

# 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<sub>2</sub> 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<sub>o.</sub> 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<sub>m</sub> = 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

$$slope = \frac{C - 1}{V_m C}$$
$$intercept = \frac{1}{V_m C}$$
$$V_m = \frac{1}{slope + intercept}$$
$$C = 1 + \frac{slope}{intercept}$$

## **Calculating surface area from V**<sub>m</sub>

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

Where:

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- S<sub>BET</sub> Total surface area under test
- V<sub>m</sub> Monolayer volume
- L Avagadro's number 6.02 x 10<sup>23</sup> molecules/mol
- $\alpha_m$  Cross sectional area of gas molecule 0.162 nm<sup>2</sup> for N<sub>2</sub>
- M molar volume 22414 L / mol

Dividing  $S_{BET}$  by sample mass gives specific surface area (m<sup>2</sup>/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<sub>m</sub>C becomes 1/V<sub>m</sub>, simplifying our equation to:

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

# 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



- 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

## 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**



## **Software Improvements - Analysis**



#### **Software Improvements – Results View**

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ata	Prep Stations Measure Stations Re-	sults View				
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Alumina-1-SP_01171028119.SA5						
Alumina-2-3MP_01171048127.SA5						
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#### **Software Improvements – Report**

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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%

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%

#### Single point analysis

#### Multi-point analysis

## **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

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

#### 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



#### **Questions????**

#### **Contact HORIBA**

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