Surface Measurement Systems
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Overview
Note 1202

TERMINOLOGY AND TECHNIQUES FOR MEASURING THE SORPTION OF VAPORS AND GASES

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Introduction

There are several commonly used experimental techniques that can be used to measure gas and vapor sorption, including **volumetric** (sometimes called manometric), **gravimetric** (DVS) and **chromatographic** (sometimes called breakthrough) techniques. These techniques have wide practical applicability, first in determining fundamental material properties such as surface area, porosity, surface energy, hygroscopicity, contact angle and second in assessing a material's performance towards various applications that rely on sorption behavior – heterogeneous catalysis, API stability, water harvesting, gas separation, etc.

The choice of experimental technique will determine the type of information obtained and have different limitations and inherent advantages. Some examples of parameters that inform the choice of technique include:

- Measurements on large or small volumes of sample, or samples with very high or very low surface area and porosity.
- Sample sensitivity to temperature, vacuum, and pressure changes.
- Importance of mimicking process and real-world conditions – multiple gases/vapors, presence of air and humidity, constant or varying temperature and pressure, etc.
- Importance of determination of sorption kinetics, equilibrium times, diffusion, and general time-resolved data.
- Number of samples and number of gases/vapors to be analyzed at the same time.
- Interest in probing the material's fundamental properties – such as density, surface area, pore size distribution, surface energy, specific gas-material interaction properties, cohesion & adhesion, etc.
- Options to combine multiple measurements at the same time (hyphenations) e.g. XRD, Raman, IR, calorimetry, etc.
- Complexity, cost, and ease of use of the instrument.

This SMS Overview Note will start with an explanation of associated terminology around the important sorption measurable variables and modes of controlling the introduction of probe molecules. It then provides a global view on the aforementioned measurement principles and discusses their advantages and disadvantages.

Note! Throughout this document, the concepts of gas and vapor will be used interchangeably, as referring to molecule in the gaseous phase used to probe the material, or the *sorbate*. In a strict definition, a gas is a fluid which cannot turn into liquid by increasing its pressure – i.e. a fluid above its critical temperature.

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Terminology governing sorption

Sorption is the accumulation of fluid phase molecules on a surface, in a pore or in a material's bulk. It includes the terms **adsorption** and **absorption** which are often specifically used for surface and bulk sorption. The extent of sorption is generally influenced by only three variables – number of probe particles coming into contact with the material, their kinetic energy and the nature of their interaction.

Units

The average kinetic energy of all molecules in the system is unambiguously defined by ***temperature***. Temperature is represented in Kelvin (K, the SI unit), degree Celsius (°C) or degree Fahrenheit (°F). Challenges associated with accurate temperature measurement and its homogeneity are not discussed here.

On the other hand, the number of target probe molecules which interact with the material at any point can be reported in a variety of ways, with terms encountered such as ***absolute/partial pressure, relative pressure, humidity, water activity, volume/molar fraction, concentration,*** etc. All these terms refer to the same concept and they are often a source of confusion.

In a fundamental thermodynamic sense, the ***pressure*** of a gas/vapor is the force exerted by molecules hitting a container's walls and the preferred way refer to this sorption parameter. The term ***absolute pressure*** is sometimes used to make the distinction clearer from other pressure modes. Absolute pressure is usually measured in *pascal* (the SI unit), *bar* or *atm*, though other units of pressure are sometimes used: *torr*, *mmHg*, *cmHg*, etc. When there is more than one type of molecule in the fluid phase, a single pressure value does not tell the full story. In this case the terms ***total pressure*** and ***partial pressure*** are defined. ***Total pressure*** is the pressure of the entire mixture while ***partial pressure*** is the pressure of each individual component, respectively. Both use the same units as absolute pressure. As an example, we can have a mixture of water vapor in nitrogen at a total pressure of 101325 Pa and with water having a partial pressure of 3000 Pa.

Partial pressure is closely related to other ways of expressing the components of a mixture, namely ***fraction*** or ***concentration***. These modes report the amount of one component in the total mixture. They can be reported as a number (out of 1) or as a percentage (out of 100%). One further complication is that the fraction can be either on a **molar, volume,** or **mass** basis of the components. The best way to represent the meaning of a fraction basis is through an example. In a balloon we put one mole of N_2 and one mole of CO_2. The ***molar fraction*** of N_2 is 1/(1+1) = 0.5 in this mixture. To get the ***volume fraction***, we must instead consider the volume contribution of each gas. If we consider both gases as ideal, a mole of each occupies 22.4 L, so for N_2 the volume fraction is 22.4/(22.4+22.4) = 0.5. Finally for the ***mass fraction***, we need to convert to weight by using the molar mass of each component, resulting in 28 g of N_2 and 44 g of CO_2. The mass fraction of N_2 is then 28/(28+44) = 0.388. To differentiate between the three, we often use notation such as *mol%*, *vol%* and *wt%*. Sometimes fractions are also expressed as ***parts of a whole***, e.g. parts-per-million or ppm. These can be converted into a regular fraction by dividing by the total number of parts. It is also important to refer to which basis these refer to, by using notation such as *ppmv* or *ppmw*, etc. These units are generally discouraged as they are confusing.

It was mentioned before that by increasing the pressure of a vapor, it eventually condenses as a liquid when the pressure reaches the saturated vapor pressure (p^0) of that compound. Since p^0 is a set limit for maximum pressure, it is useful to think of a measurement value relative to this limit. This is termed ***relative pressure***, given as the ratio of the current partial pressure to p^0.

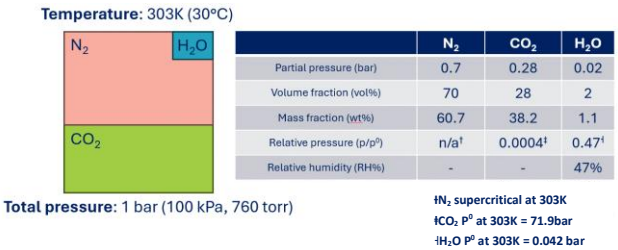
$$\textit{relative pressure} = \frac{\textit{partial pressure}}{\textit{vapour (saturation) pressure}} = p/p^0$$

Relative pressure is usually represented with the shorthand p/p^0, ranging from 0 to 1, or from 0 to 100% if using a percent value. **Humidity** (RH) or **water activity** are both relative pressure terms, specifically used when the vapor is water.

Note! Above the critical point of a compound, there is no distinction between a liquid and gas state, which means that there is no vapor pressure. Such gases (for example N_2 and CH_4 at room temperature) cannot be represented in relative pressure.

To summarize all the above terminology, we end with an example in

Figure *1*.



	N_2	CO_2	H_2O
Partial pressure (bar)	0.7	0.28	0.02
Volume fraction (vol%)	70	28	2
Mass fraction (wt%)	60.7	38.2	1.1
Relative pressure (p/p^0)	n/a†	0.0004‡	0.47‡
Relative humidity (RH%)	-	-	47%

†N_2 supercritical at 303K
‡CO_2 P^0 at 303K = 71.9bar
‡H_2O P^0 at 303K = 0.042 bar

Figure 1: A figure that graphically represents the concepts of different ways of reporting total pressure/concentration.

Pure vs carrier probe pressure control

To measure the amount sorbed, one must accurately control temperature and pressure. While the former is usually only controlled through heating/cooling, the latter can be changed in several ways. In most common techniques we find that the pressure of the probe molecule is controlled in two ways: directly controlling total pressure of a single pure probe gas, or by mixing the probe with an inert carrier gas and controlling its partial pressure at a fixed total pressure.

Pure probe introduction. Here a pure gas or vapor is put into contact with the sample. A vacuum is first created around the material, removing any residual atmosphere. Then the probe of interest is introduced, and its total pressure controlled.

Carrier probe introduction. In this mode, the gas or vapor of interest is first mixed with a carrier gas (like He, N_2 or air) and then introduced to the sample. The carrier gas is considered to be inert and should not interact with the sample. The partial pressure of the probe is controlled by changing the mixing ratio at a fixed total pressure. The mixture total pressure does not have an influence on sorption and is generally selected to be atmospheric (1 bar).

The number of probe molecules interacting with the materials is identical in both scenarios. This is easily seen through the schematic in Figure 2. In general, equilibrium uptake on the material is the same, but the kinetics of sorption may differ. The carrier gas mode more often represents the kinetics and diffusion in real-world applications.

The SMS DVS, SMS iGC-SEA and SMS BTA systems operate in carrier mode, while the SMS DVS Vacuum operates in pure mode.

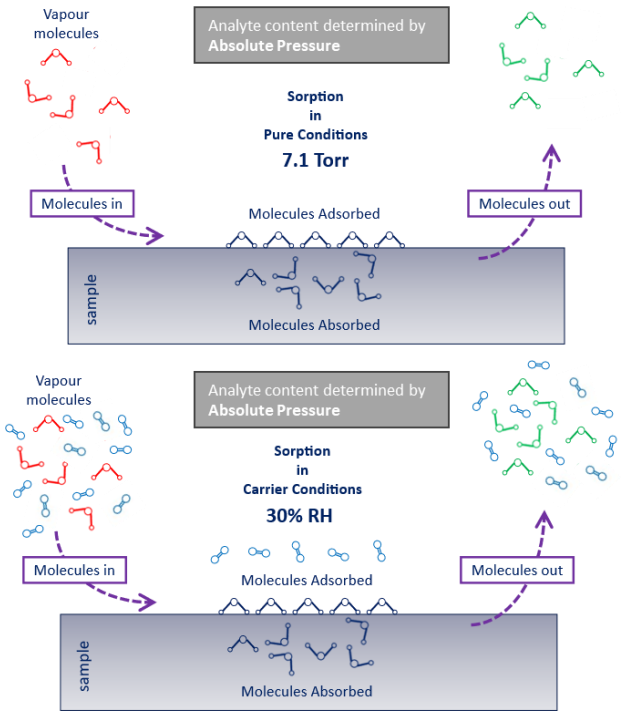


Figure 2. Principle of pure (top) and carrier (bottom) sorbate introduction – the sorbate is water (triatomic molecule) while the carrier is nitrogen (diatomic molecule).

Static vs dynamic sorbate introduction

Another common distinction in sorption methods is whether the probe molecules are dosed in single precise amounts (static introduction) or whether they are flowing around/through the sample (dynamic introduction).

Static introduction (dosing). Many sorption measurements are conducted in a static, or equilibrium mode. In this process, the gas is dosed into a chamber containing the sorbent. The chamber is then sealed, and the system is equilibrated. The method is best suited to adsorbates with fast kinetics (e.g., N_2 but not H_2O). Generally, only a pure probe is used. Diffusion coefficients and sorption kinetics are difficult to calculate as the pressure/concentration changes throughout the sorption process. Also, if the system pressure changes for various reasons besides adsorption, more commonly due to vacuum leaks or temperature changes, this may lead to errors in measurements, especially at low partial pressures.

Dynamic introduction (flowing). In the dynamic method, a continuous flow of gas or vapor is passed over the sample. The method controls both the upstream rates of entry and the downstream exit rate, effectively controlling both the pressure/concentration and flow rate of the adsorbate in the chamber. It also helps to overcome some boundary layer diffusional barriers, by ensuring little to no concentration gradients around the sample. Both pure and carrier introduction is possible. The principle of dynamic method is illustrated

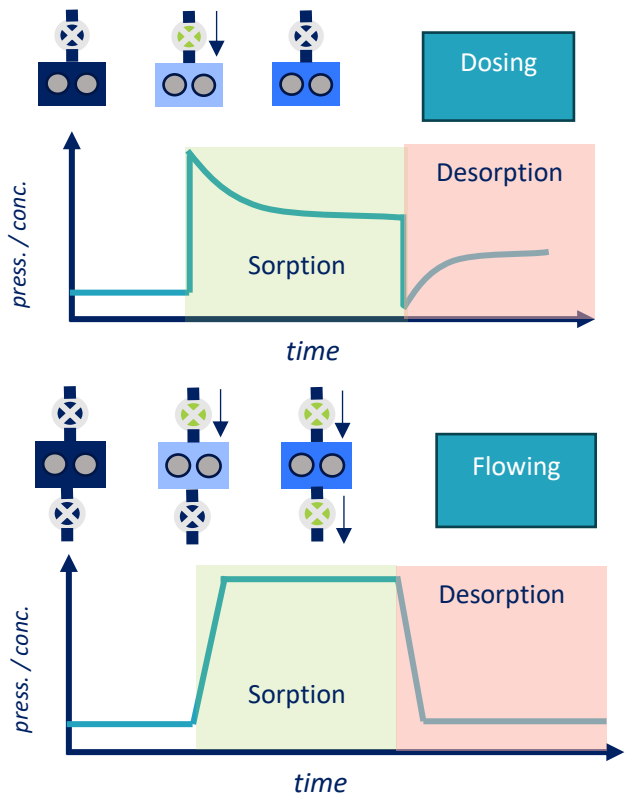


Figure 3 below.

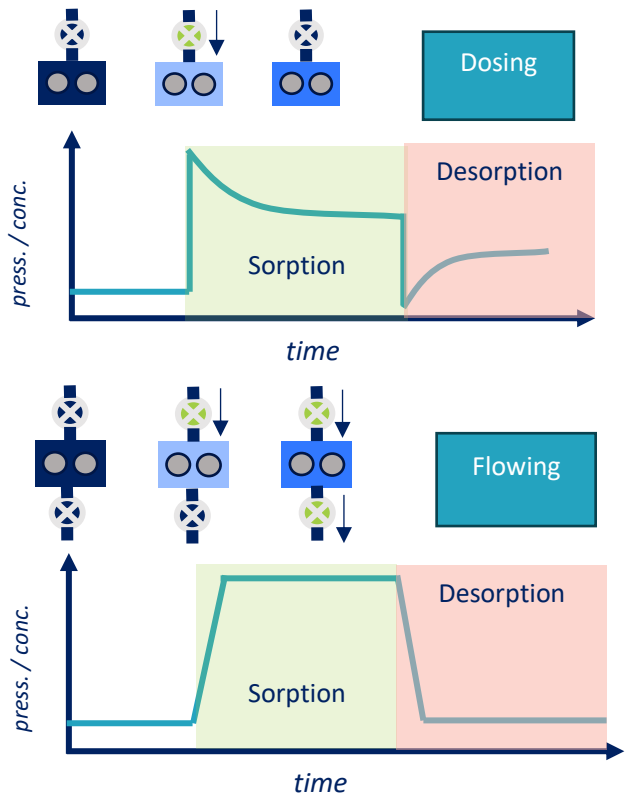


Figure 3. Principle of static (top) and dynamic (bottom) methods.

The SMS DVS, SMS iGC-SEA and SMS BTA systems operate in dynamic mode, while the SMS DVS Vacuum can perform both static and dynamic introduction.

Volumetric, gravimetric, and chromatographic methods

After discussing the terminology of sorption and some fundamental differences in working modes, we can now turn to measurement techniques. There are three common methods of determining the sorption or uptake of a gas or a vapor in a material: **gravimetric** (e.g. DVS), **volumetric**, and **chromatographic** (also called breakthrough), each with key advantages and disadvantages.

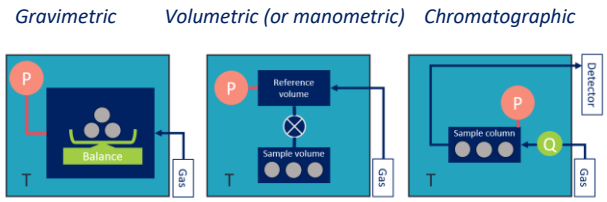


Figure 4: Schematic of different sorption methods.

Gravimetric methods

In a gravimetric method, the change in weight resulting from adsorption is directly measured using a highly sensitive microbalance. The change in net force measured by the balance as temperature and pressure/concentration change can be equated to gas uptake by the sample. Gravimetric measurements are some of the most accurate means of measuring uptakes of gases and vapors in a wide range of conditions.

In a standard experiment, the sample is loaded in the balance and isolated in a chamber. The chamber temperature is carefully monitored, alongside the pressure/concentration of the gas phase. Change in mass given by the balance has three contributions: the change in sample mass given by uptake in the sample, a change in net buoyant force given by the change in density of the gas phase and a drag force of a gas flow on the sample pan. The buoyancy force is small for experiments at ambient pressure and temperature but can play a role at high pressure (>a few bar) where corrections may be required. The drag force is only relevant when a dynamic mode is used, as the gas flow impinges on the balance parts and may need to be corrected through a blank. A way of minimizing both drag and buoyancy corrections is to construct the balance symmetrically, having a sample and a reference pan in identical configurations in the flow path.

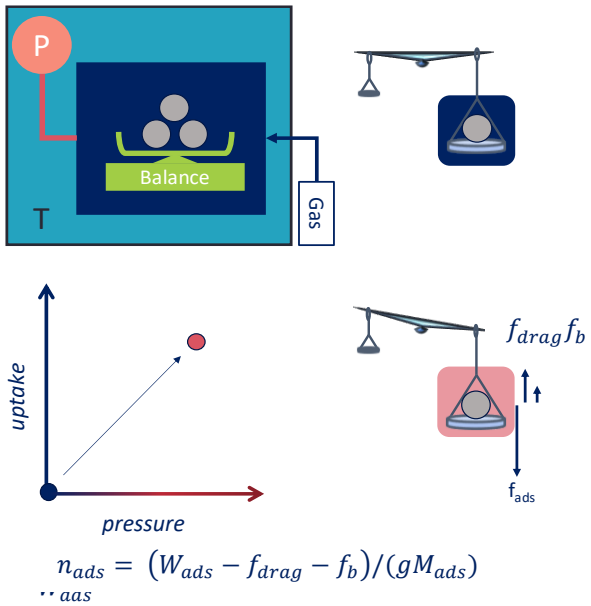


Figure 5: Gravimetric method for measuring gas/vapor sorption.

A well-known benefit of gravimetric methods is that they typically require a low amount of sample: as little as 1-5 mg can be used to obtain reliable results for single component measurements. Conversely, the upper range of mass/volume is similarly much higher, a few grams and 10s of cm^3 can be measured. Note that the mass range and accuracy depend on the performance and stability of the balance – SMS DVS balances have a total mass and resolution of 1 g / 0.01 µg for the low mass balance and 5 g / 0.1 µg for the high mass balance.

High temperature treatment under vacuum or inert gas is often required to dry and remove any residual molecules from the sample. In a gravimetric system, sample drying/activation can be followed directly and quantified. The probe molecule pressure can be controlled in a pure or in a carrier configuration. Both static and dynamic modes can be used. The uptake is measured directly as a function of time,

yielding the kinetics of mass transfer by default. Co-adsorption conditions (mixing of multiple probes) can be easily achieved in the fluid phase. Together with the ability to independently change total pressure and sample temperature, gravimetry is highly flexible when it comes to complex sorption programs: dosing or mixing of sequential components (co-adsorption), flowrate changes, temperature and pressure swings, in-situ activation under inert carrier or vacuum, stability testing, etc.

SMS DVS systems are all gravimetric systems designed around the SMS UltraBalance design. Most DVS instruments are symmetric in design, except the DVS Intrinsic, DVS Endeavour and DVS Dual Vacuum.

Volumetric methods

In volumetric methods a cell containing the adsorbent material is dosed sequentially from a known volume of gas. The pressure is monitored as the probe sorbs in the material, the equilibrium value of which is then used to calculate the final gas amount remaining in the cell using an equation of state. The difference between the initial and the final amount of gas is equal to the amount adsorbed.

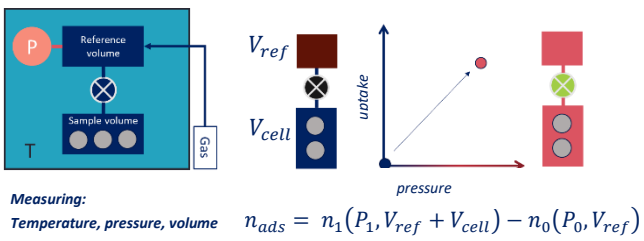


Figure 6: Volumetric method for measuring gas/vapor sorption.

In a standard volumetric experiment, the sample is weighed into a closed vial. If the material needs drying or activation, the vial is then taken to high temperature under inert gas or vacuum for a pre-defined time. The vial is re-weighed to determine the activated sample mass. It is then transferred to the sorption device and connected to the dosing volume. This reference cell has a known volume and is separated from the sample cell by a valve. All air is removed from the two volumes using a vacuum pump. Then, the volume of the sample cell must be determined, a procedure which is performed by expanding a non-sorbing gas like helium – essentially performing a pycnometry experiment. Once the free cell volume is calculated, the reference volume is pressurized to a known pressure and the valve separating the cell is opened. The pressure decays as the gas is taken up by the sample and its decay is monitored to estimate whether the sample has reached equilibrium. Adsorbed amount can then be calculated for that pressure through an equation of state, which is followed by sequential doses of the probe molecule in increasing amounts.

Volumetry is a straightforward method to measure pure single component sorption as it has few moving parts. Its simple construction also means that extreme conditions of low/high temperature and high pressure are easier to implement. It is often used for routine characterization experiments, and it can be parallelized by having the reference volume shared between two or more sample cells. The geometry and gas path of the sample cell can be easily changed, which means volumetry is easier to integrate with other measurements – XRD, FTIR, microscopy, etc.

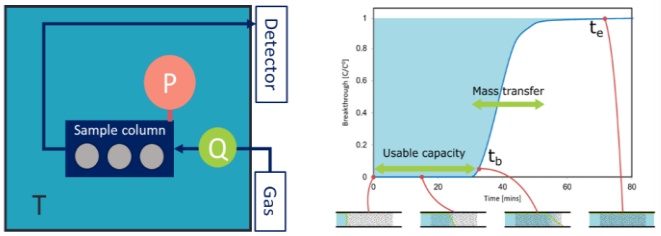
The indirect measurement of sorption uptake through pressure has several important consequences. There must be enough sample in the cell to produce a measurable pressure drop. This means that minimum sample requirements are higher, usually 50-100 mg, while maximum sample possible is limited by the volume of the system, usually up to 1 g. Another consequence is that volumetry can only operate in a static dosing mode. The amount of adsorbate dosed should be known in advance or optimized. It should also be noted that each subsequent dose after the first propagates pressure errors in previous doses, such that the uptake uncertainty compounds as more points are recorded.

Since it uses a closed system, changing the temperature also changes the pressure in the system. Isobars are therefore not commonly possible on volumetric systems. Mixtures can be potentially dosed. However, as there is no knowledge of the partial pressure of each

component in the headspace after the sorption process, assumptions must be made for an uptake calculation.

Chromatographic / breakthrough methods

In chromatographic methods, the probe molecule flows over a packed bed / column of the material to be characterized. All important variables: temperature, total pressure/concentration, and flowrate are continuously monitored at the inlet and outlet of the column, which can then be used to determine a molar mass balance over the packed bed.



Measuring:
temperature, pressure,
concentration, flowrate

$$n_{ads} = n_{in}(P,T,Q,c) - n_{out}(P,T,Q,c)$$

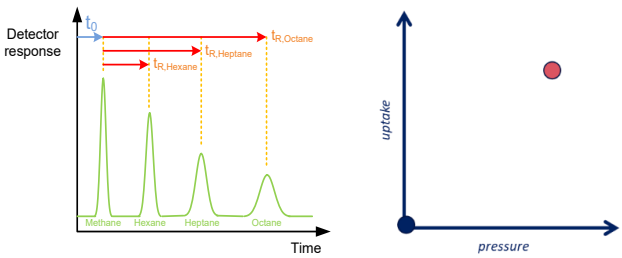


Figure 7: Chromatographic (breakthrough) methods of measuring gas sorption, including frontal and pulsed.

Chromatographic/breakthrough methods are inherently flow/dynamic methods. A pure mode of introduction can theoretically be used, though systems most often work in a carrier mode to simplify total pressure control over the column.

The probe can be introduced as a step change in inlet concentration, a mode which is often termed “frontal” or “breakthrough” due to a concentration front being generated and passing through the column until it breaks through to the other side. Thereby a mass balance can be performed to determine the amount of probe that has been retained in the column – which can be assigned to uptake on the surface and in pores. The probe can also be introduced as a pulse of concentration, similar to chromatography. This mode of operation is often known as “inverse chromatography”, since we are characterizing the sample in the column rather than the gas phase. The time for the pulse to fully elute is termed “retention time”. In all cases, the shape of the resulting concentration curve provides parameters about equilibrium uptake, transport through the bed and strength of the probe molecule’s interactions with the material.

In a common experiment procedure, a column of desired size is packed with a sample of the material. The column is weighed before and after packing to
ıact sample mass. If thermal
ed, the column can be purged
an inert gas while heated, with
termined again. The column is
sorption analyzer. The volume of
be determined for an accurate
n known as “dead volume” or
ıtion time”, which is commonly
r a pulse of a non-interacting gas
methane. The probe pulse or
sed through the column, with
let monitoring the flowrate and
he mass balance is then

The number of parameters which must be precisely controlled and measured at both column inlet and outlet – temperature, pressure, concentration, flowrate - make this method complex to accurately set up. In general, the method development takes longer while single point experiments are faster to perform. Most systems also require a larger amount of sample than previous methods, 100s of mg to a few grams, through the set-up can be scaled up to kg ranges to simulate industrial processes. Sample morphology plays a role, with fine powders and crystals often leading to blockages and over pressurization, requiring preliminary shaping. On the other hand, there is a large flexibility in the type of sensors used to monitor concentrations, and to set-up hyphenated techniques around the material in the column itself.

Chromatographic/breakthrough methods are one of the few methods which can be used to determine true multicomponent adsorption data: e.g., individual uptakes of two or more components in a mixture and surface interaction parameters. The shape of the eluted peak or breakthrough curve encodes information about the kinetics of adsorption and mass transfer through the bed, which can be crucial for process scale-up.

The iGC-SEA and the BTA Frontier systems are SMS flagship dynamic chromatographic and breakthrough analyzers, respectively.

Conclusion

In this note, we explored various experimental techniques for measuring gas and vapor sorption: gravimetry, volumetry and chromatography. These techniques play a crucial role in determining fundamental material properties and assessing material performance across diverse applications. Key considerations when choosing an experimental technique include sample volume, surface area, targeted temperature and pressure regimes, experiment complexity, number, and type of sorbed molecules and the need to mimic real-world conditions. Additionally, understanding sorption kinetics, equilibrium times, and material properties such as density and surface energy informs the selection process. Researchers can also explore hyphenations of multiple measurements to gain deeper insights. Ultimately, the choice of technique should align with research goals, complexity, cost, and ease of use.

Table of comparison between methods

A summary of the differences between the three methods is available in the following table.

	Gravimetric	Volumetric	Chromatographic
Short description	A microbalance directly measures the change in weight as the gas/vapor is adsorbed in the material.	The sample is placed in an enclosed cell, where successive doses of gas are introduced. Pressure in the cell is monitored.	A stream of known molar flowrate is passed through a column / packed bed. Concentration at the outlet is monitored and a mass balance is calculated.
Primary measured parameters.	Sample weight change. Temperature & pressure/concentration.	Pressure decay in a closed cell of known volume. Temperature & pressure/concentration.	Flowrate in/out of a packed bed. Temperature & pressure/concentration before and after the bed.
Sample minimum amount	from 1-10 mg	from ~50-100 mg	From 50-100 mg
Sample maximum amount	1 – 100 g	1-5 g	100 g – few kg
Pros	Highly accurate and flexible with samples and measurement conditions. Smallest sample amounts needed. Direct measurement of uptake. Can operate in both dynamic and static mode. Provides sorption kinetics by default. Can easily perform both isotherm (pressure scan) and isobar (temperature scan) experiments. Sample drying/activation is followed directly and quantified.	Low complexity, simple to implement and to parallelize. Straightforward to obtain wide temperature and pressure ranges. Easier to hyphenate as the sample can be located away from the instrument.	Provides true multicomponent sorption data from mixtures. Pulse retention time can be used to determine isotherms and surface parameters. IGC method can measure minute surface areas. Can provide information into process relevant parameters – mass and heat transfer.
Cons	Complex engineering required– best with bespoke instrumentation. Cannot measure true multicomponent sorption, though can measure total amount adsorbed from a mixture. Buoyancy correction may be difficult at high pressures.	Indirect measurement of uptake – must rely on equations of state. Cannot use dynamic or carrier probe introduction. Difficult to record isobars and sorption kinetics. Cannot measure multicomponent sorption. Incremental compounding error for each dose. Pressure gradients between sample and reference can be significant at low partial pressures.	Indirect measurement of uptake – must rely on equations of state. Complex to set up and correctly analyze data – best with bespoke instrumentation. Often not suitable for fine powders due to pressure drop.
Method applicable	Static & dynamic introduction Pure & carrier	Static only Pure only	Dynamic only Pure & carrier