Introducing the New HORIBA SA-9650 Dynamic Surface Area Analyzer

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First a review of some basics

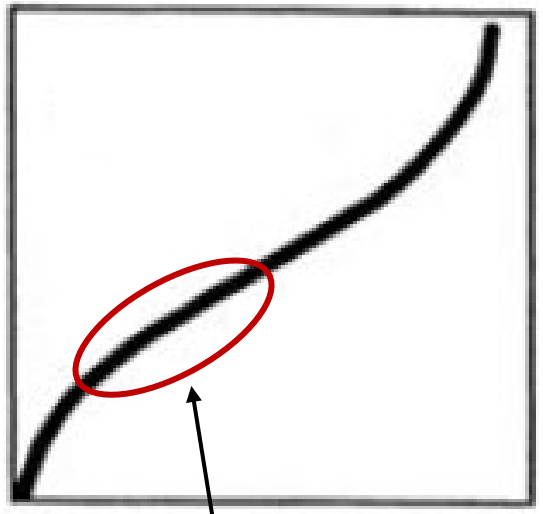
- **Gas adsorption** – the build up of gas molecules on the surface of a solid, which is reversable (leading to desorption)
- **Van der Waals forces** – unmet on the interface of a solid, they adsorb water or other vapors in nature
- **Preparation (Degassing)** – heating a sample while flowing gas over powder bed, removes naturally occurring adsorbates
- **Analysis** – utilizing cryogenic temperatures (typically liquid N_2 in a Dewar) the sample is exposed to a single or multiple pressure(s) or gas concentration(s) to determine adsorption data

Review of some basics continued

- **Isotherm** – the raw data from a test at constant temperature (typically 77.3K) plotted as volume of gas adsorbed (y axis) vs pressure (x).
- **Saturation pressure** – the pressure of a gas which is in equilibrium with its liquid – expressed as P_o
- **Relative pressure** – a means to "normalize" data from different labs which may be at differing atmospheric pressures where the absolute pressure is divided by the saturation pressure of the test gas, frequently written P/P_o. Typically expressed as 0.05, 0.1, 0.2, etc.

Isotherms and Surface Area

- The Isotherm is the raw data plot with volume of gas adsorbed (y axis) vs partial pressure or gas concentration (x axis)
- Surface area is calculated from the area of the isotherm where multiple layers of gas build up (linear region)
- Most typical model utilizes BET method
- Data collected in region from 0.05-0.3 pressure or 5 – 30% concentration
- Pressure is normalized by using saturation pressure (Po) as maximum pressure



Surface area data from this region of the isotherm

The BET equation (in linear form)

$$\frac{P}{V_a(P_o - P)} = \frac{C-1}{V_m C}\left(\frac{P}{P_o}\right) + \frac{1}{V_m C}$$

y = m(x) + b

Where: V_a = Volume of adsorbed gas

P = Absolute pressure

P_o = Saturation pressure

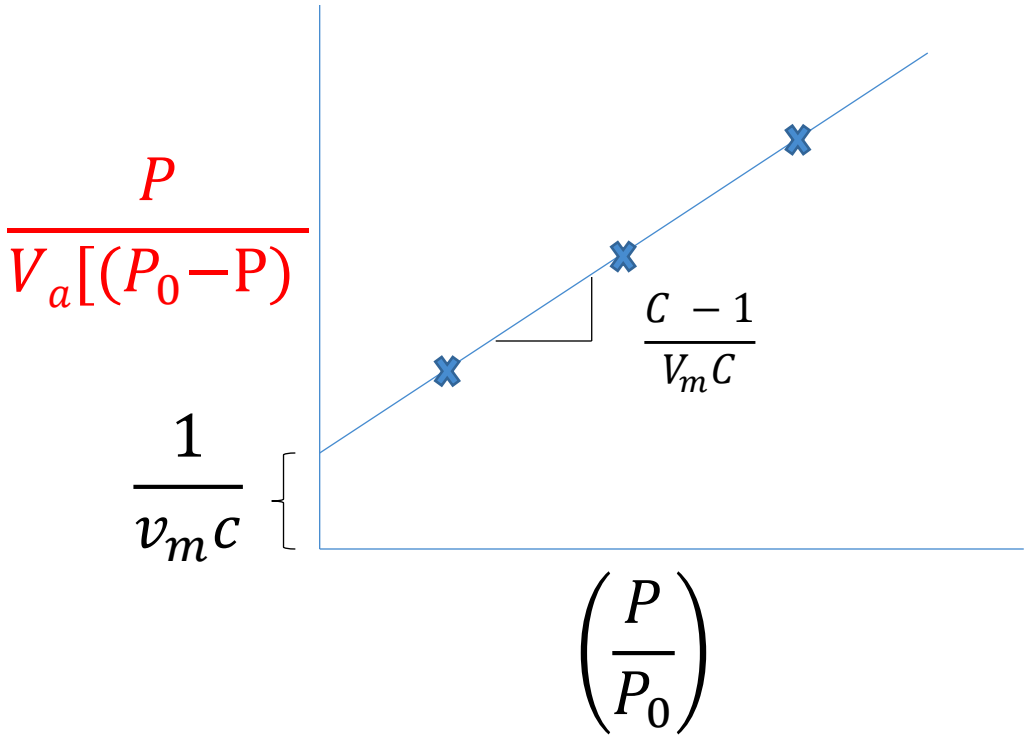
V_m = Mono-layer gas volume – what we're seeking!

C = BET C constant $\approx \exp\left(\frac{E_1 - E_L}{RT}\right)$

The BET equation for multi-point analysis

$$\frac{P}{V_a(P_o - P)} = \frac{C-1}{V_m C}\left(\frac{P}{P_o}\right) + \frac{1}{V_m C}$$

$$y = m\,(x) + b$$



And from this linear regression

$$\text{slope} = \frac{C - 1}{V_m C}$$

$$\text{intercept} = \frac{1}{V_m C}$$

$$V_m = \frac{1}{\text{slope} + \text{intercept}}$$

$$C = 1 + \frac{\text{slope}}{\text{intercept}}$$

Calculating surface area from V_m

$$S_{BET} = \frac{V_m * L * \alpha_m}{M}$$

Where:

S_{BET} – Total surface area under test

V_m – Monolayer volume

L – Avagadro's number - 6.02 x 10^{23} molecules/mol

α_m – Cross sectional area of gas molecule - 0.162 nm^2 for N_2

M – molar volume – 22414 L / mol

Dividing S_{BET} by sample mass gives specific surface area (m^2/g)

Single point calculation from the BET equation

- When C is very large – $1/V_mC$ approaches 0
- Meaning y-intercept is very close to 0
- Regression can be forced through the origin without substantial error in surface area result (change to slope)
- Likewise, when C is very large, C-1≈ C. Thus, $C-1/V_mC$ becomes $1/V_m$, simplifying our equation to:

$$\frac{\boldsymbol{P}}{\boldsymbol{V_a(P_o - P)}} = \left(\frac{\boldsymbol{1}}{\boldsymbol{V_m}}\right)\left(\frac{\boldsymbol{P}}{\boldsymbol{P_o}}\right)$$

Single point vs multi-point BET

- Single point is much faster than multi-point data collection
- Depending upon the material, single point and multi-point may be very close to one another
- Multi-point is typically more accurate since no assumption of a very large C value - meaning an accurate y-intercept for the regression analysis versus use of the origin
- However, single point is very repeatable and reproducible
- Thus, in a production environment or where quick material screening is required, single point provides a great advantage and provides useful results

Origin of surface area instruments at HORIBA

Built on a time proven dynamic SA platform!

- Originally developed in the US in early 1990's by Howard Jennings of Beta Scientific – then known as the SA-6200
- Beta Scientific distributed in Europe through ThermoFinnigan
- HORIBA Instruments originally agreed to distribute in 1995
- HORIBA Instruments purchased the product in 2005
- Improvements made to the 9600 over time, Version 1, 2 and current Version 3.
  - Software
  - Hardware and electronics

Dynamic adsorption? What is it and why?

Dynamic adsorption vs Volumetric adsorption

Dynamic

- Uses a flowing gas mixture over the sample
- Adsorption determined differentially using Thermal Conductivity Detectors (TCDs)
- Extremely fast data collection
- No need for volume calibration
- Elegantly simple design
- Robust and reliable
- Lower cost to purchase
- Lower cost to maintain
- Great for high throughput screening
- Great for production / QA / QC environments
- Single point or multi-point BET surface area

Volumetric

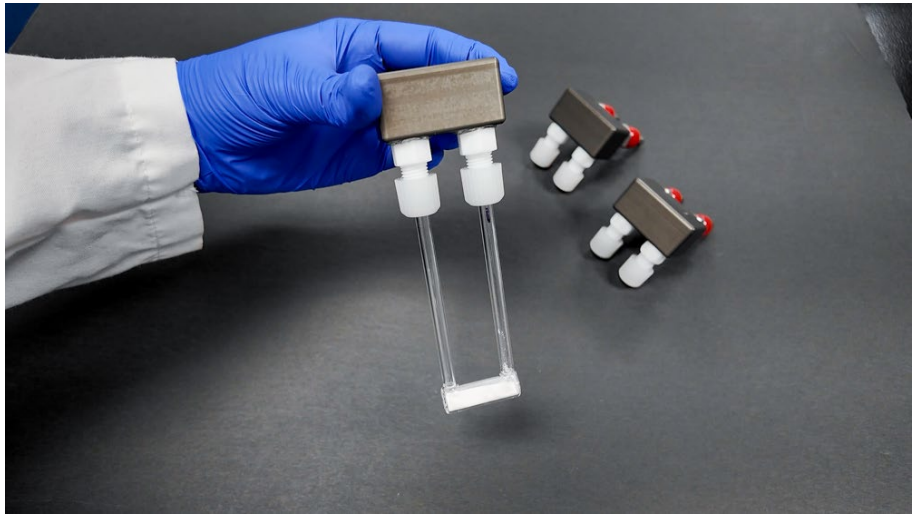
- Doses gas from a calibrated manifold
- Adsorption determined through recording of calibrated manifold, measured volume of sample holder and pressure change.
- Typically, slower data collection
- Volume calibration required (manifold stored, sample measured at outset of each test)
- More complex design – multiple valves, vacuum system and multiple transducers
- Typically, higher cost to purchase
- Higher cost to maintain
- More appropriate for research and pore size distribution measurements

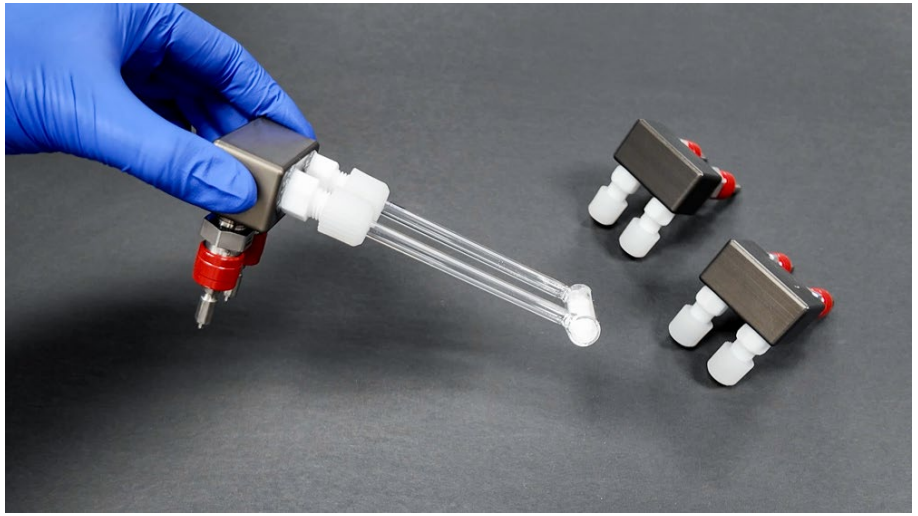
Sample preparation

Determine the empty (tare) weight of the U-shaped sample tube

Using the U-shaped sample tube and funnel provided, load the sample into the sample tube

Sample preparation





Using the nylon nuts and ferrules, attach the sample tube to the sample tube holder

Sample preparation

Install the sample tube and holder into one of the degas preparation stations, place the heating mantle around the sample tube and start the degas process with the controller

Analysis

When degassing is complete, transfer the sample tube and holder to the Test station and initiate the analysis

After automatic gas calibration, the Dewars of LN2 are automatically raised. Then adsorption process begins.

Introducing the New SA-9650

Dynamic Surface Area Analyzer

- New, modern design
- CE Mark – now available globally
- Safety covers / doors for degas and analysis compartments (latching)
- No side access required
- All models built with 3 preparation stations
- New PC based software

Introducing the New SA-9650

Degas / prep system

Internal computer control

- Everything you need in one small package
- On-board controller (or use external PC)
- Full keyboard integrated into instrument with LCD display
- Easy accessibility to degas and analysis stations

Analysis system

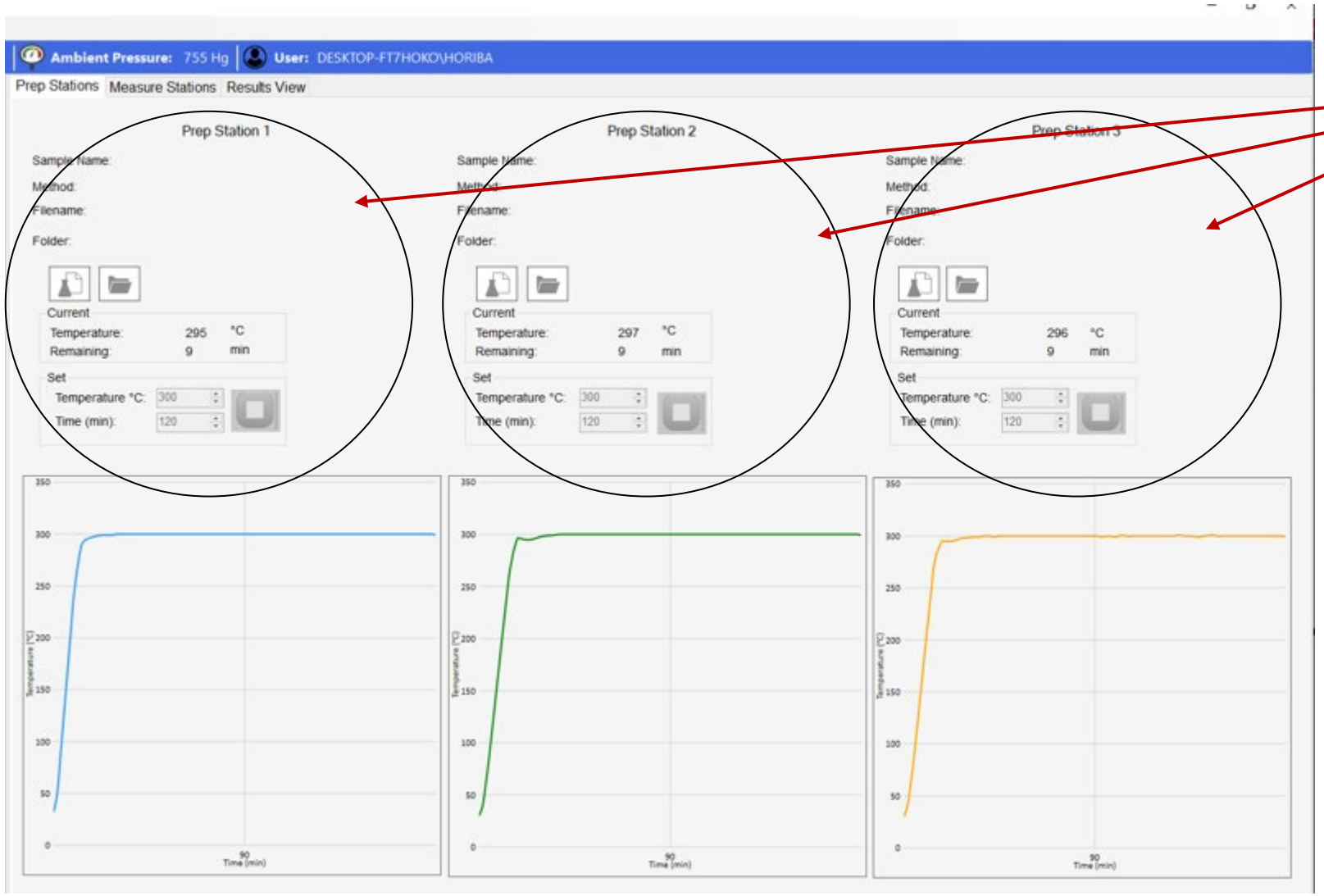
Flexible configurations to fit any need or budget

Four models to choose from

- SA-9650-1SP – Single analysis station, single point BET
- SA-9650-3SP – Three analysis stations, single point BET
- SA-9650-1MP – Single analysis station, multi-point BET
- SA-9650-3MP – Three analysis station, multi-point BET

- All configurations include 3 prep stations

Software Improvements – Prep Stations



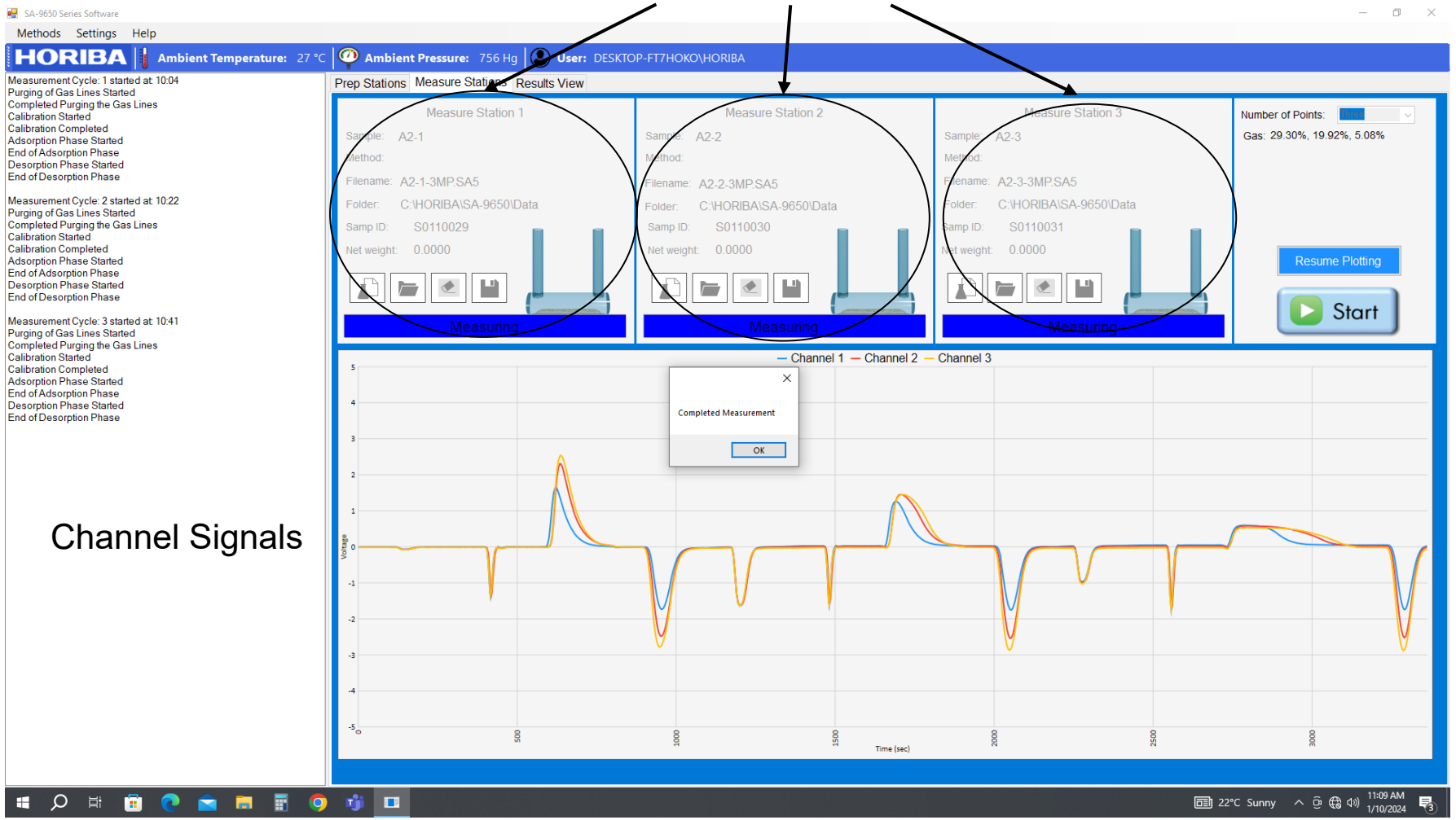
Prep Stations

Degas temperature vs time

Software Improvements - Analysis

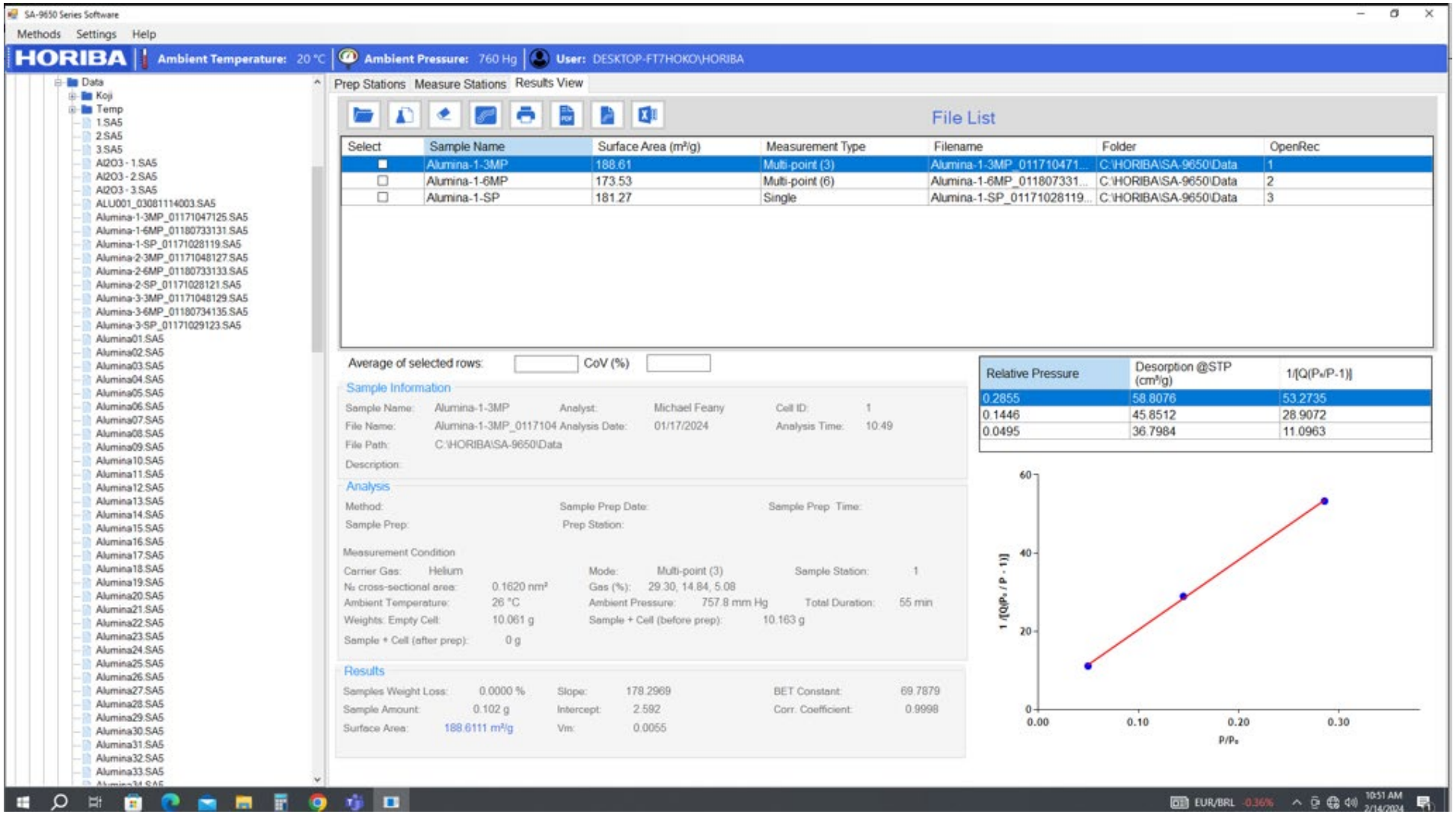
Operation Status

Analysis Stations



Channel Signals

Software Improvements – Results View



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Software Improvements – Report

HORIBA Scientific SA-9650 Series - Surface Area Analysis

HORIBA Instruments Inc. 9755 Research Drive, Irvine, CA 92618

Sample Information

Sample Name: Sample 220f | Analyst: Andy G | Cell ID:

Analysis Date: 01/29/2025 | Analysis Time: 10:13

File Name: Station 2 220f Monday 9 point SA

File Path: C:\HORIBA\SA-9650\Data

Description:

Analysis

Method: 220f Standard Method | Sample Prep Date: | Sample Prep Time:

Sample Prep: | Prep Station:

Measure conditions

Carrier Gas: Helium | Mode: Multi-point (9) | Sample Station: 2

N2 cross-sectional area: | Gas(%): Nitrogen 29.90, 14.94, 5.03

Ambient Temperature: 24 °C | Ambient Pressure: 755.6 mm Hg | Total Duration: 59 min

Weights: Empty Cell: 0 g | Sample + Cell (before prep): 0.0382 g | Sample + Cell (after prep): 0.0382 g

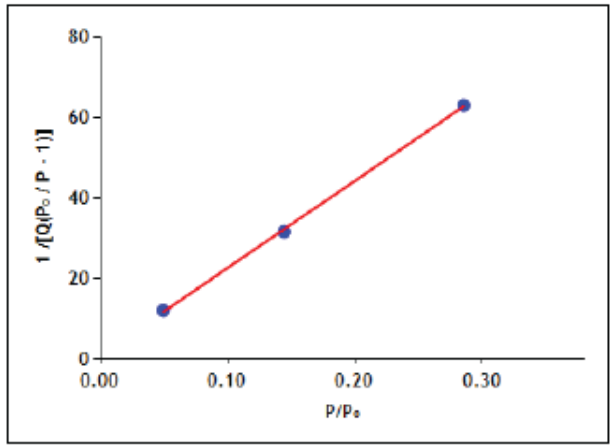
Results

Sample Weight Loss: 0% | Slope: 218.0822 | BET Constant: 217.7206

Sample Amount: 0.0382 g | Intercept: 0.9986 | Corr. Coefficient: 0.9999

Surface Area: 188.8532 m²/g | Vm: 0.0048

Relative pressure (P/Po)	Nitrogen volume desorbed @STP cm³/g	1/[Q(Po/P - 1)]
0.2854	52.3071	62.930
0.1448	44.4345	31.807
0.0495	35.3335	12.084



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Example data – Calcium Carbonate

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	2.28	2.47	2.13	
Test 2	2.31	2.36	2.2	
Test 3	2.21	2.3	2.12	
Average	2.27	2.38	2.15	2.26
STDEV	0.05	0.09	0.04	0.11
COV	2.26%	3.63%	2.03%	4.96%

Single point analysis

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	2.32	2.4	2.26	
Test 2	2.32	2.4	2.26	
Test 3	2.27	2.28	2.25	
Average	2.30	2.36	2.26	2.31
STDEV	0.03	0.07	0.01	0.06
COV	1.25%	2.94%	0.26%	2.54%

Multi-point analysis

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Example data - Kaolin

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	21.29	21.89	21.72	
Test 2	21.27	21.83	21.66	
Test 3	20.95	21.55	21.4	
Average	21.17	21.76	21.59	21.51
STDEV	0.19	0.18	0.17	0.31
COV	0.90%	0.83%	0.79%	1.42%

Single point analysis

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	21.47	21.11	21.8	
Test 2	21.26	21.77	21.48	
Test 3	20.66	21.37	21.06	
Average	21.13	21.75	21.45	21.44
STDEV	0.42	0.37	0.37	0.43
COV	1.99%	1.70%	1.73%	2.01%

Multi-point analysis

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Other materials

Material	Single point	Multi-point
Alumina	173.74	177.76
Bentonite	12.31	12.29
Calcium Hydroxide	13	13.35
Graphite	5.75	5.97
Hydroxyapatite	56.28	56.88
Kaolinite	7.9	8.1

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The New SA-9650

Dynamic Surface Area Analyzer

- Reliable, time proven platform
- Rugged performance
- Cost to purchase is very low
- Cost of ownership very low
- Smallest footprint / analysis port available
- Operated standalone or from PC
- Backed by HORIBA's global reputation for quality, support and service

Finally…..

Questions????

Contact HORIBA

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OR

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Omoshiro-okashiku

Joy and Fun

Terima kasih

நன்றி

Gracias

谢谢

Danke

Σας ευχαριστώ πάρα πολύ

Tack ska du ha

धन्यवाद

THANK YOU

شُكْرًا

Grazie

ขอบคุณครับ

Obrigado

Большое спасибо

ありがとうございました

Cảm ơn

Merci

감사합니다

Dziękuję