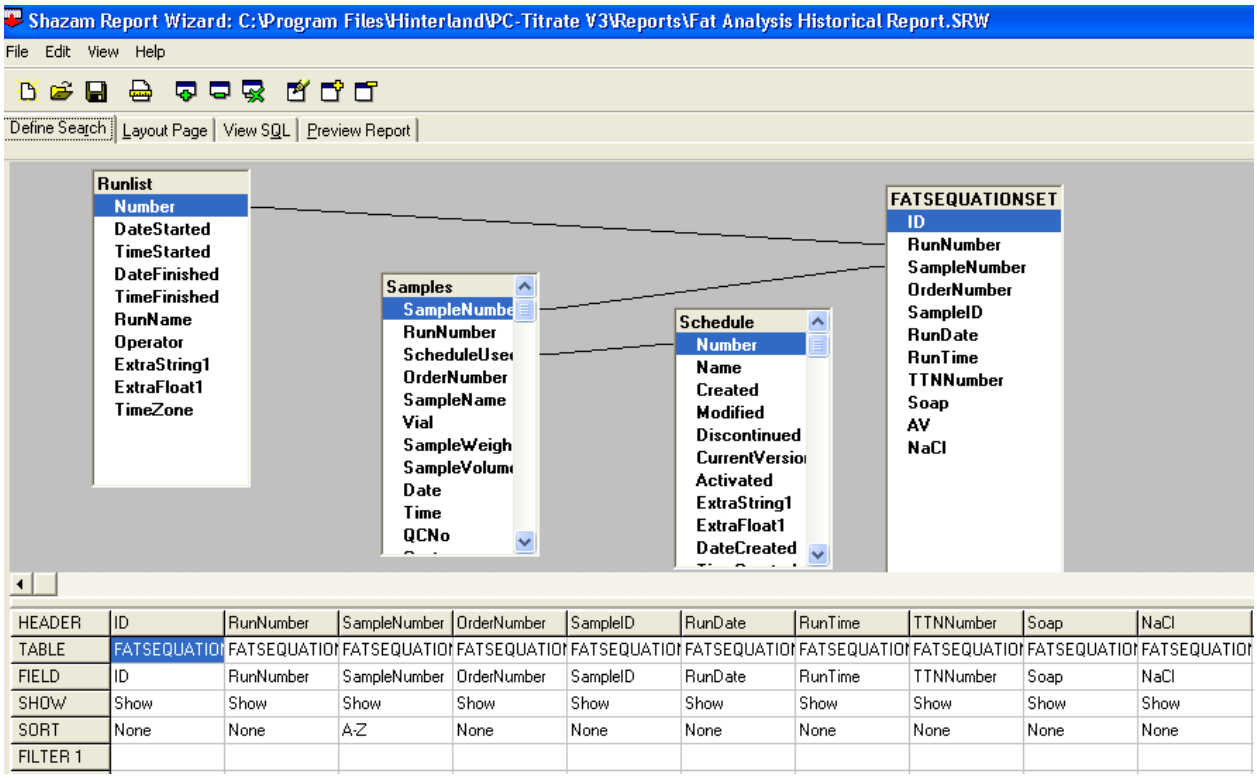


2. Click Done to Exit.

3. From the main screen go to the **Reporting** tab and select **Prepare and/or Print a Shazam Report.**

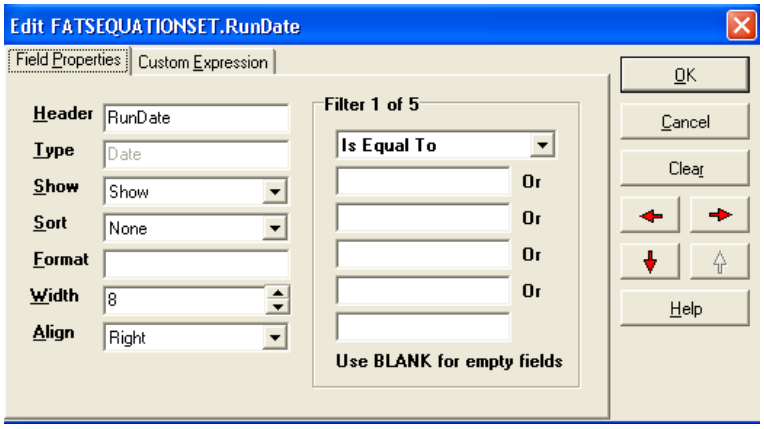
4. Go to File, Open Report and load the report you want to modify. This may be an in-run report or a historical report; typically, changes are made to both.

5. After a few moments a report will appear on the screen. The screen should be on the **Define Search** tab and may look like the one below.

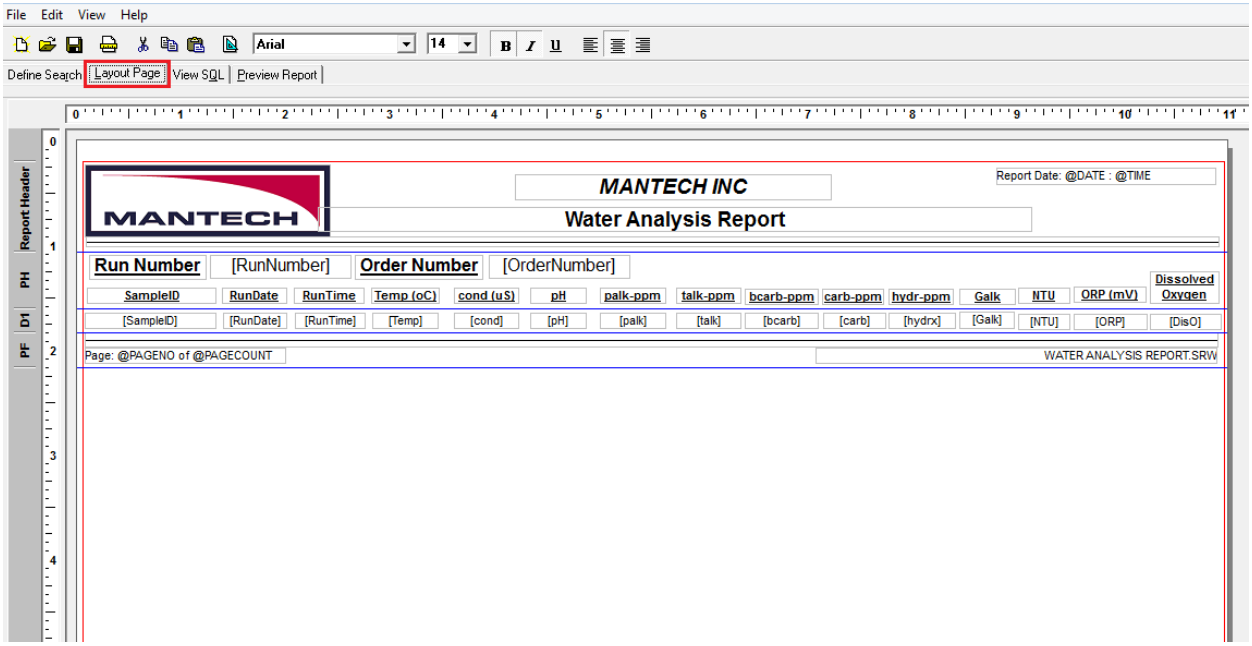


On the lower half of the screen a grid that contains all of the data types found in the report is displayed. Here the user can define filters (see section **3.01**) and change the number of decimal places reported for each parameter. To change the number of decimal places, double click under the parameter header to modify.

An **Edit** window will then appear. In the **Field Properties** tab, type in the number of decimal places in the **Format** textbox. For example, if 3 decimal places are desired, type 0.000. Click **OK** to exit the window.



Additional formatting changes can be made on the **Layout Page** tab.



Here the user can modify headers/titles (anything without square brackets around them), by clicking on the field to highlight it, then right clicking and selecting **Edit Caption**. Type in the name to use, then close the window. Fields containing square brackets should not be modified as they are linked to the result for that parameter.

Fields can be moved by dragging and dropping the desired box. The fields must not touch the lines however, or the links associated with those parameters will not work. You can also change font and other formatting by clicking on fields to highlight them and using the font editing tools at the top of the screen.

Fields can be deleted by clicking to highlight, then clicking the Delete button on the keyboard.

The sizes of the fields can be adjusted by clicking to highlight, then dragging to adjust field width/height.

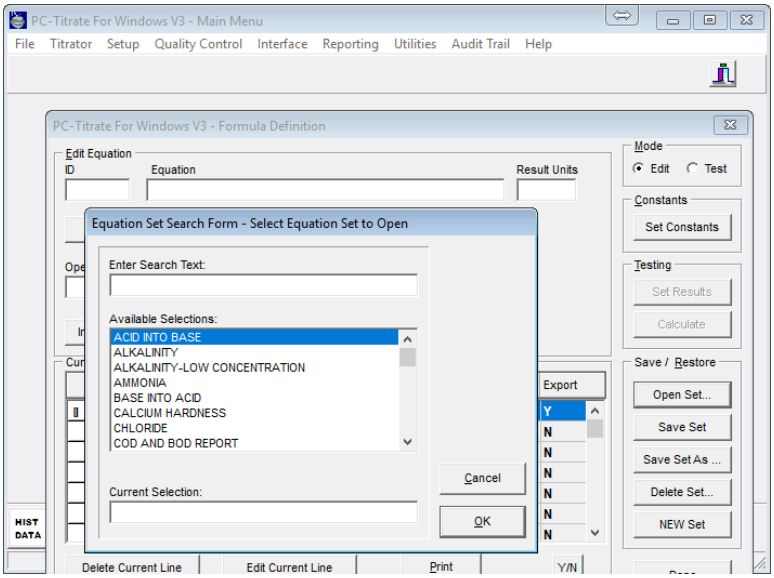
If modifying a Historical report, click on the **Preview Report** tab to see a preview of the changes. No preview is available for in-run reports unless you have a run is in progress.

To save changes, click **File, Save**. Saving As is not recommended as proper linking will not be in place.

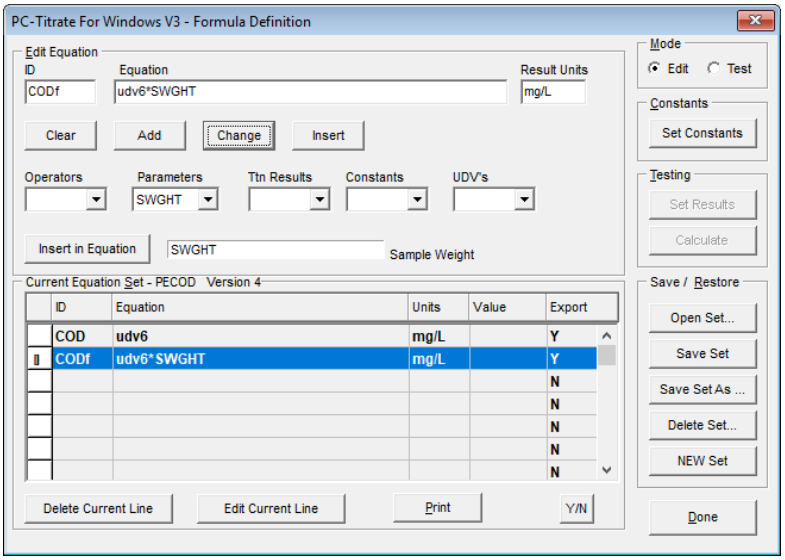
7.6 Adding a Dilution Factor to PeCOD Analysis

Samples can be diluted if the expected or known COD concentration is outside of the COD measurement range. The software can also be set to record the raw COD (CODr) value and calculate the final COD (CODf) value, based on the inputted dilution factor. Both CODr and CODf values can be included in the final report. To incorporate automated dilution factor COD calculations, follows the steps below:

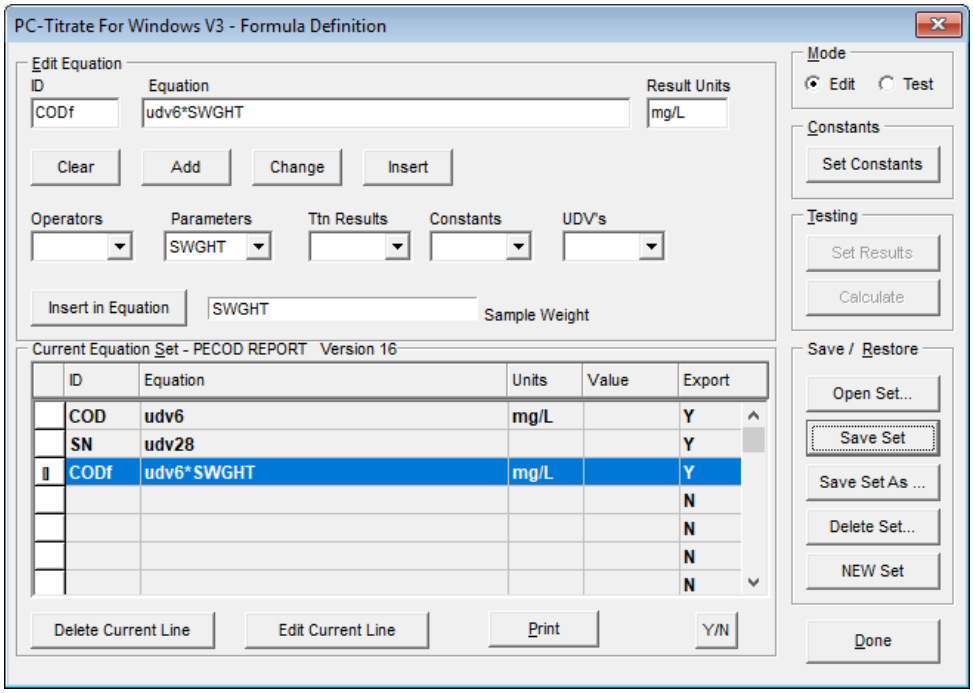
1. Go to “Setup > Formula Definition”.
2. On the right-hand side, click, “Open Set…”



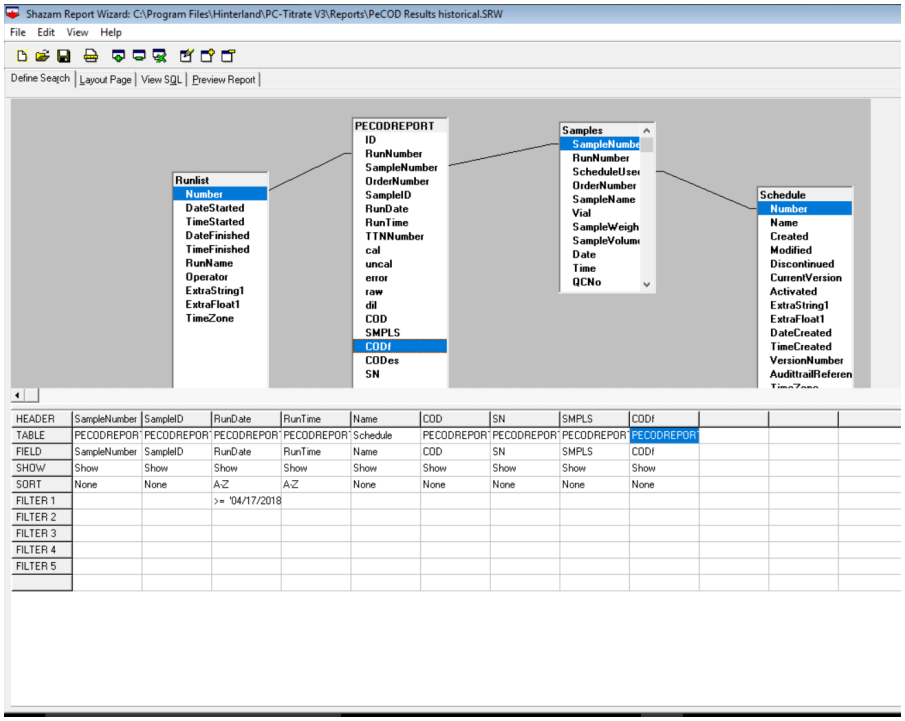
3. Scroll down and select “PECOD”.
4. There should be one row with ID “COD” and Equation “udv6”. At the top of the window, type in the following empty boxes: ID: “CODf”, Equation: “udv6*SWGHT”, Result Units: “mg/L”.
5. Click “Add” to add this row to the “Current Equation Set” below COD.
6. Click the “Y/N” button to change the Export Column to “Y”.
7. Click “Save Set”.



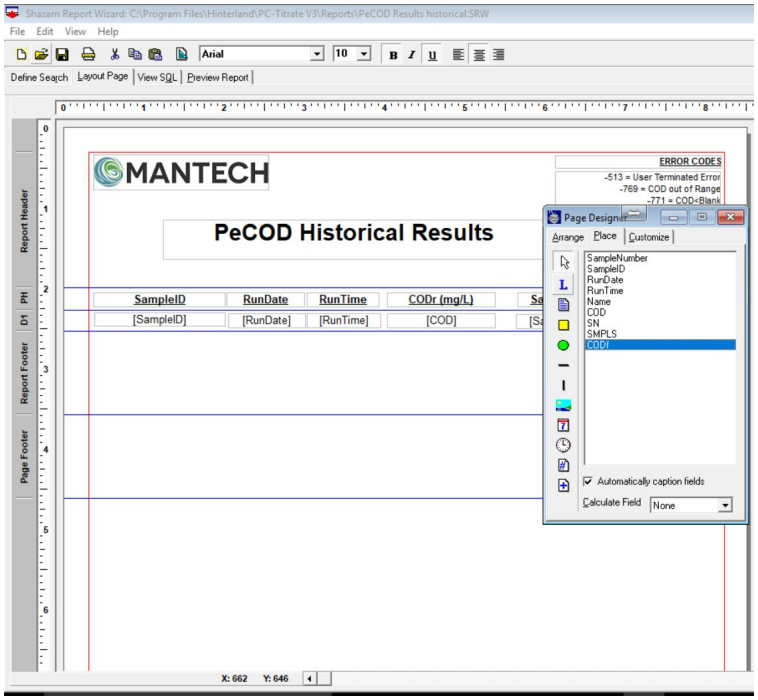
8. Next, Load the “PECOD REPORT” equation set.
9. Add the same CODf row to this equation set. Again, change the Export Column to “Y”.
10. Click **“**Save Set”.



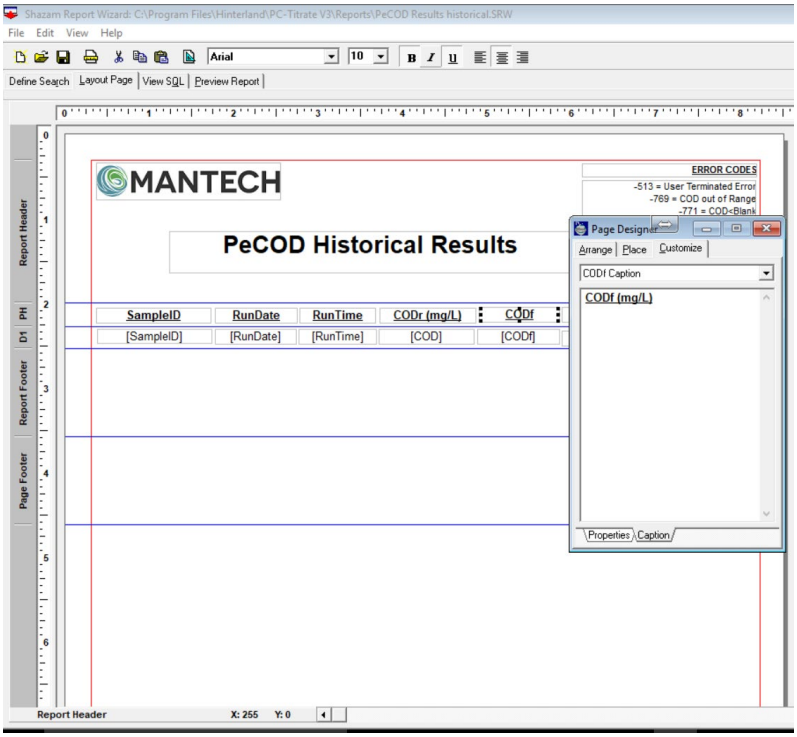
11. Click “Done” to close the Formula Definition window.
12. Next, go to “Reporting > Prepare and/or Print Shazam Reports…”
13. Click “File > Open Report > PeCOD Results Historical”.
14. Select the “Define Search” tab near the top of the window.
15. The middle of the window under PECOD REPORT, find and double click on “CODf” to add it to the report.



16. Next, click the “Layout Page” tab.

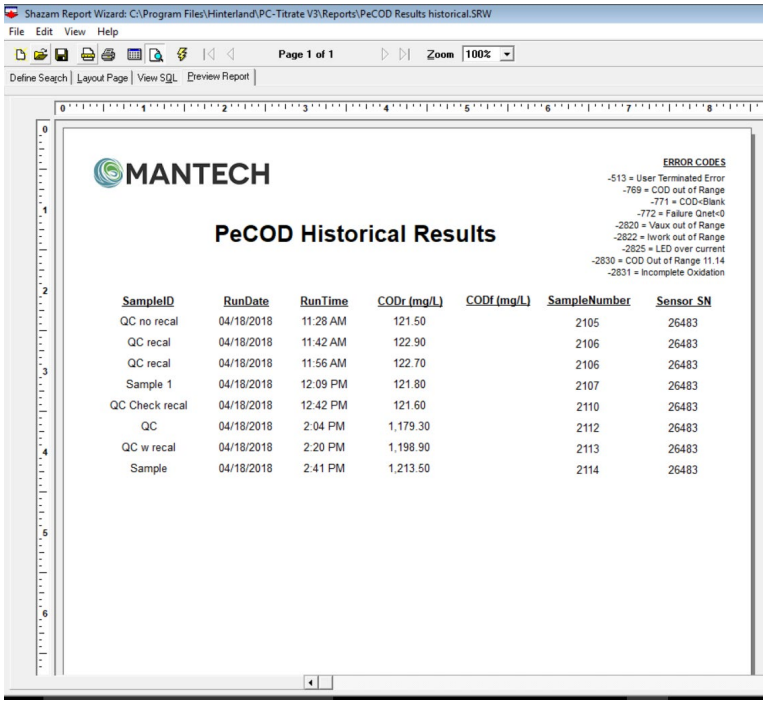


17. Right click on the report and select “Place Objects”.
18. Click and drag “CODf” onto the report page. Rearrange the report titles to fit all the columns at the top. Note that the boxes can’t be touching the blue lines. Use the font features at the top of the window to make formatting changes.
19. Right-click on the top box labeled CODf and click “Edit Caption”. In the bottom box of the next window, add “mg/L” to the caption.
20. Click the red “X” to close the window.



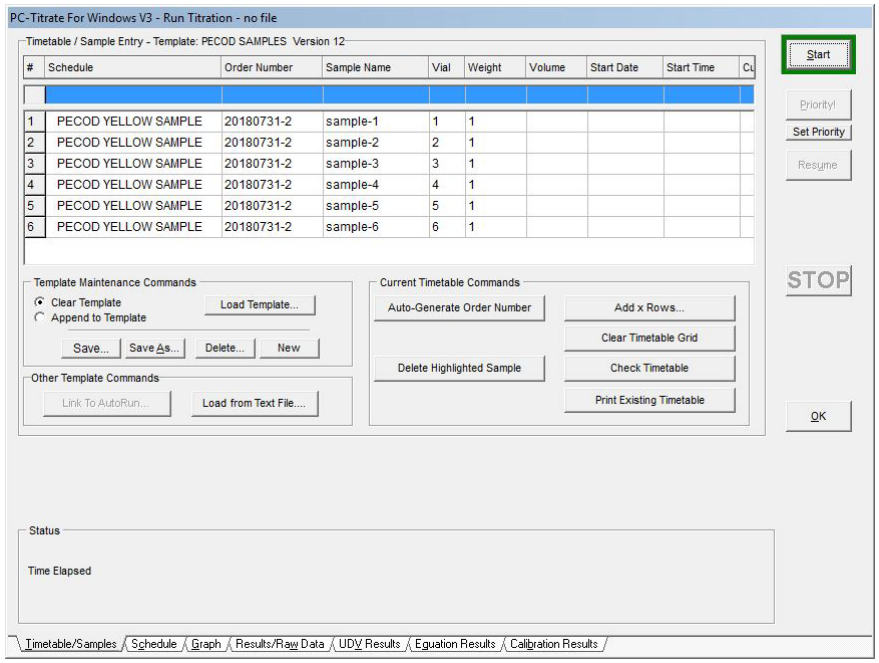
21. Right- click on the top box labeled COD and click “Edit Caption”. Rename COD to CODr to indicate raw COD (pre-dilution calculation). Click the red “X” to close the window.

22. Click the “Preview Report” tab to see the changes implemented into the report. There should now be the CODr (for the raw value) and CODf (the final value with dilution factor considered) column. Note that the CODf column will be empty until an analysis is completed after the changes to the equations sets. Close the report window and save the report when prompted.



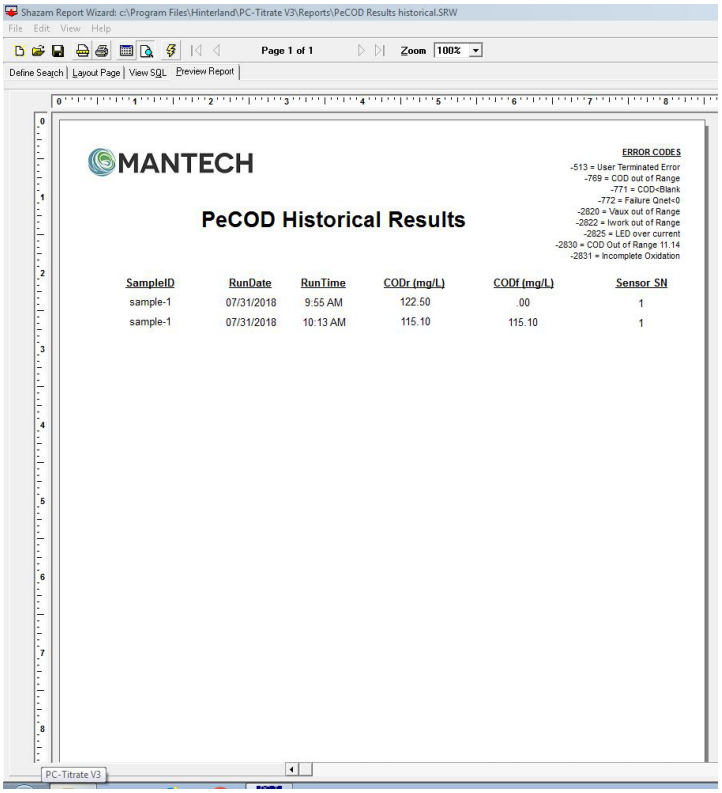
SampleID	RunDate	RunTime	CODr (mg/L)	CODf (mg/L)	SampleNumber	Sensor SN
QC no recal	04/18/2018	11:28 AM	121.50		2105	26483
QC recal	04/18/2018	11:42 AM	122.90		2106	26483
QC recal	04/18/2018	11:56 AM	122.70		2106	26483
Sample 1	04/18/2018	12:09 PM	121.80		2107	26483
QC Check recal	04/18/2018	12:42 PM	121.60		2110	26483
QC	04/18/2018	2:04 PM	1,179.30		2112	26483
QC w recal	04/18/2018	2:20 PM	1,198.90		2113	26483
Sample	04/18/2018	2:41 PM	1,213.50		2114	26483

23. The software will multiply the CODr value by the dilution factor, which must be written in the “Weight” column of the “Run Titration” window. For example, if the sample was 2x diluted, then a “2” should be written in the “Weight” coulumn. If the sample hasn’t been diluted, the “Weight” column should say “1”. If no number is placed in the “Weight” column, the CODf result will report as 0mg/L. The CODr value will still report the result on the PeCOD screen.



#	Schedule	Order Number	Sample Name	Vial	Weight	Volume	Start Date	Start Time	Cu
1	PECOD YELLOW SAMPLE	20180731-2	sample-1	1	1				
2	PECOD YELLOW SAMPLE	20180731-2	sample-2	2	1				
3	PECOD YELLOW SAMPLE	20180731-2	sample-3	3	1				
4	PECOD YELLOW SAMPLE	20180731-2	sample-4	4	1				
5	PECOD YELLOW SAMPLE	20180731-2	sample-5	5	1				
6	PECOD YELLOW SAMPLE	20180731-2	sample-6	6	1				

24. The report below shows that the first sample had a dilution factor of “0” and the second had a dilution factor of “1”.



25. Go to “File > Open Reports > PECOD REPORT”.
26. Repeat steps 14 -21 to apply the same changes to the PeCOD REPORT.

The CODf column has now been implemented into the software.

7.6. Appendix F – Troubleshooting Guide

The following tables give a list of possible problems that could arise. They have been divided into different categories of problems and include a variety of solutions with each issue.

Table 1: Standard/Sample Results Incorrect

Category	Potential Problems	Solutions
Chemical	Titrant off/contaminated	• Standardize titrant • Use fresh titrant
	Chemical interferences from leaky tips	• Raise reagent tips (all except for burets) out of solution • Move reagent bottle down below pump to reduce head pressure • Tighten fittings • Replace tubing/fittings
	Reagents contaminated	• Check expiry date • Make/use fresh solutions
	Incorrect/not enough ISA being added	• Use correct ISA • Check that ISA pump is plugged in/turned on and set to AUTO. • Make sure software is programmed to add enough ISA from correct digital output number.
	Sample carryover	• Use clean or new beakers • Check for loose fittings or air bubbles in rinse lines • Adjust tubing height at rinse station to ensure adequate rinsing of tips and probes • Check that rinse station is not clogged and that water is draining adequately • Increase rinse volume/time • Ensure that tips are not blocking drain hole • Check for sticky drain tubing – if stuck, cut off that portion and reattach
	Rinse water contaminated	• Check conductivity of water supply (should be <30µS)
Electrode	Electrode not conditioned	• Rinse out electrode, refill with fill solution, soak in pH 4 buffer or low standard for at least an hour
	Electrode old	• Replace electrode (depending on use and care, lasts 6 months - 1 year)
	Electrode broken/cracked	• Replace electrode
	Calibration invalid	• Clean, refill, and soak in pH 4 buffer or low standard before recalibrating
	Fill solution low	• Top up fill solution
	Fill solution incorrect	• Use correct fill solution
	Low flow rate	• Make sure fill hole is open • Rinse out electrode to clear out any salt crystals blocking junction
	Electrode junction not covered	• Lower electrode farther into solution

	Electrode not connected properly	• Ensure secure connection to TIS on correct port • Unscrew and reconnect avoiding cross-threading • Remove O-ring from cap of electrode • Replace cable
	Incorrect Grounding	• If there is an electrode in port 1, remove all red jumpers • If port 2, 3 or 4 electrodes are in a separate solution from the electrode in port 1, use grounding switches • If there is no electrode in port 1, use a jumper cable between port 1 and the port in use
	Electrode not stabilizing	• Increase stability settings in titration method or schedule • Rinse, refill and soak electrode in pH 4 buffer or low standard to recondition it • Replace electrode
Hardware	Stirrer not working	• Take out rod and clean and then push back in securely • Check that the paddle is not hitting against other tips, electrodes, or the sides of the beaker • Check that cable is connected to TIS securely • Replace stirrer
	Buret tip is out of solution	• Move tip below the liquid level
	Flow rate of reagent/sample pumps are off	• Check flow rates and enter the value into the Hardware Setup
	Sample/reagent pumps leaking	• Replace gaskets and lip seals in pumps and replace pump head securely • Tighten fittings
	Sample pump is erratic	• Ensure pump head is on securely • Replace belt
	Sample needle is not submerged	• Adjust height of sample needle • Fill tubes/beakers with more sample
	Buret Valve Sticking	• Clean out valve • Replace valve
	Drain is leaking	• Check that tubing is in drain valve completely • Replace drain valve
	Reagent pump not turning on	• Check that pump is turned on/plugged in • Check that pump is in auto mode (if applicable) • Check that power bar is turned on/plugged in • Check outlet • Check fuse • Check power cord
	Electrode board blown	• Use port 2 if port 1 blown, and port 4 if port 3 blown. Be sure to change the Titration Method and Calibration Template to reflect this change and adjust grounding if taking electrode off port 1.

Software	Incorrect sample weight entered in template	• Manually calculate the results using the correct weights, and remember to enter weights next time
	Incorrect flow rate of reagent pumps entered into Hardware Setup	• Check flow rate and enter into Hardware Setup
	Incorrect syringe size set up in Hardware Setup	• Set up correct syringe size in Hardware Setup
	Sample volume in titration method(s) does not match volume pumped into TitraSip in schedule.	• Change so that volumes match
	False endpoint being selected	• Increase filter • Increase smoothing settings
	Endpoint being missed	• Decrease filter • Decrease smoothing
	Error in equation	• Check equations for missing brackets, decimal places or incorrect terms
	Titration Settings not Ideal	• Change injection control settings • Change stability control settings
	Wrong calibration template selected in schedule	• Use correct calibration template
	Incorrect electrode port set up in Titration Method	• Setup Titration Method for correct port

Table 2: Calibration Invalid

Category	Potential Problems	Solutions
Electrode	Electrode not conditioned	• Rinse out electrode, refill with fill solution, soak in pH 4 buffer or low standard for at least an hour
	Electrode old	• Replace electrode (depending on use and care, lasts 6 months - 1 year)
	Electrode broken/cracked	• Replace electrode
	Fill solution low	• Top up fill solution
	Low flow rate	• Make sure fill hole is open • Rinse out electrode to clear out any salt crystals blocking junction
	Fill solution incorrect	• Use correct fill solution
	Electrode junction not covered	• Lower electrode farther into solution
	Electrode not connected properly	• Ensure secure connection to TIS • Unscrew and reconnect avoiding cross-threading • Remove O-ring from cap of electrode • Replace cable

	Incorrect Grounding	• If there is an electrode in port 1, remove all red jumpers • If port 2, 3 or 4 electrodes are in a separate solution from the electrode in port 1, use grounding switches • If there is no electrode in port 1, use a jumper cable between port 1 and the port in use
	Electrode not stabilizing	• Increase stability settings in Calibration Template • Rinse, refill and soak electrode in pH 4 buffer or low standard to recondition it
Chemical	Buffers/standards in wrong order	• Recalibrate with buffers in correct (ascending) order
	Buffers/standards contaminated	• Use new buffers
	Carryover from previous buffer/standard	• Check for loose fittings or air bubbles in rinse lines • Adjust tubing height at rinse station to ensure adequate rinsing of tips and probes • Ensure that the rinse station and TitraSip are not clogged and is draining adequately between buffers/standards • Increase rinse volume
	Rinse water contaminated	• Check water supply
Hardware	Stirrer not working	• Replace stirrer • Take out rod and push back in securely • Check that the paddle is not hitting against other tips or the sides of the beaker or tube • Check that cable is connected to TIS securely
	Electrode board blown	• Use port 2 if port 1 blown, and port 4 if port 3 blown. Be sure to change the Titration Method and Calibration Template to reflect this change and adjust grounding if taking electrode off port 1.
Software	Validation Settings too tight	• Change validation settings: Slope = -65 to -53, Intercept = +/- 100, Correlation = 0.995 for a pH calibration
	Incorrect electrode port set up in Calibration Template	• Setup template to look at correct port
	Wrong buffers set up in Calibration Template	• Setup correct standards in the Calibration Template

Table 3: Possible Titration Problems

Symptom	Problem	Solutions
False endpoint being selected	Filter set too low	• Increase filter setting
	Smoothing set too low	• Increase smoothing settings
	1st/largest endpoint is not the correct one	• Set up equation to use ve2 instead of ve1 as the endpoint, and check the box "Return 2 largest endpoints" in Titration Method
Endpoint being missed	Filter set too high	• Decrease filter
	Smoothing set too high	• Decrease smoothing
	Endpoint windows being used, electrode has drifted, and endpoint moved	• Stop using endpoint windows or adjust window
Injection sizes too large/too small	Injection sizes set too large/too small in titration method	• Change injection sizes
	If injections too large through endpoint, hold is too high	• Reduce hold
Titration taking too long	Injection sizes too small	• Increase maximum injection size
	Stability control settings set too high	• Reduce stability time out
Choppy/noisy curves	Electrode not stabilizing	• Change stability control settings • Recondition electrode • Recalibrate electrode • Replace electrode
	Electrode is not in solution	• Submerge electrode so that the junction is completely covered
	Electrode fill solution low	• Top up fill solution
	Low flow rate of electrode fill solution	• Make sure fill hole is open • Rinse out electrode to clear out any salt crystals blocking junction

	Bad electrode cable connection	• Unscrew from top of electrode and reconnect avoiding cross-threading • Remove O-ring from cap of electrode • Make sure connection is secure at TIS end of cable • Replace cable
	Incorrect Grounding	• If there is an electrode in port 1, remove all red jumpers • If port 2, 3 or 4 electrodes are in a separate solution from the electrode in port 1, use grounding switches • If there is no electrode in port 1, use a jumper cable between port 1 and the port(s) in use
	Stirrer not working	• Replace stirrer • Take out rod and push back in securely • Check that the paddle is not hitting against other tips or the sides of the beaker • Check that cable is connected to TIS
	Buret tip is not fully submerged	• Submerge buret tip below the liquid level

Table 4: Common Error Messages

Error Message	Potential Problem	Solutions
Cannot Perform Injection	No power to buret	• Check that buret is turned on/plugged in • Check that power bar is turned on/plugged in • Check power cord • Check outlet • Check fuse
	Buret has lost communication with TIS	• Check serial cable connection/reset power to buret
	Buret not set up in hardware setup	• Set up buret in Hardware Setup
	Buret port in titration method does not match the physical setup	• Change the buret port in titration method or physically change the port to match the titration method.
Buret/Meter Not Found on Port 1/2/3/4	No power to buret/meter	• Check that buret/meter is plugged in and turned on • Check that power bar is plugged in and turned on • Check power cord and outlet • Check fuse
	Serial cable not plugged in or has come loose	• Ensure there is a secure serial cable connection between meter and TIS

	Buret/meter not set up in hardware setup	• Set up buret in Hardware Setup
	Buret/meter port in titration method does not match the physical setup	• Change the buret/meter port in titration method or physically change the port to match the titration method.
Cannot connect to TIS	No power to TIS	• Check that TIS is plugged in and turned on • Check that power bar is plugged in and turned on • Check power cord and outlet • Check fuse
	Communication cable between TIS and computer not connected	• Plug in/tighten cable connection
	Communication cable physically connected to different com port than setup in Hardware Setup	• Connect cable to correct com port (com port 2)
	Com port numbers assigned incorrectly in Control Panel	• Change com port settings in Control Panel
Unable to open Com Port	No power to TIS	• Check that TIS is plugged in and turned on • Check that power bar is plugged in and turned on • Check power cord and outlet • Check fuse
	Communication cable between TIS and computer not connected	• Plug in/tighten cable connection
	Communication cable physically connected to different com port than setup in Hardware Setup	• Connect cable to correct com port (com port 2)
	Com port numbers assigned incorrectly in Control Panel	• Change com port settings in Control Panel
Com 1 error **(when schedule attempts to communicate with PeCOD)**	Software cannot connect to peCOD	• Ensure Com port drivers are installed (part of PeCOD Pro™ software package). • Ensure Com port driver is set to Com 6 in Device Manager and Hardware Setup. • Ensure USB cable is connected. • Unplug/re-connect USB cable.

Index out of date	Files that are being accessed have become corrupted	• Install backup files/backup database • Run Paradox Utility program
Table does not exist	Files that are being accessed have been corrupted or removed	• Install backup files/backup database • Run Paradox Utility program
Timetable contains errors*	Timetable has been setup incorrectly	• Make sure there are no empty cells under the Schedule, Order Number, Sample Name, and Vial columns. • Make sure you have not used the same sample name more than once
Autosampler Time Out Exceeded	No power to autosampler	• Check that autosampler is plugged in/turned on • Check that power bar is plugged in/turned on • Check that power cord/outlet • Check fuse
	Autosampler has lost communication with computer	• Tighten communication cable/Reset power to autosampler
	Com port setup in Hardware Setup is incorrect.	• Change com setting in Hardware Setup
Unknown Gilson Error	Sampler arm has felt resistance	• Move source of resistance and reset power to autosampler
Z motor position error	Sampler arm has felt resistance	• Move source of resistance and reset power to autosampler
Z-arm height exceeded	Sampler is being told to move outside the possible limits	• Check sampler move step for errors • Reload tray file
Z target less than minimum	Unknown	• Check sampler move step for errors • Reload tray file
Unable to open driver GSIOC32.dll	Problem with autosampler communication	• Check sampler com port setting and baud rate • Reserve com port for sampler • Using incompatible Windows version/computer issue

Output file error	Trying to print to non-existing printer	• Set up printer/take off automatic printing
The software has performed an illegal operation	Computer/network issue	• Reboot/remove network connection
	Database too large	• Archive database
Invalid field name	Report does not exist/field in report does not exist/linking become corrupt	• Create report/field, Re-link report/field.
An unspecified error has occurred	General error message	• Shut down the software and restart it
Fatal Error: Aborting Timetable	General error message	• Shut down the software and restart it
Database Error	General error message	• Shut down the software and restart it
"String to Number" or "Number to String" internal conversion error	Unknown	• Computer Regional settings must be set to US English • Re-link step that error occurs on • Run Paradox Utility program
Invalid floating point operation	Unknown	• Re-boot computer • Re-link step that error occurs on • Run Paradox Utility program
Range Check Error	Unknown	• Re-boot computer • Re-link step that error occurs on • Run Paradox Utility program

Z target less than minimum Z - Is the Vial Number Missing or Incorrect?	Unknown	• Shut down the software and restart it
Inject? OK	Unknown	• Click OK, and your run will continue
Z target less than minimum Z - Is the Vial Number Missing or Incorrect?	A sampler move step has attempted to move beyond the set range of motion	• Shut down the software and restart it
Inject?	A communication error has occurred between the interface and the buret	• Click OK, and your run will continue
Exception on event date conversion YYYY/MM/DD **Exception on run date conversion YYYY/MM/DD**	PeCOD system-related error message. The computer's date format is likely incorrect	• Check that the Regional Settings of the computer are set to US English. Dates must be set up MM/DD/YYYY.

***There is a "Check Timetable" button that can be selected after setting up a timetable that will highlight any errors.**

**** Always shut down the software after getting any sort of error, otherwise other general error messages will populate. Always write down exactly what the error message says, or take a screen shot. If known, take note of exactly what was done when the error occurred. If in the middle of the run, take note of what step the error occurred on.**

Table 5: PeCOD Troubleshooting

Problem	Solutions
Calibrations or QC Checks Failing	1. Examine the calibration values on the latest calibration and QC Check and verify if they're within the COD range-specific passing criteria listed 4.3. PeCOD Calibration and QC Checks If the M and/or C values are outside the passing criteria and the sensor has been used for approximately one month, or

	greater than 150 samples, the sensor may be expired. Install a new sensor and perform a NEW SENSOR ROUTINE. 2. If the M and C values are outside the passing criteria, but the sensor is less than one month old and has analyzed less than 150 samples: a. Visually inspect the sensor for discolouration or white spots. If either are present, install a new sensor and run the NEW SENSOR ROUTINE. b. remake the pre-mixed blank and pre-mixed calibrant solutions. Improper mixing and contamination of peCOD reagents can lead to failed calibrations and QC Checks. 3. Ensure that the reagent bottles have sufficient solution for the peCOD tubing to be submerged, and that no air is within the tubing. 4. Ensure there is no clogging or partial clogging within the peCOD. Verify that each prime of Port A or Port B is between 1.8 and 2.2 mL. If the prime volume is less than 1.8mL or air remains within the tubing after priming each port 3 times, proceed to 7.7.1. Removing Blockages within the PeCOD Analyzer.
Samples Results are far from expected values	1. Ensure that the peCOD is in the correct working COD range. See 7.7.3 Changing COD Ranges for instructions on changing COD range. 2. Ensure that the sample and electrolyte volumes are mixed at the appropriate ratio for the working COD range. 3. Ensure the sample contains no particulates >50µm. 4. Ensure that the sample pH is between 4 and 10. 5. Ensure that the chloride concentration within the sample is within the limits outlined in 7.7.2. Allowable COD/Chloride Concentration Combinations for PeCOD Analysis.

Table 6: PeCOD Error Codes

PeCOD Error	PCT Error	Name	Description of Problem	Suggested Actions
2.1	-513	Terminated by User	The exit button on the peCOD display was selected	• Error indicating the user has terminated the current analysis. No further action required. • If the error is generated when using MANTECH software, the time delay set for sample analysis is too short which is causing the analysis to be interrupted.

				Contact MANTECH or your local MANTECH distributor for assistance in increasing the time delay.
PeCOD Error	**PCT Error**	**Name**	**Description of Problem**	**Suggested Actions**
2.2		Sensor Uncalibrated	Error indicating the sensor is not calibrated	• Run new sensor routine or run calibration.
3.1	-769	COD out of Range	Sample concentration is too high.	• Dilute original sample with COD free water and re-mix with electrolyte (remember to multiply this dilution factor to obtain the final COD value). • Alternatively, switch to a different COD range. You will need the appropriate electrolyte and calibrant for the new range. Remix the calibrant and blank solution and calibrate the peCOD. Mix sample in the new working range ratio.
3.2	-770	Reference < Blank	Reference (calibrant) solution charge obtained is less than the zero (blank) solution	• Check that the calibrant solution is correctly mixed with electrolyte and recalibrate
3.3	-771	COD Less Than Blank	COD result is less than the blank solution	• Ensure that sample is mixed with electrolyte in proper ratio and lines are primed. • Check electrical contacts between the connection pins on analyzer board. Very gently clean if necessary using isopropanol and a lint free cloth. • If the above do not rectify the problem, the parameters/settings in Labterm may need to be adjusted. Contact a MANTECH representative for assistance.
3.4	-772	Failure Q_{net} < Zero	Resultant charge from sample or calibrant is too low (i.e. not enough signal detected)	• Ensure that sample is mixed with electrolyte in proper ratio and lines are primed. • Check electrical contacts between the connection pins on analyzer board. Very gently clean if necessary using isopropanol and a lint free cloth. • If the above do not rectify the problem, the sensor or electrode block may need to be replaced.
7.1		Pump Failure	Pump Error	• Prime lines, and check that there is strong flow from the waste tubing. • If this does not rectify the problem, please contact a MANTECH representative for pump maintenance.

PeCOD Error	PCT Error	Name	Description of Problem	• Suggested Actions
7.2		Pump did not Initialize	Pump Error	• Prime lines, and check that there is strong flow from the waste tubing. • If this does not rectify the problem, please contact a MANTECH representative for pump maintenance.
8.4		Solution not Presented	User did not press enter upon system prompt	• Only applies for running a calibration or sample analysis using the PeCOD touch screen menu. • Restart the calibration and ensure to press enter when prompted to present solution.
11.2		Analyzer Lid Open	Lid is open, or analyzer lid is not securely latched.	• Make sure analyzer lid is closed and correctly secured via the front latch. • If this does not rectify the problem, take out the sensor and electrode block to ensure the o-rigs are in place.
11.4	-2820	V_{aux} out of Range	Auxiliary voltage is over range	• The current and voltage applied may be too high • Remove the sensor and electrode block. Flush out the electrode block several times with DI water • Check electrical contacts between the connection pins on analyzer board. Very gently clean if necessary using isopropanol and a lint free cloth. • Prime the lines to make sure there are no bubbles present, then recalibrate. • If the above do not rectify the problem, the electrode block may need to be replaced.
11.6	-2822	I_{work} out of Range	Current is over-range	• The current and voltage applied may be too high • Remove the sensor and electrode block. Flush out the electrode block several times with DI water • Check electrical contacts between the connection pins on analyzer board. Very gently clean if necessary using isopropanol and a lint free cloth. • Prime the lines to make sure there are no bubbles present, then recalibrate. • If the above do not rectify the problem, the electrode block may need to be replaced.

PeCOD Error	PCT Error	Name	Description of Problem	Suggested Actions
11.9	-2825	LED Over Current	Occurs during normalization step of calibration. The LED output was too high to obtain the desired baseline.	• Common Error for new sensors • If using a new sensor, run the "New Sensor Routine" to reset the serial number and calibrate the PeCOD • Run 3-4 calibrations. If the problem persists, please contact a MANTECH representative.
11.10		FIFO Overrun	Too much processor activity	• Erase logs and run sample again.
11.14	-2830	COD Out of Range	Sensor calibration did not achieve reproducibility target.	• Make sure there are no bubbles present in the lines. • Prime lines and recalibrate
11.15	-2831	Incomplete Oxidation	The sample concentration may be too high (sample oxidation was not complete in the required amount of time).	• Dilute original sample with COD free water and re-mix with electrolyte (remember to multiply this dilution factor to obtain the final COD value). • Alternatively, switch to a different COD range. You will need the appropriate electrolyte and calibrant for the new range. Remix the calibrant and blank solution and calibrate the PeCOD. Mix sample in the new working range ratio.
14.1		Burn-in Failed	System failed to stabilize.	• Prime lines and recalibrate • If problem persists, the sensor may need to be replaced.

7.7 Appendix G – Additional PeCOD Resources

7.7.1. Removing Blockages within the PeCOD Analyzer

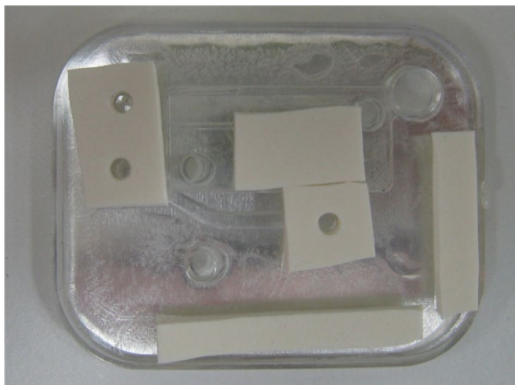
Samples with suspended solids can sometimes cause blockages in the PeCOD COD analyzer. The PeCOD COD method only oxidizes dissolved organics; therefore, it is suggested to filter samples before analysis.

If there is no solution flowing from the waste port when priming **Port A**, there is likely an internal blockage within the fluidics path. Follow the instructions below to back flush the lines and clear the electrode block.

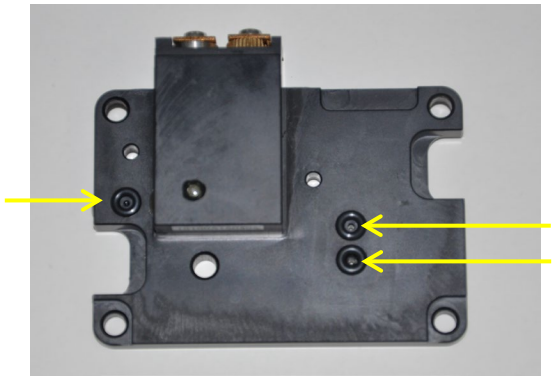
NOTE: If priming **Port B** does also not result in solution flowing from the waste port and/or you cannot hear the pump turning on, the blockage may be deeper into the fluidics which may require service from a MANTECH representative.

General Checks

1. Open the PeCOD lid and remove the sensor.
2. Look at the back of the sensor – all 3 holes should be completely clear and not partially obscured by the white rubber seals. (Example of a good sensor shown below).



3. Ensure that the electrode block is sitting flat in the analyzer block. If not, remove the 4 thumbscrews and make sure the 3 o-rings are seated at each port. When installing the electrode block back into the analyzer, ensure that each screw is tightened evenly.

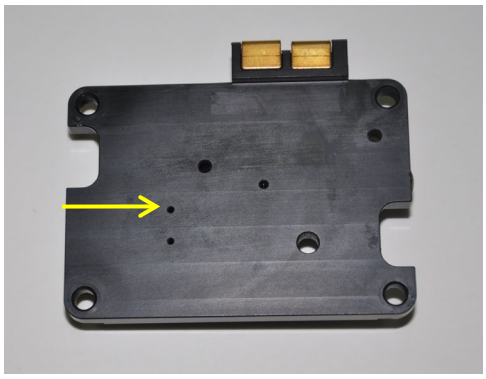


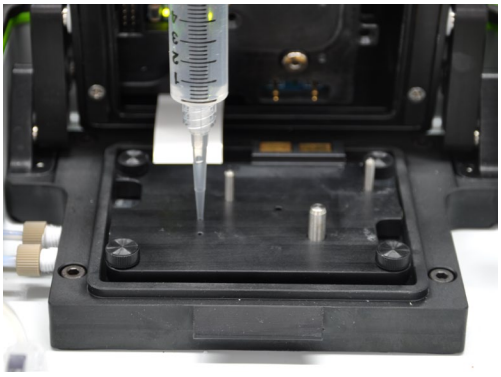
Back-flushing Port A

You will require a syringe fitted with a modified 200uL pipette tip to perform this operation. These have been provided with the PeCOD system, part number PQA-85014.

1. Fill the syringe with DI water, and attach the narrowest pipette tip.
2. Open the PeCOD lid and remove the sensor. Place Port A tubing into a waste container as shown below.

3. Insert the syringe into the hole shown below. The tip should fit snuggly into the hole so that no air gets in.





4. Go into MENU/OPERATION/PRIME LINES/PRIME PORT A. Press ENTER, and at the same time gently push on the plunger of the syringe. You must prime Port A to open the valves of the internal fluidics path. Observe the flow of water out of the Port A tube. Stop pushing the plunger when you hear the pump stop.

5. Repeat step 4 a few times to ensure the flow out of Port A is strong.

6. If there is no solution coming out the waste port while priming **Port B**, the same process can be repeated by selecting prime Port B instead of Port A. Use the same hole for the syringe tip, as shown in the picture above.

NOTE: This operation back-flushes fluid lines between the sensor inlet and Port A, which is the most likely place for particles to be lodged. This back-flushing procedure usually clears any blockages. A flow of water out of Port A during this operation indicates this part of the fluid path is clear. Verify this by placing the Port A line into a beaker of water and attempting to prime as usual. If this does not clear the blockage, continue to the next section.

Flushing the Electrode Block

1. With a lint-free tissue wipe the top of the block to remove any liquid. If there are white salt deposits on the electrode block, gently wipe them off with lint-free tissue that has been dampened with DI water.

2. Remove the electrode block by unscrewing the 4 thumbscrews.

3. Observe the 3 fluid ports on the underside of the electrode block.

4. Fill a syringe with DI water and attach the larger pipette tip. Insert the tip into each hole to flush out the port.

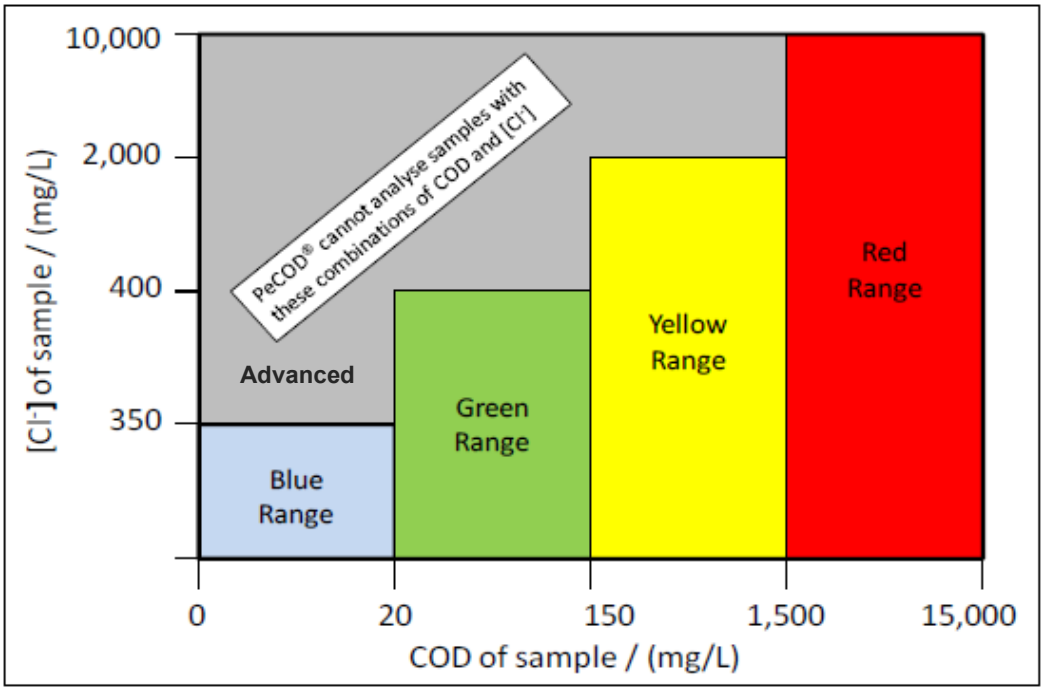
5. Ensure there is a strong flow in both directions. Note that two of the ports are “straight through” and one is an “Internal Channel”.

If these procedures do not result in a steady flow of solution from the waste port during priming operations, please contact a MANTECH representative for assistance.

7.7.2. Allowable COD/Chloride Concentration Combinations for PeCOD Analysis

High chloride can interfere with both the dichromate and PeCOD techniques. While the dichromate method makes use of the hazardous compound mercuric sulfate to bind chloride, the PeCOD employs a special “doping” effect in the sensor to reduce its sensitivity to the ion. There are still limitations however, therefore to reduce its effect on PeCOD analysis, ensure that after dilution with electrolyte the chloride concentration will be <200mg/L. This means that the allowable chloride concentration of the original sample varies depending on the COD range (outlined in the chart below). If necessary, do a pre-dilution of sample with deionized water before mixing with electrolyte.

Note that the central sensor element of a chloride-tolerant sensor appears black in color. A white sensor element indicates that the sensor has lost some/all chloride tolerance, even if the sensor is passing calibrations. To test whether a sensor has lost its chloride tolerance, one may wish to spike a known COD standard with a chloride solution to check recovery.



Recommended COD/[Cl-] Combinations for peCOD Analysis. The coloured regions indicate the allowable combinations of COD & [Cl-] for the different measurement ranges. The grey region indicates those combinations of COD & [Cl-] that are not suitable for analysis by peCOD without prior pre-dilution

7.7.3 Changing COD Ranges

The peCOD method has four COD ranges: Advanced Blue (<25mg/L), Green (<150mg/L), Yellow (<1,500mg/L), and Red (<15,000mg/L). To switch COD ranges, follow the steps below:

1. On the peCOD touchscreen, press Enter until the Main Menu is displayed. The Main Menu shows the Date and Time and firmware version.

2. Once on the Main Menu screen, select the following:
    a. Menu
    b. Setup
    c. Analysis Method
    d. COD Range
    e. Use the arrows to select the desired COD range
    f. Enter

3. Once the desired range is set in the peCOD, ensure that the correct PC-Titrate schedules are used for the corresponding COD range.

7.7.4 PeCOD solution mixing ratios

Select the appropriate electrolyte for your COD range. Blank, Calibrant and Sample solutions must be mixed with the same colour electrolyte, and in specified ratios:

Advanced Blue	<25 mg/L	Advanced Blue…3 parts with 1 part blue electrolyte
Green	<150 mg/L	Green……..1 part with 1 part green electrolyte
Yellow	<1,500 mg/L	Yellow……..1 part with 9 parts yellow electrolyte
Red	< 15,000 mg/L	Red……..1 part with 49 parts red electrolyte

<u>How to Prepare the QC Check, Blank, and Calibrant Slurries</u>

Prepare your sample before preparing your solutions. Note: Solutions will only need to be prepared once until used up.

Select the appropriate electrolyte and calibrant for your COD range:

• Prepare your Blank Slurry by mixing Distilled/ D.I Water with Blank Slurry

• Prepare your Calibrant Slurry by mixing the Calibrant Slurry with Distilled/D.I. Water

• Prepare your QC Check Slurry by mixing the QC Check Slurry with Distilled/D.I. Water

• Ensure that your samples do NOT contain particulates >50um, are within the specified pH (4-10) and chloride limits, and adjust as necessary

Reference Table 7 for solution and sample preparation. Note that if the system has automated electrolyte addition, the electrolyte doesn't need to be pipette into the sample tube. If the system has a TitraSip configuration, the sample does not need to be measured and can be free poured into the sample tube.

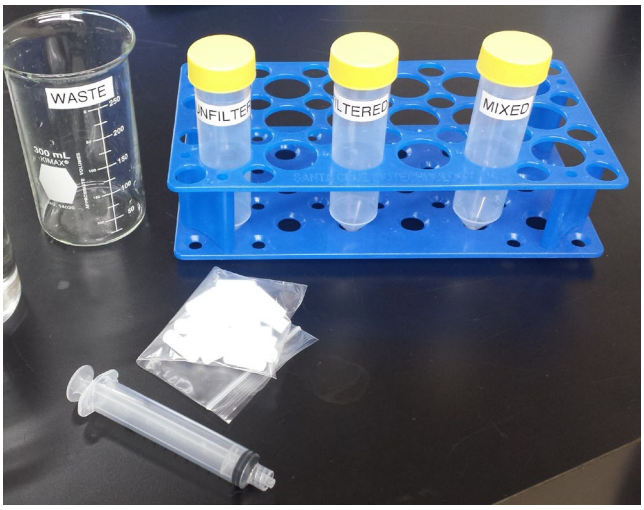
Table 7: PeCOD solution and sample preparation

ADVANCED BLUE RANGE		
Blank Solution (500mL bottle)	**Calibrant Solution (1L bottle)**	**Sample**
300mL DI Water 100mL Blue Electrolyte	750mL Original Blue Calibrant 250mL Blue Electrolyte	15mL Sample 5mL Blue Electrolyte
GREEN RANGE		
Blank Solution (500mL)	**Calibrant Solution (1L)**	**Sample**
250mL DI Water 250mL Green Electrolyte	500mL Original Green Calibrant 500mL Green Electrolyte	10mL Sample 10mL Green Electrolyte
YELLOW RANGE		
Blank Solution (500mL)	**Calibrant Solution (1L)**	**Sample**
50mL DI Water 450mL Yellow Electrolyte	100mL Original Yellow Calibrant 900mL Yellow Electrolyte	2mL Sample 18mL Yellow Electrolyte
RED RANGE		
Blank Solution (500mL)	**Calibrant Solution (1L)**	**Sample**
10mL DI Water 490mL Red Electrolyte	20mL Original Red Calibrant 980mL Red Electrolyte	0.5mL Sample 24.5mL Red Electrolyte

7.7.5 PeCOD Filtering Guide

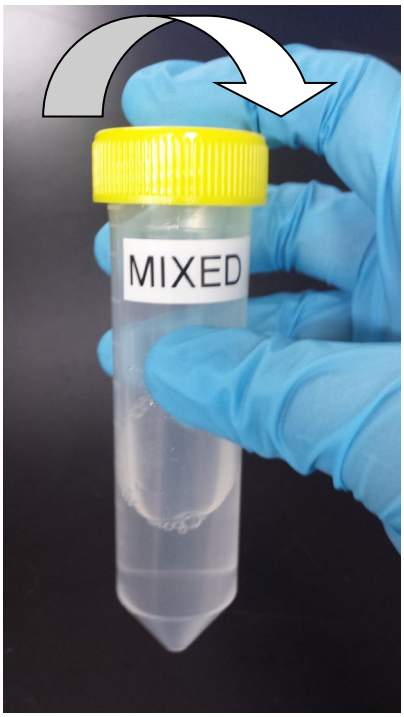
Samples must be filtered prior to peCOD analysis to ensure that no particulates greater than 50 micron (um) are primed into the peCOD. Particulates larger than 50um can cause clogging, which can lead to damage of the internal fluidics of the machine. To prevent clogging and damage, follow the steps below:

1. Gather the following supplies: 10mL syringes, 35um PE syringe filters (or similar filter that doesn't contribute COD to the samples), sample tubes and lids, and the unfiltered samples.



2. Fill the syringe with the unfiltered sample. **Attach the filter** and ensure it is fastened securely. Push the sample through into a new tube labeled Filtered. If the automated system has a TitraSip configuration, the sample can be filtered directly into the sample tube on the sampler rack, as the correct volume will be pumped to the TitraSip cell by the dosing pump.

3. If the automated system does not have a TitraSip, the correct volume of sample must be pipetted from the aliquot of filtered sample. Use Table 7: PeCOD solution and sample preparation to pipette the correct amount of sample, for the working COD range, into a new sample tube, to be place onto the sampler rack (labeled Mixed in the photo below).
    a. If the system does not have automated electrolyte addtion, add the correct volume of electrolyte for the COD working range to the tube. Screw on the sample tube lid and invert several times to mix the sample.
    b. Place the well-mixed sample tube onto the sampler rack for automated analysis.



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