APPENDIX IV.

Molecular Probe Analysis Procedure

Procedure for Molecular Sieve Gas Adsorption testing

1. Load clean sample pans (clean by blowing out with freon duster). Sample pans are kept in a plastic holder by carousel position number. The order must not be mixed, since the weight of each pan in vacuo is not measured for each run, but is determined separately and used for following runs.

The sample weight in each pan is adjusted so that the full pans all have the same weight within + 2 mg and no pan is more than 90% full. It is important to have all the full pans the same weight so that you do not have to constantly change weight ranges on the Cahn balance.

2. Place full sample pans in carousel, make sure they go into the correct position.

3. Carefully insert carousel inside vacuum tube. Use one hand to center and guide the carousel, steady this hand on the bottom of the vacuum tube. Use the other hand to slowly push the carousel into place. With practice this step becomes easier. When the carousel is fully inserted, place clamp on O-ring connector and seal finger tight. Do not over tighten seal or you will not be able to rotate the carousel freely and the carousel can become cocked to one side due to uneven pressure on the O-ring.

4. Make sure the outlet valves on all the gas regulators are closed. Switch gas selector valve to the first gas that will be adsorbed, carbon dioxide.

5. Change valving on the vacuum pump station to the rough pump position (so that the mechanical pump is connected directly to the gas adsorption system and the oil diffusion pump is isolated). Very slowly crack open the large vacuum valve on the gas adsorption system, while watching the system pressure. Open valve just wide enough to cause a pressure drop of about 1 torr every second. It is critical that the samples, especially fine powder with high surface area, are not evacuated too fast. Adsorbed water and other material will be desorbed as the sample is evacuated. If the desorption is too rapid, the force of the gas evolution will cause the powder to burst out of the sample pan. If this happens the samples will have to be reloaded and the vacuum tube cleaned.

Monitor the pressure drop, opening the vacuum valve a little wider as the pressure is reduced in order to keep the same rate of pressure drop. Continue until system pressure is below one torr, then slowly open vacuum valve completely. Switch vacuum pump station to oil diffusion pump position (close roughing valve then open oil diffusion pump valve and then main valve).

6. The system is now ready for thermal desorption of the samples. The wizard is already programed for the correct heating cycle. Connect the heater power and thermocouple leads from the carousel to the wizard. Turn on zone one on the Wizard and run

program. This will heat sample at 10 deg C/minute to 110 deg C and then at 30 deg C/minute to 350 deg C, soak at 350 deg C for one hour and then cool to room temperature.

7. When Wizard program is completed, attach stainless steel tubing from pump to heat exchanger leads on the carousel. Put ice water in stainless steel dewar feeding pump (inlet tube to pump will rotate allowing the dewar to be removed and replaced). Turn on pump in forward direction. The first water going through the heat exchange will be super heated to steam, which will come out the outlet line. For this reason make sure the outlet line is inside the dewar and do not touch the outlet line for the first minute, it gets quite hot. The carousel cools off very quickly, usually in five to ten minutes.

8. When the carousel is at 25 deg C turn off water pump. Allow system to equilibrate for five minutes (do not want thermal gradients when weighing sample pans).

9. Starting with carousel position one, pick up each pan and record its weight in your notebook. To pick up the pan, position the carousel so that the hang down wire is between position one and two by rotating the carousel (disconnect heater, thermocouple and water pump lines first). Then using electronic position control, lower hang down wire to its lowest position. Now slowly rotate carousel clockwise until hang down wire is touching sample pan one's wire loop. Then use electronic position variable control to raise hang down wire slowly until hook on hang down wire is touching the wire loop, but the pan is still resting on the carousel. There is a little delay in the electronic position controller between the time you move the knob and the hang down wire moves. Now switch the electronic position control to the raised position, causing the sample pan to be raised off the carousel. If the pan is swinging, rotate the carousel until the hanging pan is touching a pan that is still resting on the carousel, this will stop the swinging. Then very slowly, so that you do not cause any new swinging, rotate the carousel to allow the sample pan to hang freely. Make sure the pan is not rubbing but looking at the weight pen on the recorder. It should show a smooth line with no noise. Rubbing usually causes random noise spikes.

Note: The electronic position controller must be in the raised position to get a correct weight from the Cahn balance! If it is not you have introduced some electronic weight suppression.

10. Now you know the weight of the clean sample in vacuum (you previously recorded the weight of the clean sample pans in vacuum) by difference. The next step is to expose the sample to the first gas.

11. The first gas adsorbed is carbon dioxide. Close the vacuum valve on the gas adsorption system to isolate the balance chamber. Since the gas selector valve was placed in the carbon dioxide position previously, the line to the regulated was

evacuated and no air will be allowed into the system when the carbon dioxide valve is opened. Open the valve on the carbon dioxide regulator allowing the gas into the balance chamber. The gas flow is restricted by the selector valve and it will take several minutes to reach the desired pressure of 700 torr. This is a good feature since too rapid an inflow of gas might blow the powder samples out of the pans.

12. When the adsorbate gas is at the correct pressure, close the valve on the regulator. The correct pressures are shown below for 25 deg C.

Adsorbate	Pressure (torr)	Relative Pressure
carbon dioxide	700	0.015
neopentane	347	0.27
isobutane	705	0.27
n-butane	492	0.27

13. When the correct pressure is reached, allow the sample to equilibrate for one hour (set the timer) and then weigh each sample as in step 9 and record the values in your notebook.

14. Then evacuate the samples as in step 5 (there is not as great a chance of bursting since there is no water adsorbed on the surface). Then thermally desorb the carbon dioxide as in step 6 through 8.

15. Weigh the samples at 25 deg C in vacuum as before and compare with initial weight in vacuum. The difference should be less than + 0.05 mg, the repeatability of the Cahn balance at this range. If the difference is larger there is hysteresis and not all the adsorbate was removed or some of the sample could have been lost from the pan.

16. Introduce the next gas in the series, following the order in the table: carbon dioxide, neopentane, isobutane and then n-butane.

17. Repeat the process until all the gases have been completed.