

Dynamic Dual Vapor/Gas Gravimetric Sorption Analyzer

Capabilities:

- Dynamic/Static isotherms and isobars
- Competitive Adsorption
- *In-situ* degassing
- Real time sorption kinetics



DVS Vacuum

Dynamic Gravimetric Vapor Sorption System

The DVS Vacuum is the only gravimetric vapor sorption system which offers static and dynamic sorption experiments. It accurately and precisely measures adsorption-desorption isotherms and adsorption-desorption isobars over a broad range of temperatures. It provides insights about the interactions and total adsorption capacities of studied materials with water vapor, organic vapors, gases and their mixtures. More importantly, it provides data on the fundamental understanding of adsorption processes which can be used in theoretical models. The DVS vacuum is versatile due to its unique upstream and downstream sorbate control for real-time adsorption and desorption kinetics. It can be used to mimic industrial conditions, and thus assess the performance of materials prior to their deployment in adsorption based technologies.

This is particularly attractive for chemical engineers and researchers pursuing novel energy-related applications through systematic tailoring of sorption properties to specific needs such as thermally driven heat pumps, adsorption based thermal storage systems, drying, purification and separation of gases and CO₂ capture from power plant flue gas. Additional DVS Vacuum applications are found in fundamental drying and sorption studies of nanoporous materials, composites, membranes, porous ceramics, activated carbons and pharmaceutical actives and processes. The DVS Vacuum's experimental flexibility enables studying adsorption and desorption under dynamic isothermal or isobaric conditions. It performs multi-component experiments using vapor and/or gas sorbate molecules with *in-situ* sample degassing up to 400°C and high vacuum. Multiple adsorption/desorption and sample regeneration cycles can be performed with real-time sorption kinetics and thermodynamics for sample masses from 5 to 1000 mg. This greatly expands the physisorption characterization capabilities available for such materials.

Zeolites, porous polymers, composites, Aluminophosphates (AlPOs) and Silica aluminophosphates (SAPOs), silica gels, activated carbons and Metal Organic Frameworks (MOFs) are important classes of materials used in various sorption based technologies. The combination of hierarchical pore structure control and selection of appropriate adsorbents enables entry and adsorption of small molecules on internal surfaces. Such processes are typically controlled by physisorption mechanisms governed by molecular size, polarity and chemical nature of the sorbent surfaces. In some cases specific chemical interactions can give rise to more strongly bound chemisorbed species, which are an essential part in the design of heterogeneous catalysts.

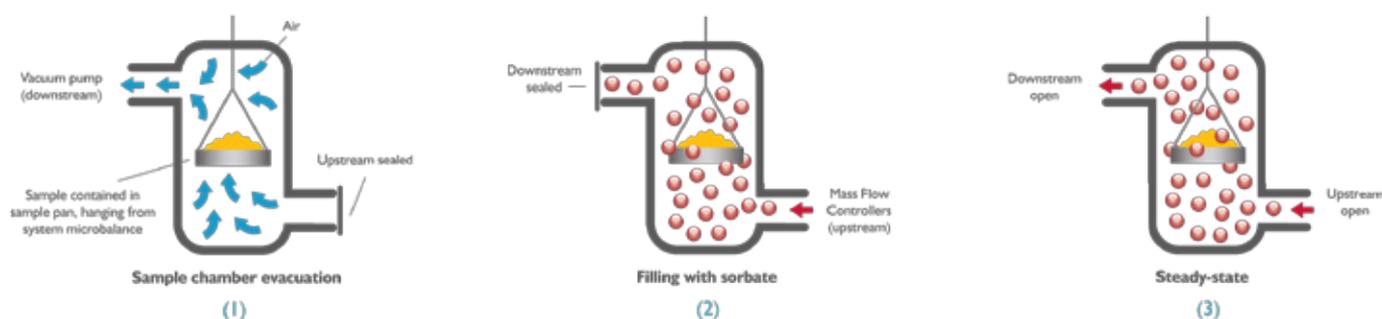
Key Measuring Capabilities

- Adsorption and desorption under dynamic/static, isothermal, or isobaric conditions.
- Competitive adsorption of two probe molecules (i.e. CO₂-H₂O, Toluene-H₂O, MeOH-H₂O).
- Perform multi-component experiments using vapor and/or gas sorbate molecules.
- Unique vapor temperature and delivery control.
- *In-situ* sample degassing up to 400°C and high vacuum (2x10⁻⁶ Torr).
- Multiple adsorption/desorption and sample regeneration cycles.
- Real-time sorption kinetics and thermodynamics.
- Experimental background pressures as low as 1x10⁻⁶ Torr.
- Adsorption measurements at relative pressures as low as 0.005 Torr.
- Minimum deliverable relative water vapor pressure at 25°C of 0.05%.
- Sample masses from 5-1000 mg.

The principle of DVS Vacuum

A unique principle of the DVS Vacuum is the ability to control and measure sorbate entry and exit flows simultaneously while recording changes in sample mass. The benefits include: broad range of sorption experimental partial pressures, real time sorption kinetics, sorbate molecule residence time control and thermal cycling. The DVS Vacuum also covers a wide range of sample and vapor temperatures allowing for sample thermodynamic properties determination. This includes capability for *in-situ* sample degassing at elevated temperatures and high vacuum. A wide range of molecules, both gas and vapor phase, are controlled through a sophisticated flow control system. Additionally, as the entire DVS Vacuum vapor generation delivery system and sample chamber are at thermal equilibrium in the temperature controlled enclosure, variable sorbate molecules and temperature can be easily changed without condensation and decontamination concerns. Tailoring the sorbate molecule gives access to many physico-chemical parameters.

The principle of dynamic adsorption

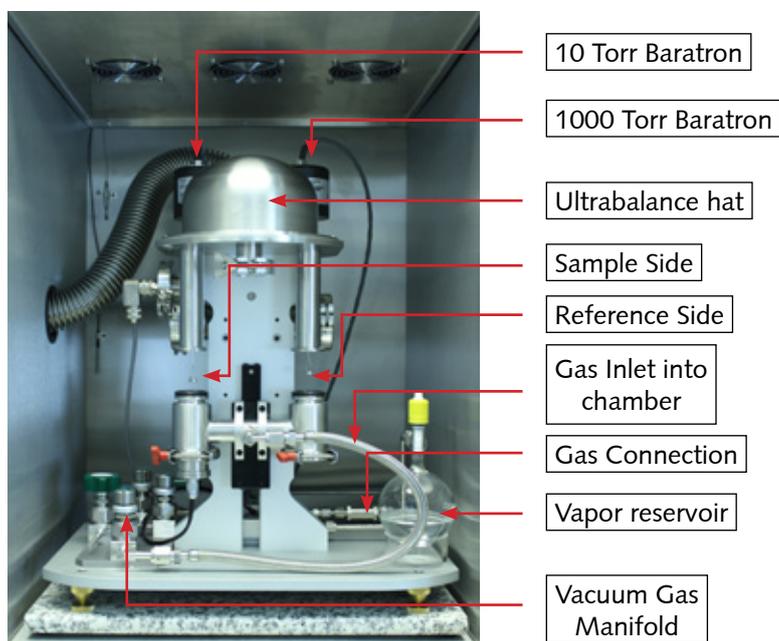


1. *In-situ* degassing of sample under high vacuum and high temperature. Downstream consisting of butterfly valve controlling pumping speed is fully open, while upstream controlled by mass flow controllers is closed.

2. Filling the chamber with sorbate molecules. Upstream is open, while downstream is closed.

3. Dynamic state whereby the amount of sorbate molecules entering and leaving the chamber is controlled simultaneously.

DVS Vacuum layout and capabilities



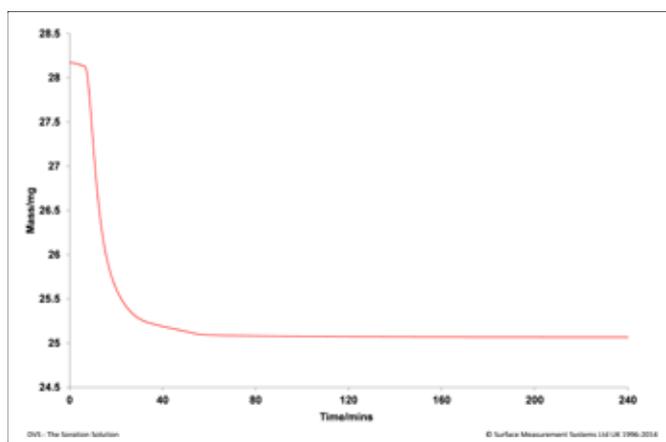
- Dynamic (or static) operational mode
- Upstream and downstream vapor/gas flow controls
- Lowest measurable pressure 0.005 Torr
- Smallest step size 0.05% P/Po
- Temperature controlled enclosure operating in the range from 20 to 70°C
- *In-situ* sample degassing up to 400°C (using pre-heater) and high vacuum
- Multi vapor and/or gas injection system for sorbates (2 gasses or 2 vapors or 1 gas and 1 vapor)
- Water vapor adsorption in the temperature range 20 to 70°C up to 90% P/Po and above 70°C in a limited P/Po range.
- Highly accurate Baratrons for pressure measurements
- Transducer for vacuum pressure measurement

Applications of DVS Vacuum

Drying kinetics and *in-situ* degassing of samples

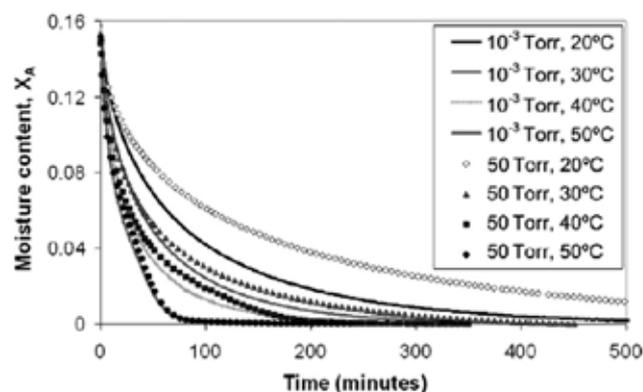
DVS Vacuum extends the capability of sample degassing to drying kinetics and mass equilibrium prior to sorption measurements. Samples can be *in-situ* degassed at temperatures of up to 400°C using various heating rates and vacuum pressures down to 10^{-7} Torr. This is immediately followed by sorption experiment at desired sorption temperature upon cooling the sample to experimental temperature. Sample transfer is not required for degassing.

Degassing of 13X Zeolite



Drying curve of 13X zeolite, which was degassed *in-situ* at 400°C and high vacuum.

Drying kinetics of a pharmaceutical powder

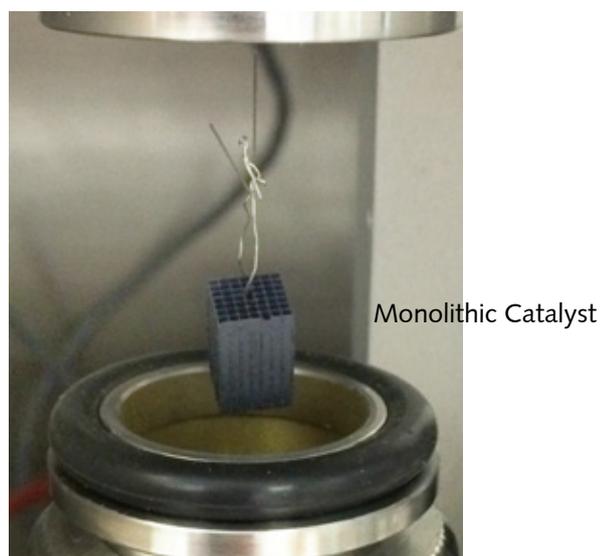


The effect of temperature and vacuum pressure is shown to provide information on dehydration kinetics of carbamazepine dihydrate.

High temperature vacuum preheater and housing for variable sample geometries



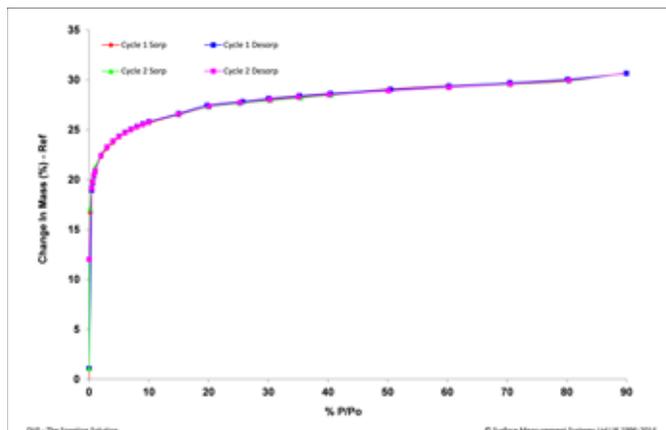
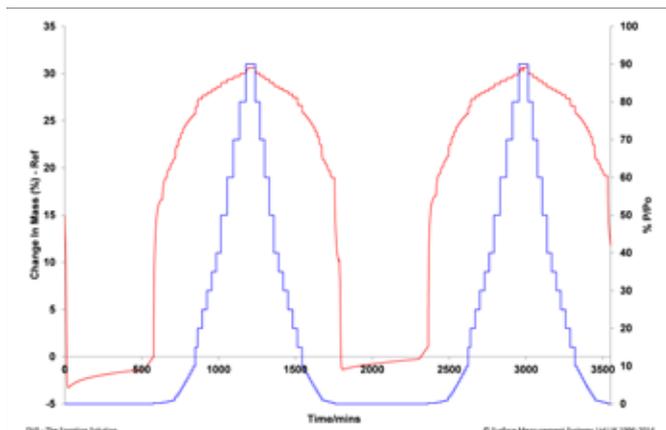
High temperature pre-heater for *in-situ* degassing/regeneration of samples up to 400°C. Temperature is measured by Pt-100 thermocouple, which is placed below the stainless steel sample pan.



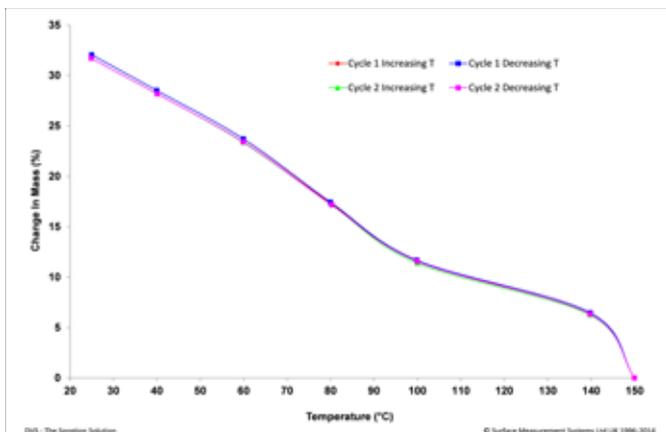
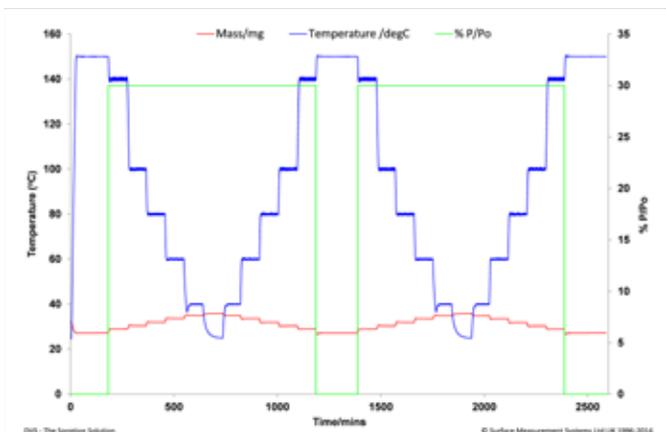
Variable samples such as catalytic converters, thin films and porous membranes can be measured in the system. The sample is connected directly on the hangdown wire. In typical experiments, where powders, pellets or beads are used, samples are loaded in stainless steel pans. Other experimental cells are available for a wide range of sample types and applications such as diffusion/permeation and Knudsen vapor pressure.

Water vapor adsorption in zeolites and MOFs for thermal adsorption storage and heat transformation

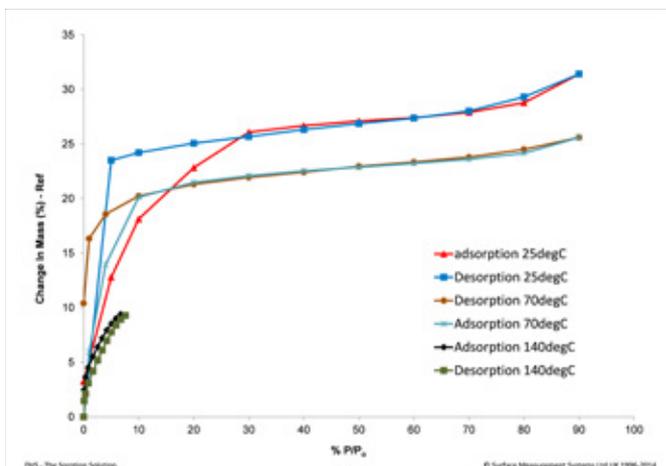
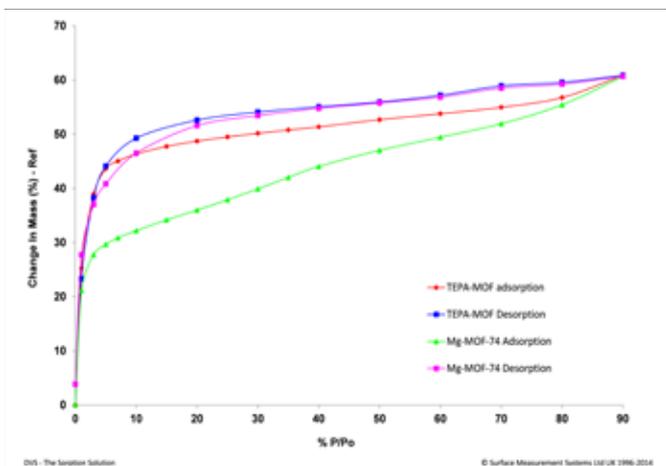
Micro- and meso-porous materials such as zeolites 4A, A10 Sylosiv, 13X, MCM-41 respectively, aluminophosphates including SAPO-34, and MOFs have gained much interest recently due to their promising applications in novel heating and cooling technologies, exploiting thermo-adsorptive effects. These materials show interesting sorption properties; high or low uptakes in the low partial pressure range in which water can be considered as an adsorbate for cooling applications. Therefore, adsorption by these materials in the presence of water vapor is extensively studied in order to understand water vapor sorption kinetics at low partial pressures, the total adsorption capacity, stability of material after several adsorption/desorption cycles over wide range of temperatures and energy requirements for the regeneration of adsorbents. In addition, the selection of various probe molecules and their mixtures (water- alcohol) give access to physico-chemical parameters that are critical for understanding the material performance in extreme conditions. Examples of isobars and isotherms including sorption kinetics of promising adsorbents are shown below.



A10 (powder, Grace Chemicals) water vapor sorption at 40°C. Prior to sorption measurements A10 was *in-situ* degassed at 180°C under high vacuum of 10^{-5} Torr for 480min and subsequently cooled down to sorption temperature of 40°C. Sample was regenerated between cycles using the same degassing conditions. Resulting water adsorption-desorption isotherms of A10 is shown on the right.



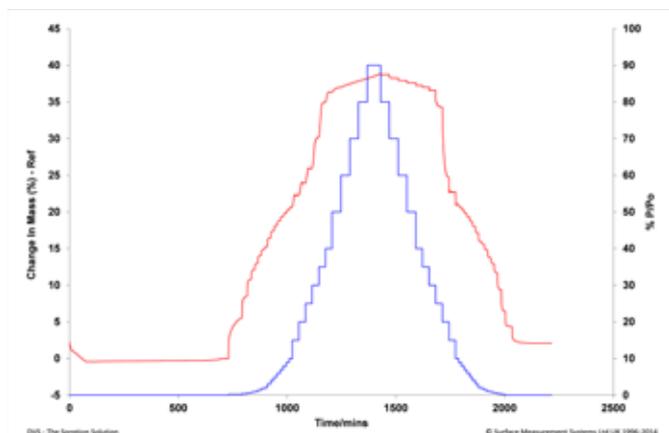
A10 water vapor isobars at 7.14 Torr (Figure left). Two cycle of A10 showing change in the mass (in red) during stepping down (adsorption) and stepping up (desorption) temperature (in blue) at pressure (in green) of 7.14Torr. A10 water vapor isobar at 7.14 Torr (Figure right).



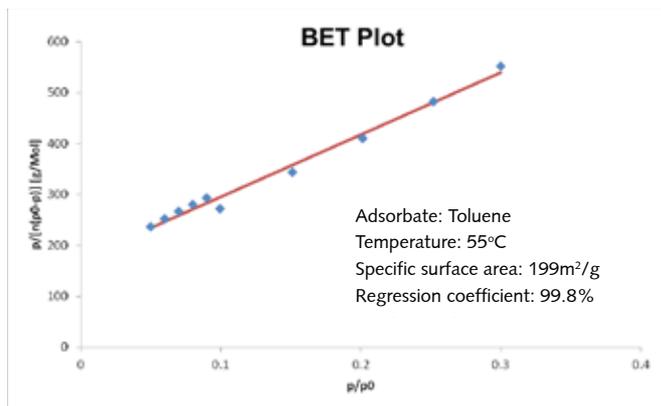
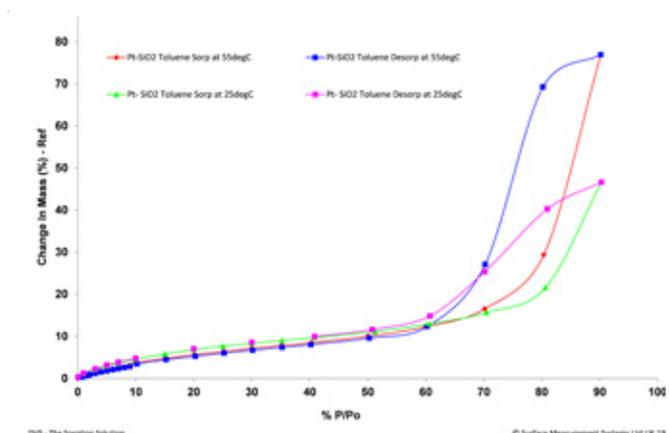
Comparison of 25°C water vapor adsorption-desorption isotherms for Mg-MOF-74 and TEPA-MOF-74. Mg-MOF and TEPA-MOF were prepared by Xiao Su & Lev Bromberg from MIT, Chemical Engineering. (Figure left). Comparison of 4A (Sigma Aldrich, 1/16inch diameter, 1-2mm pellets) water adsorption- desorption isotherms measured at 25, 70 and 140°C (Figure right). The large hysteresis at 25°C is due the fact that mass equilibrium at low P/P0 was not reached.

Molecular separations of catalysts and zeolites

A wide range of sorbate molecules including water, organic vapors (i.e. alcohols, toluene, benzene, cyclohexane, xylene, acetaldehyde, etc.) and gases are controlled through a sophisticated flow manifold. The selection of sorbate molecules for specific adsorption based applications gives access to many physico-chemical parameters, such as size selectivity and or chemical selectivity of the sample.



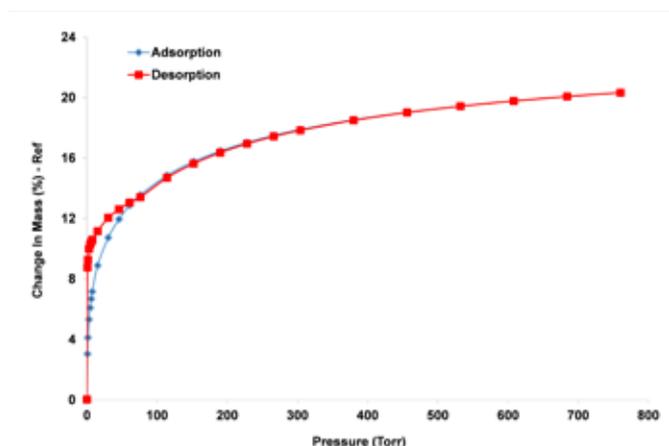
Zeolite Y benzene sorption at 25°C. Adsorption-desorption cycle showing benzene sorption kinetics (left) and corresponding isotherm (right) at 25°C. The inset shows the isotherm in the Henry region where pressure was increased by 0.2 % P/Po.



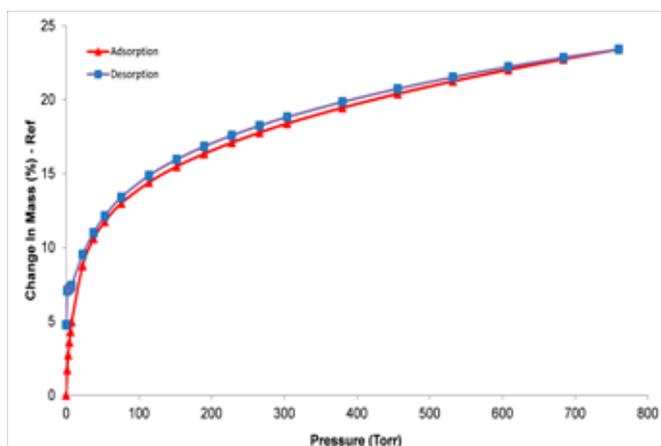
Comparison of Pt-SiO₂ toluene adsorption-desorption isotherms at 25 and 55°C (left). Determination of specific surface area using BET equation for toluene sorption at 55°C (right).

MOFs and zeolites as adsorbents for CO₂ capture and storage

MOFs and zeolites are promising porous crystalline materials for CO₂ capture. Both materials are strong candidates due to high adsorption capacities, the economic feasibility of its reagents as well as ease of synthesis.



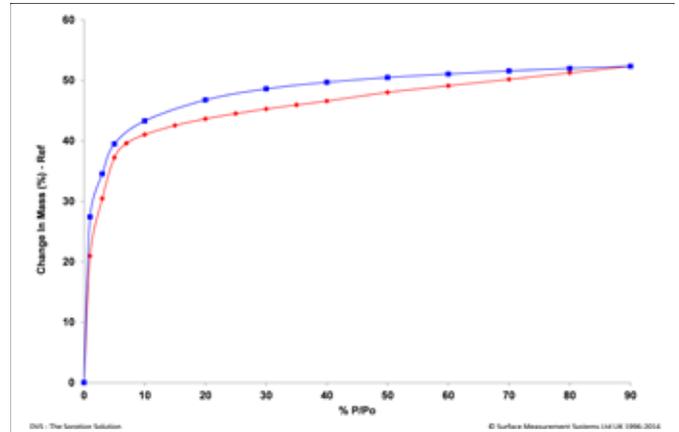
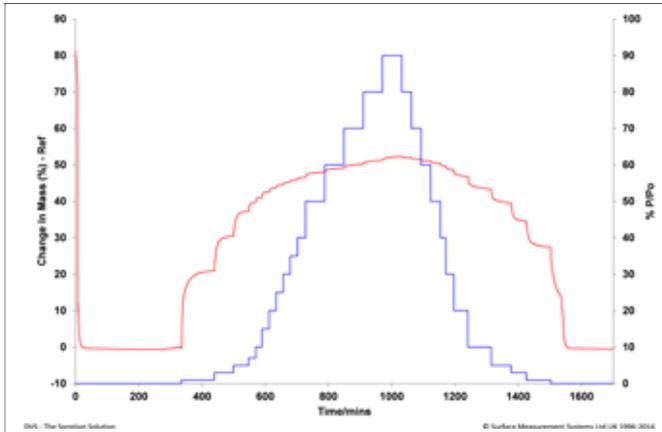
13X adsorption-desorption of CO₂ in the pressure range from 0 to 760 Torr at 25°C. 13X was in the form of beads having 1-2mm diameter.



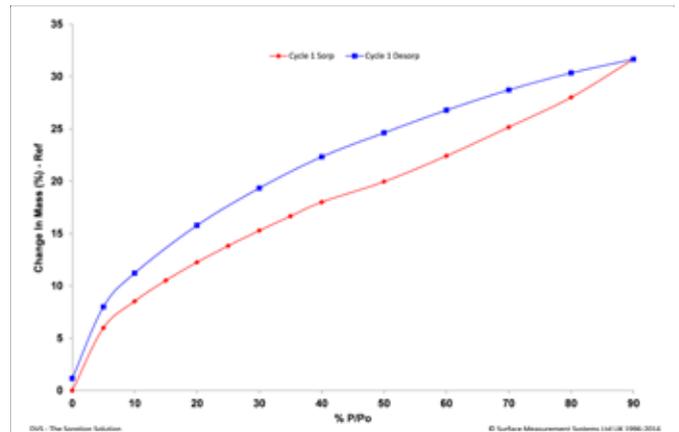
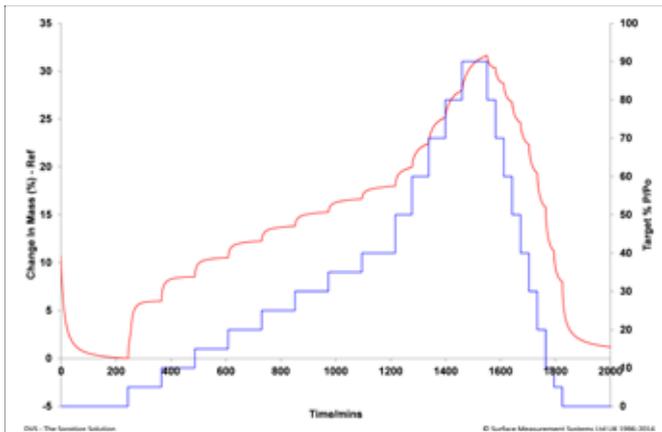
Mg-MOF-74 adsorption-desorption of CO₂ in the pressure range from 0 to 760 Torr 25°C.

Co-Adsorption on MOFs and fibers

Many industrial processes, such as gas purification, drying, filtration and carbon capture, use MOFs, porous solids or porous polymers to adsorb gases or organic molecules. Water vapor often co-exists with gases or organic molecules and its concentration can vary from very low to saturated. Therefore, it is important to understand the effects of the presence of water vapor on adsorption of gases or organic molecules. DVS Vacuum can be used to study co-adsorption of two adsorbates over broad temperature and relative pressure ranges.



50/50 CO₂/H₂O Mg-MOF-74 sorption at 25°C. Sorption kinetics shown on left and corresponding isotherms on right with adsorption in red and desorption in blue.



Natural fiber 50/50 Toluene/Water sorption at 25°C. Prior to sorption measurements the fiber was dried at 25°C and under high vacuum for 240min. Adsorption/desorption cycles showing water-toluene kinetics (left) and resulting isotherms (right).

High temperature preheater for *in-situ* degassing/activation

Maximum temperature: 400°C
Heating ramp rates: up to 10°C/min
Sensors: Pt-100 thermocouple

Gas /vapor injection system (Upstream control)

Injection system consists of mass flow controllers (upstream) which can deliver vapors and gases of desired flow rates.

Number of Mass flow controllers: 2

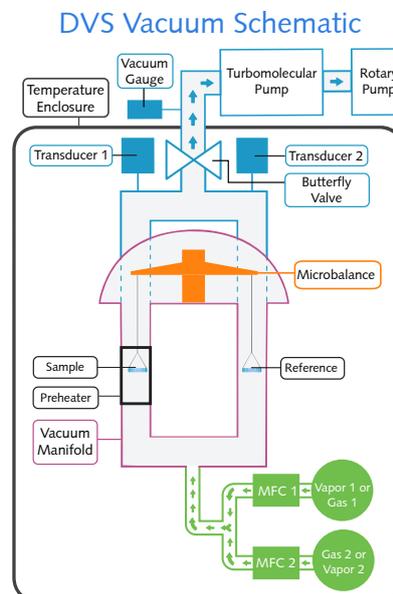
Full scale: 200 sccm

Adsorptive species: organic solvents i.e. water, toluene, methanol, ethanol, benzene, acetaldehyde

Gases: CO₂, N₂, 2000 ppm NH₄, H₂S

Butterfly valve (downstream control)

The butterfly valve regulates the amount of vapors or gases in the system by opening and closing depending on the pressure inside the chamber, while total pressure is kept constant.



Water vapor and organic vapors

Water vapor is generated up to 90% P/Po in the temperature range between 20 to 70°C. Water vapor can be generated in a limited P/Po range above 70°C up to 150°C. Organic vapor generation is limited to solvents' boiling point temperatures.

Gases

Gas adsorption up to atmospheric pressure can be performed using pure or mixtures of gases.

Vacuum system

Vacuum pump: rotary vane pump

Ultimate vacuum 1x10⁻³ Torr

High vacuum pump: Turbomolecular pump

Ultimate vacuum: 4x10⁻⁸ Torr

Vacuum stand

Manifold: 316 stainless steel

Diaphragm valves orbital welded

Seals: Viton, Kalrez (MFCs), Cu gaskets

Tubing: 1/4 inch stainless steel

Specifications

Temperature

Temperature controlled enclosure
Control range: 20°C to 70°C
Regulation accuracy: $\pm 0.2^\circ\text{C}$
Enclosure also provides anti-condensation protection.

Weight measurement

High Resolution microbalance
Sample mass: between 1 and 1000mg
Mass change: $\pm 150\text{mg}$
Resolution (precision): $0.1\ \mu\text{g}$
Peak to peak noise: $\leq 0.3\ \mu\text{g}$

Pressure measurement

1000 Torr Baratron full scale from 0.01 up to 1000 Torr (standard)
10 Torr Baratron: full scale from 0.005 up to 10 Torr (standard)
Other ranges available upon request (100 and 500 Torr)
Accuracy: ± 0.5 of Reading
Resolution: 0.01% of full scale

Vacuum pressure measurement

Vacuum pressure transducer: full scale from 1×10^{-8} Torr up to 760 Torr

Computer hardware and software

The system is fully automated and controlled by purpose-built software. Data can be analyzed in real time using analysis software.

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