3P INSTRUMENTS

Department of Porous Materials

3P INSTRUMENTS

Characterization of

particles · powders · pores

Overview

- 0.) Altamira Company History
- 1.) What is Chemisorption
- 2.) Altamira AMI-300 family
- 3.) Altamira µBench-cat and Bench-cat systems

Company History

HISTORY OF ALTAMIRA INSTRUMENTS

- Founded in 1985 in Pittsburgh, Pennsilvania
- Pioneered automated catalyst characterization
- More than 400 instruments installed
- Global Customer base
- Recognized for excellence in customization

Company History

- AMI CATALYST CHARACTERIZATION FAMILY
- µBenchCAT BENCH-TOP REACTOR SYSTEMS
- BENCHCAT and BenchCAT-HTS CUSTOM REACTOR SYSTEMS

Company History

- Cooperation with 3P Instruments started in June, 2018
- OEM-supplier of the Quantachrome ChemStar until 2019
- Cooperation between Altamira and Anton Paar / QuantaTec was apparently terminated

What is Chemisorption?

Physisorption

- Physisorption = Adsorption based on weak van-der-Waals-Wechselwirkungen

- Reversible
- Monolayer-/Multilayeradsorption **on the complete available surface area**

Typical systems:

N_2, Ar, Kr at 77 or 87 K, CO_2 at 273 K

Inert gas on the complete available surface area of the material within the sample cell

What is Chemisorption

Physisorption

- Physisorption = Adsorption based on weak van-der-Waals-Wechselwirkungen
- Reversible
- Monolayer-/Multilayeradsorption **on the complete available surface area**

Typical systems:

N_2, Ar, Kr at 77 or 87 K, CO_2 at 273 K

→ **Inert gas on the complete available surface area of the material within the sample cell**

Chemisorption

- Chemisorption = Adsorption by formation of a chemical bond (usually covalent) between adsorbate and adsorbent
- Irreversible
- Monolayer adsorption on the **active surface area of a catalyst**

Typical Systems:

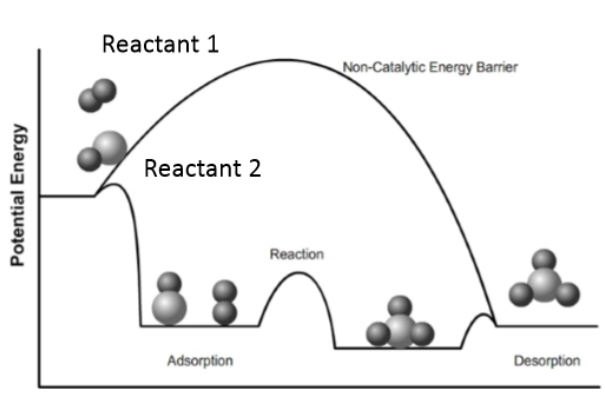
CO, H_2, NH_3, O_2, SO_2 on Pt, Pd, Ni, etc…

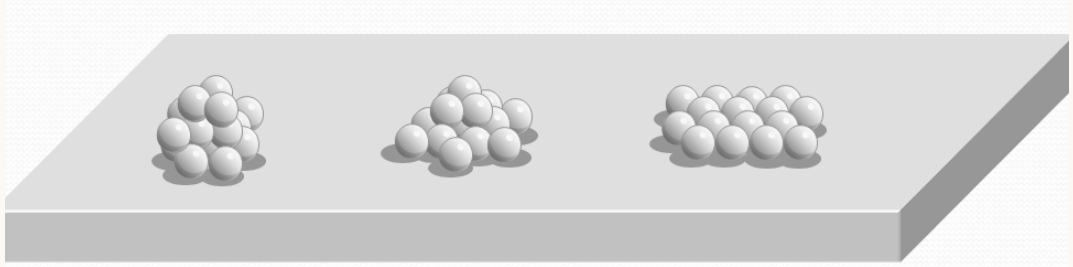
→ **Reactive gases on metal centres at T > RT**

What is Chemisorption?

Chemisorption to determine the active metal surface area

- The most important information of a functionalized substrate carrier is:
  How many metal centres are available for a chemical reaction on the surface?





- **Atoms on the inside of crystallite deposits do not participate in the reaction!**

→ **Amount of active centres can be deduced from the chemisorbed amount of gas**

→ **How much energy is required to produce and activate a catalyst?**

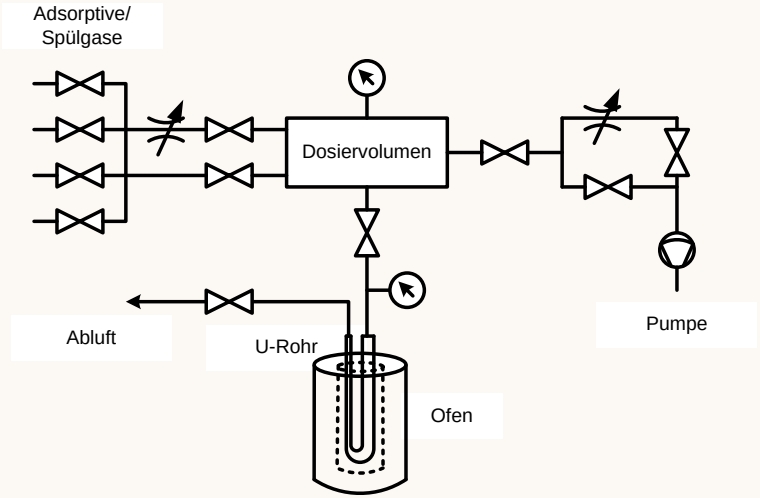
What is Chemisorption? - Methods

(Vacuum) Volumetric Method

Isotherm-Analysis, comparable to physisorption measurements

Determines:

- Monolayer capacity
- Dispersion
- Crystallite size
- Adsorption enthalpy



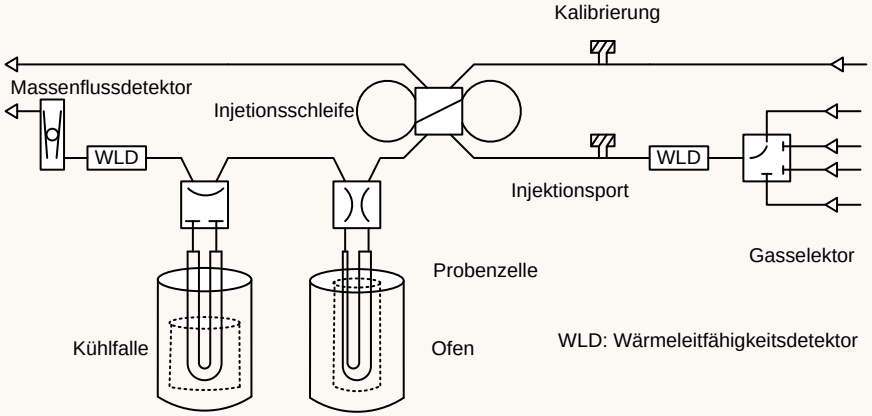
Dynamic flow method

Temperature Programmed Reactions TPX

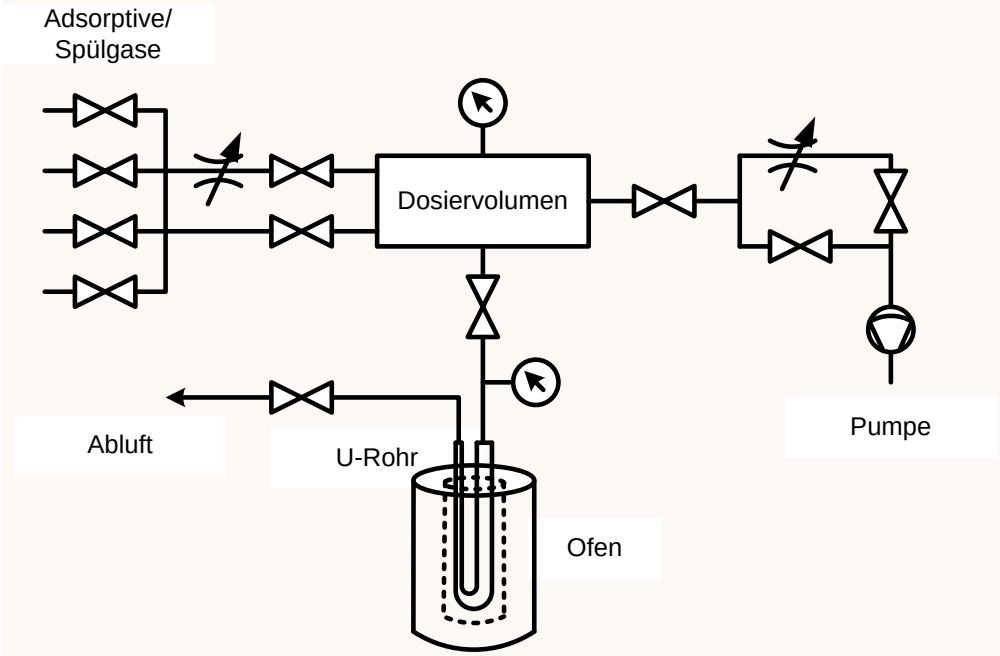
- **TPR** (TP Reduction)
- **TPO** (TP Oxidation)
- **TPD** (TP Desorption)

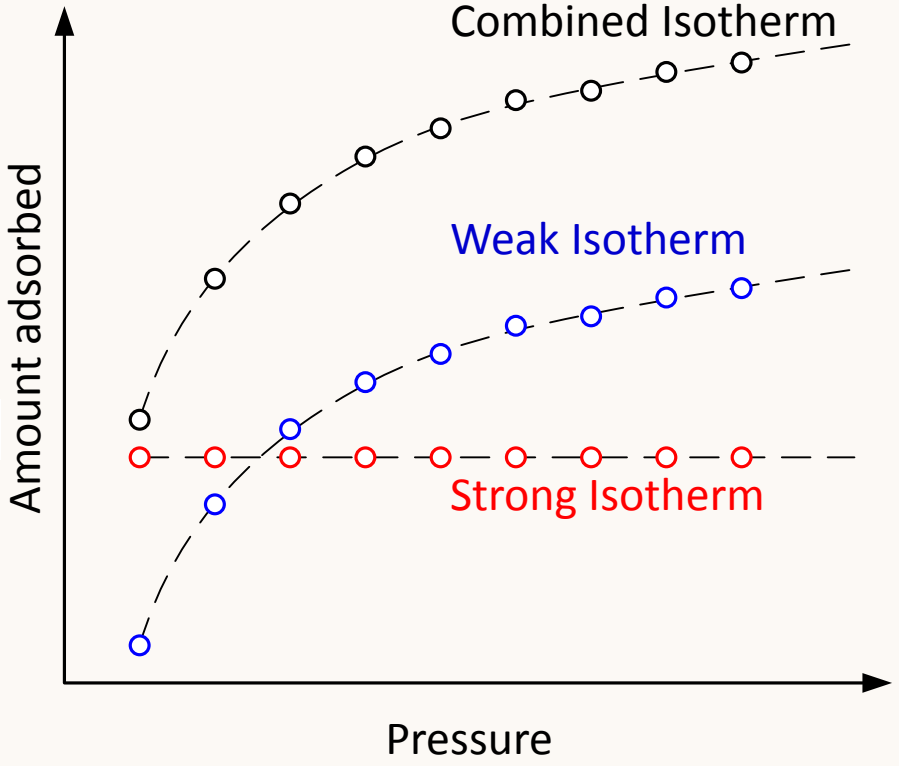
Puls-Titration

Determination of monolayer capacity



What is Chemisorption? - Methods



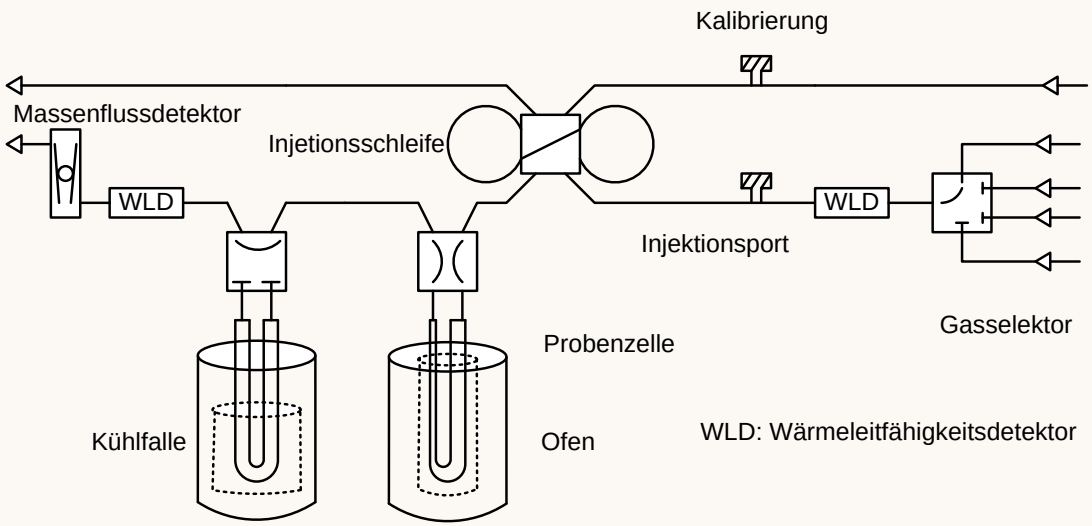


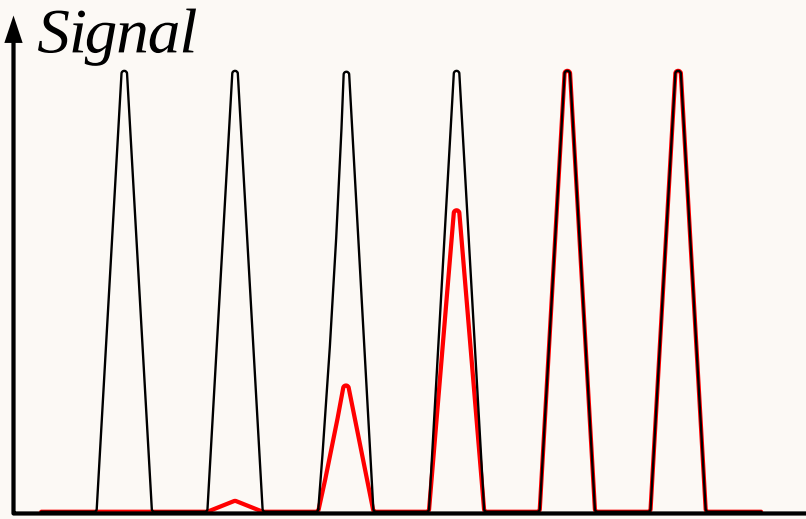
First recorded isotherm is the combined isotherm – contains both physi- and chemisorption

Second recorded isotherm is the weak isotherm – contains only physisorption

Difference between the two is the strong isotherm – contains the chemisorption information

What is Chemisorption? - Methods



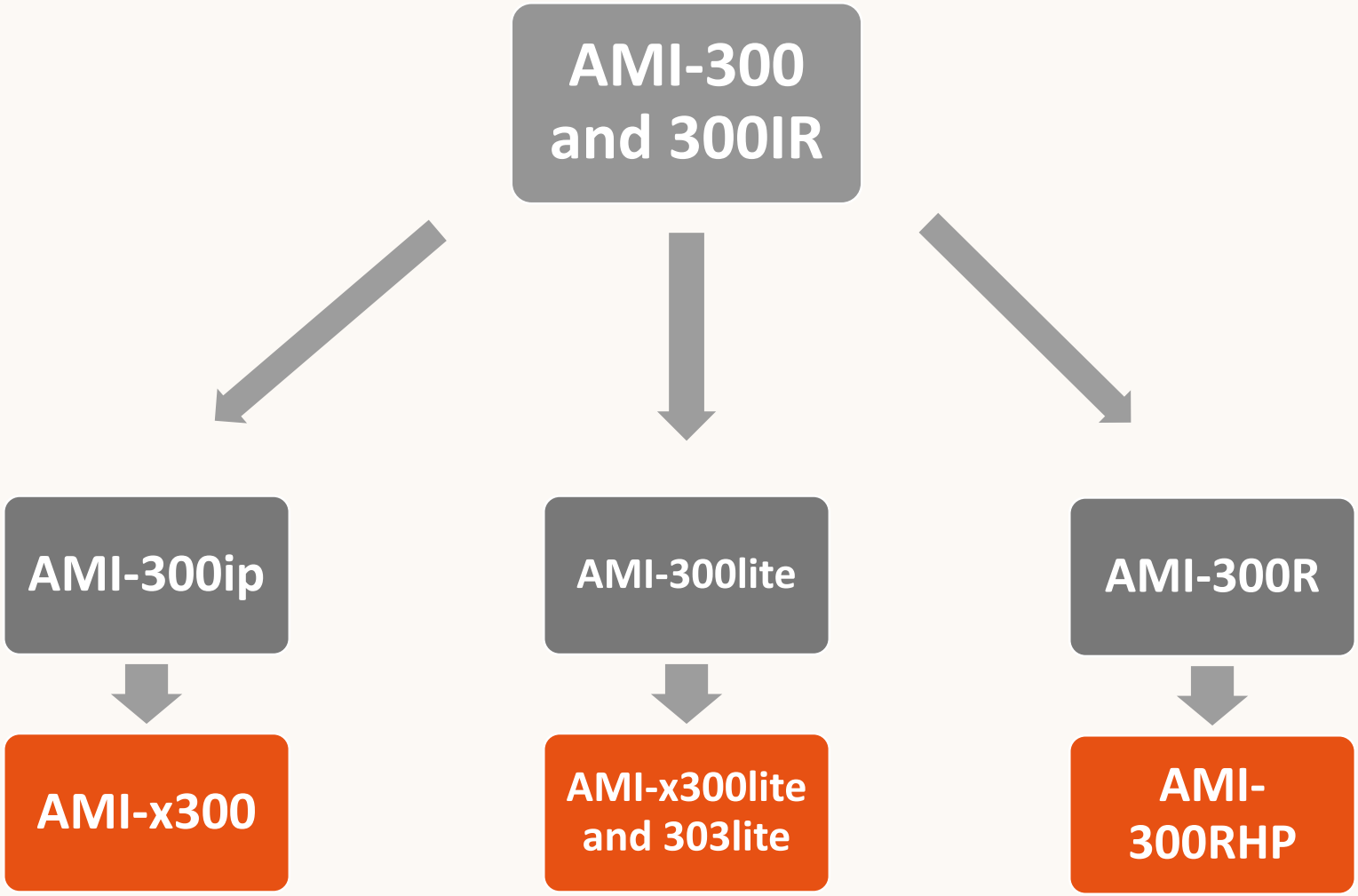


Puls-Titration

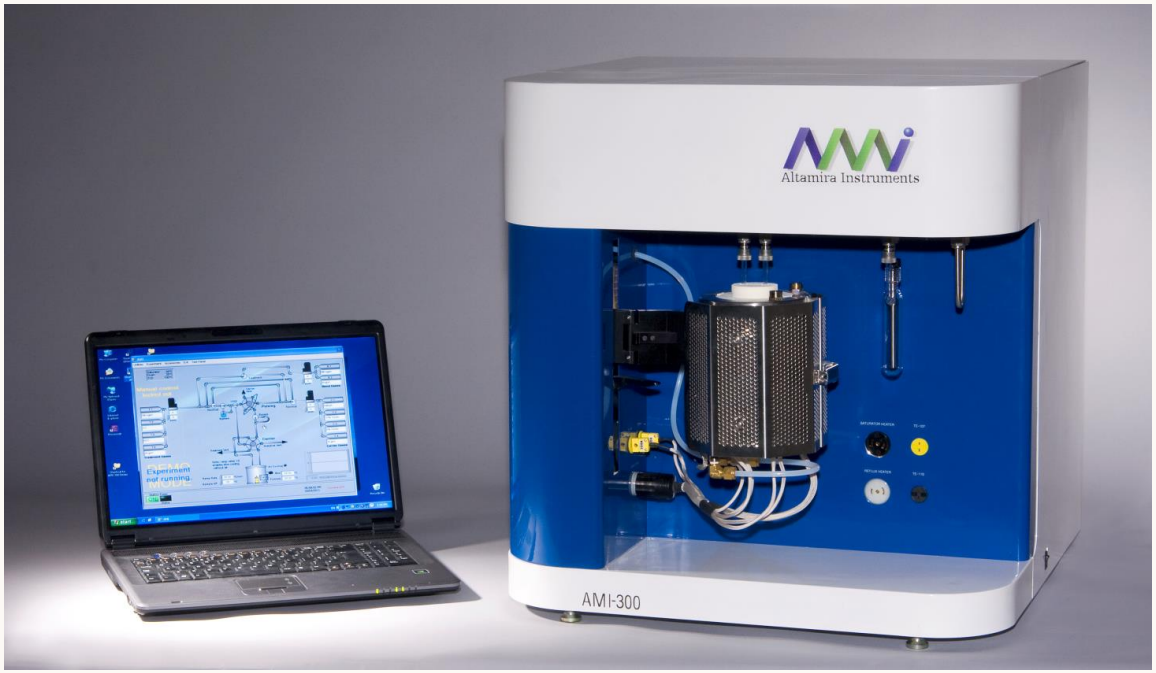
$$V_{ads} = V_1^{inj} - \left(\frac{A_1^{inj}}{A_1^{sat}} V_1^{inj} \right) + V_2^{inj} - \left(\frac{A_2^{inj}}{A_2^{sat}} V_2^{inj} \right) + \dots$$

Note, that after each pulse, weakly bound molecules will be carried away by the carrier gas, which means the adsorbed amount **corresponds to the strong adsorption from the volumetric method.**

The AMI Characterization Family

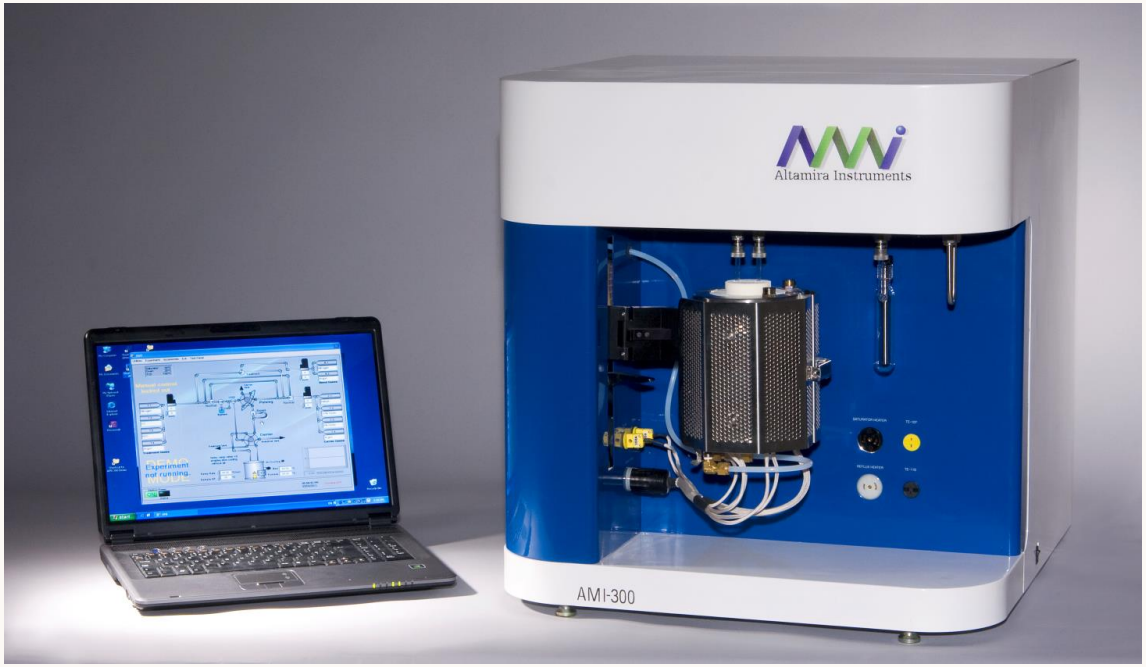


AMI -300: THE TESTS



- TEMPERATURE PROGRAMMED REDUCTION
- TEMPERATURE PROGRAMMED OXIDATION
- TEMPERATURE PROGRAMMED DESORPTION
- ISOTHERMAL REACTIONS
- PULSE CHEMISORPTION
- DYNAMIC BET

AMI -300: COMPONENTS



- INTERNAL TCD
- OPTIONAL SECONDARY DETECTORS (GC, MS, FID)
- HIGH TEMPERATURE FURNACE (1200C)
- GAS BLENDING INSIDE INSTRUMENT
- VAPOR SPARGING
- TEMPERATURE SAFETY SWITCH

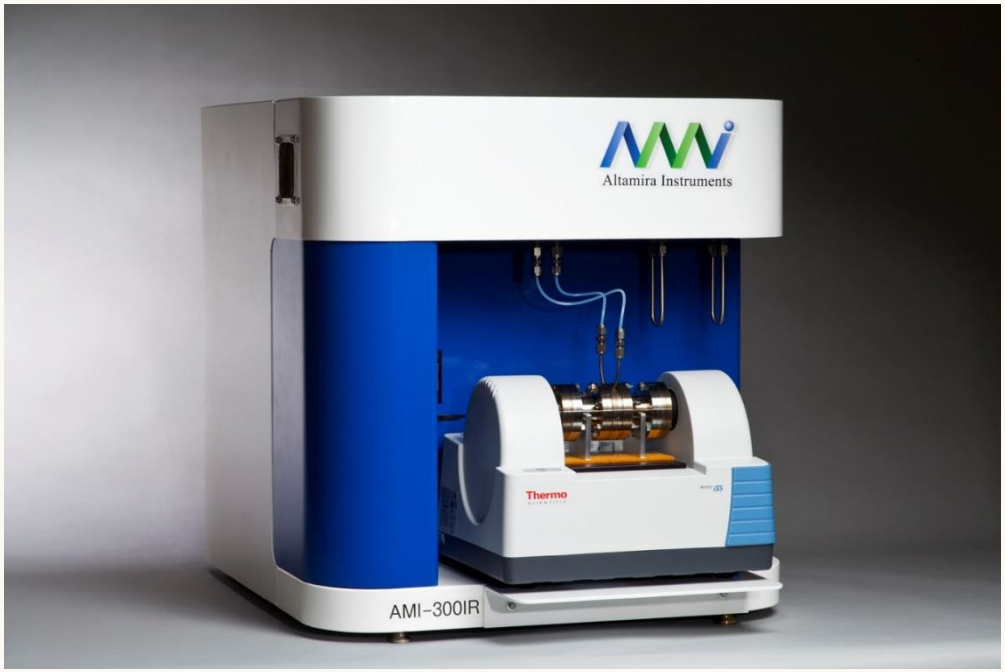
WHY BUY AN AMI?

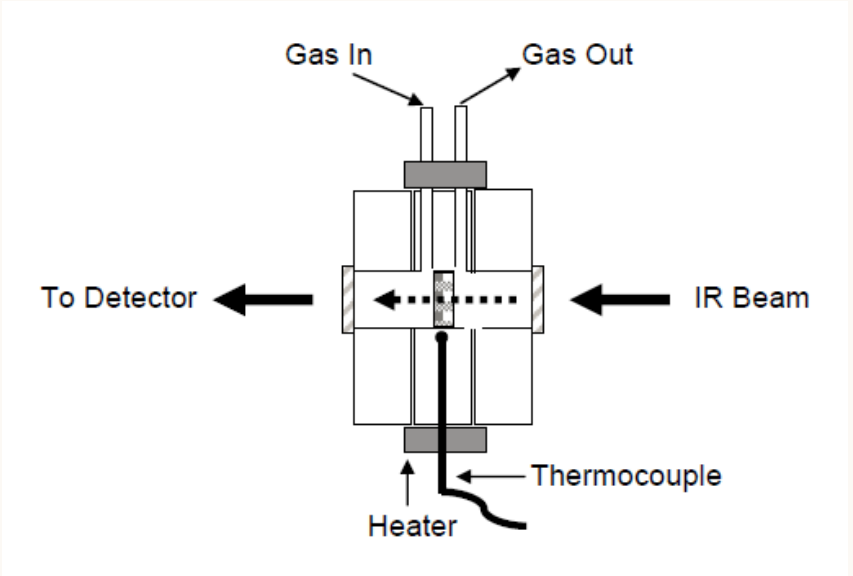
- FULLY AUTOMATED
- SAFETY COMPONENTS
  - Check valves on each gas inlet line
  - Hardwired TSS (redundant thermocouple)
  - Alarm Matrix for all process variables
  - Options for:
    - Gas flow stoppage if reactor breaks
    - Seismic mounts
- MASS SPEC
  - Can be connected at reactor or at vent
  - MS data is incorporated into the AMI data file
  - Custom fragmentation software gives gas pressures and not just mass numbers
- CRYO-OPTION to -130°C
- "OPTIONS"
  - Vapor generator is standard with the AMI
  - Analysis software is standard with the AMI

AMI -300: OPTIONS

- ANALYTICAL DEVICES
  - MS
  - GC (AMI can trigger at customer defined intervals)
  - FID (yield total hydrocarbon amount)
  - FID with methanizer
- EXTRA GAS BLENDING
  - Altamira's 4th MFC is strictly for gas blending and not for TCD reference
- CRYO-OPTION
  - -130°C minimum
- HARSH SERVICE APPLICATIONS
  - High percentage sulfur compounds (H_2S, SO_2)
  - Halides

AMI -300*ir*





- IN-SITU OBSERVATION OF ADSORBED SPECIES TO DETERMINE TYPE AND MODE OF ADSORBTION
  - TEMPERATURE PROGRAMMED OXIDATION/REDUCTION
  - TEMPERATURE PROGRAMMED DESORPTION
  - PULSE CHEMISORPTION

AMI -300*ir*

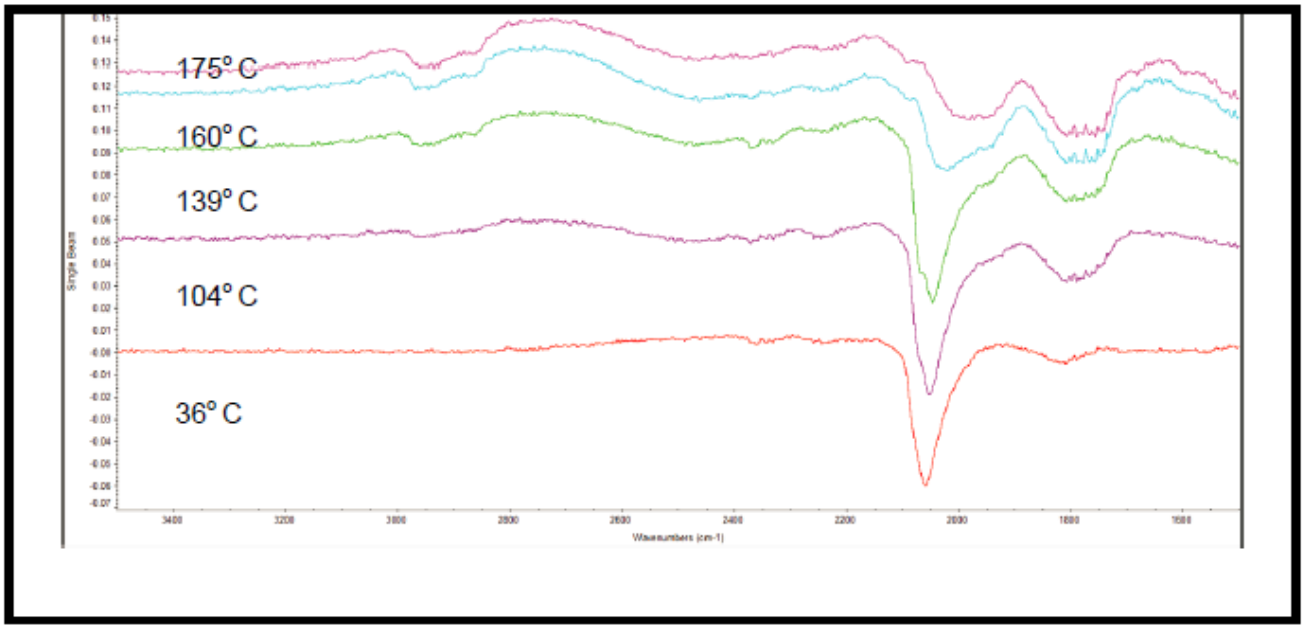


Figure 5. CO signal as a function of temperature.

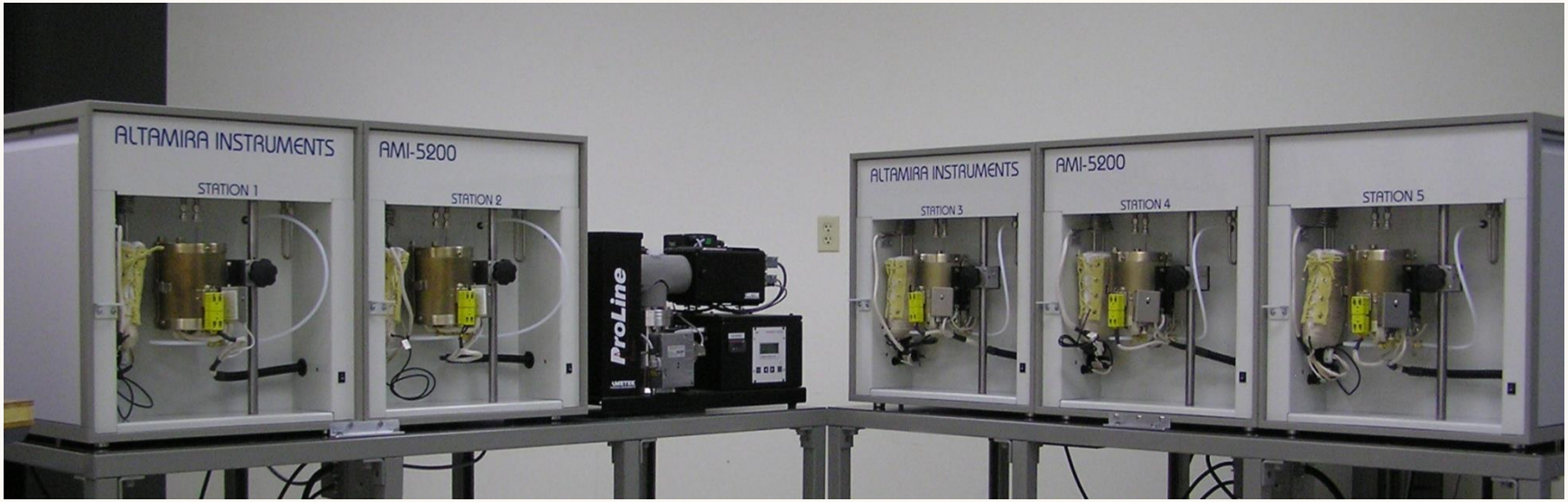
- **CUSTOM TRANSMISSION CELL**
  - **Temperatures to 500°C (variable of inert/carrier gas)**
  - **May be used in conjunction with other detectors (TCD, MS)**
  - **Cells are also available for RAMAN or other applications (i.e. photo-catalysis)**

AMI -300*ip* = Higher Throughput

AMI-300*ip* is:

- **Two Work Stations**
  - **-1 for Pretreatment**
  - **-1 for Characterization**
- **Switch functions automatically**

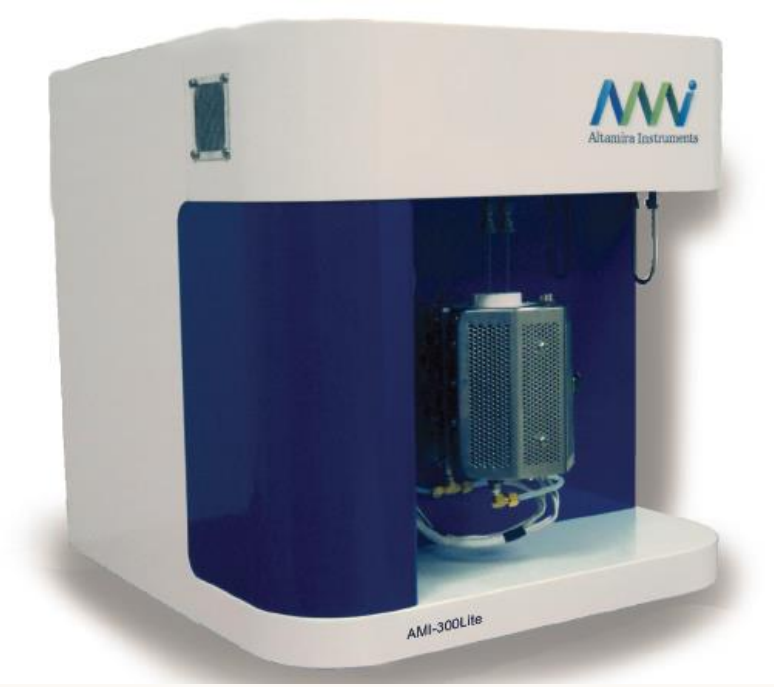
AMI -x300



AMI-5300

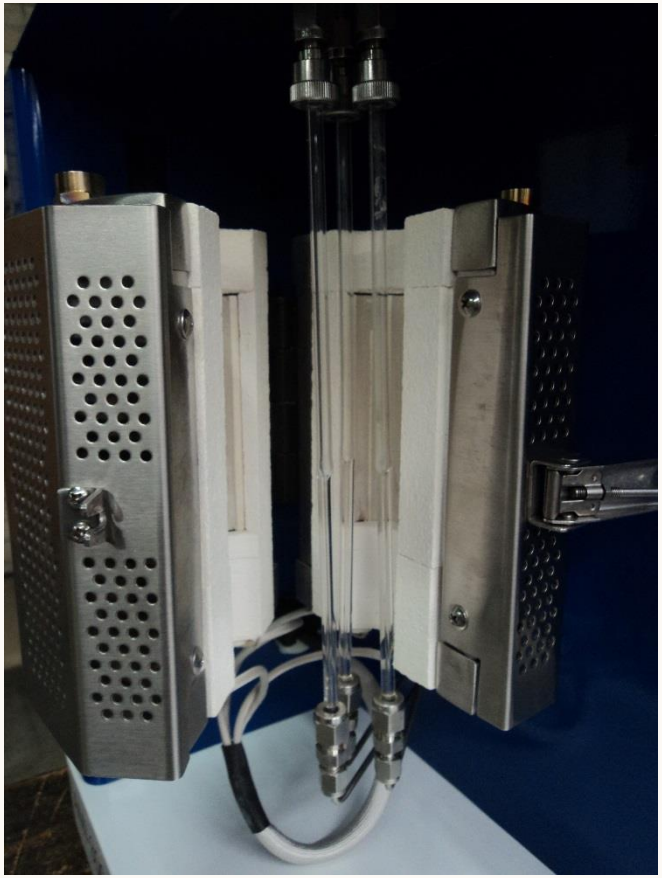
- 5 times the through-put!
- Fully automated from a single PC
- Each station is fully independent
- Multi-port Mass spectrometer allows for queue of stations and sampling
- X300 gives you the option to have as many stations as you want

AMI – 300lite



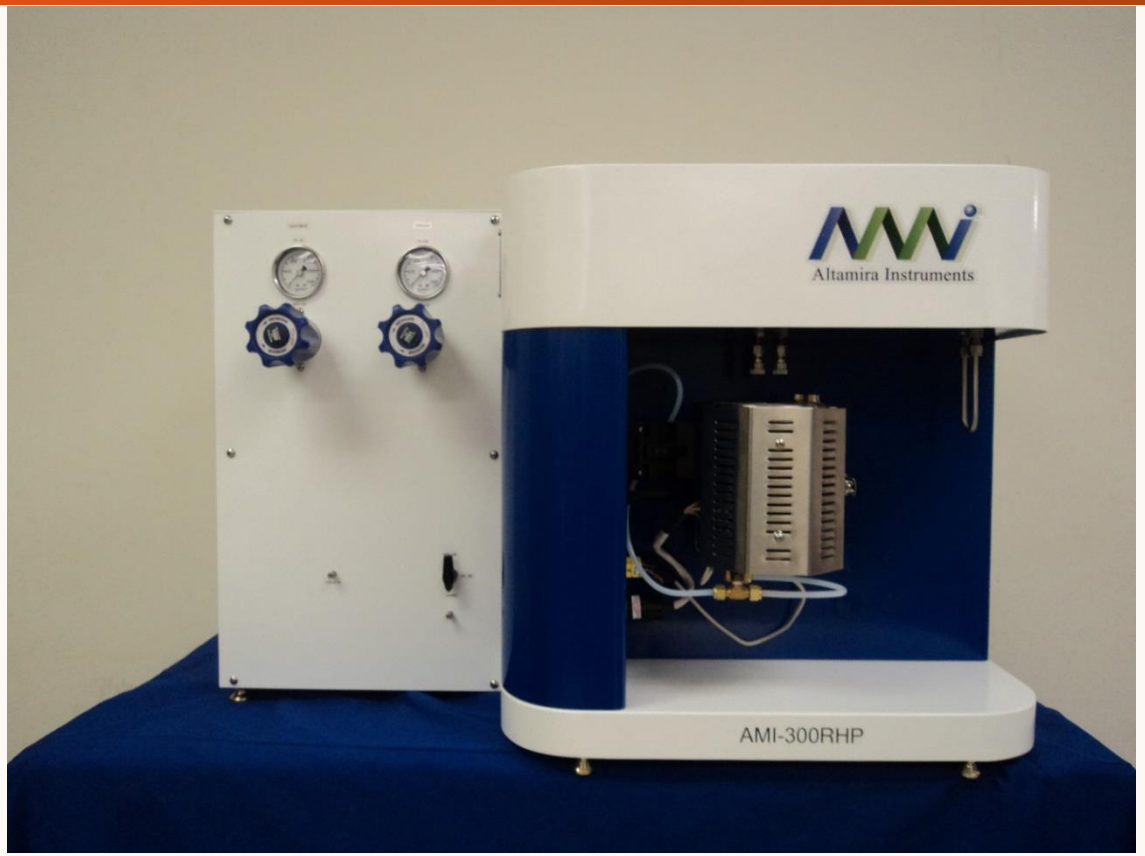
- "Economy" version but can perform TPR, TPO, TPD, Pulse Chem and a single point BET
- The only fully automated "lite" instrument in the industry
- Optional pre-treatment station at the same time as TPR/TPO/TPD/Pulse Chemisorptions!
- Optional multi-station available for higher throughput!

The New AMI – 303lite



- Run 3 samples at one time!
- 3 TCDs, 3 reactors (in one furnace), 3 MFCs (one per station)
- TPR, TPO, TPD, Pulse Chemisorption

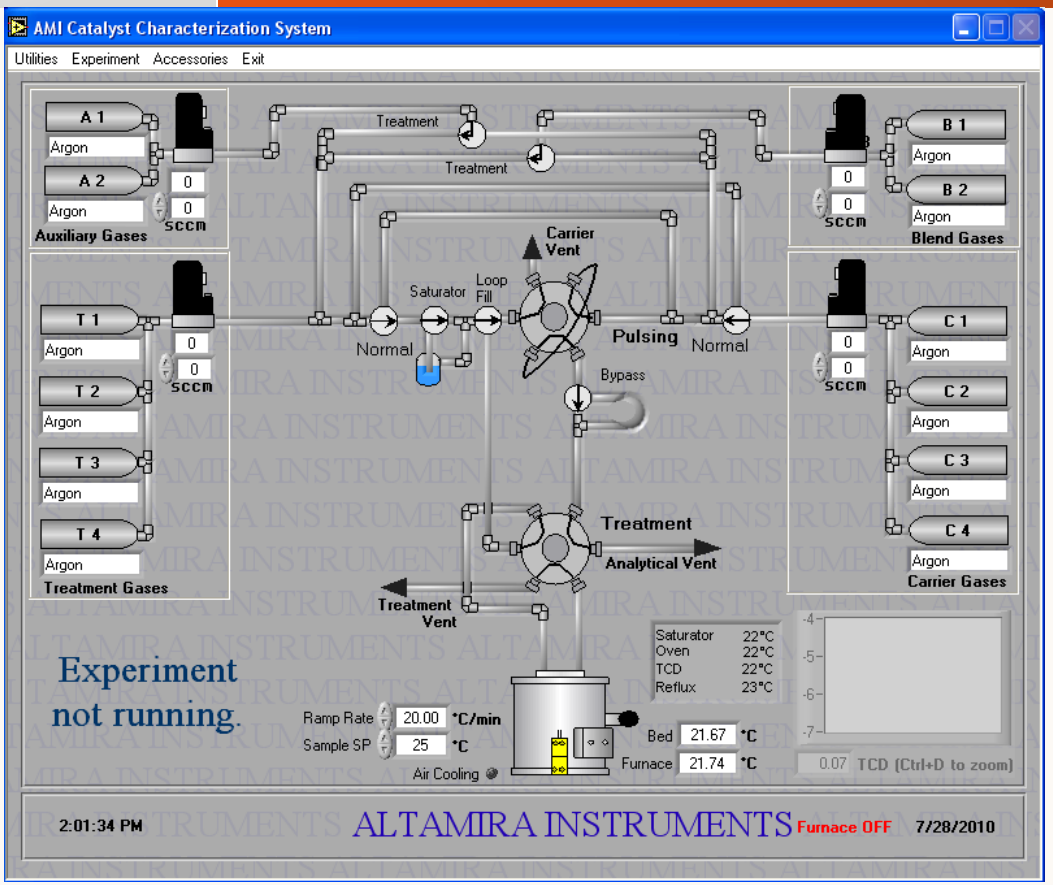
AMI - 300 RHP



AMI-300 RHP

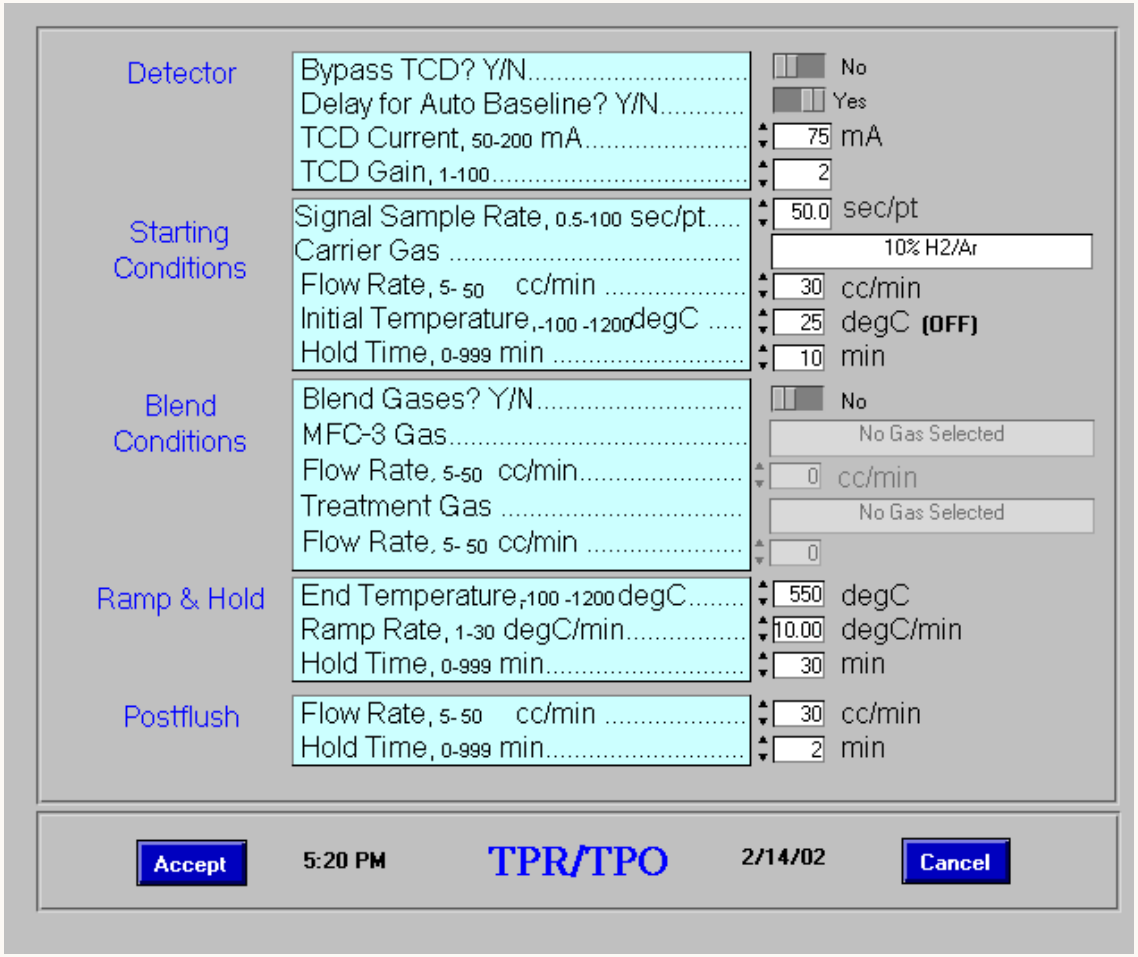
- R = pump; HP = high pressure
- Liquid pump
- High pressure reaction experiments (two in one: micro-reactor AND chemisorption)
- High Pressure characterization (to 100 bar)
- Auxiliary Detection Valve(s) for reaction experiments to external device
- Automatic pressure regulation

AMI 300 SOFTWARE

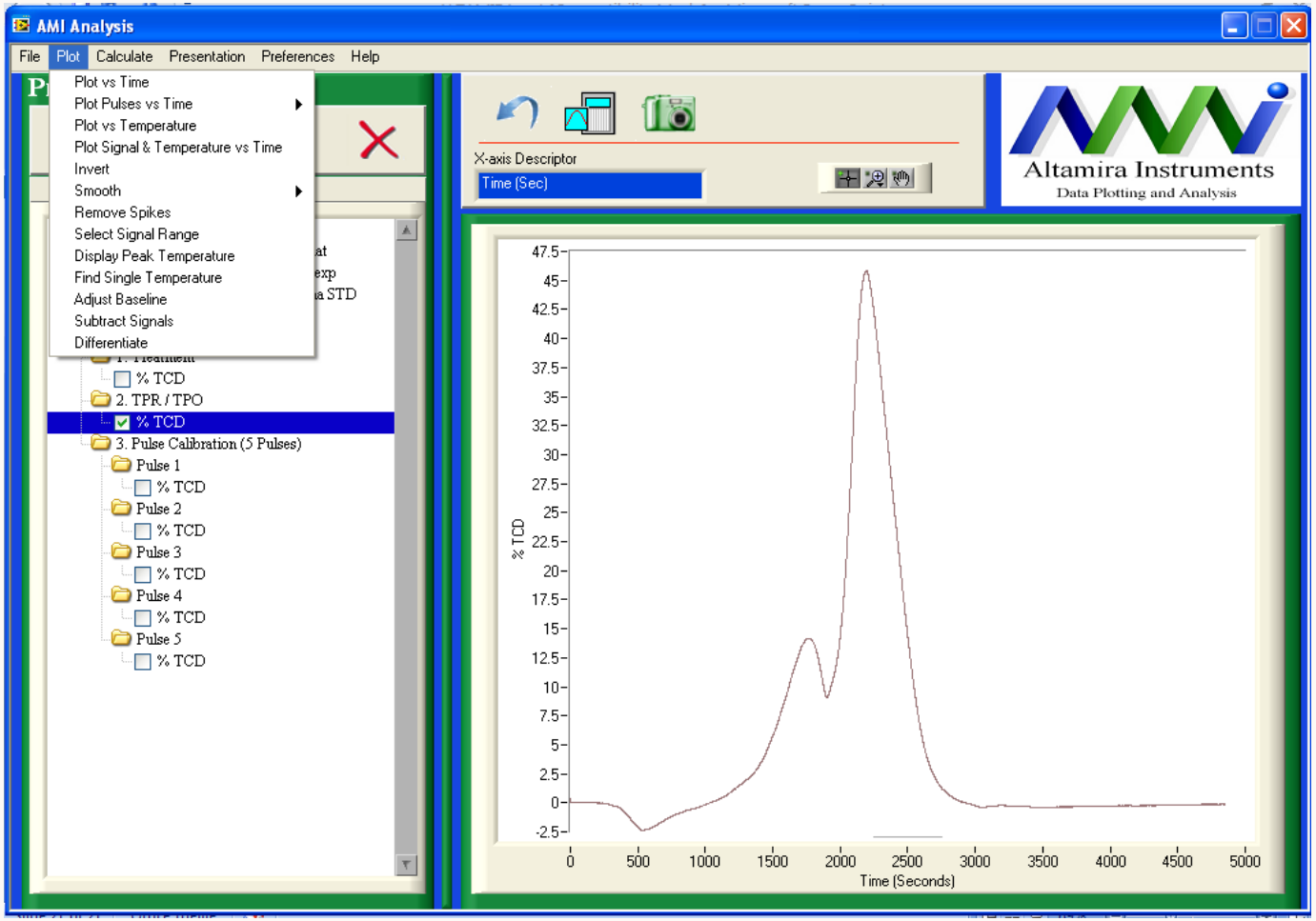


- Software operates on Windows platform via LabVIEW
- Fully Automated designed for unattended operation
- User Friendly experimental setup and control via P&ID-like screen
- Control and/or trigger MS, GC, FID, etc…

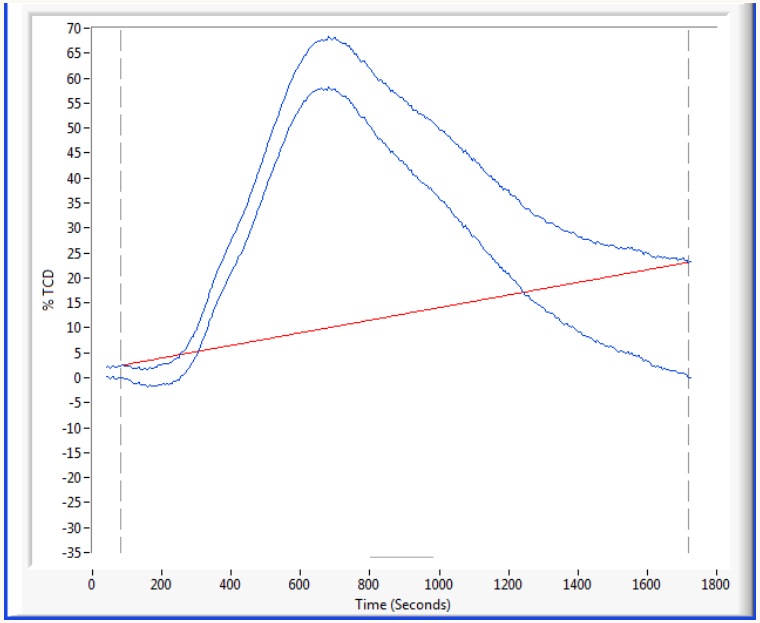
DEFINING PARAMETERS FOR PROCEDURES



ALTAMIRA ANALYSIS PROGRAM

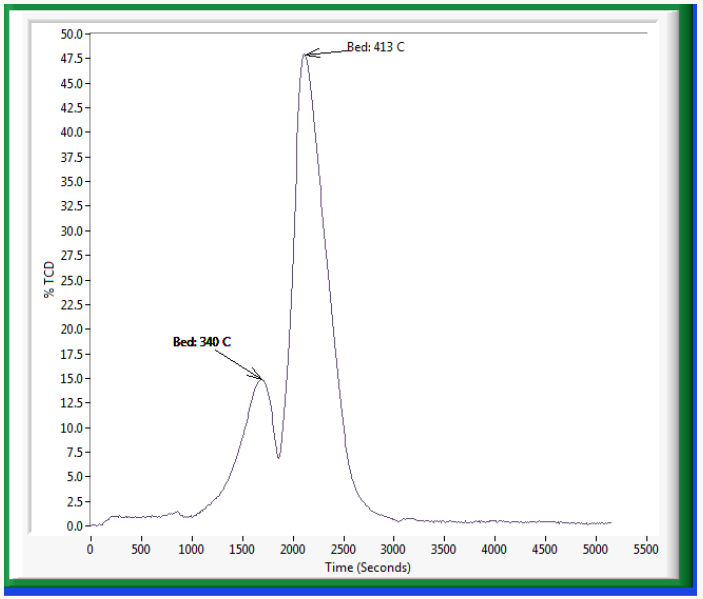


ADJUST BASELINE AND DISPLAY PEAK TEMPERATURES



- Adjust your baseline automatically by a simple click and drag!

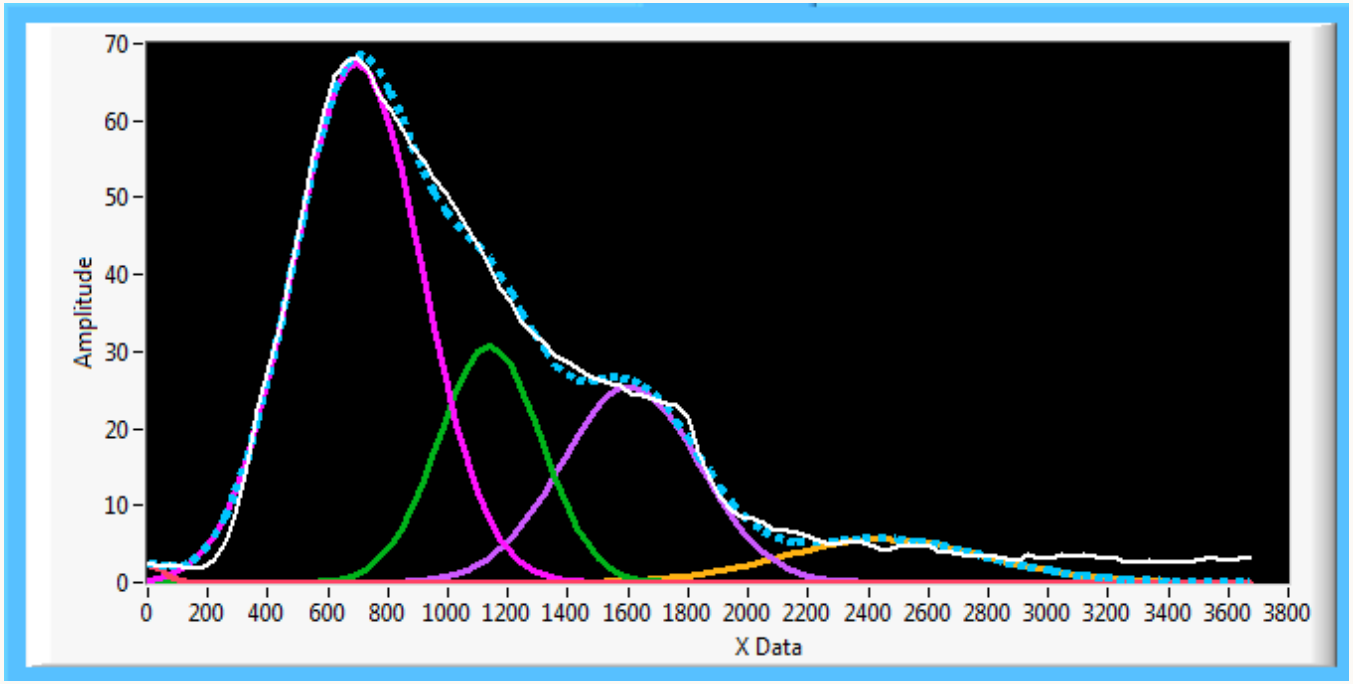
- Locate peak temperatures with a simple click of the mouse.



PEAK FITTING OF COMPLEX CURVES

Peakfit of a TPD

- Gaussian fit of a 64% Ni/SiO2 TPD
- R^2 = .9934



COMMON QUESTIONS: AMI

- How do the results between static and dynamic chemisorption processes compare?
- What kind of samples are suitable for testing?
  - Supported metal catalyst
  - Acid catalysts
  - Oxidation catalysts
  - Even some samples for gas-sorption measurements
- Spec-manship/Performance specifications?

µBENCHCAT REACTOR SYSTEMS

µBenchCAT

- Fully automated *standardized* bench-top reactor for catalytic studies.
- Gas or liquid phase possibilities
- Standard options for pumps, pressures, and material

µBENCHCAT REACTOR SYSTEMS

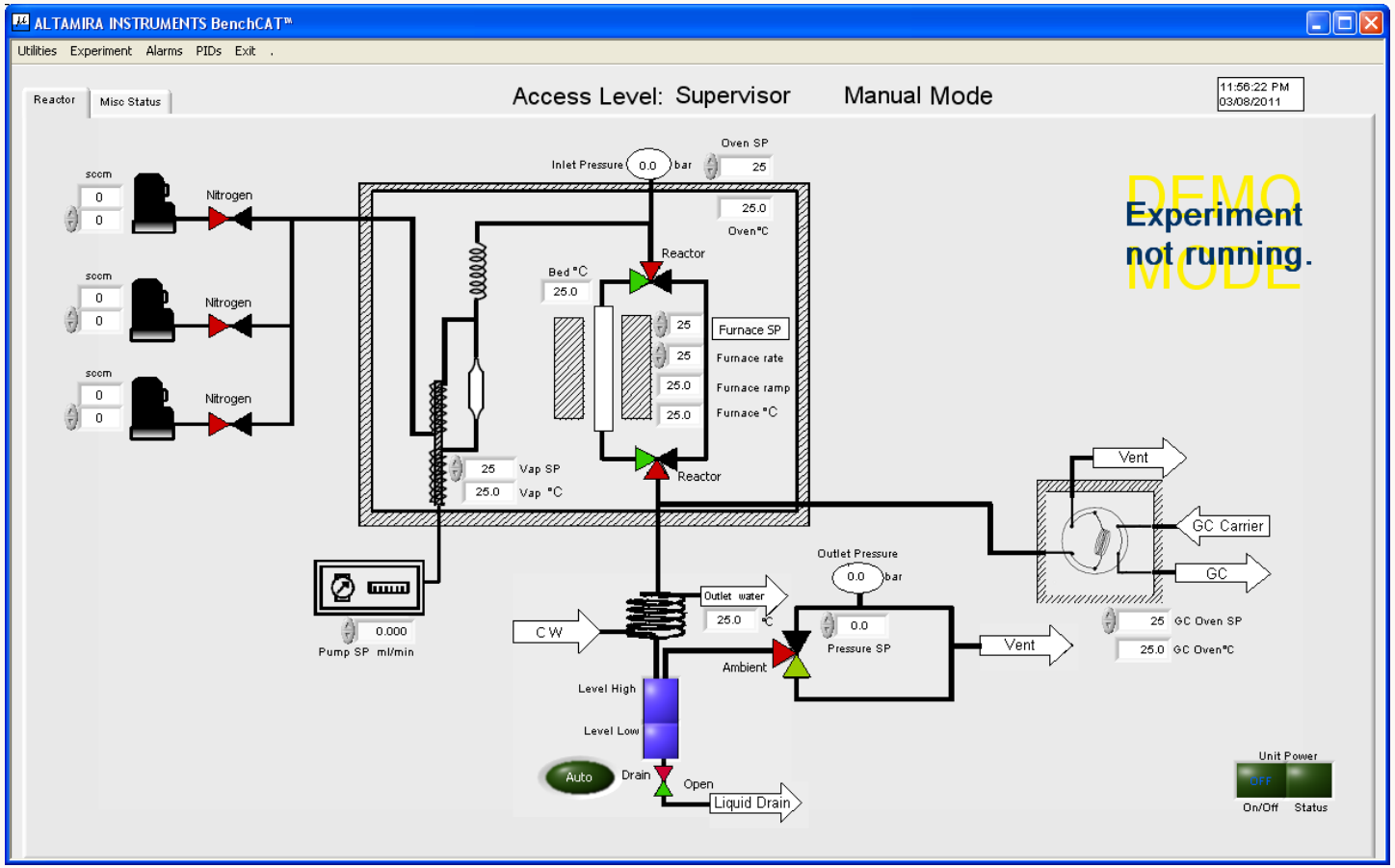
µBenchCAT

- Up to 6 gases
- Up to 2 liquids
- 650C to 1200C depending upon reactor material
- Heated oven to 200C for liquid/gas preheating and vaporizations
- Hardware, Firmware, and Software safety measures
- Connection to external analytical devices

WHY BUY a µBENCHCAT

- SAFETY COMPONENTS
  - Check valves on each gas inlet line
  - Hardwired TSS (redundant thermocouple)
  - Alarm Matrix for all process variables
  - Flow Safety (automatic positive shut-off valves)
  - Pressure Relief Valve(s) built in
  - PLC Alarms
  - Multiple User Profiles
- FUNCTIONALITY
  - MFCs are set once with an inlet pressure, no “ramp-up”
  - Every component is fused
  - Open frame design
  - Optional vaporizer design with carrier gas or atomizer
- CHEMISORPTION MODULE (external detector)
- PHOTO-CATALYSIS and RAMAN MODULE
- DUAL STATION MODULE (series/parallel)

µBENCHCAT REACTOR SYSTEMS



µBenchCAT

- Valve positions, flow rates, temperatures, pressures, and product sampling are all automated
- Experiments are easily written in minutes

COMMON QUESTIONS: µBENCHCAT

- Can a µBenchCAT be adapted to perform spectroscopic measurements?
- Can a system run in series or parallel mode?

BENCHCAT™ REACTOR SYSTEMS

BenchCAT

Fully automated *customized* reactor, for example:

- -Diesel Catalyst Studies
- -Fuel Cell Catalytic Membrane Studies
- -Fisher Tropsch Studies
- -Gasification
- -Hydrocarbon Dehydrogenation Studies
- -Reactions Studies of Acetic Acid

Application: Study of Reactions involving Membranes for Fuel Cells

-Custom designed stainless and quartz reactor for various temperatures and pressures
-Analysis performed upstream and downstream of membrane

Application: Trans-Esterification of Oil with Methanol (Biofuels)

-Liquid pressures to 350 bar
-Level Control for liquid collection

Application: Studies of Hydrocarbon Hydrogenation

-Pressures to 100 bar and temperatures to 800°C
-Multiple detectors: FID, GC
-4 station instrument

Application: Oxidation Reaction Studies

-Four station instrument with sampling valve to MS that allows for station queues.
-Added lexan covers for safety

Application: Pyrolysis of Methyl Chloride

-Fluid Bed Reactor
-Wet Test Meter for mass balance calculations

Application: Petroleum Studies

-Six-station plug-flow reactor in 1 oven
-Liquid sampling system with level control

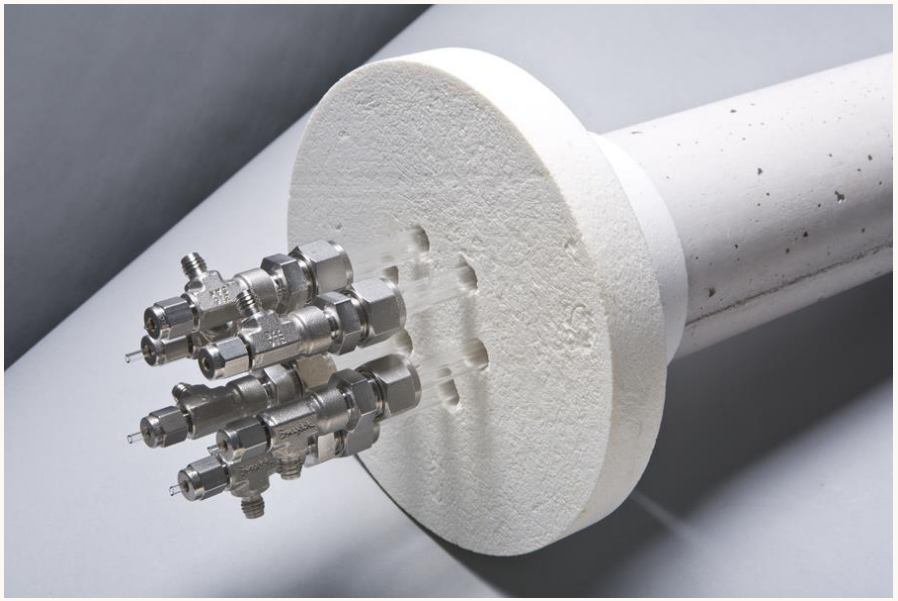
Application: Oxidation Reactions

-6 Stations in a single furnace
-Separate Electrical Cabinet

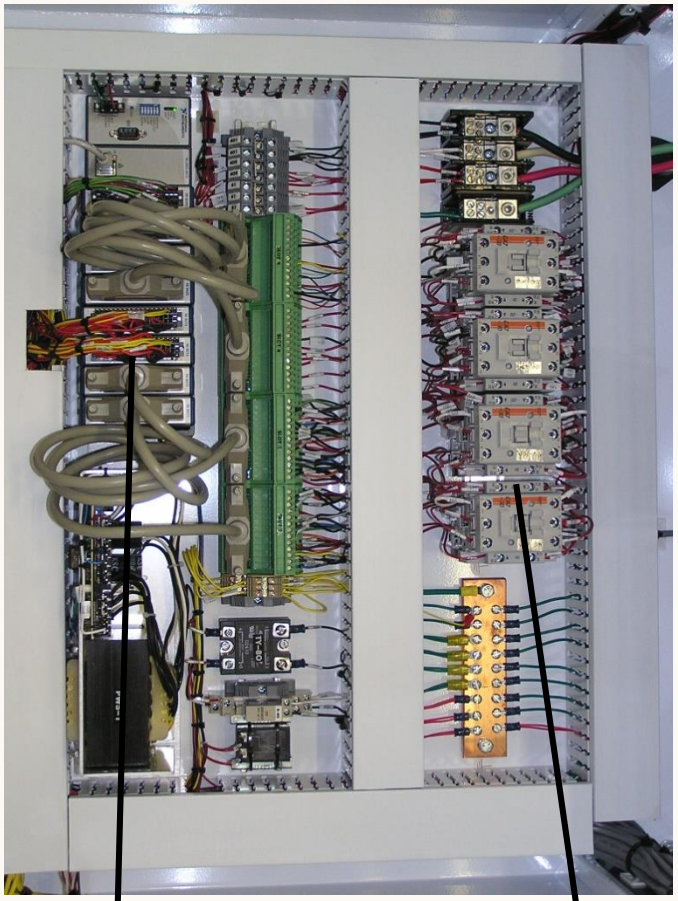
Application: Methanol Synthesis

-Slip-stream sampling to MS
-20 bar inlet charged to 100 bar before reactor with compressor
-Recycle loop with purge

Quartz Reactors in a Single Furnace

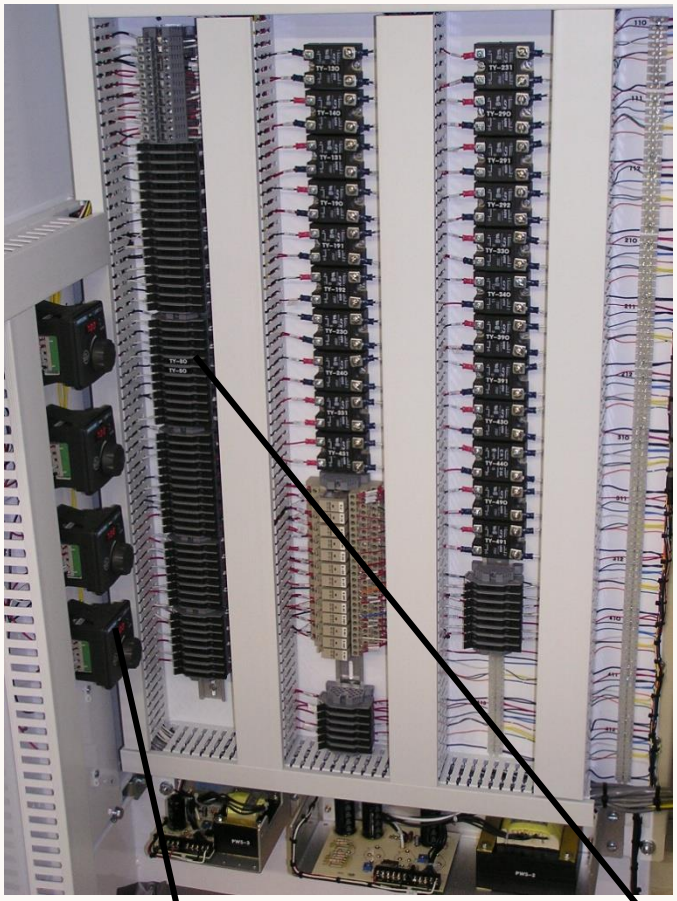


Inside the Electrical Cabinet



Data Sampling up to 50 Hz

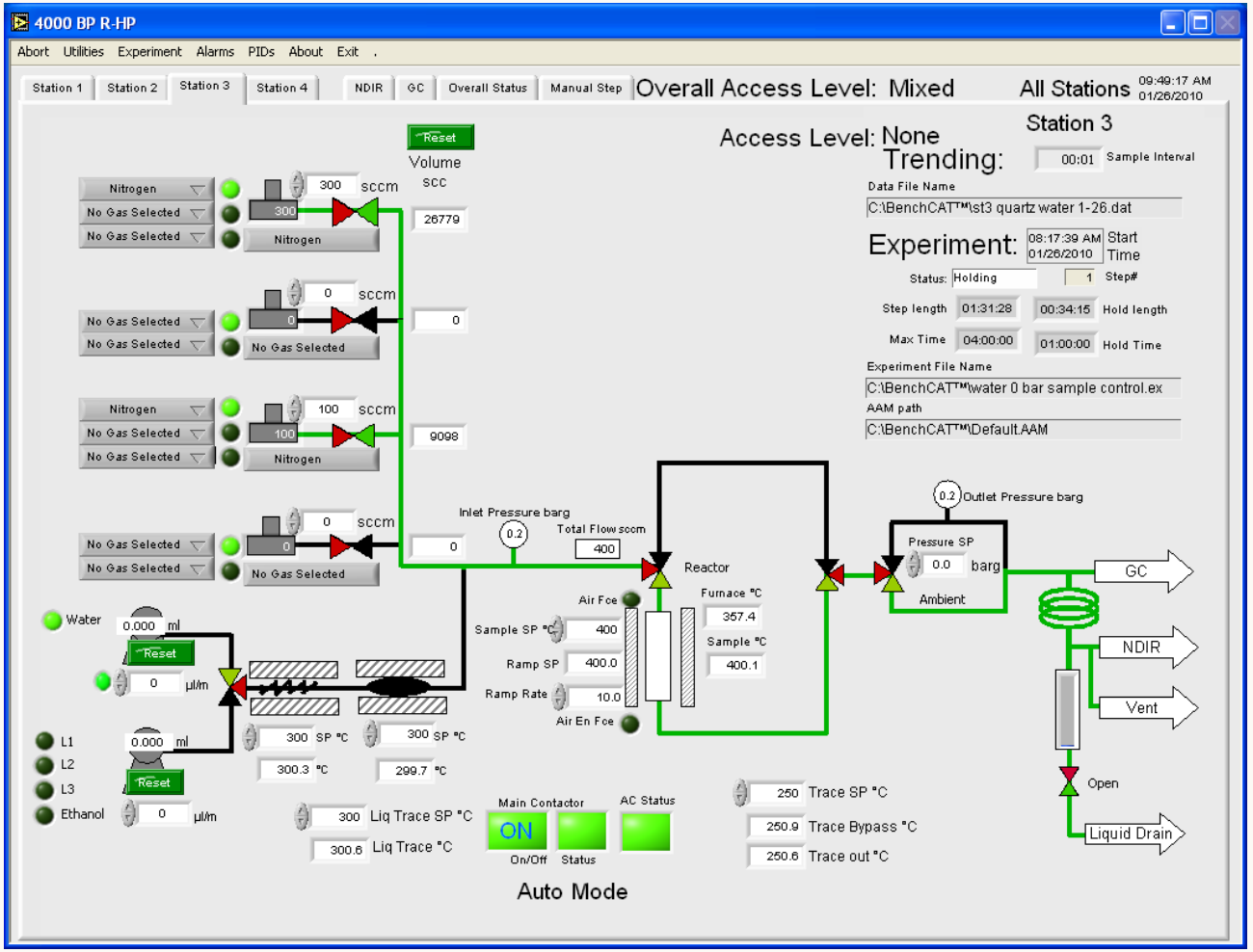
Independent power to all stations



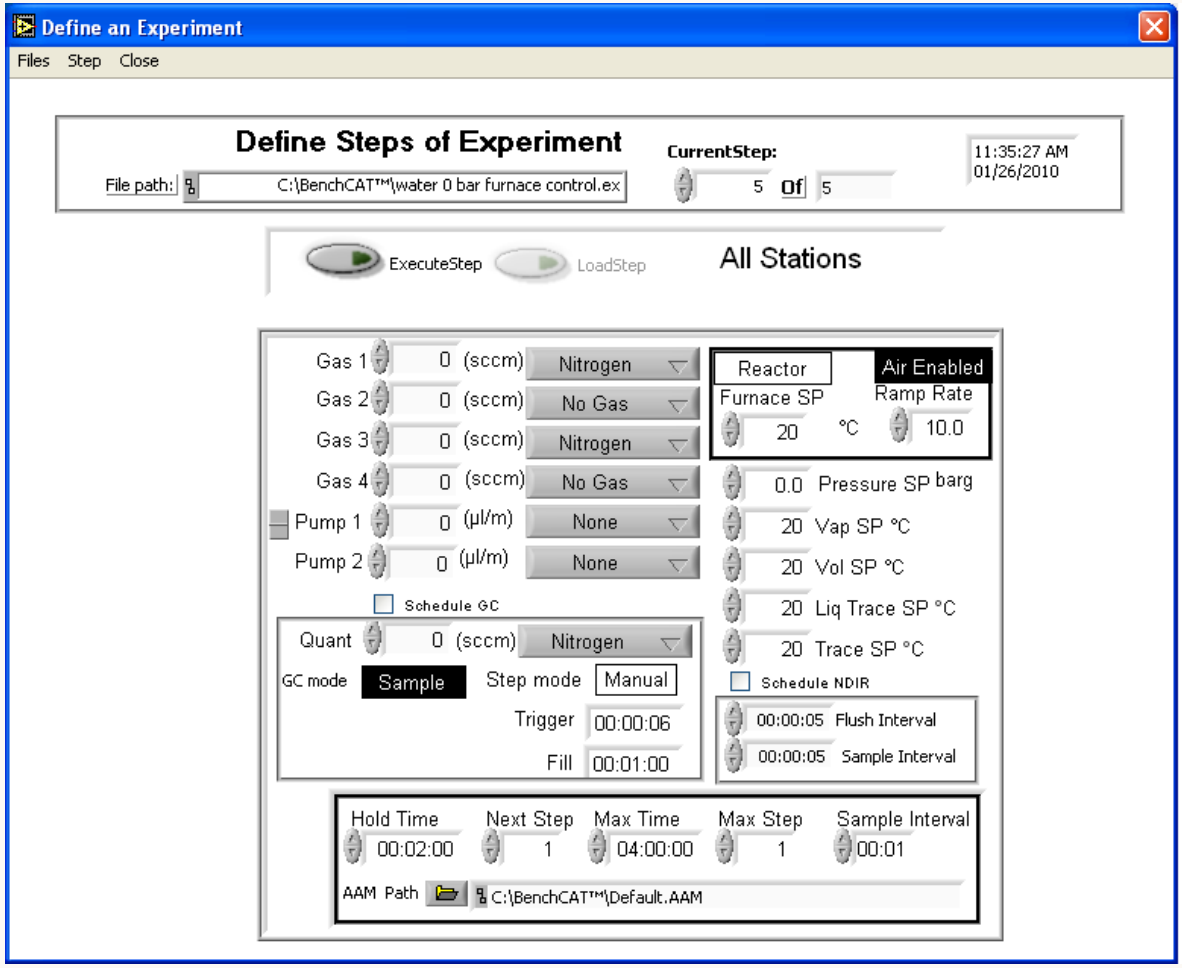
Temperature Safety Switches

Fusing on all heaters and circuits

BENCHCAT™ SOFTWARE



BENCHCAT™ SOFTWARE



COMMON QUESTIONS FOR A BENCHCAT CUSTOMER

- What are the temperature and pressure conditions?
- What is the catalyst loading?
- How many and what type of gases?
- How many and what type of liquids?
- Number of stations?
- Are there any physical size requirements?
- What external analytical devices do you need?
- What is the mode of the reactor?
  - PFR
  - CSTR
  - Trickle-bed

3P INSTRUMENTS

DEPARTMENT OF POROUS MATERIALS

THANK YOU!

Characterization of
particles · powders · pores

3P INSTRUMENTS

Characterization of

particles · powders · pores