10. Water Analysis in OLI Studio: A Tour

Reconciling a Brine from an Oil Field

The Application

This application involves reconciliation of a water sample from an oil well. Reconciliation is done for both electroneutrality and pH.

In this application we will take brine from an oil well that is producing water along with the oil. We will not consider the oil phase in this example.

It is quite common when reviewing laboratory analysis of water samples for the positive ions in solution (cations) and the negatively charged ions (anions) not to balance each other. This may be due to the precision limits of the various experimental procedures used to measure the ions and/or due to the fact that some ions may not have been analyzed. In reality, these solutions must have a neutral charge. **OLI Studio will reconcile the charges to make a solution that is neutral.**

The pH of the solution is frequently measured. However, since the analysis is experimental and subject to errors, the pH that is calculated by the Water Analysis tool may be different from what is measured experimentally. OLI Studio can reconcile this difference.

Finally, the reconciled sample can be converted into a molecular representation which can be used in other simulators. We will use OLI Studio to perform a simple calculation on our reconciled sample.

The power of the OLI Studio becomes apparent as we consider different reconciling options and pH considerations.

Tour Conventions

In this tour, we will use the following conventions:

Type Face	User Action
Bold and Italic	The user is required to enter this information
Bold and Underlined	The user is directed to look for this feature in the program windows
Click	Left-mouse button
Right-Click	Right-mouse button

The tour Starts here!

We have been given the produced water sample from an oil well in Thailand. The sample is listed below:

Table 10-1 Thailand Brine Sample data

Cations	***Concentration (mg/L)***	***Anions***	***Concentration (mg/L)***
Ba^{+2}	0.07	Cl^{-1}	39137
Ca^{+2}	3700	HCO_3^{-1}	561
Fe^{+2}	2.89	HS^{-1}	0.09
K^{+1}	402	SO_4^{-2}	2200
Mg^{+2}	262.8		
NH_4^{+1}	104	pH	6.1
Na^{+1}	20400		

Start the OLI Studio program by ***double-clicking*** the OLI Studio icon on the desktop or by using the Start menu.

The main window for the OLI Studio will display after the splash screen. The main window is similar to other OLI Studio products. There is a **Tree-view** or **Navigator** displayed on the left-hand side of the window. This shows all the objects currently in the document. Currently the display shows no objects. The bottom-left panel is the **Actions** or the **Explorer** view and shows the icons of the objects.

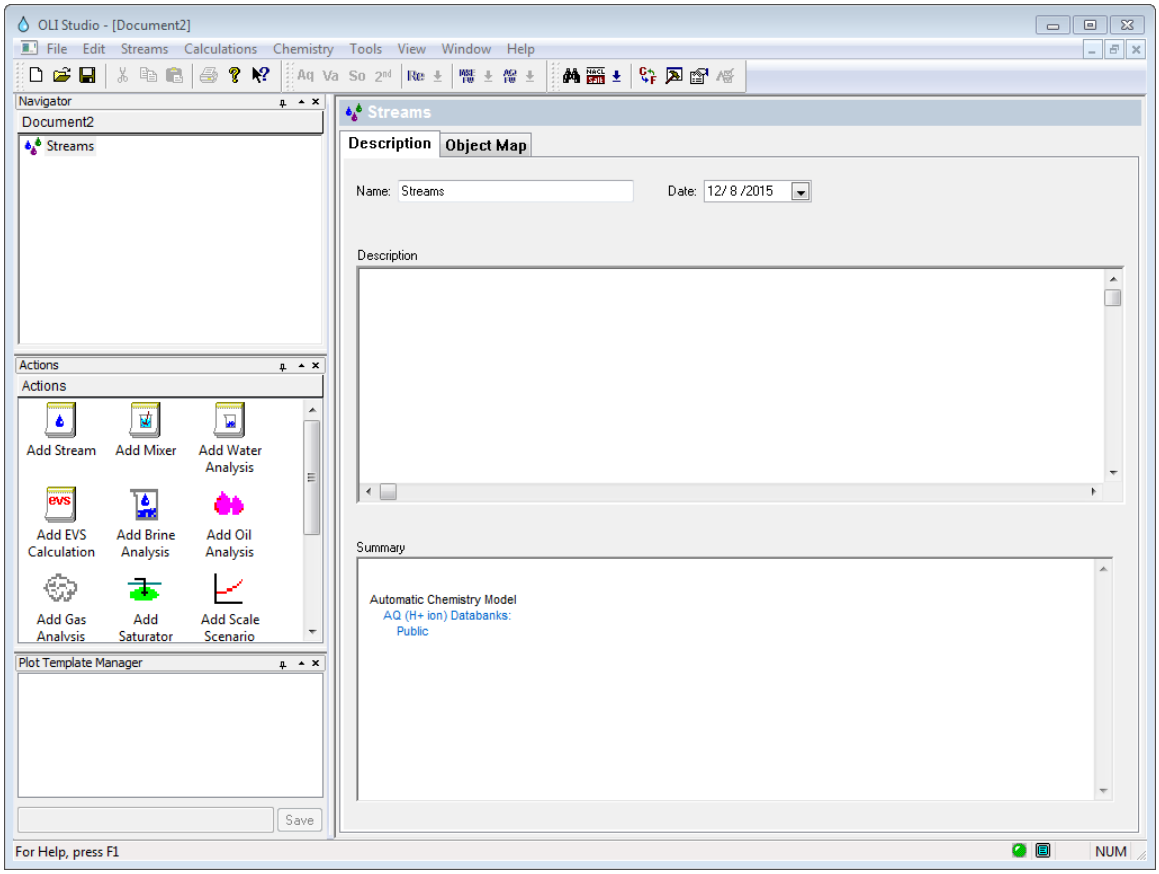


Figure 10-1 the OLI/LabAnalyzer main window.

To set up this tour, we need to change some settings. Please locate and ***click*** on the ***Tools*** menu in the menu bar.

This will display a drop-down menu. We will not dwell on each of the items in this tour. Please select **Names Manager** by ***Clicking*** on the item.

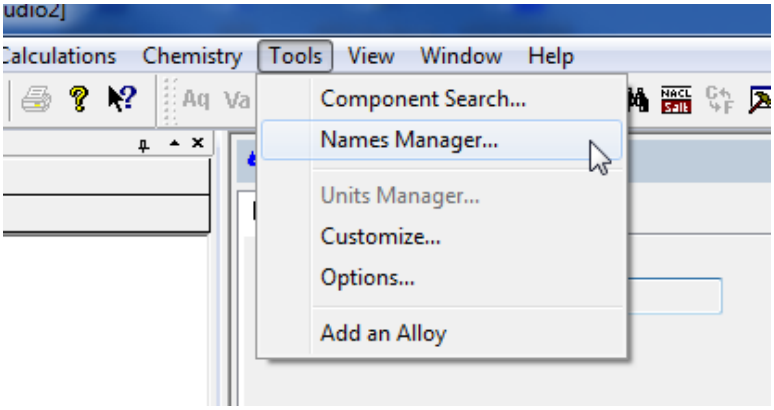


Figure 10-2 The Tools menu items.

There are several methods of displaying component names. For the moment we wish to use the formula names for our ions. ***Click*** the **Formula** radio button. ***Click*** the **OK** button when done.

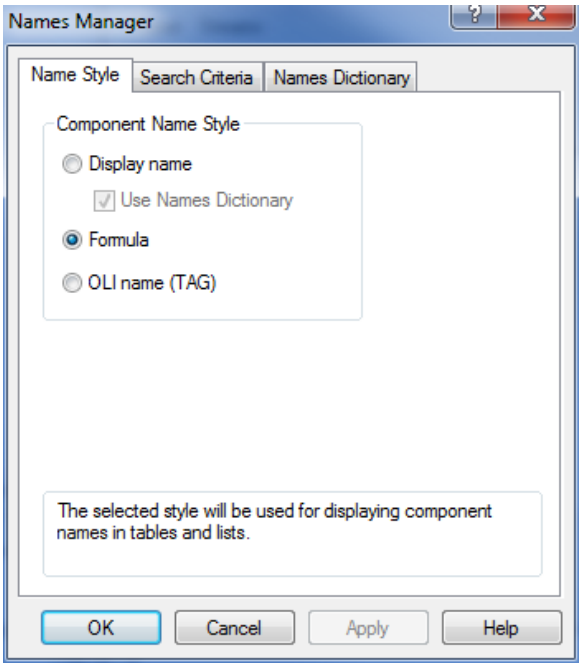


Figure 10-3 The Names Manager

When you return to the main window, locate the **Add Water Analysis** icon in the explorer view and ***double-click*** on the icon.

A "Water Analysis" object will be added to the Tree View. The **Explorer** view will now shows three new icons. You should now be on the **Analysis** tab, if not, please click it.

For this tour, we want you to rename the default analysis to the name ***Thailand.***

Right-click the new object in the tree-view and select **Rename.** Enter the name ***Thailand.***

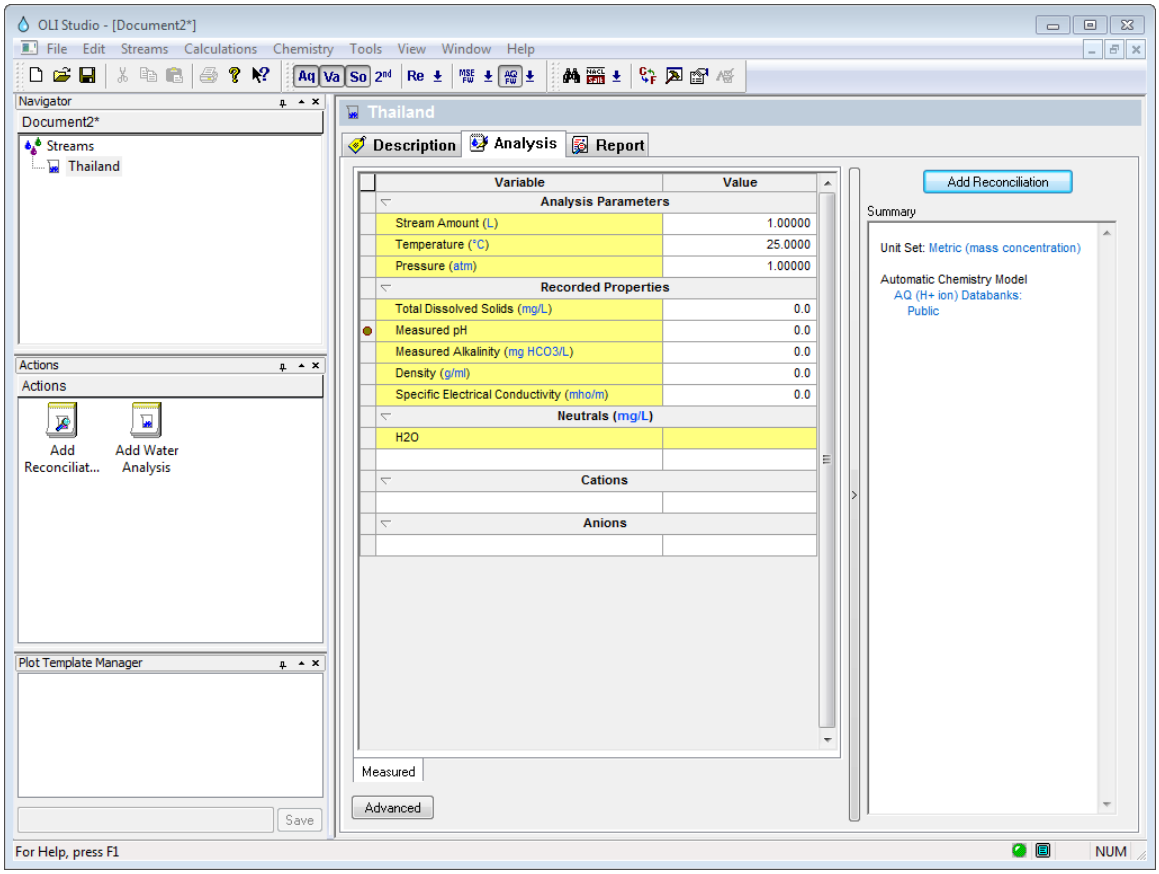


Figure 10-4 The Water Analysis Definition.

This window has several parts. The main part is the input grid in the center of the window. Here the user will enter the species concentrations as well as reportable items such as density. The field is scrollable and is divided into several sections:

Analysis Parameters

This section has the total stream amount, the temperature and pressure of the sample. The default values are 1 liter, 25 ^{o}C and 1 Atmosphere.

Recorded Properties

These are values reported from the lab. The pH of the solution, density, total dissolved solids and electrical conductivity may be entered.

Inflows

These are the molecular (neutral) species in solution. Water is entered by default but the user may not alter this value. Other neutrals such as dissolved gases (e.g., methane) may be entered in this section.

Cations

These are the positively charged species in solution.

Anions

These are the negatively charged species in solution.

Enter the cations listed in the table. The grid will scroll down to accept more entries.

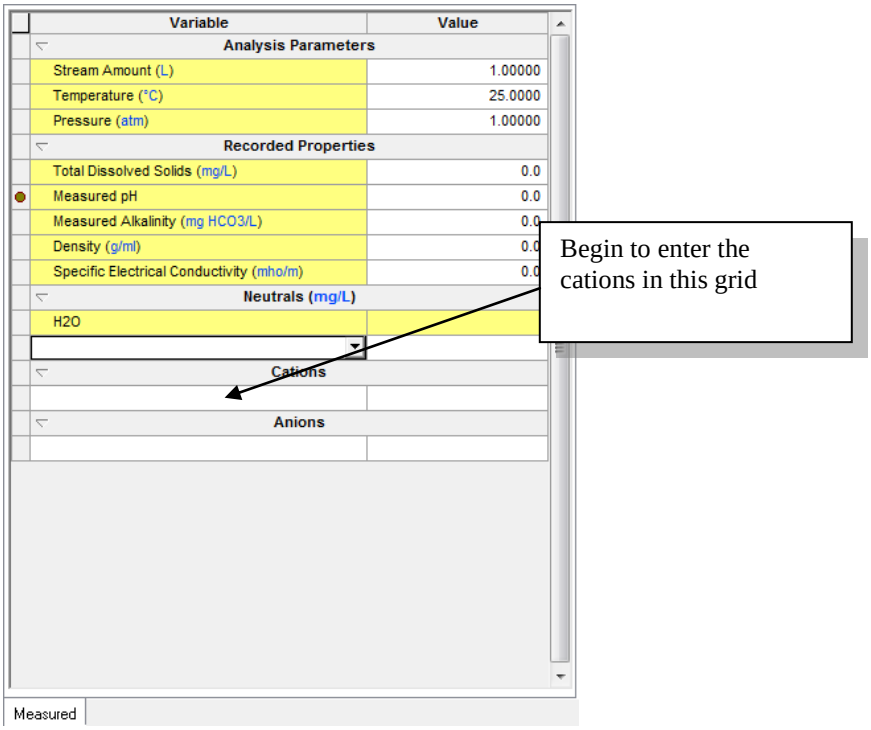
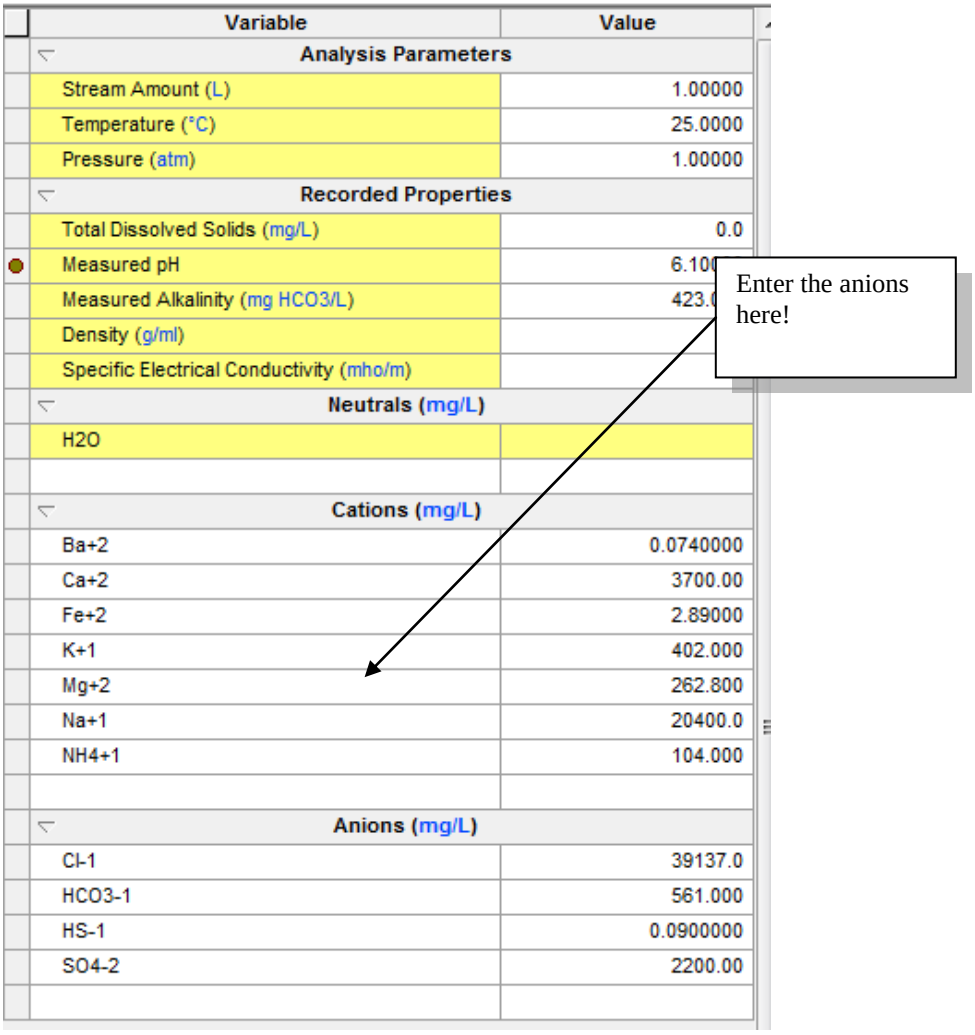


Figure 10-5 Entering the cations

Scroll down the grid and enter the anions:



Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.10
Measured Alkalinity (mg HCO3/L)	423.
Density (g/ml)	
Specific Electrical Conductivity (mho/m)	
Neutrals (mg/L)	
H2O	
Cations (mg/L)	
Ba+2	0.0740000
Ca+2	3700.00
Fe+2	2.89000
K+1	402.000
Mg+2	262.800
Na+1	20400.0
NH4+1	104.000
Anions (mg/L)	
Cl-1	39137.0
HCO3-1	561.000
HS-1	0.0900000
SO4-2	2200.00

Figure 10-6 Entering the anions

We are now ready to perform some reconciliation calculations for this sample.

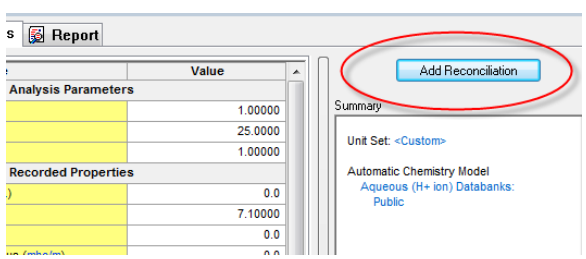


Figure 10-7 Finished data entry

Click on the **<u>Add Reconciliation</u>** Button.

This will display more tabs for entering data about the reconciliation. A new object will appear under the **<u>Thailand</u>** object in the tree view. This is an indication that the new object, in this case a reconciliation, is related to the parent object.

There are several items on this display. The entered analysis is displayed in the input grid. It is important to note that this is a copy of what you originally input. The values may be changed without altering the values in the parent analysis.

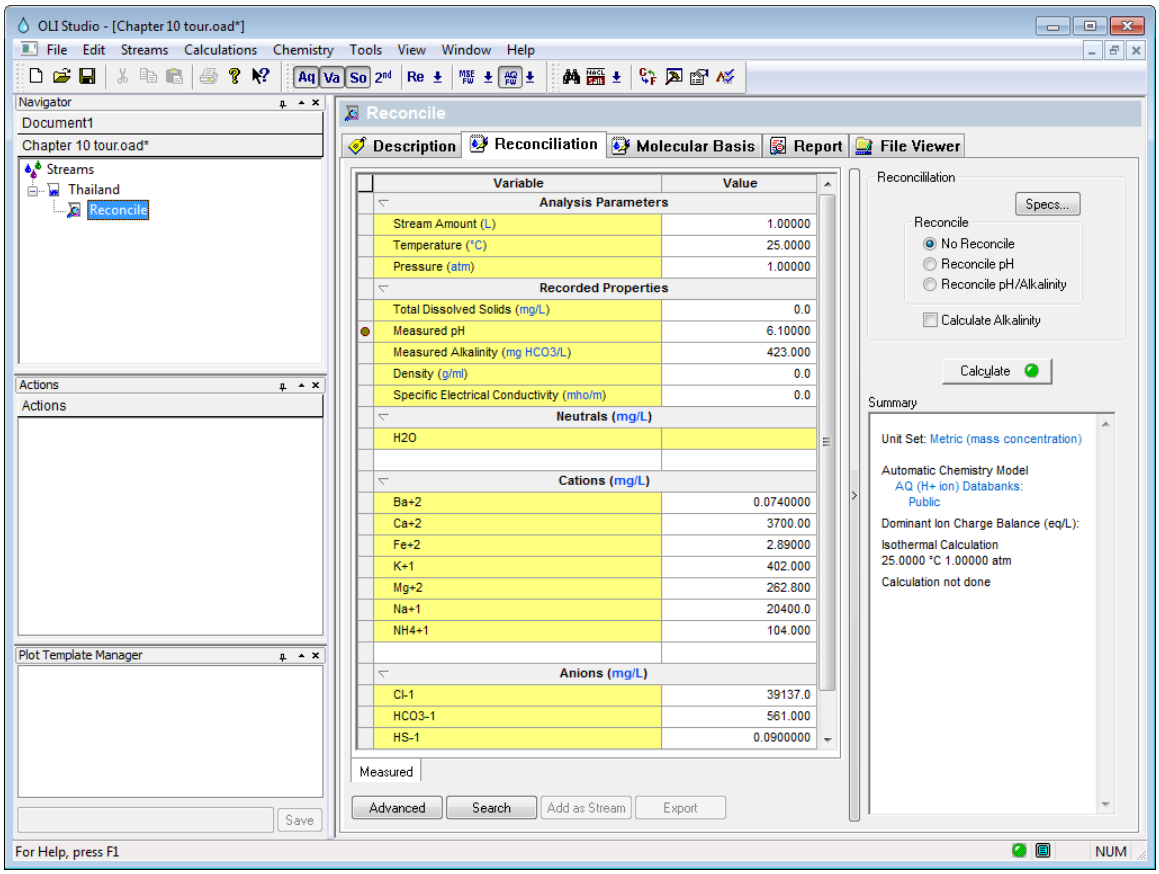


Figure 10-8 Starting the reconciliation.

In addition to the input grid, there is a **Reconciliation** box and a **Summary** box.

Reconciliation
This box sets up both the electroneutrality reconciliation and the pH reconciliation. The user may allow the program to pick the species to adjust for reconciliation or they may manually choose the adjustment.

The pH of the solution may be adjusted (automatically by adding either hydrochloric acid or sodium hydroxide) or the user may adjust these acids and bases.

The pH and alkalinity can also be calculated from this box or if the ***Calculate Alkalinity*** check box is selected then just the alkalinity is reported.

Summary
This box will display a quick list of what was performed in this section.
Please *click* on the **Specs…** button. We will now review the options for electroneutrality.

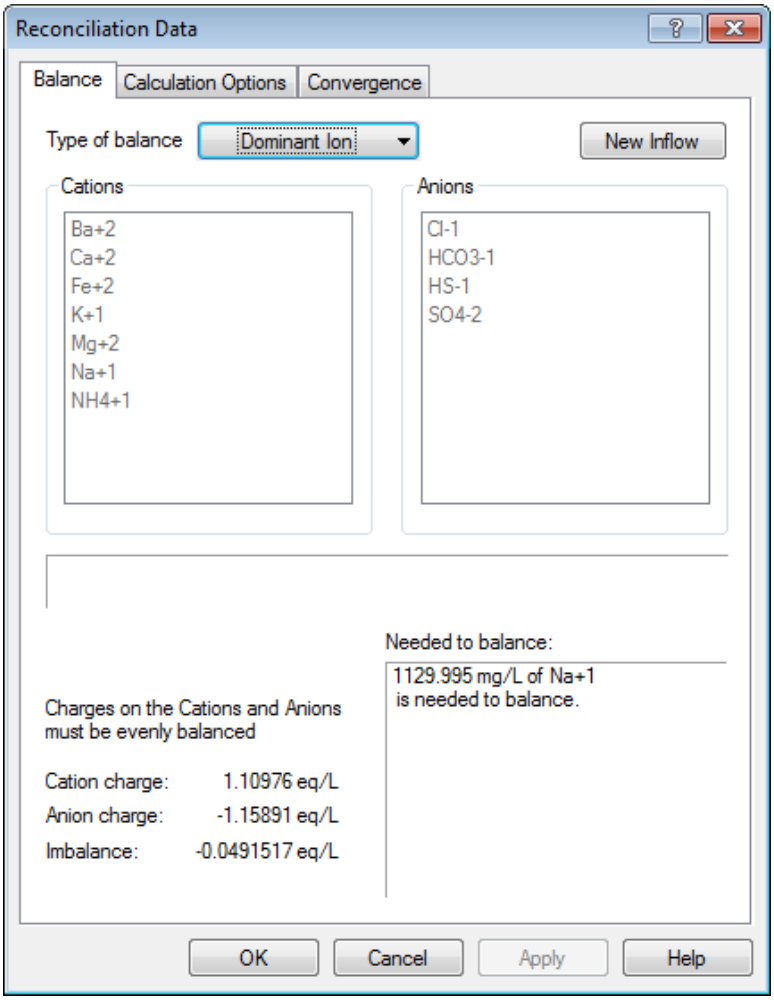


Figure 10-9 choosing electroneutrality

The default option for reconciling electroneutrality is the **Dominant Ion** method. This method determines the amount of imbalance in charge then uses the counter ion with the largest concentration on an equivalent basis. This sample currently has too much negative charge (approximately 0.049 equivalents). The largest counter charge will be added. In this case the value is 1139.995 mg/L of Na^{+1}.

There are other options that may be used:

To see all options for balancing charge ***Click*** the **Type of balance** button. The options are:

Dominant Ion

This is the default method. The largest counter ion is used to adjust the electroneutrality, as was noted.

Prorate Ion

In our example, there is too much positive charge. The Prorate Ion method, if employed, would keep the relative amounts of all the negatively charged species the same and add a percentage multiplier to all such species until the electroneutrality was achieved.

Na/Cl

This method chooses either sodium ion or chloride ion as the adjusting species (depending on imbalance) regardless of the largest species concentration.

Make-up Ion

This option allows for a single ion species to be adjusted. In this example, there is too much positive charge. If the Magnesium ion was chosen, then it would be reduced in concentration to make the sample electrically neutral.

User Choice

The user may pick the cation/anion pair to use for adjusting. Unlike the Make-up ion method, this method always adds material since both a cation and an anion are provided.

For this tour, we will use the default method of **Dominant Ion**.

Click the **OK** button to continue.

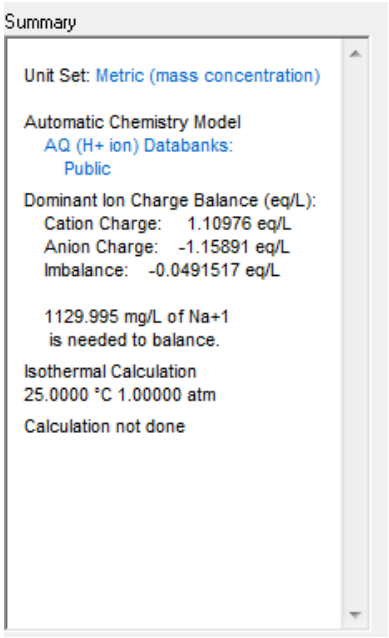


Figure 10-10 the summary box

The summary box will update to show our selection.

We now want to reconcile for pH. We know that the measured pH is 6.1. We want to ensure that the solution pH is 6.1 when we are done. This will involve adding either an acid or a base to adjust the pH.

We need to add the pH value to two locations in the grid. The first is the target pH and this is required for the calculation. The second location is the reported pH. The reported pH may differ from the target pH. The user may want to see the effects on the solution at some other condition than the reported pH, hence the need for two locations.

In the **Reconcile pH** box *Click* on the **Reconcile pH** radio buton**.** The titrants HCl and NaOH are the default titrants and we will use them in this tour.

Enter a pH value of ***6.1*** in the **Recorded Properties** **pH - Aqueous** section.

Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.10000
Measured Alkalinity (mg HCO3/L)	423.000
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Calculation Parameters	
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Neutrals (mg/L)	
H2O	
Cations (mg/L)	
Ba+2	0.0740000
Ca+2	3700.00
Fe+2	2.89000
K+1	402.000
Mg+2	262.800
Na+1	20400.0
NH4+1	104.000
Anions (mg/L)	

Figure 10-11 Entering pH information

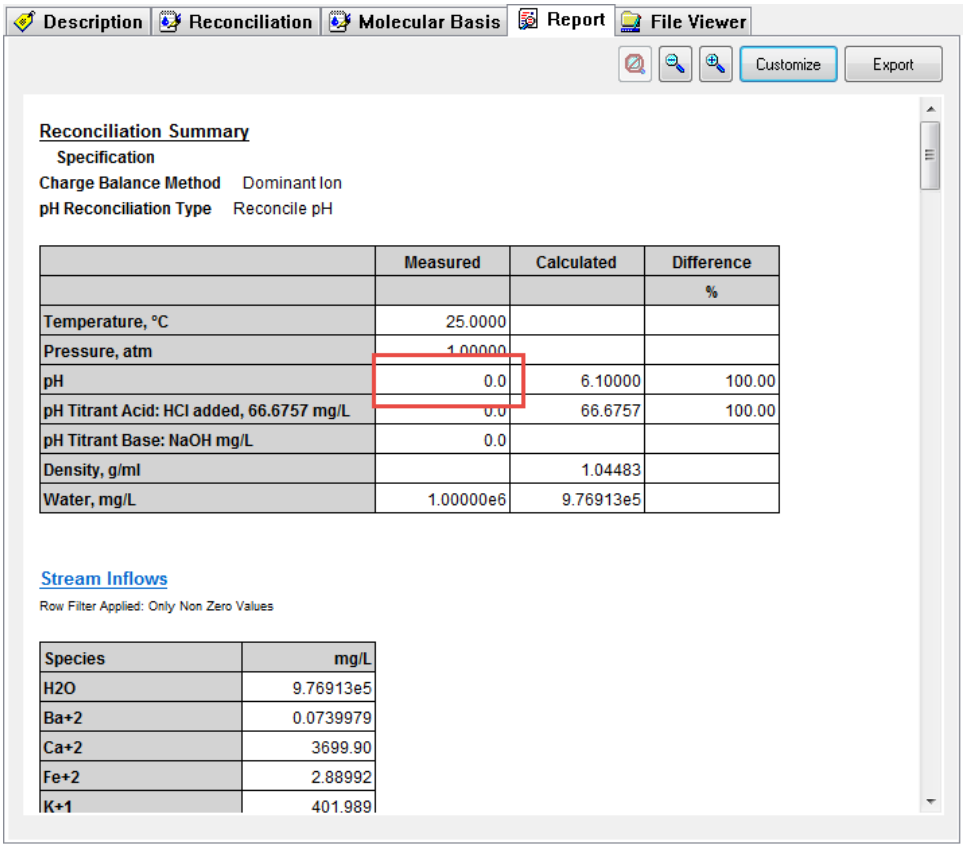
Click on the **Calculate** button to start the calculation.

When the calculation has finished, scroll down the **Summary** box to see that NaOH was added. Also, click on the **Calculated** tab to see the results of the calculation.

Click on the **Report** tab.

Notice that the Calculated pH is now 6.1. You can scroll down to see additional information for the sample

You may want to highlight the report area with your mouse in order to refresh the page. Even though the report is calculated, sometimes it is not visible immediately.



Description | Reconciliation | Molecular Basis | Report | File Viewer

Customize | Export

Reconciliation Summary

Specification

Charge Balance Method Dominant Ion

pH Reconciliation Type Reconcile pH

	Measured	Calculated	Difference
			%
Temperature, °C	25.0000		
Pressure, atm	1.00000		
pH	0.0	6.10000	100.00
pH Titrant Acid: HCl added, 66.6757 mg/L	0.0	66.6757	100.00
pH Titrant Base: NaOH mg/L	0.0		
Density, g/ml		1.04483	
Water, mg/L	1.00000e6	9.76913e5	

Stream Inflows

Row Filter Applied: Only Non Zero Values

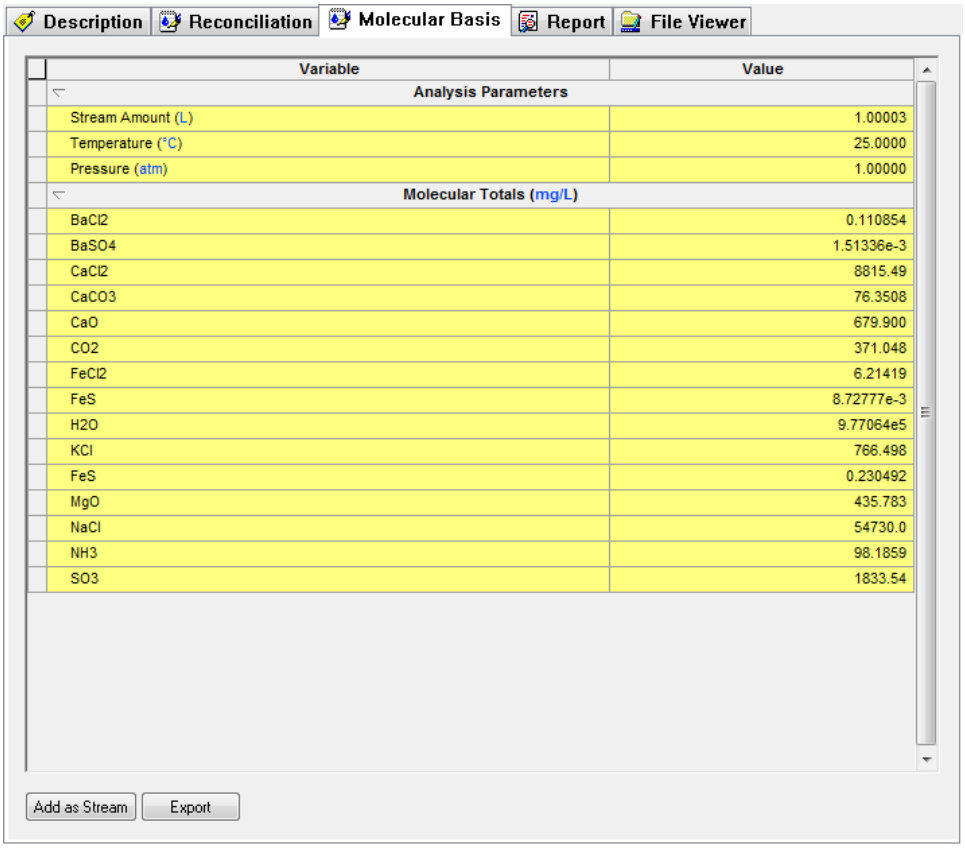
Species	mg/L
H2O	9.76913e5
Ba+2	0.0739979
Ca+2	3699.90
Fe+2	2.88992
K+1	401.989

Figure 10-12 The Report tab[39]

Click on the **Molecular Basis** tab.

This will display the sample in terms of molecular (neutral species). You can scroll down to see additional information.

[39] In Version 9.2.7 there is a bug in the report. The measured pH is the value you entered but it is not displayed in the report. This will be fixed in later versions.



Description | Reconciliation | Molecular Basis | Report | File Viewer

Variable	Value
Analysis Parameters	
Stream Amount (L)	1.00003
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Molecular Totals (mg/L)	
BaCl2	0.110854
BaSO4	1.51336e-3
CaCl2	8815.49
CaCO3	76.3508
CaO	679.900
CO2	371.048
FeCl2	6.21419
FeS	8.72777e-3
H2O	9.77064e5
KCl	766.498
FeS	0.230492
MgO	435.783
NaCl	54730.0
NH3	98.1859
SO3	1833.54

Add as Stream | Export

Figure 10-13 The molecular view.

Calculating Alkalinity

Let us now determine the alkalinity of this pH reconciled sample. On the **Reconciliation Tab** locate the ***Calculate Alkalinity*** check box.

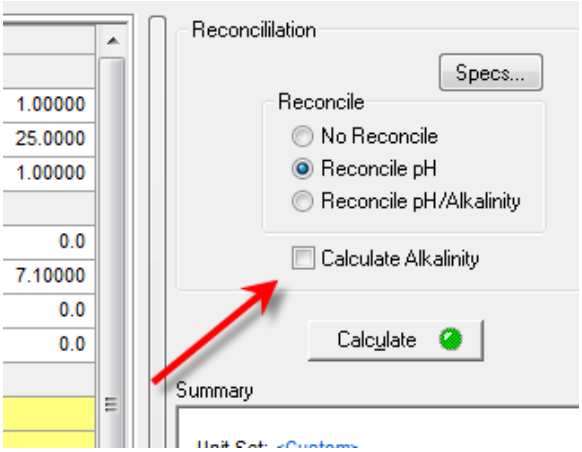


Figure 10-14 Calculate Alkalinity

Check the box

The input grid updates with a new set of parameters in the **Calc Parameters** section.

Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.10000
Measured Alkalinity (mg HCO3/L)	425.000
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Calculation Parameters	
Alkalinity pH Titrant	H2SO4
Alkalinity End Point pH	4.50000
pH Acid Titrant	HCL
pH Base Titrant	NAOH
Neutrals (mg/L)	

Figure 10-15 Added the Alkalinity titrant H2SO4

The OLI Analyzer will perform a pH titration for total Alkalinity. This means the sample will be titrated down to a pH of 4.5 and the amount of acid used is converted into Alkalinity. The box is a drop-down box and several other titrants are available:

Calculation Parameters	
Alkalinity pH Titrant	H2SO4
Alkalinity End Point pH	H2SO4
pH Acid Titrant	HCL
pH Base Titrant	HNO3
	NAOH

Figure 10-16 Additional Alkalinity Titrants

The Alkalinity Titrant is defaulted to H2SO4 and it is recommended that you use this value.

It is important to note that although a real equilibrium calculation is being performed, no species (such as the added H2SO4) is being added to the stream.

Click the Calculate button.

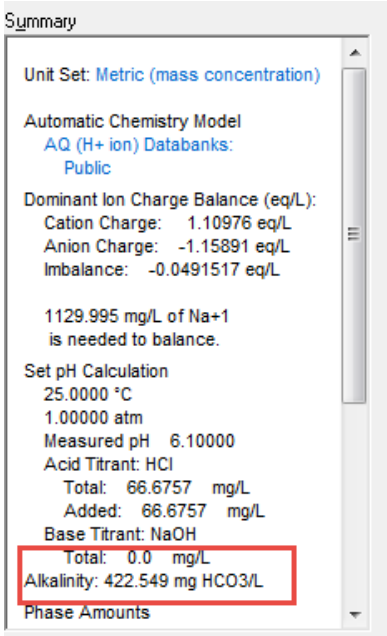


Figure 10-17 Calculated Alkalinity

From the summary box we can see that the solution's calculated alkalinity is approximately 623 mg/L as HCO3.

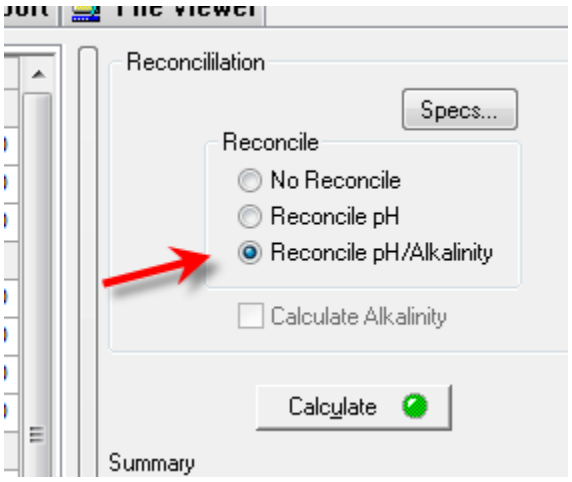


Figure 10-18 reconciling both pH and alkalinity

Recorded Properties	
Total Dissolved Solids (mg/L)	0.0
Measured pH	6.10000
Measured Alkalinity (mg HCO3/L)	425.000
Density (g/ml)	0.0
Specific Electrical Conductivity (mho/m)	0.0
Calculation Parameters	
Alkalinity Titrant	CO2
Alkalinity pH Titrant	H2SO4
Alkalinity End Point pH	4.50000
pH Acid Titrant	HCL
pH Base Titrant	NAOH

Figure 10-19 User entered values note that the original pH of 6.1 is still used

Summary

Unit Set: Metric (mass concentration)

Automatic Chemistry Model
AQ (H+ ion) Databanks:
Public

Dominant Ion Charge Balance (eq/L):
Cation Charge: 1.10976 eq/L
Anion Charge: -1.15891 eq/L
Imbalance: -0.0491517 eq/L

1129.995 mg/L of Na+1
is needed to balance.

Alkalinity Calculation
Calculated Alkalinity: 425.000 mg HCO3/L
Titration End Pt: 4.50000
Alkalinity Titrant: CO2
Added: 0.957544 mg/L
Alkalinity pH Titrant: H2SO4
pH Reconciliation:
Measured pH: 6.10000
pH Titrants:
Acid: HCl

Figure 10-20 The red box shows the alkalinity values

Creating a stream from the sample

We now need to convert this sample to a molecular stream. ***Click*** the **Add as Stream** button.

The program will allocate the ion concentrations into molecules. The combination of these species is usually not unique, but however allocated; the elemental material balances will be preserved.

You have the option of separating phases during this step. Each phase can be removed from the created stream as well as saved as a new stream. This step, in effect, becomes a phase splitter.

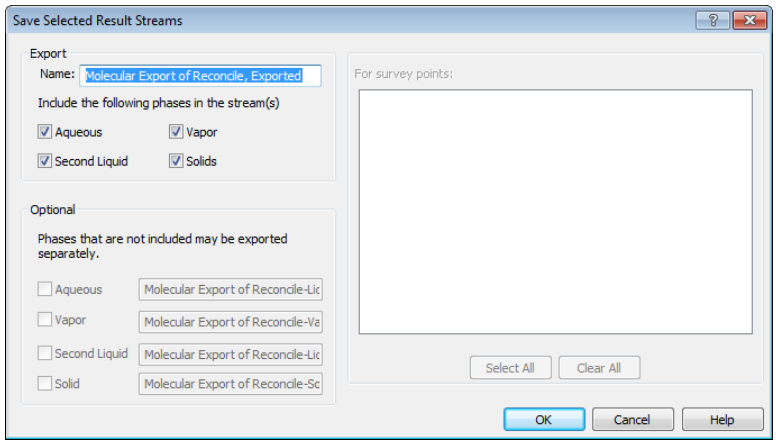


Figure 10-21 Save As Stream dialog, default options selected

Click the ***OK*** button to save all the phases as a new stream.

The tree-view will be updated to display a new stream.

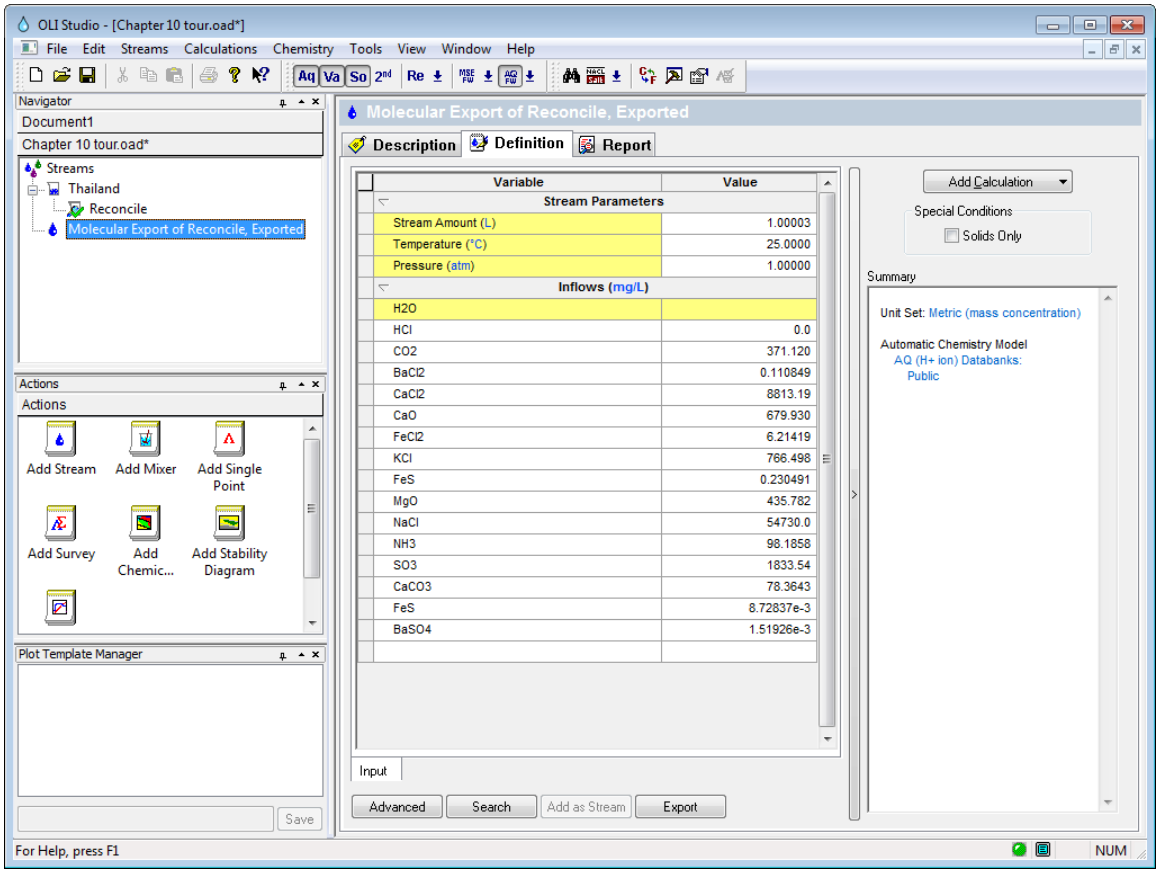


Figure 10-22 A new stream object is displayed.