Characterizing Adsorbents for Gas Separations

Pressure-swing adsorption (PSA) and temperature-swing adsorption (TSA) separate a specific gas species from a mixture of gases. This article explains how to evaluate the performance of an adsorbent for a given separation.

Separations account for a significant proportion of worldwide energy consumption (1). Energy-intensive distillation dominates the chemical process industries (CPI), but more-efficient alternatives, such as membrane technology and adsorption by porous materials, are also in widespread use. Pressure-swing adsorption (PSA) and temperature-swing adsorption (TSA) are two common gas separation processes. In a PSA process, adsorbents are regenerated by reducing pressure; in a TSA process, they are regenerated by applying heat (2–4).

Adsorbent performance as a function of temperature, pressure, and gas composition is a crucial aspect of PSA and TSA. To determine whether an adsorbent will be appropriate for a specific application, you must assess its working capacity, isotherm shape, selectivity, heat of adsorption, and sorption kinetics. Such data can be obtained using laboratory gas adsorption measurement techniques, prior to testing and optimizing process designs in a pilot plant.

Two previous articles, “Adsorption Basics: Part 1” (5) and “Adsorption Basics: Part 2” (6) introduced the fundamentals of adsorption, including equilibrium and mass-transfer considerations, the mass-transfer zone concept, and column sizing, and discussed the most widely used adsorbents.

This article discusses how to characterize adsorbents in the lab. It covers the performance parameters and data required for gas separations and the laboratory techniques used to obtain this information. The article also discusses methods for assessing multicomponent adsorption and identifies future challenges in the field.

Working capacity and isotherm shape

The performance of an adsorbent for a particular separation depends on several factors. One of the most important is its working capacity. For PSA, it is the difference between the uptake at the feed pressure and the uptake at the regeneration pressure. For TSA, it is the difference between the uptakes at the feed temperature and the regeneration temperature at the working pressure (Figure 1).

For any given adsorbent, working capacity depends partly on isotherm shape. For PSA, for example, the steeper the isotherm in the operating pressure range at the process temperature, the greater the working capacity (for an adsorbent with a given saturation uptake). Isotherms measured at different temperatures, however, are also required to accurately and realistically simulate a process (4).

At the temperatures and pressures typically used for gas separation, isotherms for most nanoporous adsorbents follow the trend shown by the Langmuir equation. These are known as favorable isotherms and are concave to the pressure axis (5), as shown in Figure 1. Loading as a function of pressure, however, often increases more gradually than described...
by the Langmuir equation (the Langmuir model assumes adsorption occurs on a homogeneous surface, which is physically unrealistic for most adsorbents). When this is the case, other models, such as the Tóth and Sips (or Langmuir-Freundlich) equations, which describe heterogeneous adsorption, are more appropriate (4).

**Selectivity**

Working capacity and isotherm shape are basic properties that define a material’s ability to adsorb gases. For separation, however, selectivity is more important. Selectivity can be defined in different ways depending on the separation mechanism, of which there are two general types — equilibrium and kinetic. Most commercial separation processes are equilibrium-based, although the recovery of nitrogen from air using carbon molecular sieves, for example, is a kinetics-based separation (4, 7).

Equilibrium selectivity, $S_{eq}$, is usually defined as:

$$S_{eq} = \frac{n_1}{n_2} \frac{p_1}{p_2} \quad (1)$$

where $n_1$ and $n_2$ are the molar loadings of Species 1 and 2 at partial pressures of $p_1$ and $p_2$, respectively, under the process conditions.

Kinetic selectivity, $S_{kin}$, meanwhile, can be expressed as:

$$S_{kin} = \frac{K_1}{K_2} \left( \frac{D_1}{D_2} \right) \quad (2)$$

where $K_1$ and $K_2$ are the Henry’s law constants and $D_1$ and $D_2$ are the diffusivities of Species 1 and 2, respectively (7).

Equilibrium selectivity therefore depends on the relative equilibrium quantities of each component adsorbed under the process conditions, whereas kinetic selectivity depends on differences in diffusion rates. Both types of selectivity can be calculated from data obtained using the lab techniques described later in this article.

**Heat of adsorption**

The heat of adsorption, usually expressed in kJ/mol, indicates the strength of interaction between the adsorbate and the adsorbent. Purely physical adsorption, or physisorption, has a low heat of adsorption, whereas chemical adsorption, or chemisorption, has a higher heat of adsorption (2).

The heat of adsorption defines the temperature and pressure at which adsorption occurs, but a higher value also means that more heat will be generated during the adsorption process. Particularly large temperature increases in adsorbent beds are possible, which can lower the transient or dynamic bed capacity, because the amount of adsorbate adsorbed decreases with increasing temperature. And, higher heats of adsorption can adversely affect process efficiency, particularly for TSA, because more energy will be required for adsorbent regeneration.

Heats of adsorption can be defined in different ways (8), but the most practically useful is the isosteric heat, $q_i$ (4). To calculate isosteric heat, measure isotherms at two or more temperatures (that are close in value) and use the following (Clausius-Clapeyron-type) relationship:

$$q_i = RT^2 \left( \frac{\delta \ln P}{\delta T} \right)_{n_i} \quad (3)$$

where $R$ is the universal gas constant, $T$ is temperature, $P$ is pressure, and $n_i$ is the uptake.

To calculate $q_i$, plot the natural logs of the pressures for isotherm points at constant uptake against $1/T$. A straight-line fit through these data has a slope of $q_i/R$. Using this process, $q_i$ can be calculated for different values of $n_i$.

For pure gases, $q_i$ typically decreases with loading, as the most strongly interacting sites or pores are occupied first. Increases at higher loading can occur due to adsorbate-adsorbate interactions, which become more significant at higher pressures and gas densities. (At lower loadings, adsorbate-adsorbent interactions dominate because the gas molecules are mostly interacting with the surface, rather than each other.) However, it is worth noting that calculated values of $q_i$ can be quite sensitive to the method used, so some observed changes may simply be a result of the fitting process (9).

**Sorption kinetics**

Equilibrium uptakes determined from isotherms are required to define working capacities and isotherm shape, and to calculate equilibrium selectivities and heats of adsorption; however, the kinetics are also crucial. Process simulations require kinetic data, regardless of the separation

![Figure 1](image-url)
mechanism. Kinetic data are also needed to calculate kinetic selectivities. Although simple in principle, detailed analysis of sorption kinetics and diffusion is a complex topic (2, 9, 10). However, for engineering purposes, the kinetics can be approximated because the need for mathematical simplicity is often more important than having an accurate description of the microscopic processes occurring in a full column. For simulations, kinetics are most commonly described using the linear driving force (LDF) model (2, 4, 11). This simple approach is often sufficient for process simulation, because the differences in the kinetic curves for different models that describe diffusion at a microscopic level can be lost during the integration processes required to describe the performance of a full column (11).

The importance of adsorbent and adsorbate properties

The equilibria and kinetics of gas adsorption depend on the properties of the adsorbate and the adsorbent (2). Maximum equilibrium capacities, for example, generally increase with the total pore volume of a material. However, the amount of uptake as a function of pressure (at any given temperature) depends on several other properties, including pore size, the strength of adsorbate-adsorbent interactions, and adsorbent heterogeneity. An adsorbent’s pore size affects the equilibrium uptake, as narrow pores result in greater overlap of the adsorption potentials of opposing pore walls. This increases the adsorption strength, leading to more adsorption at lower pressures. However, interactions between an adsorbate and a particular surface also depend on the properties of the adsorbate, such as its polarizability and dipole and quadrupole moments, and the chemistry of the adsorbent (2). For example, CO₂ typically adsorbs more strongly than other gases such as H₂, N₂, and CH₄, because it has a larger quadrupole moment, whereas He interacts more weakly than H₂, N₂, and CH₄, because it has no dipole or quadrupole moment and it has a relatively low polarizability. Polar surfaces also interact more strongly with polar adsorbates.

Pore size also affects the kinetics. Particularly narrow pores can inhibit diffusion, whereas wider pores permit more rapid mass transfer, although diffusion rates may decrease if the adsorbate binds strongly to the pore walls. In larger pores, surface diffusion — the hopping of adsorbate molecules from one adsorption site to another — can occur alongside Knudsen diffusion (i.e., the diffusion that occurs in the free molecule regime, where collisions with the pore walls are more likely, or occur more frequently, than intermolecular collisions or interactions) at lower pressures. At higher pressures, surface diffusion can occur alongside viscous flow through a bulk fluid phase. The microscopic behavior of adsorption and diffusion in different nanoporous materials, particularly for mixtures when competitive effects become important, can therefore be quite complex (10, 12).

Gas adsorption measurement

All of the factors discussed thus far need to be considered when selecting an adsorbent for a given separation. However, you can use the measurements discussed in the following sections to practically assess the performance of a particular material. The presence of binder in commercial adsorbent pellets and beads can affect both equilibrium and kinetic properties. So, for practical purposes, it is important to experimentally characterize each adsorbent on a case-by-case basis.

Gas adsorption is most commonly measured using volumetric and gravimetric techniques (8). The volumetric (or manometric) technique usually measures changes in pressure in a fixed-volume system to determine the amount of gas adsorbed, while the gravimetric technique measures changes in sample weight.

Volumetric (or manometric) techniques

A basic manometric system consists of a calibrated dosing volume connected to a sample cell by a valve (Figure 2). A vacuum pump is required to evacuate both the sample cell and the dosing volume. Before starting any measurement, the sample must be degassed to remove environmental contaminants or remnants of the synthesis process from the pores of the material. Thus, a measurement begins at vacuum, with the sample degassed and the valve between the dosing volume and the sample cell closed.

To start a measurement, the dosing volume is pressurized and the gas is allowed to reach thermal equilib-
rium. The number of moles of gas, \( n \), in the dosing volume can be calculated using the real gas law:

\[
P V = n Z R T
\]

(4)

where \( V \) is volume and \( Z \) is the compressibility factor. Accurate pressure and temperature measurement is essential for calculating \( n \).

The valve is then opened to dose gas to the sample cell. The amount adsorbed (\( \Delta n \)) is given by:

\[
\Delta n = \frac{PV_i}{Z_{i,T} RT} - \frac{P_f (V_1 + V_2)}{Z_{f,T} RT}
\]

(5)

where \( V_i \) is the dosing volume and \( V_2 \) is the dead volume of the sample cell, \( P_i \) and \( P_f \) are the initial and final pressures in \( V_1 \) and \( V_1 + V_2 \), respectively, and \( Z_{i,T} \) and \( Z_{f,T} \) are the compressibility factors under the relevant conditions.

You can then determine an entire isotherm by sequentially dosing more gas to the sample cell and measuring the pressure at each step. The adsorbed quantity at the \( m \)th isotherm point, \( n_m \), is:

\[
 n_m = \sum_{i=1}^{m} \left( \frac{P_{i,T} V_i}{Z_{i,T} RT} - \frac{P_{f,T} (V_1 + V_2)}{Z_{f,T} RT} \right)
\]

(6)

In practice, the dosing volume and the sample cell are often held at different temperatures, which must be accounted for. There is typically a temperature gradient between the dosing valve and the sample cell. It can therefore be assumed that a fixed dividing line exists between the part of \( V_2 \) held at the temperature of the dosing volume, \( T_{dose} \), and the part held at the sample temperature, \( T_s \). This can be defined by a decimal fraction, \( f \), so that \( fV_2 \) is at \( T_{dose} \) and \( (1-f)V_2 \) is at \( T_s \). Equation 6 can then be modified accordingly. It should be noted that even small errors in \( P, V, Z, \) and \( T \) can propagate to cause large errors in the calculated value of \( n_m \).

**Gravimetric techniques**

Gravimetric measurements, meanwhile, usually use a system equipped with a microbalance. A common choice is the compensating electronic beam balance. In these devices, the sample is mounted in a pan on one side of the balance beam and a counterweight is suspended from the other side (Figure 3). Another option is the magnetic suspension balance; these are often single-sided, so no counterweight is required.

Regardless of the balance type, it must be mounted in a vacuum-compatible chamber. Glass can be used up to atmospheric pressure, but metal construction is now more common. A vacuum pump is required to degas the sample and provide a reference point for isotherm measurement, and a method of controlling or dosing gas to the microbalance.
Reactions and Separations

chamber is needed to measure adsorption as a function of pressure, as shown in Figure 3.

Both the microbalance and sample chamber must be maintained at a controlled temperature, and accurate pressure measurement is essential. The inability to measure pressure accurately may limit a gravimetric instrument’s ability to measure adsorption in a given pressure regime, so different transducers covering different ranges are recommended.

An isotherm measurement typically begins with the sample held under vacuum after an appropriate degassing period. Next, the gas is dosed into the microbalance chamber and the system is allowed to reach equilibrium. The final microbalance reading provides a measure of the amount of adsorption exhibited by the sample, while the transient weight signal allows for analysis of kinetics. To determine a full isotherm, increase the gas pressure incrementally and record the microbalance reading at each equilibrium point.

With all gravimetric measurements, it is important to correct the microbalance reading for buoyancy effects. Without accurate buoyancy corrections, the measured weight will not accurately represent the amount of adsorption, particularly at high pressures.

The force on the microbalance due to adsorption, \( f_{\text{ads}} \), is:

\[
f_{\text{ads}} = m_{\text{ads}} g\]

(7)

where \( m_{\text{ads}} \) is the mass adsorbed and \( g \) is the acceleration due to gravity.

The buoyancy of the sample, however, creates a force, \( f_{\text{buoyancy}} \), that depends on the mass of the sample, \( m_s \), the sample density, \( \rho_s \), and the gas density, \( \rho_g \), at the measurement temperature and pressure:

\[
f_{\text{buoyancy}} = m_s g \left( \frac{\rho_g}{\rho_s} \right)\]

(8)

These two forces create a total force on the microbalance, \( f_{\text{tot}} \):

\[
f_{\text{tot}} = f_{\text{ads}} - f_{\text{buoyancy}} = m_{\text{ads}} g - m_s g \left( \frac{\rho_g}{\rho_s} \right)\]

(9)

If \( \rho_g \) and \( \rho_s \) are known, \( m_{\text{ads}} \) can then be calculated. Practical calculations are usually more complex because other components — such as balance hangdowns (i.e., the wire from which the counterweight and sample holder are suspended) and the sample container — contribute to the total buoyancy force.

Other techniques

The volumetric and gravimetric techniques are the most common ways to measure gas adsorption, but others are available, including variations on the manometric method — such as dynamic (or flowing) (8) and differential techniques (13) — and gas chromatography. The latter can also be used, together with frequency response techniques and other approaches such as isotope exchange (14, 15), to study kinetics (10).

Dynamic manometric methods involve controlling the flow of gas into the sample cell and measuring the pressure response to determine either the equilibria or kinetics of adsorption. Differential manometric techniques determine the amount adsorbed by measuring the pressure difference between the sample cell and a reference cell held under the same conditions (13).

Gas chromatography involves packing the adsorbent into a column and measuring the response at the outlet to changes in the inlet gas composition. Various types of chromatography are used, and they differ in the way the inlet gas composition is changed. Frontal chromatography, for example, introduces a step change in the inlet concentration, which allows you to determine the breakthrough curve for the adsorbent bed.

Frequency response techniques use a system containing an adsorbent bed in which one of the properties, most commonly the volume (15), is varied in a controlled manner. Varying volume cyclically in a closed system induces corresponding pressure changes that typically lag behind the volume change due to adsorption or desorption in the bed. Measuring this lag, or the pressure response, therefore allows you to analyze the sorption kinetics.

Isotope exchange is a more specialized approach to characterizing adsorption. In this method, the isotopic composition of the gas is varied and the response is used to analyze the equilibria or kinetics of adsorption (14).

Measurement pitfalls

When making gas adsorption measurements, take care to avoid several common pitfalls.

When using a manometric system, it is especially important that all measurements are accurate, because error propagation can be severe due to the large number of readings required for Eq. 6.

Also pay careful attention to gas purity, as contaminants can preferentially adsorb to samples; gravimetric measurements are most susceptible to such problems, assuming the contaminant species are heavier than the measurement gas, as is often the case.

Two problems specifically affect isotherm measurements at high pressure (16). The first is uncertainty of the gas density, which must be calculated using an equation of state (EOS). Accurate EOSs are available — in the NIST REFPROP database, for example — but small errors in pressure and temperature measurement can cause large errors in \( Z \), and these may propagate further, particularly in manometric measurement.
The second issue affecting isotherm measurement is that significant uncertainties can arise because of the complexity of defining the adsorbent and adsorbate volumes (16). The two traditional methods of defining an adsorbed quantity are excess adsorption (17) and absolute adsorption (18). With these traditional methods, large errors in the sample volume or density invalidate calculations of the adsorbed quantity, which can have serious implications when assessing an adsorbent for a given application, particularly at higher pressures. Recently, Gumma and Talu (19) have suggested a method for defining the adsorbed quantity, called net adsorption, that eliminates the need for sample volume measurement.

More generally, measurements of gas adsorption can be affected by:

- instrument design — unnecessary dead volume can increase errors in manometric systems and lengthen response times in gas chromatography and other dynamic methods
- the exothermic nature of adsorption — which can create non-isothermal conditions
- the different physical behavior of different gases — including differences in the thermal conductivities of different species and as a function of pressure, and adiabatic gas expansion that occurs when gas passes through orifices, such as valves. Flowrate restrictions through valves can also affect kinetic measurements (20).

### Multicomponent adsorption

Measuring multicomponent adsorption is a more technically challenging subject than measuring single-component adsorption, but it is of high practical importance (15, 21, 22). For pure gases, the weight, volume, temperature, and pressure are all required to measure adsorption. Errors in any of these variables can propagate, affecting adsorption measurement accuracy. To measure multicomponent adsorption, however, it is necessary to additionally determine — or infer — changes in composition of both the adsorbed and gas phases. This adds additional uncertainty.

### Volumetric multicomponent measurements

Talu (22) identified three different approaches to measure multicomponent adsorption based on volumetric (manometric) principles. The first is a closed system in which different gases are delivered from calibrated volumes (as in the manometric system described previously for pure gas measurements). When using two species, this forms a binary mixture, which is circulated in a loop so that the gases mix and pass through the adsorbent bed (Figure 4). After equilibrium is achieved, the adsorbent bed is isolated and the pressure is measured. You can then determine the amount of each component adsorbed by analyzing the composition of the gas phase (21, 23).

The molar balance expression for this system contains additional variables expressing the gas-phase composition, and also includes more volume terms. Accuracy is therefore affected by error propagation, as for pure gas measurements, but with additional uncertainty in the gas-phase concentration. These measurements are also laborious, as equilibrium can take hours to achieve, and each run provides only a single datapoint.

The second approach employs an open system in which mass flow controllers (MFCs) direct a gas of known composition through the bed, as shown in Figure 5. A gas chromatograph (GC) or a mass spectrometer (MS) analyzes the downstream composition and a backpressure regulator controls the pressure.
The amount of each component adsorbed can then be calculated by an open-system molar balance expression of the form:

$$n_i m_s = \int \left( [F y_i]_{\text{in}} - [F y_i]_{\text{out}} \right) dt - \frac{y_i PV}{ZRT}$$  \hspace{1cm} (10)

where \(n_i\) is the amount of component \(i\) adsorbed per unit mass, \(m_s\) is the degassed sample mass, \(F\) is the molar gas flowrate, \(y_i\) is the gas-phase concentration of component \(i\), and \(t\) is time. The terms in the integral, \((F y_i)_{\text{in}}\) and \((F y_i)_{\text{out}}\), are the flowrates of component \(i\) at the inlet and outlet, respectively, and the volume \(V\) is the dead volume of the column.

In this case, accurately determining the gas-phase concentration and flowrate is the main technical challenge. Flowrate is particularly difficult to measure to sufficient accuracy, so it is often a source of significant uncertainty.

The third approach involves first equilibrating the adsorbent under a flowing gas mixture. After equilibration, the column is isolated and the adsorbates desorbed. The total content of the column is analyzed, allowing the amount of each component present to be calculated. High accuracy can be achieved with this method, but the measurements are particularly laborious (22), since here, too, each measurement yields only a single datapoint.

**Gravimetric multicomponent measurements**

Multicomponent adsorption can also be measured gravimetrically, with a GC or MS used to determine the gas-phase composition (Figure 6) (23). The gas mixture must be circulated around the system to ensure thorough mixing and to achieve equilibrium, after which the total weight change is recorded, the gas is sampled and analyzed, and the amount of each species adsorbed by the sample is calculated.

This method requires relatively large sample sizes to ensure that the change in the gas-phase composition is detectable. The amount of adsorption required depends on the internal volume of the microbalance chamber, which is usually larger than the volume of manometric systems. Additional adsorbent can be added to the chamber to increase the amount of adsorption, but this still relies on the use of large sample quantities and it increases the difficulty in ensuring equilibrium has been achieved under relatively homogeneous conditions of temperature and pressure.

The accuracy of this approach depends on the amount of adsorption. When there are insufficient differences in the amount of each component adsorbed (in a system of a given volume), a meaningful measurement is not possible. Minimizing the internal volume of a system helps, but there are technical limits for microbalance chambers.

**Combined volumetric-gravimetric measurements**

An alternative is to combine the volumetric and gravimetric techniques. In this approach, a gas mixture is delivered to a microbalance chamber from a set of calibrated volumes (Figure 7). When equilibrium is achieved, the total weight change, the internal volume of the system, the molar mass of each gas, and the EOS for the mixture are used to calculate the amount of each component adsorbed. However, even for binary mixtures, the accumulated errors can be large, and the accuracy decreases as the molar masses of the species approach each other (22, 23). For multicomponent systems with three or more gases, accurate measurements can become prohibitively complex.

It is challenging to make accurate measurements of multicomponent gas adsorption using this technique because accurate volumetric measurements require a small system volume, as well as accurate temperature and pressure measurement. However, microbalance chambers tend to have large internal volumes. Uncertainties in mixture EOSs also add difficulty.

**Future challenges**

Measuring multicomponent adsorption is technically demanding and can be a time-consuming process. Equilibration times can be long and the required optimization process
can be laborious; the various experimental parameters need to be adjusted to investigate the effects on the results. Careful instrument calibration is also essential.

A large number of datapoints is required to properly characterize multicomponent adsorption for any given system. For pure gas adsorption, temperature and pressure are varied and the total uptake (net, excess, or absolute) determined, for example, by measuring the amount adsorbed as a function of pressure at a series of fixed temperatures. In multicomponent adsorption, both the gas-phase and adsorbed-phase compositions and the total pressure can be varied, introducing additional degrees of freedom. If measuring a single datapoint takes hours, total experimental times can be prohibitively long. In addition, in closed systems, the datapoints are essentially random because it is not possible to control the final state of the system.

These factors add to the challenges of multicomponent gas adsorption measurement, even if high accuracies can be achieved. For routine characterization, chemical engineers require a quick and easy method of determining the multicomponent adsorption behavior of a given set of adsorbates and an adsorbent. Much effort has been expended on trying to develop such techniques, but success has so far been elusive. If such a method were found, it would be invaluable to chemical engineers working on separation problems. It would also be useful to synthetic chemists developing new adsorbents, who could use it for rapid screening purposes.

Despite the practical importance of multicomponent adsorption and the long history of the study of gas adsorption, there are still considerable opportunities for developing new methods to allow quick and easy characterization of adsorbents, particularly for small samples.

**Literature Cited**


