APPLICATION NOTE 026

How to Use the MCCTC Configuration of the PID EFFI to Perform Pulse Chemisorption Experiments

The MCCTC (Micro Catalyst Characterization and Testing Center) configuration of the PID EFFI is designed to equip the EFFI with the ability to both characterize and perform activity testing of catalysts in-situ. By paring the MCCTC configuration of the EFFI with a mass spectrometer, the user has a powerful tool that allows them to characterize their catalyst, perform activity testing, and then characterize it again to see how the catalyst surface has changed after being subjected to industrial conditions. One of the characterization techniques employed by the MCCTC option is pulse chemisorption, a method commonly used to measure active metal dispersion. This is made possible because of the inclusion of an extra gas feed via Mass Flow Controller (MFC) and a known volume loop, typically 0.5 cc in volume, used for gas dosing. Here, we will explain the experimental procedure, how to set up the Process@ software of the EFFI to automatically perform the pulse chemisorption experiment, set up the Process Eye software of the MKS Cirrus2 Mass Spec to collect relevant data for the experiment, and how to use MicroActive from Micromeritics to import the mass spec data and calculate results.

Experimental Procedure

For this example, the Platinum-Alumina (Pt-Al) reference material from Micromeritics will be analyzed via pulse chemisorption using pure CO as the active species to fill the known volume loop for dosing. 10% H_2/Ar is used as the feed to reduce the sample and to be the carrier gas during gas dosing. For this test, 1 g of sample is used but note that because sample mass is an input parameter for calculations, varying quantities of sample can be used for this characterization technique. It is important to keep in mind the quantity of sample; too much sample will adsorb high quantities of gas and will require many gas doses but too little sample will not adsorb enough gas to provide high resolution data. Diluted CO mixtures (CO/He) can be used but will require more doses because of the reduced quantity of the active species in the dosing loop. In addition, H_2 and H_2 mixtures can be used as the active species when paired with an inert carrier feed such as N_2 or He.

Building a Session Table in Process@ to Perform the Pulse Chemisorption Experiment

Process@ gives the user the ability to program an automated experiment by building a session table. Each session is given a finite amount of time and any or all of the system parameters (temperatures, flows, pressure, etc.) can be changed moving from session to session. Moving forward, this document will explain how to build the session table for automatically analyzing the Pt-Al reference material.

Prior to gas dosing, the Pt-Al reference material should be reduced under a flow of 50 ml/min of H_2/Ar while being ramped to 400°C at a rate of 10°C/min. Once 400°C is achieved the sample should be held at this temperature for 30 additional minutes to allow for a complete reduction of the sample. After the reduction is complete the sample should be cooled to room temperature–the fastest way to achieve this is by opening the hot box door. Once the sample has cooled, the mass spec can begin recording and the active species, CO, can be dosed to the sample via the 6-way valve with the known volume loop. The session table should look similar to the one built in Figure 1.

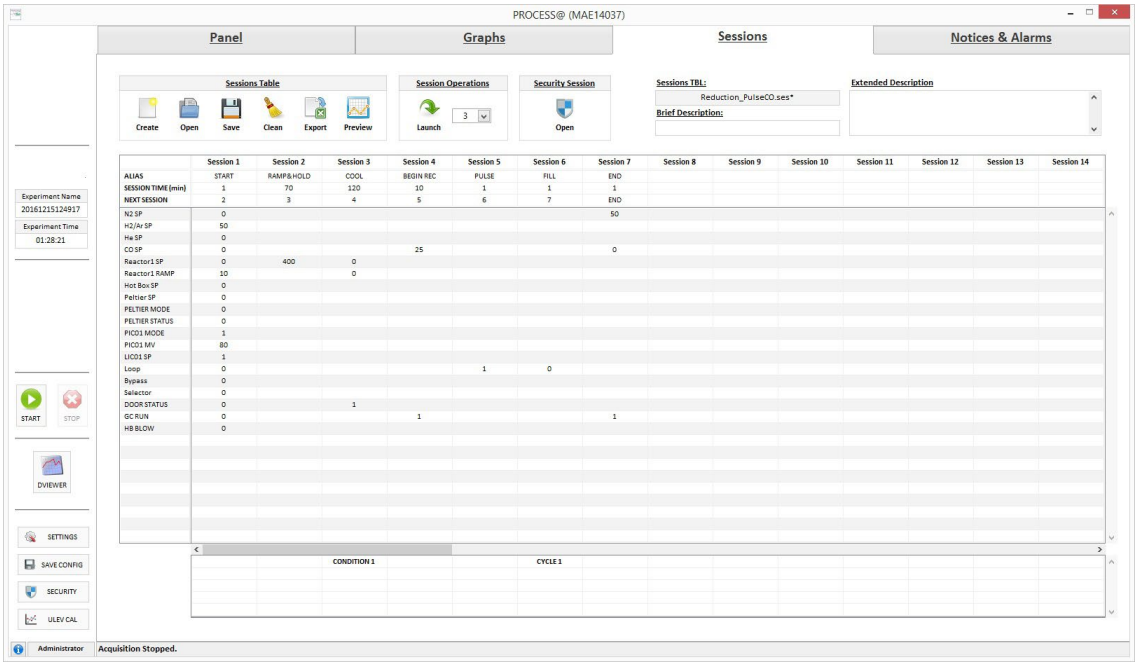

Figure 1: A Process@ session table built to reduce and dose active species onto the catalyst

There are a few items to note in this session table. First, the pressure control valve (PCV) is set to manual operation (PIC01 MODE = 1) and the valve is fully open (PIC01 MV = 80%). This ensures the system will be operating at atmospheric pressure for the duration of the analysis. Second, the door is opened by setting DOOR STATUS to "1". Likewise, when it is set to "0" it will close. Third, CONDITION 1 is set up in Figure 2. It is designed to save time; even though the system is given 120 minutes to cool to room temperature when the reactor temperature reaches 30°C or below the software will automatically jump to Session 4 to begin the data collection (GC RUN = 1) and move forward with the analysis.

Sessions 5 and 6 are looped for nine total injections of CO into the carrier stream. Session 5 is used to inject the full loop into the carrier stream (Loop = 1) and Session 6 is used to re-fill the loop (Loop = 0). A time of 1 minute for each of these sessions is sufficient. The nine total injections is achieved via CYCLE 1, seen in Figure 3. To build the cycle, enter "9" in the Repetitions field and select Session 5 and click Include Cycle and then click OK. The final session terminates the analysis and stops the data acquisition by the mass spec (GC RUN = 1). Note that the logic of the software requires the GC RUN parameter to be set to "1" for both starting and stopping. This can be manipulated to the user's advantage where multiple sets of data can be collected at varying times throughout the duration of the analysis by continuing to set the GC RUN parameter to "1". Therefore each odd iteration of setting GC RUN to "1" will begin the collection of data and each even iteration will end the collection of data.

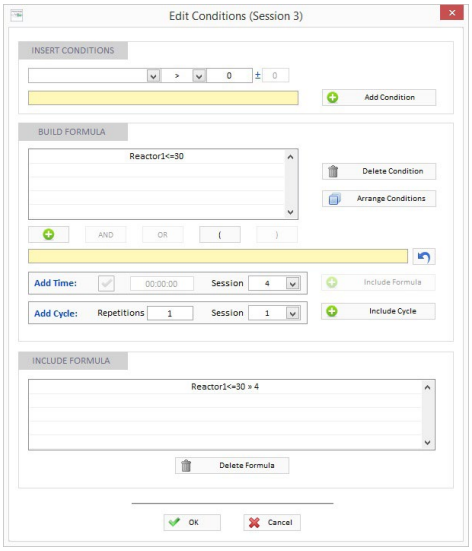

Figure 2: Creating a conditional jump to move the experiment forward once the reactor reaches 30°C

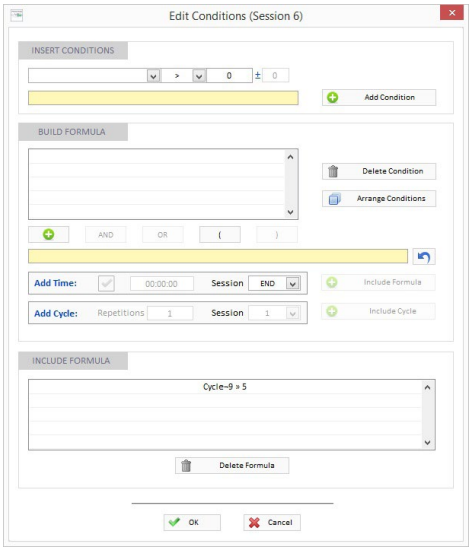

Figure 3: Editing the analysis conditions to include a nine repetition cycle between Session 5 and Session 6

Creating and Running an Automatic Sequence in Process Eye to Automatically Collect Data

The user can setup Process Eye to automatically collect data when triggered. The digital signal cable between the EFFI and Cirrus2 Mass Spec is the interface used to transmit the trigger signal mentioned in the previous section (GC RUN = 1). With Process Eye open, click Start Create/Edit Recipe and either select an existing recipe from the menu or enter a name for a new recipe as shown in Figure 4 and click OK.

Next, enter the atomic mass of the active species. The Faraday detector is typically used for this application and Skip on Saturation should be selected. Properly configuring the Accuracy setting is critical for generating high resolution results. When this parameter is increased, the reading is more accurate but it requires more time. Likewise, when the parameter is decreased, the reading is less accurate but can be recorded more frequently. For this application choosing an Accuracy setting of "4" is an excellent compromise. The Cycle Time becomes "0.100", meaning that Process Eye will record data every 0.1 seconds. This can be seen in Figure 5. Optionally, the user can click the green plus icon to add additional mass readings for more complex applications but this is not needed for the pulse chemisorption application.

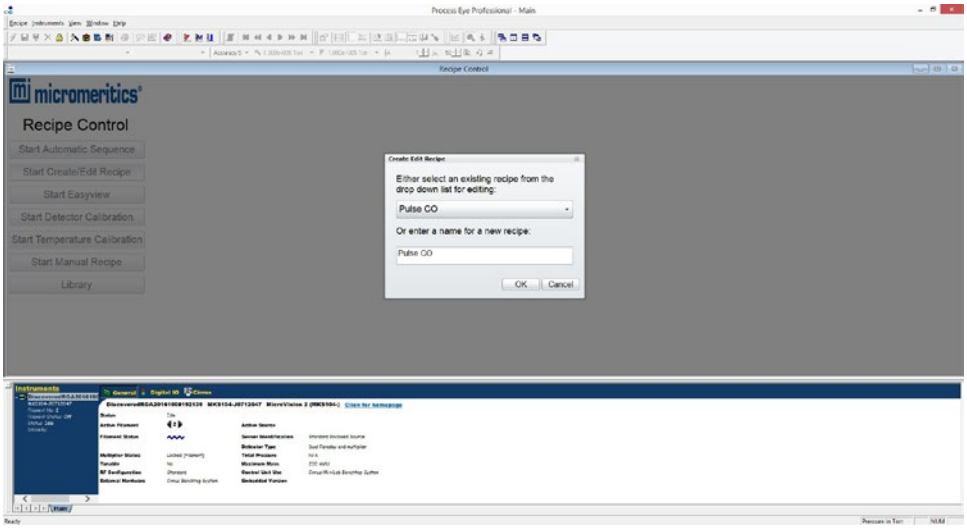

Figure 4: The window which appears when clicking Start Create/Edit Recipe in the Process Eye software

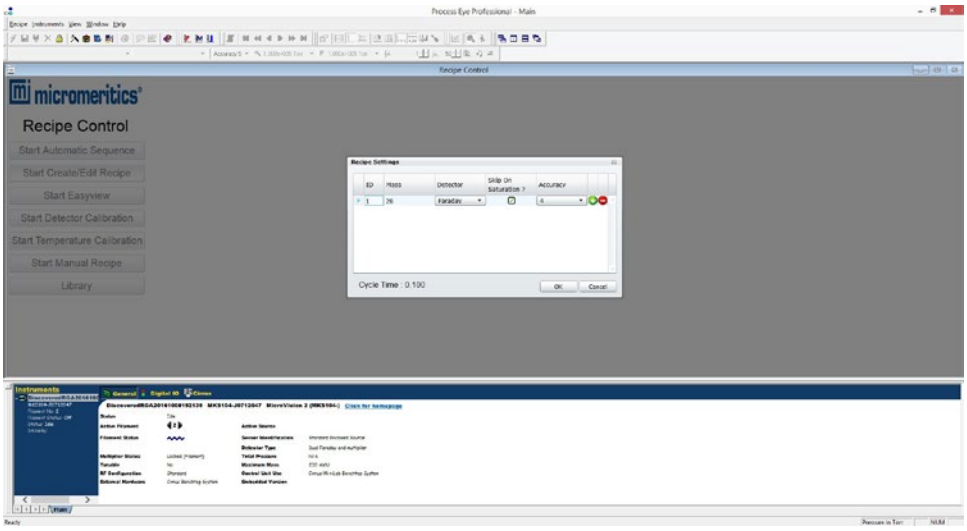

Figure 5: Adjusting the Recipe Settings

When Start Automatic Sequence is selected, the view seen in Figure 6 will appear. The newly created recipe should be selected from the Recipe Name menu. The string entered into the Save As field will be the name of the new data file created during the analysis. Both Export As Text and Filament Enabled should be selected. When Begin Automatic Sequence is chosen the Process Eye software will begin the automatic sequence and will be ready to receive the trigger signal from the EFFI to begin recording data as seen in Figure 7. Note that for more complex applications multiple recipes can be run in sequence when combined with the multiple trigger signals mentioned in the previous section. If Restart After Sequence Completion is selected then the automatic sequence will run the recipes in an infinite loop that must be stopped by the user by clicking Stop Automatic Sequence or Abort Automatic Sequence.

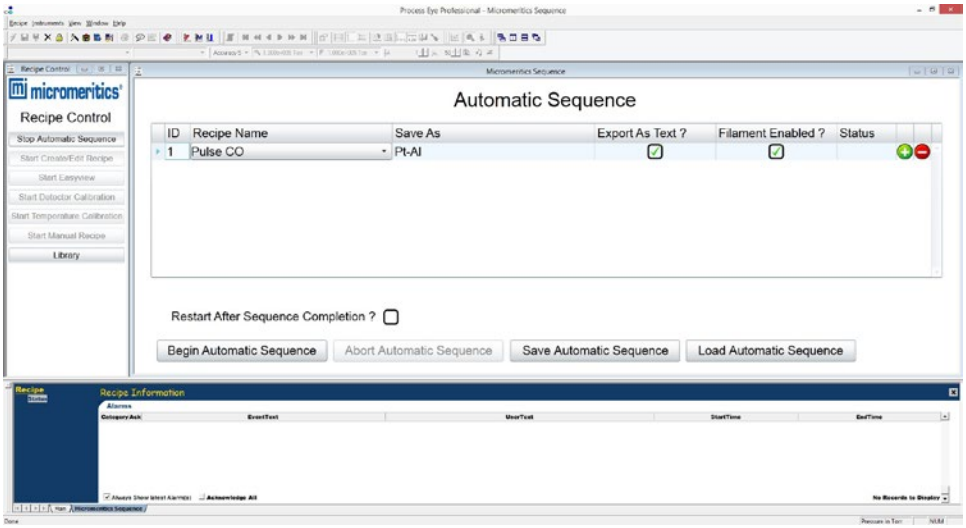

Figure 6: Building the Automatic Sequence in Process Eye

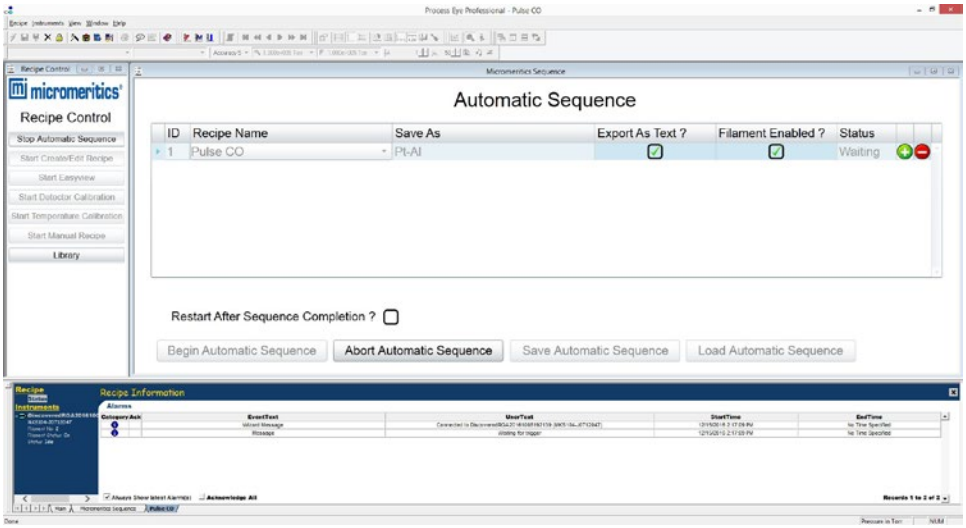

Figure 7: The automatic sequence waiting to receive a trigger signal to begin data acquisition

Session 4 in the Session Table is when the mass spec is first triggered to begin data acquisition. Its duration is 10 minutes for two reasons. First, it allows the mass spec to establish a steady baseline and second, it allows flushing of the loop with the active species. Once the active species has been injected into the carrier stream the automatic sequence will look similar to Figure 8. Here, the first injection was performed at minute 10. It took about 40 seconds for the active species to travel from the loop, first to the reactor through the catalyst bed and then out the exhaust to the mass spec connection. The first injection should have a smaller peak than the subsequent injections because the catalyst will chemically adsorb some of the active species but note that a logarithmic scale is used by default for the y-axis so the peaks may appear to be the same size. If part of the live data plot disappears, as seen in Figure 8 prior to the 9 minute mark, the data is still successfully being written to the data file. Upon completion of the analysis the second trigger signal will be sent to the mass spec to stop data recording. This will complete the experiment and save the data file in a format that can be imported by MicroActive.

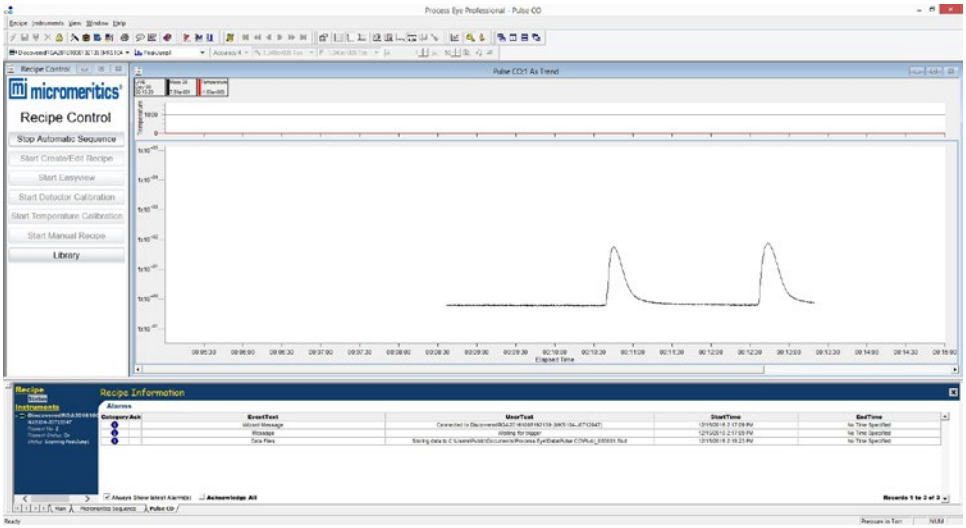

Figure 8: Live recording of data during the pulse chemisorption experiment

Importing the Mass Spec Data with MicroActive and Calculating Results

Versions 4.04 and newer of MicroActive includes the ability to import mass spec files and use the data for calculations. To do this, select the File menu and select Import... then browse to the Process Eye data folder. Make sure to specify the file type in the bottom right corner; MKS file should be selected for files generated by Process Eye as seen in Figure 9.

When importing data into MicroActive, the user can either add this data to an existing sample file or create a new file. In this example a new file is created. For a new file, enter the sample name, the operator, and sample mass, as seen in Figure 10.

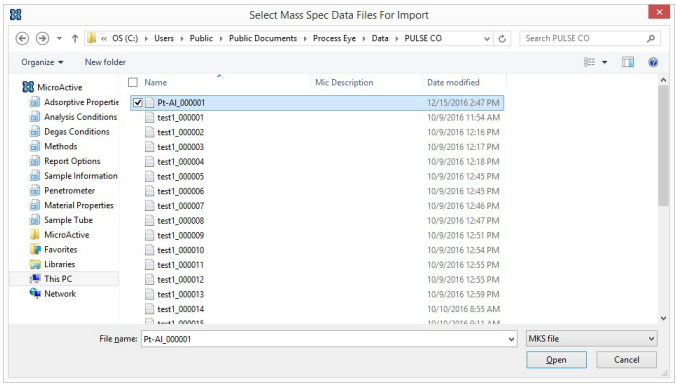

Figure 9: Selecting the mass spec data file to import into MicroActive

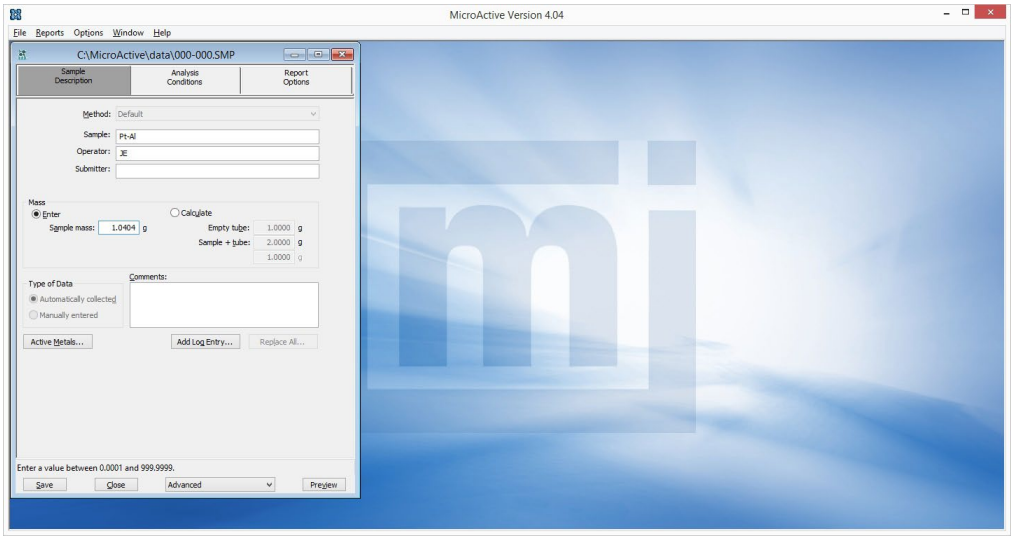

Figure 10: Entering the sample information into the .SMP file

For a pulse chemisorption experiment, the percentage of active metal (catalyst) in the sample must be specified. This is done by clicking the Active Metals... button. The Pt-Al reference material is 0.5% Platinum– this should be entered as seen in the Active Metals table in Figure 11.

Next, the Analysis Conditions should be entered as seen in Figure 12. Here, the description Mass Spec will already be entered. The Type of analysis should be selected as Pulse Chemisorption. The carrier gas and its flow rate can be entered, but this is optional but useful to have as a reference. The analysis gas must be selected so the proper stoichiometric factor can be applied in calculations. Loop injection should be selected and the calibrated loop volume should be entered. The loop temperature should remain 0.0°C – this will ensure the full entered loop volume entered in the previous step is used in the calculations. Finally, the entered ambient temperature and atmospheric pressure values should remain as defaults.

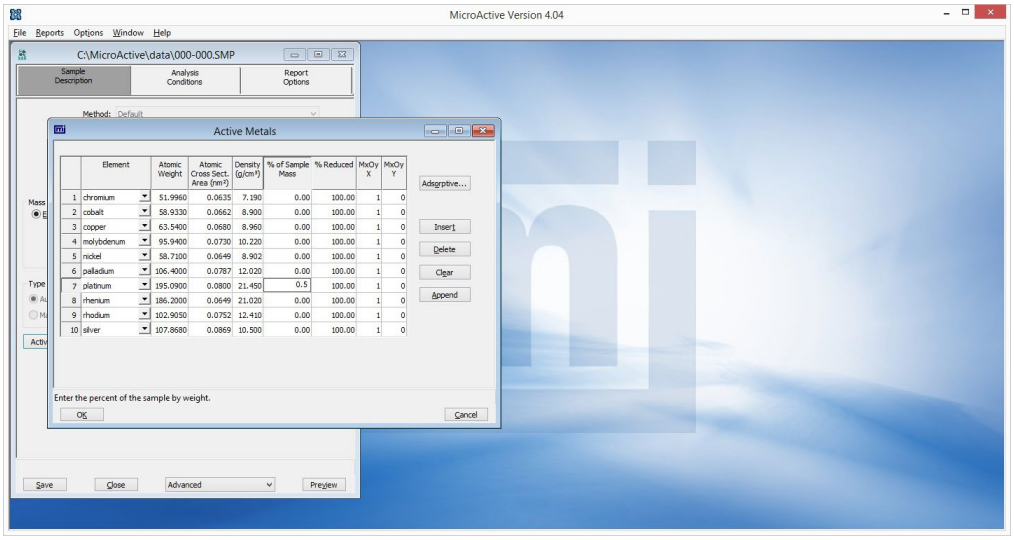

Figure 11: The Active Metals table

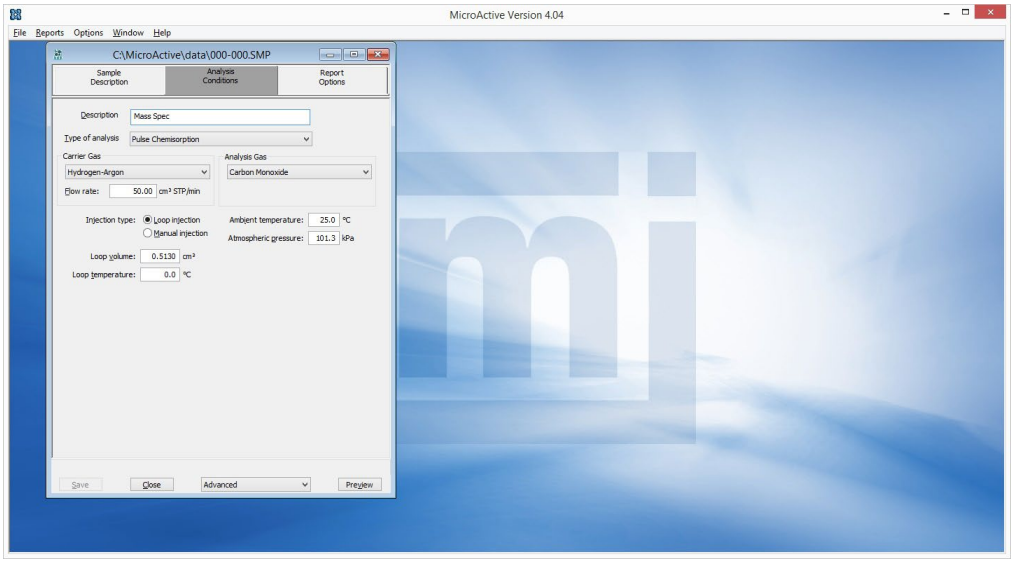

Figure 12: Entering the Analysis Conditions into the sample file

Pulse Chemisorption should be selected under Report Options. The number of peaks used for saturation can be edited as seen in Figure 13. In this case, the last 5 peaks will be used. When using approximately 1g of the Pt-Al material with a 0.5cc injection loop and pure CO as the active species, adsorption will occur during only the first 2-3 injections. The number of peaks used for saturation should be edited to reflect the analysis conditions.

Once the sample information, analysis conditions, and report options have been edited, Peak Editor–Mass Spec should be selected from the drop-down menu at the bottom of the sample file window. Click Find All Peaks and MicroActive will automatically find and integrate the peaks generated by the gas injections during the experiment. The peak information will be displayed in a table on the left side of the window as seen in Figure 14.

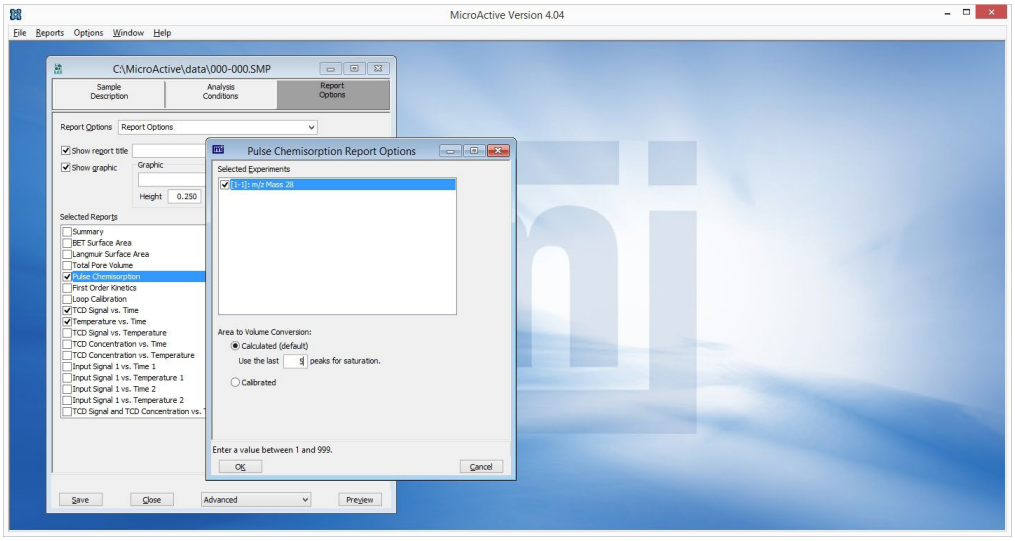

Figure 13: Editing the Pulse Chemisorption Report Options

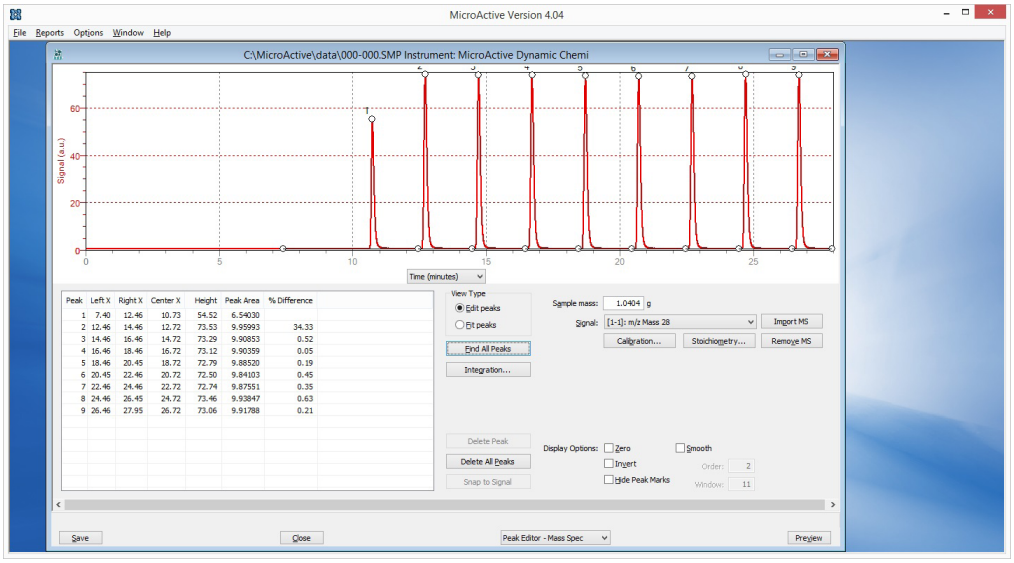

Figure 14: Using the Peak Editor in MicroActive

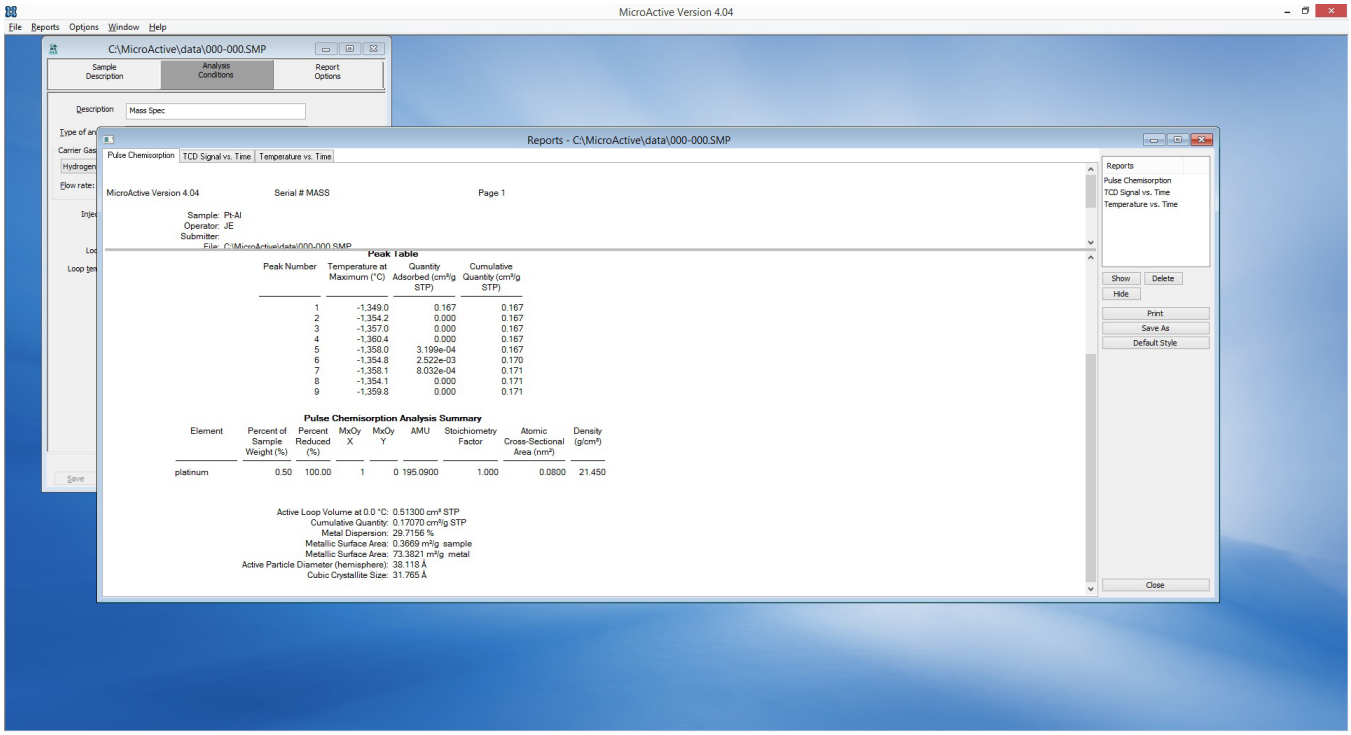

Figure 15: The Pulse Chemisorption report

Click Save and then Preview to generate the pulse chemisorption report. The dispersion will be calculated and reported as seen in Figure 15. Note that the dispersion values will be low if the final sample mass is not entered. The sample will lose some mass via water loss during the reduction phase of the analysis. The final sample mass can be entered into the analysis file and the report can then be regenerated.