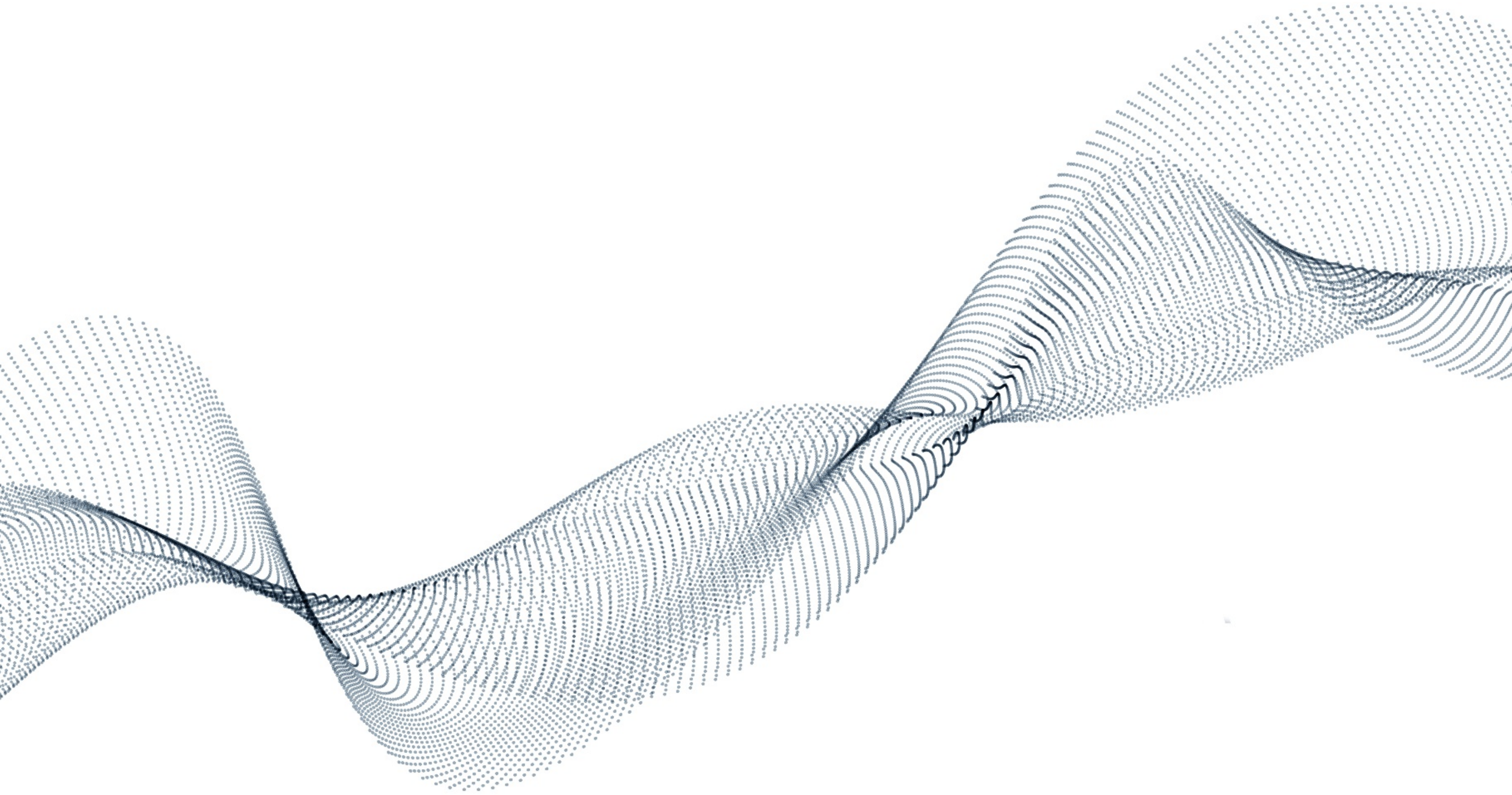
Characterizing adsorbents for gas separations

Measurement needs and laboratory techniques

White Paper



Contact information
Address: 422 Europa Boulevard, Warrington, WA5 7TS, United Kingdom
Email: info@hidenisochema.com
Tel: +44 (0) 1925 244678

www.hidenisochema.com

Publication details
Author: Darren Broom
dbroom@hidenisochema.com

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About Hiden Isochema
Hiden Isochema is a world leader in the design and manufacture of sorption instruments. We offer a range of fully automated gravimetric and manometric instruments for determining the equilibria and kinetics of gas and vapor sorption by liquids and materials. Our full product range includes DVS analyzers, dedicated breakthrough analyzers and unique permeation and climate control systems.

Porous adsorbents such as zeolites and activated carbons are widely used in industrial gas separations. In order to select a material for a given separation, and to subsequently design and optimize a process, each adsorbent must be thoroughly characterized. Key performance parameters include working capacity, heats or enthalpies of adsorption, and selectivity, each of which can be determined using established laboratory techniques. Although commercial instruments are widely available for this purpose, gas adsorption, particularly at higher pressures, can be challenging to measure accurately, and so careful attention must be paid to potential sources of error. Furthermore, despite the maturity of adsorption technology for producing and purifying industrial gases, considerable scope still exists for further advances in both measurement techniques and instrumentation.

This white paper introduces the information required to characterize the performance of adsorbents for gas separations and describes the main measurement techniques, together with some of the measurement pitfalls. Areas in which further work is required are also highlighted, and advantages and disadvantages of each technique discussed. The aim is to provide useful, practical information for anyone interested in characterizing adsorbents for gas separations. A reference list is also provided for further reading on the topic.

Contents

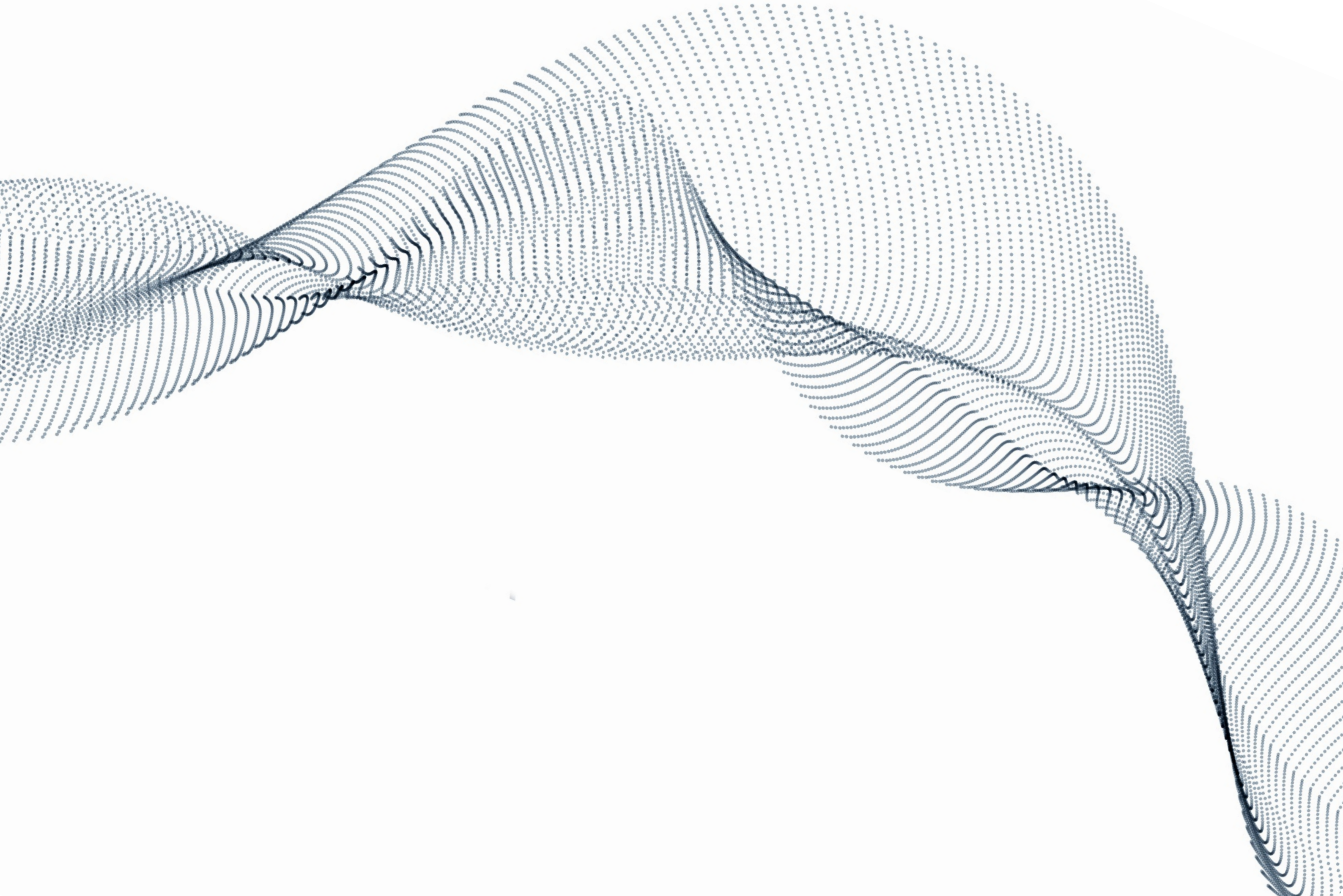
Introduction

Chemical separations account for a significant proportion of worldwide energy consumption.[1] Energy-intensive distillation dominates, but more efficient alternatives such as membrane technology and adsorption by porous materials are also widely used. To separate gases, pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are the two most common processes. In PSA, the adsorbent is regenerated by reducing pressure, while in TSA it is regenerated by heating.[2-4]

Adsorbent performance as a function of temperature, pressure, and gas composition is a crucial aspect of this technology. Important parameters for assessing materials for practical applications, and for process design and optimization, include working capacity, isotherm shape, selectivity, heats or enthalpies of adsorption, and sorption kinetics. This information can be obtained from laboratory gas adsorption measurements, prior to testing and optimizing process designs using pilot plants.

This white paper, based on an earlier article published in *Chemical Engineering Progress*,[5] discusses this process. It introduces the performance parameters and data required for gas separations, and the laboratory techniques used to obtain this information. Methods for determining multicomponent adsorption are also discussed and future measurement challenges identified. It concludes with a comparison of the most established measurement techniques.

Performance parameters



Performance parameters

Working capacity and isotherm shape

Working capacity is an important parameter for any adsorption application. For separations, it can be defined as the reversible uptake between the adsorption and regeneration conditions of the process. In the case of PSA, working capacity is the difference in uptake between the feed pressure and the pressure at which the adsorbent is regenerated. For TSA, it is the difference between the uptakes at the feed and regeneration temperatures, under the working pressure (see **Figure 1**).

For any given material, working capacity will depend partly on isotherm shape. In PSA, for example, the steeper the isotherm in the operating pressure range at the process temperature, the greater the working capacity (for a material with a given saturation uptake). Isotherm measurements are therefore important for determining practical working capacities. Isotherm data measured at different temperatures, however, are also required to accurately and realistically simulate a given separation, as processes will usually operate under non-isothermal conditions. Knowledge of the temperature dependence of adsorption is also required to assess materials for TSA.[4]

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

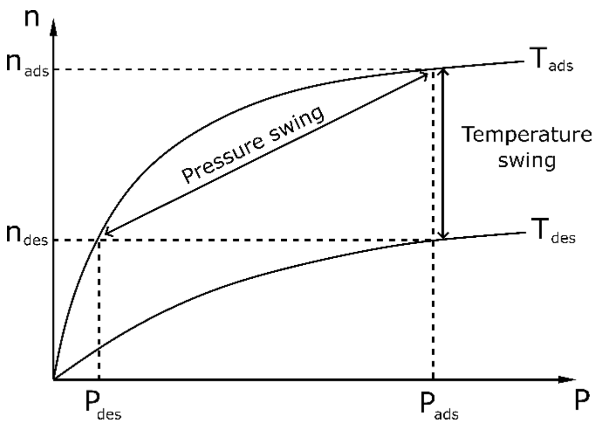


Figure 1. *An illustration of pressure swing and temperature swing cycles used in PSA and TSA.*[2,3] *n is the equilibrium amount adsorbed and P is pressure, and the working capacity in each case is given by* $n_{ads} - n_{des}$*. Lowering* P_{des} *for the pressure swing would increase* $n_{ads} - n_{des}$*; as would increasing* T_{des} *in the temperature swing case.*

Selectivity

Working capacity and isotherm shape are basic adsorption properties of an adsorbent, defining its ability to adsorb the relevant gases. For separations, however, *selectivity* is more important. This can be defined in different ways, depending on the separation mechanism, but there are two general types: *equilibrium* and *kinetic*. Commercial separation processes usually use the former, although kinetic separation is exploited, for example, to produce N_2 from air using carbon molecular sieves.[4,6]

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

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

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,

$$S_{kin} = \frac{K_1}{K_2}\sqrt{\frac{D_1}{D_2}} \qquad (2)$$

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.[6]

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 can be calculated from data obtained using the techniques described later in this paper.

Heat of adsorption

The *heat of adsorption* is another important parameter. It indicates the strength of the adsorbate-adsorbent interactions, and is usually expressed in kJ mol^{-1}. Purely physical adsorption, or *physisorption*, results in a low heat of adsorption, while chemical adsorption, or *chemisorption*, results in higher values.[2] The actual numerical quantities, however, for any given adsorbent, differ for different adsorbates. H_2, for example, which physisorbs weakly, will have low values, whereas heavier hydrocarbons usually have higher values.

Aside from simply defining the temperature and pressure at which adsorption occurs, the magnitude of the heat of adsorption has two main practical consequences. Firstly, a high value leads to more heat being generated during the adsorption process. Large temperature increases in adsorbent beds are possible, which can lower the transient or dynamic bed capacity, since the amount adsorbed decreases with increasing temperature. Secondly, higher heats of adsorption can adversely affect process efficiency, particularly for TSA, because more energy is then required to regenerate the adsorbent.

Heats of adsorption can be defined in different ways,[7] but the most practically useful is the *isosteric heat*, q_i.[4] This can be determined by measuring isotherms at two or more closely spaced temperatures, and then applying the following (Clausius-Clapeyron type) relation,

$$q_i = RT^2 \left[\frac{\delta \ln P}{\delta T}\right]_{n_i} \tag{3}$$

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

To calculate q_i, the natural logs of the pressures for isotherm points at constant uptake are plotted against $1/T$. A straight line fit through these data will then have a gradient, q_i/R.

Using the above method, q_i can be calculated for different values of n_i. For pure gases, q_i usually decreases with loading, as the most strongly interacting sites or pores are occupied first. Increases at higher loading can occur, however, due to increasing adsorbate-adsorbate interactions, which become more significant at higher pressures and hence gas densities. Despite this plausible physical explanation for changes in q_i, as a function of uptake, it is worth noting that calculated values of q_i can be rather sensitive to the precise method used, so some observed changes may simply be artefacts of the fitting process.[8]

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 mechanism, but they are also needed to calculate kinetic selectivities.

Although simple in principle, detailed analysis of sorption kinetics and diffusion in porous materials is a complex topic.[2,8,9] Different scenarios can be envisioned and there are several competing effects. One straightforward situation, for example, is to assume that uptake rates are purely due to micropore diffusion in each particle in the bed. In this case, the kinetics can be described by Fick's law. However, this neglects the effects of non-isothermal conditions, surface barriers, macropore diffusion in pellets consisting of smaller microporous crystals, and other possible mass transfer resistances.[2,9]

For engineering purposes, the kinetics can be approximated, as there is a trade-off between the required accuracy of the physical description of the microscopic processes occurring in a full column and the need for mathematical simplicity. For simulations, they are most commonly described using the *Linear Driving Force* (LDF) model.[2,4,10] This simple approach is often sufficient for process simulation because the differences between the forms of the kinetic curves for different models, describing diffusion at a microscopic level, can be lost during the integration processes required to describe the performance of a full column.[10]

Importance of adsorbent and adsorbate properties

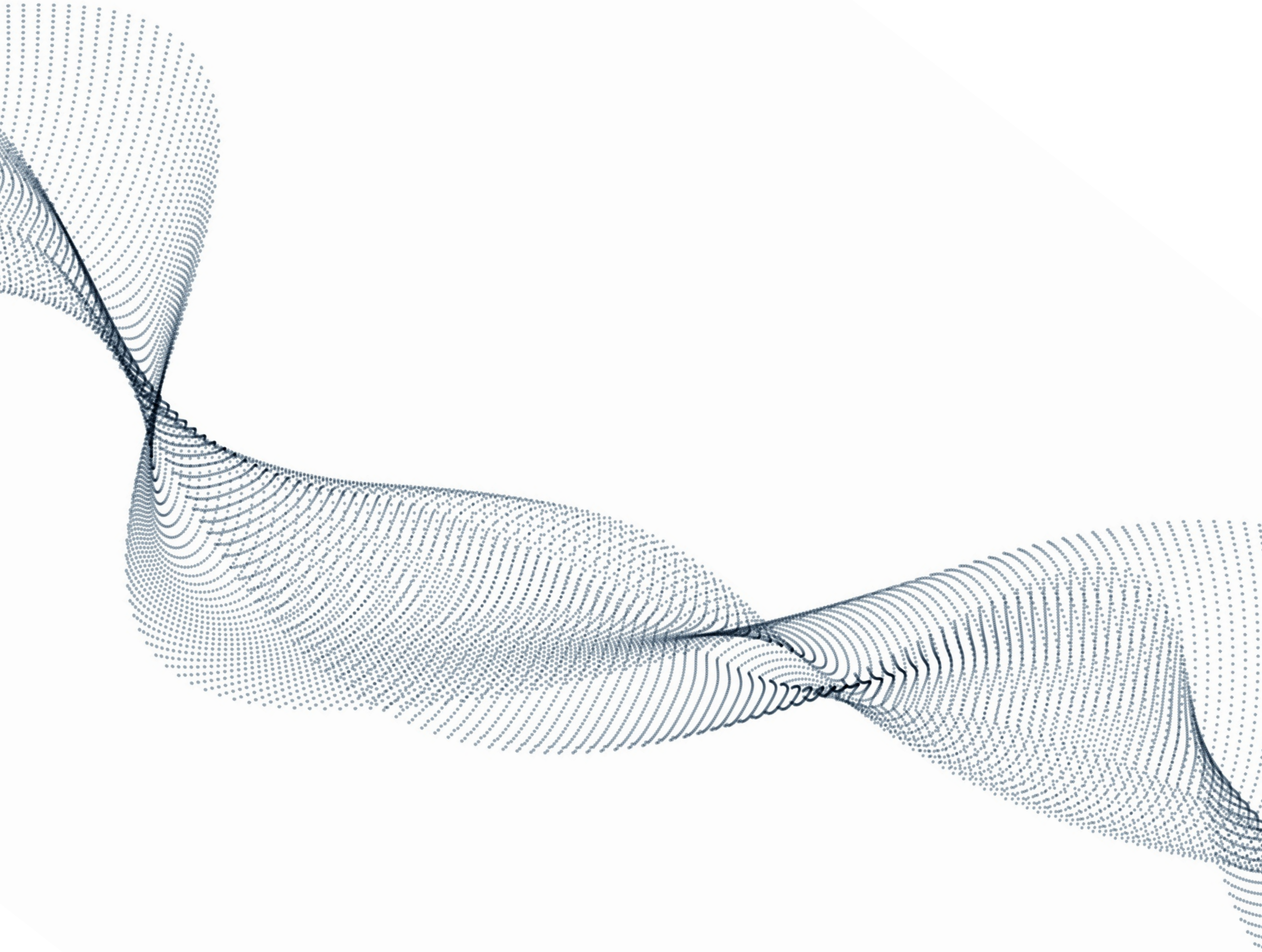
Both the equilibria and kinetics of gas adsorption depend on the properties of the adsorbate and the adsorbent.[2] Maximum equilibrium capacities, for example, generally increase with the total pore volume of a material, but the form of the uptake as a function of pressure, at any given temperature, will depend on pore size, the strength of adsorbate-adsorbent interactions, and adsorbent heterogeneity.

Narrow pores result in greater overlap of the adsorption potentials of opposing pore walls. This increases their adsorption strength, leading to more adsorption at lower pressures. Interactions with a particular surface, however, also depend on the properties of the adsorbate, such as its polarizability and dipole and quadrupole moments, and the chemistry of the adsorbent.[2] Compared to other gases such as H_2, N_2 and CH_4, for example, CO_2 typically adsorbs more strongly due to its larger quadrupole moment; while He interacts weakly, as it has no dipole or quadrupole moment and a relatively low polarizability. Polar surfaces also interact more strongly with polar adsorbates. All these factors therefore affect the working capacity of an adsorbent for a given gas, the heat of adsorption, and the selectivity of one species over another.

Pore size also affects the kinetics. Particularly narrow pores can inhibit diffusion, while wider pores will 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, at lower pressures, or viscous flow through a bulk fluid phase, at higher pressures. The microscopic picture of adsorption and diffusion in different nanoporous materials, particularly for mixtures, when competitive effects become important, can therefore become rather complex.[9,11]

All the factors discussed so far need to be considered when selecting an adsorbent for a given separation. The performance of a particular material can be practically assessed by making the measurements discussed next. Presence of a binder in commercial adsorbent pellets and beads can affect both equilibrium and kinetic properties, and so, for practical purposes, it is important to experimentally characterize each adsorbent on a case-by-case basis.

Gas adsorption measurement



Gas adsorption measurement

Pure gas (single component) adsorption is most commonly measured using the volumetric and gravimetric techniques.[7] Volumetric (or manometric) measurements usually use changes in pressure in a fixed volume system to determine the amount of gas adsorbed, while gravimetric techniques use 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 (see **Figure 2**). A vacuum pump is required to evacuate both the sample cell and the dosing volume. A measurement begins at vacuum, with the sample degassed, and the valve between the volumes closed. Sample degassing is required to remove environmental contaminants, or remnants of the synthesis process, from the pores of the material, prior to a measurement.

The dosing volume is then pressurized and the gas allowed to reach thermal equilibrium. The number of moles of gas, n, in the volume can then be calculated using the real gas law,

$$PV = nZRT \tag{4}$$

where P is pressure, V is volume, Z is the compressibility factor, R is the universal gas constant, and T is temperature. Accurate pressure and temperature measurement is therefore essential.

The valve is then opened to dose gas to the sample cell. If the dosing volume is V_1 and the dead volume of the sample cell, V_2, the amount adsorbed is given by,

$$\Delta n = \frac{P_i V_1}{Z_{i,T} RT} - \frac{P_f (V_1 + V_2)}{Z_{f,T} RT} \tag{5}$$

where 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.

An entire isotherm can then be determined by sequentially dosing more gas to the sample cell and measuring the pressure at each step, so the adsorbed quantity at the mth isotherm point, n_m, is given by,

$$n_m = \sum_{i=1}^{m} \left(\frac{P_{f,j-1,T} V_2}{Z_{f,j-1,T} RT} + \frac{P_{i,j,T} V_1}{Z_{i,j,T} RT} - \frac{P_{f,j,T} (V_1 + V_2)}{Z_{f,j,T} RT} \right). \tag{6}$$

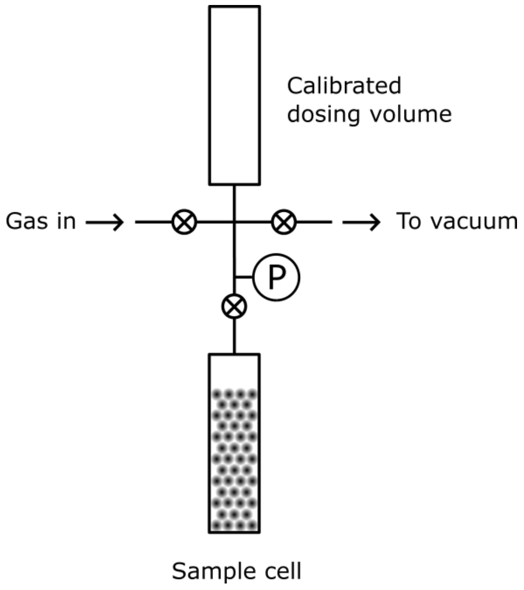


Figure 2. *A schematic diagram of a basic manometric gas sorption measurement system.*

In practice, the dosing volume and sample cell are often held at different temperatures, so this 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. Eq. (6) can therefore be modified accordingly. It should be noted that even small errors in P, V, Z and T can lead to large errors in the above calculations.

Gravimetric techniques

Gravimetric measurements, meanwhile, usually use a system equipped with a microbalance. A common choice is the compensating electronic beam balance, such as those manufactured in the past by Sartorius and Cahn. In this case, the sample is mounted in a pan on one side of the balance beam, with a counterweight suspended from the other (see **Figure 3**). Another option is the magnetic suspension balance. These are often single sided, so no counterweight is required. In both cases, it is necessary to correct the microbalance reading for buoyancy effects. Without accurate corrections, the measured weight will not accurately represent the amount of adsorption, particularly at high pressures.

Regardless of the balance type, however, it must be mounted in a vacuum and pressure-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 chamber, as shown in **Figure 3**, is needed to measure adsorption as a function of pressure. Long term balance stability is also critical.

Both the microbalance and sample chamber must be temperature-controlled, and accurate pressure measurement is essential. Inability to measure pressure accurately may limit a gravimetric instrument's ability to measure adsorption in a given pressure regime, so separate sensors covering different pressure ranges are often required.

An isotherm measurement typically begins with the sample held under vacuum, after an appropriate degassing period, as for the volumetric method. Gas is then dosed into the microbalance chamber and the system 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 analysis of kinetics. The gas pressure is then increased incrementally, with the microbalance reading recorded at each equilibrium point, in order to determine a full isotherm.

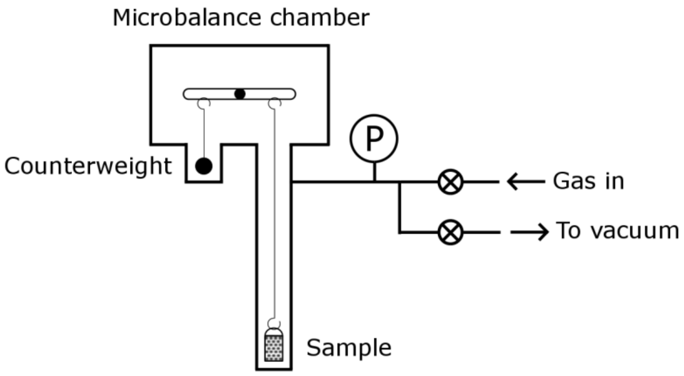


Figure 3*. A schematic diagram of a basic gravimetric gas sorption measurement system.*

Buoyancy corrections at each pressure can be applied in the following way. The force on the microbalance due to adsorption, f_{ads}, is given by,

$$f_{ads} = m_{ads} g \tag{7}$$

where m_{ads} is the mass adsorbed and g is the acceleration due to gravity. The buoyancy of the sample, however, creates a force, $f_{buoyancy}$, that depends on the mass of the sample, m_s, its density, ρ_s, and the gas density, ρ_g, at the measurement temperature and pressure. This is given by,

$$f_{buoyancy} = m_s g \left(\frac{\rho_g}{\rho_s}\right) \tag{8}$$

These two contributions result in a total force on the microbalance, f_{tot}, given by,

$$f_{tot} = f_{ads} - f_{buoyancy} = m_{ads} g - m_s g \left(\frac{\rho_g}{\rho_s}\right). \tag{9}$$

If ρ_g and ρ_s are known, m_{ads} can then be calculated.

Practical calculations are often more complex because other components, such as balance hangdowns and the sample container, contribute to the total buoyancy force. But the above description explains the basic principle.

Other methods

The above techniques are the most common, but various other approaches are available, including variations on the volumetric or manometric method, such as dynamic or flowing[7] and differential techniques,[12] and gas chromatography. The latter can also be used to study kinetics,[9] together with frequency response techniques and other approaches, such as isotope exchange.[13,14]

Dynamic volumetric 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, meanwhile, determine the amount adsorbed by measuring the pressure difference between the sample cell and a reference cell held under the same conditions.[12]

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 are used, and they differ mainly in the way the inlet gas composition is changed. Pulse injection is standard for gas chromatography, more generally, but *frontal chromatography*, which involves introducing a step change in the inlet concentration, rather than a pulse, allows determination of *breakthrough curves*.

Frequency response techniques, meanwhile, use a system containing an adsorbent bed, in which one of the properties, most commonly the volume,[14] can be 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. Analyzing this lag, or the pressure response, therefore allows determination of the sorption kinetics.

Finally, isotope exchange is a more specialist approach in which the isotopic composition of the gas is changed and the response, measured by a mass spectrometer, is used to analyze the equilibria or kinetics of adsorption.[13]

Measurement pitfalls

A number of practical pitfalls can be encountered when making pure gas adsorption measurements, so care must be taken. *Error propagation* due to the large number of readings required for Eq. (6), in the manometric case, for example, can be particularly severe. Careful attention must also be paid 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.[15] The first is knowledge of the *gas density*, which must be calculated using an equation of state (EOS). Accurate EOSs are available – in the NIST REFPROP database,[16] for example – but small errors in pressure and temperature measurement can lead to large errors in Z, even if the EOS is accurate; and these may propagate through a measurement, particularly in the manometric case. The significance of such problems depends on the gas, and on the measurement temperature and pressure regime. CO_2 adsorption measurements close to its critical point, for example, can be particularly susceptible to these errors.

The second, more fundamental, issue is knowledge of the sample volume, which is typically determined using helium, under the assumption that it does not adsorb.[15] Problems associated with this approach – including possible He adsorption and size differences between He and other adsorbates – led to the recent proposal by Gumma and Talu[17] to use *net adsorption*, an alternative definition of the adsorbed quantity that avoids the need to know the sample volume. The two traditional definitions, however, are *excess*[18] and *absolute* adsorption.[19] These two quantities are related to one another by the following expression,

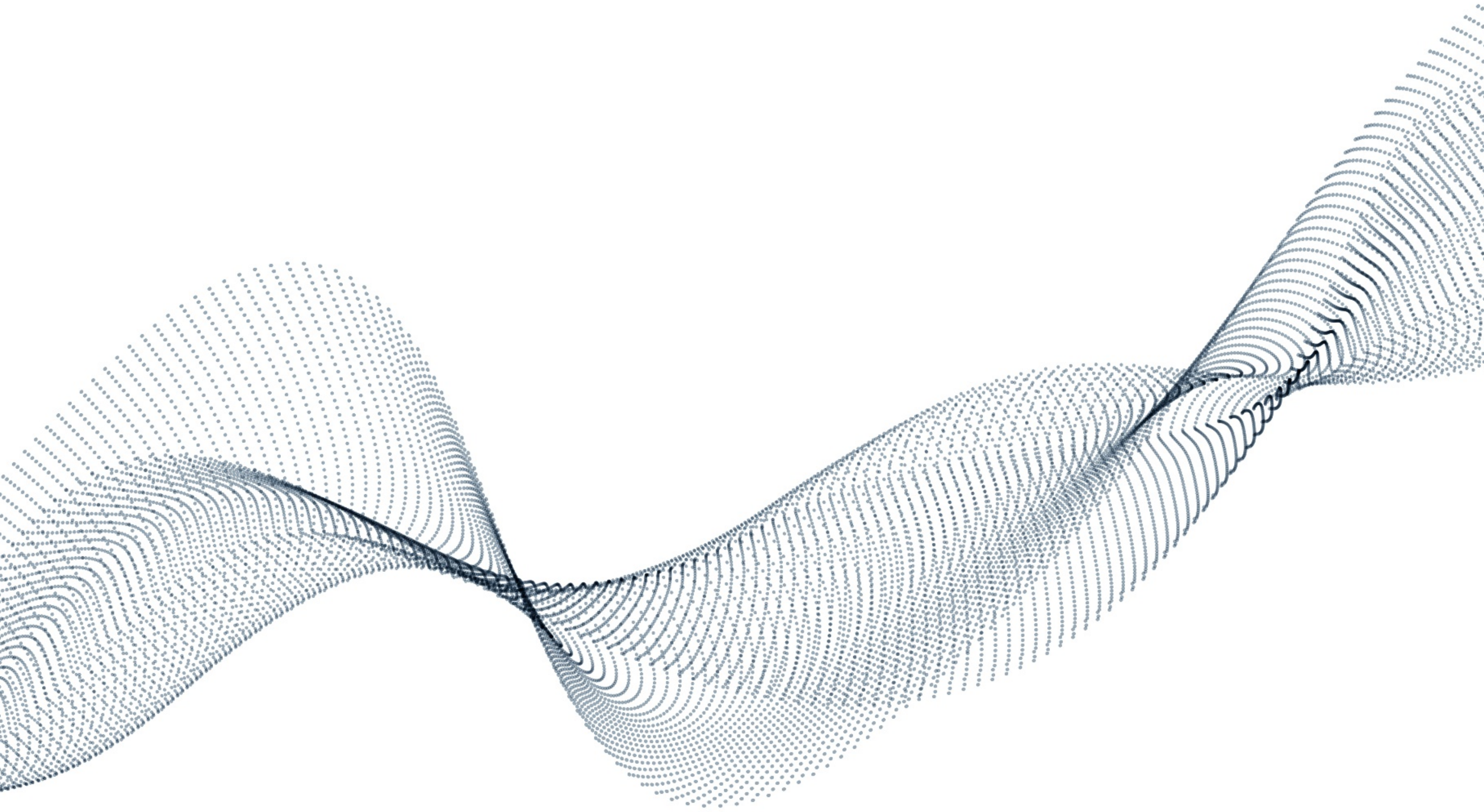
$$n_{abs} = n_{ex} + V_a \rho_g \tag{10}$$

where n_{abs} and n_{ex} are the absolute and excess adsorbed quantities, V_a is the volume of the adsorbed phase, and ρ_g is the gas phase density.

Significant uncertainties are associated with both quantities, due to the complexity or difficulty of defining the adsorbent and adsorbate volumes. Large errors in the sample volume or density will invalidate calculations of the adsorbed quantity, which can have serious implications when assessing an adsorbent for a given application, particularly at higher pressures.

More generally, aspects of instrument design, the exothermic nature of adsorption, and the differing physical behavior of different gases can all affect measurements of gas adsorption. Instrument design issues include the presence of unnecessary dead volume that can increase errors in manometric systems and lengthen response times in gas chromatography and other dynamic methods. The exothermic nature of adsorption, meanwhile, can lead to non-isothermal conditions, while aspects of gas behavior that must be considered include differences in thermal conductivity between different species and as a function of pressure, and adiabatic gas expansion effects that occur when gas passes through orifices, such as valves and mass flow controllers. Flow rate restrictions through valves can also affect kinetic measurements.[20]

Multicomponent adsorption



Multicomponent adsorption

Despite its practical importance, measuring multicomponent adsorption is a more specialist and technically challenging topic.[14,21,22] For pure (single component) gases, weight, volume, temperature, and pressure measurements are combined to calculate the amount of adsorption. Errors in any of these variables can propagate, affecting adsorption measurement accuracy, as discussed in the last section. 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. Different approaches are available, but the errors and uncertainties in these measurements can become rather large.

Volumetric or manometric multicomponent measurements

Talu[22] identified three different approaches to multicomponent measurements based on volumetric 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 using a pump, resulting in the gases mixing and being passed through the adsorbent bed (see **Figure 4**). After equilibrium is achieved, the adsorbent bed is isolated and the pressure measured. The amount of each component adsorbed can then be determined by analyzing the gas phase composition.[21,23]

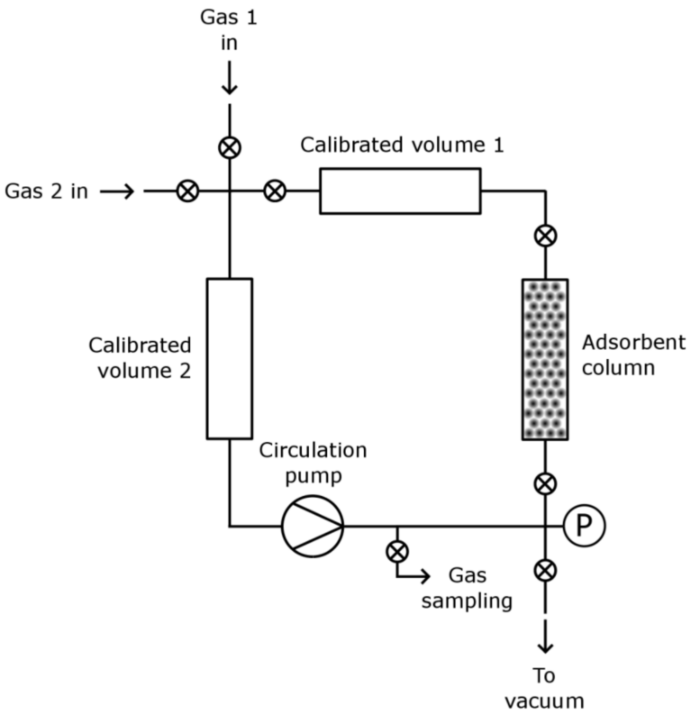


__Figure 4__. A schematic diagram of a closed manometric multicomponent gas sorption measurement system.[21,22]

A molar balance expression is still used, but it contains additional variables expressing the gas phase composition. There are also more volume terms. Accuracy is therefore affected by error propagation, as for pure gas measurements, but with additional uncertainty in the gas phase concentration. Note that the total pressure and gas phase composition cannot be controlled using this method, because the pressure will decrease as adsorption occurs, with the equilibrium concentrations varying depending on the amount of adsorption. These measurements are also laborious, as equilibrium can take hours to achieve, and this provides only a single data point. The adsorbent is typically regenerated before the next measurement is made.

The second volumetric approach involves using an open system – sometimes called a *dynamic column breakthrough*, or DCB, apparatus[24,25] – in which a known gas composition is flowed through the bed using mass flow controllers (MFCs), as shown in **Figure 5**. The downstream composition is analyzed using a gas chromatograph (GC) or a mass spectrometer, and the pressure controlled by a back-pressure regulator.

The amount of each component adsorbed can then be calculated using an open system molar balance expression of the form,

$$\Delta n_i m_s = \int((fy_i)_{in} - (fy_i)_{out})dt - \frac{y_i PV}{ZRT} \quad (11)$$

where n_i is the amount of component i adsorbed per unit mass of adsorbent, m_s is the degassed sample mass, f is the molar gas flow rate, y_i is the gas phase concentration of component i, and t is time. The terms in the integral, $(fy_i)_{in}$ and $(fy_i)_{out}$, are the molar flow rates of component i at the inlet and outlet, respectively, and V is the dead volume of the column.

In this case, accurately determining the gas phase concentration and outlet flow rate is the main technical challenge. Flow rate is particularly difficult to measure to sufficient accuracy, so significant uncertainties can result. At the outlet, the concentration of the gas mixture will be changing as a function of time, so this complicates the measurement process.

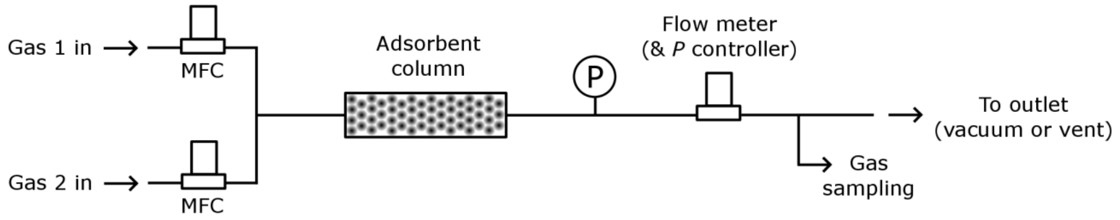


Figure 5*. A schematic diagram of an open (flowing) volumetric multicomponent gas sorption measurement system.*[21,22]

The third volumetric option, sometimes known as the *total desorption method*,[14] involves first equilibrating the adsorbent under a flowing gas mixture. After equilibration, the column is isolated and the adsorbates desorbed into a separate volume. The total contents of the column – held in the separate volume – is then analyzed, allowing the amount of each component present to be calculated. High accuracy can be achieved using this method, but the measurements are particularly laborious.[22] The collection volume is often cooled, while the bed is heated, to ensure full desorption of the adsorbates, before analysis. Again, each measurement, involving multiple stages, yields only a single data point.

Gravimetric multicomponent measurements

Multicomponent adsorption can also be measured gravimetrically in a closed system, with the gas phase composition determined using a GC or mass spectrometer,[23] as shown in **Figure 6**. The gas mixture must again be circulated around the system using a pump, to ensure thorough mixing and to achieve equilibrium, after which the total weight change is recorded and the gas sampled and analyzed to calculate the amount of each species adsorbed by the sample.

This method requires relatively large sample sizes, to ensure the resultant 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 large compared to the volume of a manometric system.

Additional adsorbent can be added to the chamber, to increase the amount of adsorption,[26] 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 the system will help, but there are technical limits for microbalance chambers.

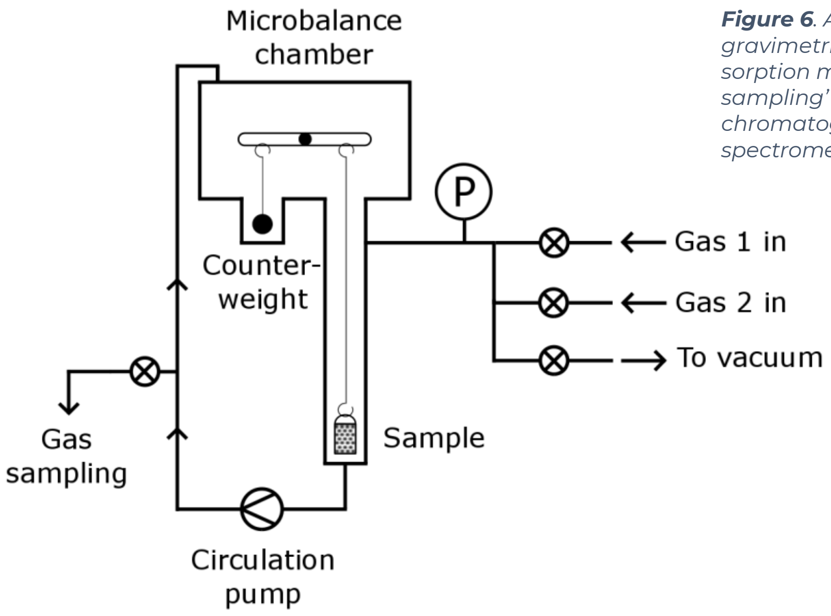


***Figure 6**. A schematic diagram of a gravimetric multicomponent gas sorption measurement system. 'Gas sampling' indicates either a gas chromatograph or a mass spectrometer.*[23]

Combined volumetric-gravimetric methods

An alternative is to combine the volumetric and gravimetric techniques in a closed system. In this case, a gas mixture is delivered to a microbalance chamber from a set of calibrated volumes (see **Figure 7**). When equilibrium is achieved, the total weight change, the internal volume of the system, the molar masses of each gas, and the EOS for the mixture, are combined to calculate the amount of each component adsorbed. This method, however, is limited to binary mixtures and only works when the molar masses of the gases differ sufficiently. Accuracy decreases as the molar masses of the species approach one another,[22,23] and so it is inappropriate for some adsorbate-adsorbate pairs.

The limitations of this technique can be understood by considering that accurate volumetric measurements require a low system volume, combined with accurate temperature and pressure measurement; yet microbalance chambers tend to have large internal volumes, compared to the most accurate volumetric systems, as noted above. The conflict between these two requirements means it is challenging to make accurate measurements of binary gas adsorption in this way. Uncertainties in mixture EOSs also add to the difficulties.

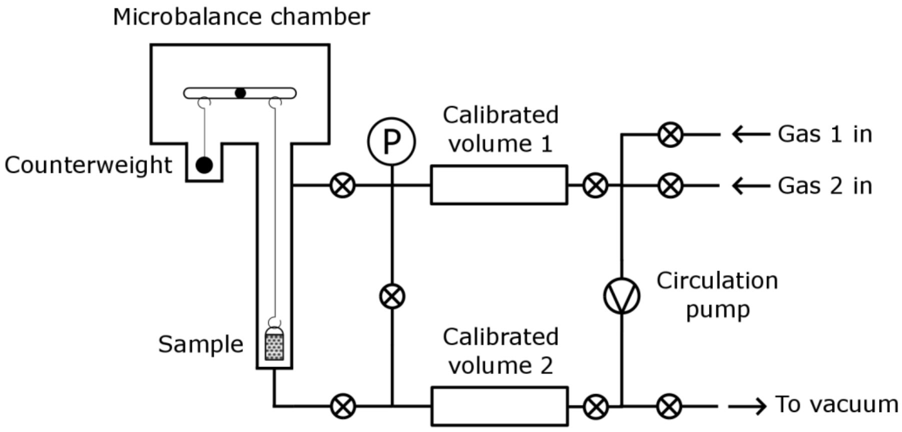


Figure 7. *A schematic diagram of a combined volumetric-gravimetric multicomponent gas sorption measurement system.*[23]

Integral Mass Balance (IMB) method

An alternative way of combining volumetric and gravimetric measurements, called the Integral Mass Balance (IMB) method, was recently introduced by Hiden Isochema. It involves combining an open (flowing) volumetric system with in-situ gravimetric measurement.[27] A controlled gas mixture is introduced at the base of a column beneath a microbalance. The weight of the sample is determined as a function of time, using the microbalance, following a step change in the inlet gas composition, and the outlet gas composition above the sample is determined using a mass spectrometer.

In contrast to the molar balance calculation performed for open volumetric systems (Eq. (10)), a mass balance integration is instead used to calculate the amount of each component adsorbed. This approach eliminates the need to measure the total outlet flow rate – the main weakness, with regard to accuracy, of open system volumetric approaches. Using a microbalance, the weight change as a function of time, $\mathrm{d}w/\mathrm{d}t$, can be determined to high accuracy. Multipoint isotherms can also be measured in a single experiment, without the need to regenerate the adsorbent between data points.

Full details can be found in a recent report,[27] in which binary N_2/O_2 adsorption isotherms were measured at a pressure of 0.915 MPa, using a 3.5 g zeolite 5A sample, and found to agree with previously published data. Twenty point binary adsorption isotherms were measured in only four hours, which represents a step change in measurement speed, compared to other techniques of comparable accuracy.

Future challenges

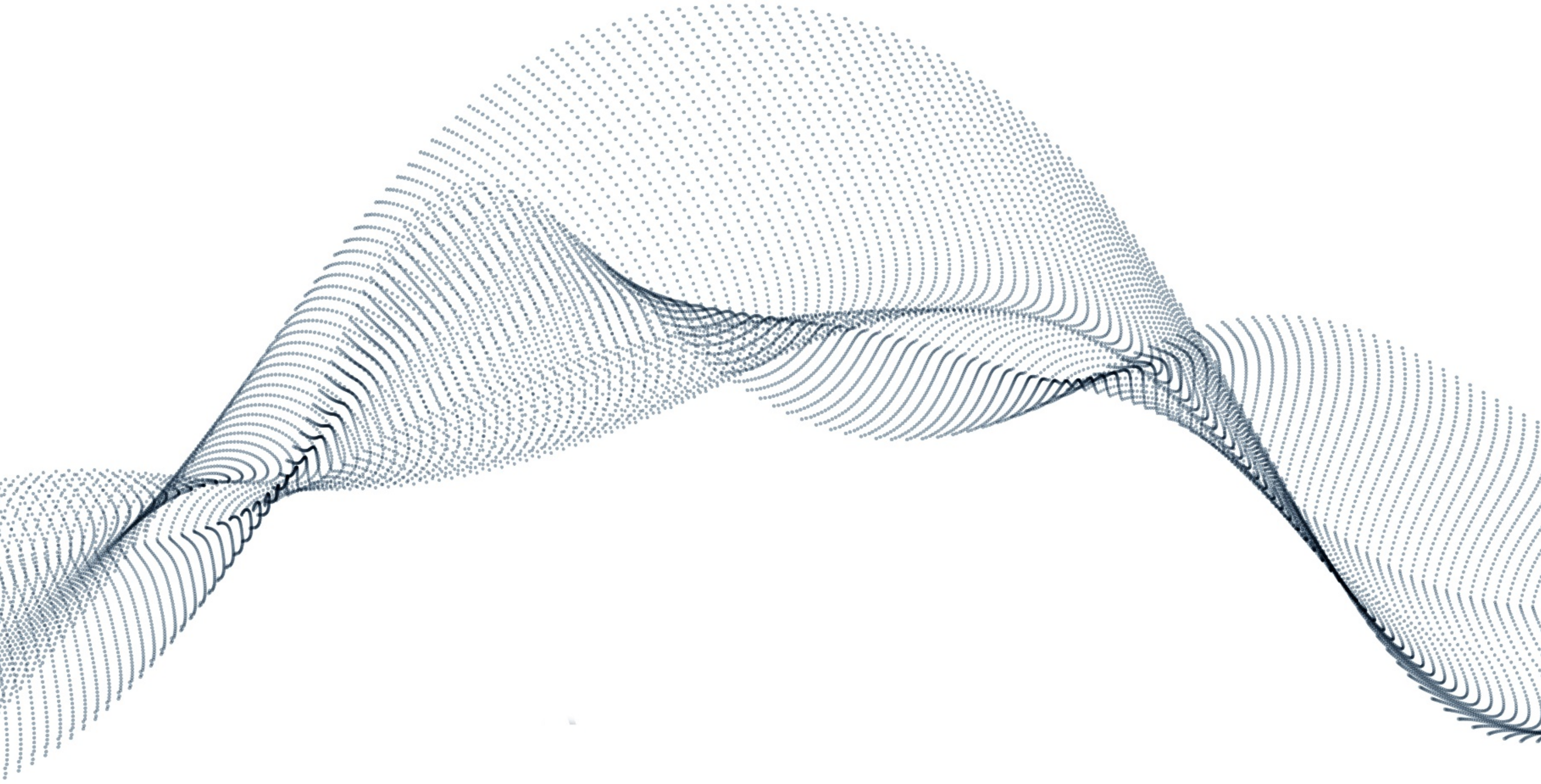
This section has emphasized the technically demanding nature of measuring multicomponent adsorption. For any given adsorbate-adsorbate pair, or combination of different adsorbates, it is possible to find a way of making accurate multicomponent adsorption measurements, but it can be a time-consuming process. Equilibration times may be lengthy and the required optimization procedure can be laborious, requiring changes in the various experimental parameters to be made to investigate the effects on the results. Careful instrument calibration is also essential.

A large number of data points are also required to thoroughly 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 the multicomponent case, both the gas and adsorbed phase composition and total pressure can be varied, introducing additional degrees of freedom. If measuring a single data point takes hours, total experimental times can become prohibitively long. In addition, in closed systems, the data points are essentially random,[14] because it is not possible to control the final state of the system.

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

The IMB method, introduced recently by Hiden Isochema, offers much promise in this regard. It has so far been properly validated for binary mixtures of N_2 and O_2 at pressures below 1.0 MPa, and further investigation of its applicability under a wider range of measurement conditions, including higher pressures, and for ternary or higher mixtures, is underway.

Comparison of different laboratory techniques



Comparison of different laboratory techniques

The study of pure gas (single component) adsorption is dominated by the manometric and gravimetric techniques. These two approaches measure the amount of gas adsorbed by a material in different ways, and this leads to different advantages and disadvantages.

Cost and ease-of-use

Manometric instruments are generally more robust, as they do not require the use of a microbalance, and simple, manually-operated systems can be built from off-the-shelf pressure and vacuum components. This means it is a cheaper way of characterizing gas adsorption. Higher pressure operation is also more straightforward, as there is no need to house a microbalance in a pressure-rated chamber.

Gravimetric systems, in contrast, must be operated in a vibration-free environment, as physical disturbance of the microbalance will result in measurement errors. Samples must also be loaded onto the microbalance, so it can be argued that they require more dexterity to operate. In terms of hardware, as implied above, gravimetric instruments also tend to be more expensive, although fully automated commercial manometric instruments for high pressure operation may be comparable in cost.

Accuracy and throughput

The achievable accuracy of the two techniques differs. In the manometric case, error propagation is inherent to the method usually used to determine an isotherm. The sample is first degassed and then gas is dosed into the sample chamber. Subsequent isotherm points are then determined by summing each quantity of gas adsorbed at each step, using Eq. (6) or the equivalent expression for the system under consideration. This can result in significant error accumulation, which can be problematic, particularly at higher pressures.

In the gravimetric case, the uptake at each isotherm point is determined relative to the degassed sample mass, and so errors do not accumulate in the same way. The gravimetric technique also involves the measurement of sample weight, in addition to temperature and pressure, which are required by both methods. This, therefore, provides an additional test of the physical plausibility of experimental data.

The potential molar sensitivity of a manometric instrument can be estimated using the real gas law (Eq. (4)), as the measurable molar quantity is determined using a change in pressure, ΔP. For a given measurable pressure change, which depends on the accuracy and resolution of the sensor, the measurable molar amount of adsorption, Δn, is given by,

$$\Delta n = \frac{\Delta PV}{ZRT} \qquad (12)$$

For a given value of ΔP, assuming fixed accuracies of T and Z, the magnitude of Δn will depend on the magnitude of V, the internal volume of the system. Lower volume manometric systems will therefore be able to measure smaller molar quantities of adsorption, and so they will be more accurate.

Direct comparison between the achievable accuracies of manometric and gravimetric instruments – for a single isotherm point – can therefore be made by comparing Δn, for the manometric case, to the measurable weight change in a gravimetric system. The latter depends on the resolution and long term stability of the microbalance, which is typically of the order of a microgram. Even for H_2, the lightest of all gases, it is difficult to achieve a Δn, using a manometric system, as low as the minimum detectable weight change in a gravimetric instrument.

An important consequence of the ability of the gravimetric technique to detect smaller adsorbed quantities is that less sample can be used, without compromising the quality of experimental data. For new adsorbents, such as metal-organic frameworks (MOFs), which are often initially synthesized only in small amounts, this is a significant advantage.

There is, however, a trade-off between accuracy and throughput – the number of samples that can be analyzed in a given time. The nature of gravimetric systems allows for a more direct pumping path between the vacuum system and the microbalance chamber, compared to a typical pumping path between the vacuum system and sample cell in volumetric instruments. Valve orifices, in the volumetric case – and generally narrower tubing – reduce the conductivity required to achieve high vacuum conditions at the sample position.

Gravimetric systems also allow in-situ measurement of the sample weight during degassing, thus providing a precise value of the degassed sample mass for calculation of the uptake at each isotherm point. This is another accuracy advantage; but the need to degas the sample in situ is a disadvantage, in terms of throughput, as volumetric systems can use separate degassing stations. One sample can be degassed while an isotherm is being measured on another. Commercial volumetric systems with multiple measurement ports are also available, which provide even higher sample throughput, compared to typical gravimetric instruments.

Versatility

A further consideration is the potential versatility of an instrument. Gravimetric instruments can often operate in more than one way, so that – for example – standard thermogravimetric analysis (TGA) can be performed in an instrument also capable of measuring accurate gas adsorption and desorption isotherms, over a wide range of pressures and temperatures. Furthermore, a mass spectrometer can be coupled to an instrument capable of flowing an inert carrier gas over the sample, allowing the performance of TGA-MS. Although less common, gravimetric instruments can also be used to measure isobars and to perform other types of experiments that involve changing the sample temperature and monitoring the change in sample weight. The gravimetric technique is also better suited to measuring vapor sorption, as bulk condensation – although best avoided – is unlikely to affect measurement accuracy. Gravimetric instruments therefore tend to be more versatile than their volumetric or manometric counterparts.

Summary and Outlook

This white paper has covered the various performance parameters required to assess an adsorbent for a given gas separation, including working capacity and isotherm shape, selectivity, heat of adsorption, and sorption kinetics. The importance of adsorbent and adsorbate properties has also been discussed. The volumetric and gravimetric techniques for determining pure gas adsorption have been described, and other methods briefly covered, together with some practical measurement pitfalls.

For separations, multicomponent adsorption is important, so the various approaches have been discussed. The technical difficulties involved have also been emphasized. 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. Such developments would have a significant impact on the field.

A comparison of the main techniques for measuring pure gas adsorption has also been provided, focusing on their cost, ease-of-use, accuracy, sample throughput, and versatility. Manometric instruments are undoubtedly easier to construct, but the gravimetric technique can be shown to be more sensitive and thus capable of making more accurate measurements on small samples. On the other hand, manometric instruments can provide higher sample throughput, due to flexibility with regard to sample degassing. Gravimetric instruments, however, are more versatile, as additional measurement types, such as TGA-MS and vapor sorption, can be performed using the same apparatus.

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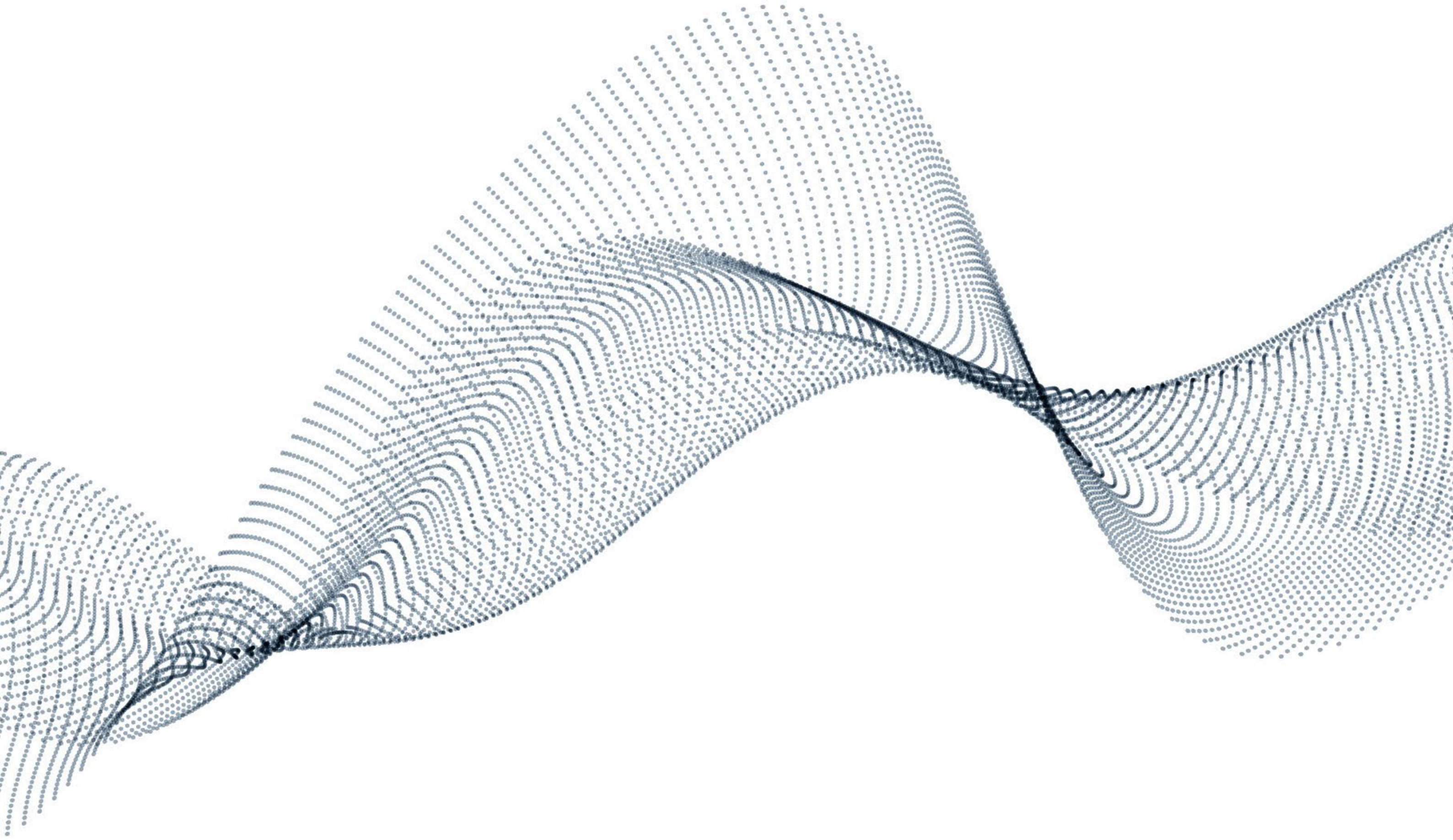

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