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DVS Application Note 50

An Overview of Dynamic and Gravimetric Vapour Sorption Vacuum System

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SMS DVS Vacuum system makes use of Dynamic and gravimetric vacuum methods which offer a number of advantages over other sorption methods for studying vacuum adsorption processes. SMS DVS Vacuum instrument can offer measurements on vapour pressure and heat of evaporation of solids, low pressure vapour/gas sorption and vacuum drying.

Introduction

There are a number of different sorption measurement methods available, for example, gravimetric and volumetric methods, ambient flow and vacuum methods, static vacuum and dynamic vacuum methods. A common question asked by many potential users of Gravimetric instrument systems is whether a vacuum method is superior to an ambient flowing gas method.

Advantages of DVS vacuum method:

Compared with ambient flow sorption instruments, there are a number of advantages offered by DVS Vacuum instrument.

1) DVS Vacuum can virtually dry all sorts of materials

Some materials need extensive drying/outgassing, which is not possible with traditional drying methods like dry gas flow and thermal convection heating. These may be:

- Micro-porous solids
- Chemical absorbents
- Nano-powders and fillers
- Complex inorganic solids
- Some strong hydrates and
- Bio-materials

2)DVS Vacuum can study co-adsorption of gases, gas mixtures or vapour/gas mixtures easily

Gas sorption measurement is nowadays extremely useful for environmental protection, filtration, fuel cell, catalysts etc.

3)DVS Vacuum can measure very low vapour pressure (10-10 Pa) and heat of evaporation of solid materials

The vapour pressure of solids is a key parameter for predicting their thermodynamic stability and for determining atmospheric inhalation exposure levels due to volatilization.

4)DVS Vacuum can work over a very large range of partial pressures (from atmospheric pressure down to 10-6 Torr)

This is important for some sub-atmospheric applications, e.g. low pressure gas capture etc.

Measurement methodology

a) Static and dynamic methods:

1)Static method

Traditional vacuum sorption measurements are conducted at static mode using the volumetric sorption method. In this process, once the vapour enters the sample chamber, the chamber is sealed and the experiment occurs under static conditions, i.e. no gas flow. Static method is acceptable at relatively higher partial pressures. The limitation with static measurements is that during experimental period, the system pressure can change for various reasons, more commonly due to vacuum leaks. This may lead to errors in measurements, especially at low partial pressures.

2)Dynamic method

In the dynamic vacuum method the instrument controls both upstream rates of vapour entry via a MFC and the downstream exit rate of vapour via a butterfly valve, effecting control over the residence time of the vapour in the chamber, and establishing contact with the sample. The principle of dynamic vacuum method is illustrated Figure 1 below.

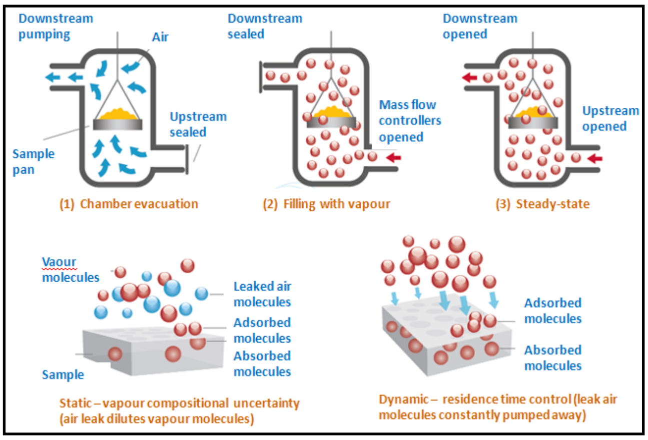

Figure 1. Principle of dynamic vacuum method

b) Volumetric and gravimetric methods:

As mentioned before, volumetric method is a static process which may not be very accurate at low pressures due to system leaks. Furthermore the parameter measured directly in volumetric system is pressure change which is then converted to volumetric change using standard relationship viz. $PV = NkT$

Where P and V are pressure and volume of the gas respectively. N is number of particles in the gas, T is the temperature of the gas and K is Boltzmann constant (1.38066 x 10^{-23} J/K).

Gas or vapour pressure measurement is not as accurate and sensitive as weight change measurement, so the volumetric method in general is less accurate than gravimetric method. In order to obtain the same sensitivity, volumetric method needs much more sample, which takes longer time to reach sorption equilibrium. Samples can be expensive in some cases, e.g. drug samples for formulation research, this may substantially increase experimental costs.

SMS DVS Gravimetric Vacuum System

SMS DVS Vacuum system is a gravimetric system and can work at both static and dynamic modes, which offers flexibility for studying adsorption processes under vacuum.

Physical properties measurable

The DVS Vacuum system measures the following physical properties:

- Adsorption and desorption isotherms
- Vapour pressure and heat of evaporation of solids

With Advance Analysis software, further properties can me measured as detailed below:

- Activation energy
- BET surface area
- Diffusion constants
- Heat of sorption

- Micro/meso-pore size distributions
- Glass transition, etc

Application examples

1) Vapour pressure measurement of pesticide, bifenthrin

Vapour pressure of bifenthrin is too low to be measured at 25°C, but it can be extrapolated from the DVS Vacuum data recorded at elevated temperatures. The raw data shown in Figure 2 was measured at 65°C. Its vapour pressure at 25°C and heat of evaporation are calculated to be 5.42 x 10^{-7} Torr and 5.2 x 104 J.Mol^{-1} respectively. The details of the calculation was addressed somewhere else [1][2].

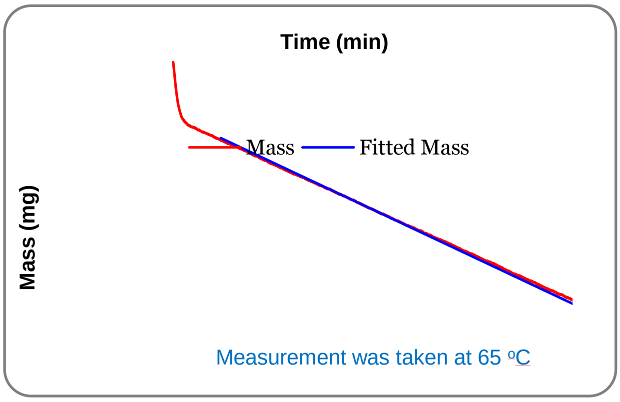

Figure 2. Linear mass loss of bifenthrin at 65°C

2) CO_2 sorption on MOFs at 25°C

Metal organic frameworks (MOFs) are highly crystalline clusters of metal ions connected by organic linkers. Their nano-sized pores and large specific surface areas (up to 5,000m^2/g) facilitate high-capacity storage of natural gasses and other compounds. Figure 3 shows the sorption behaviour of CO_2 gas on MOFs substance. One can notice that the sorption has not reached equilibrium. Much more can be absorbed above atmospheric pressures, indicating that MOFs can be a potential material for CO_2 gas capture, storage and transportation.

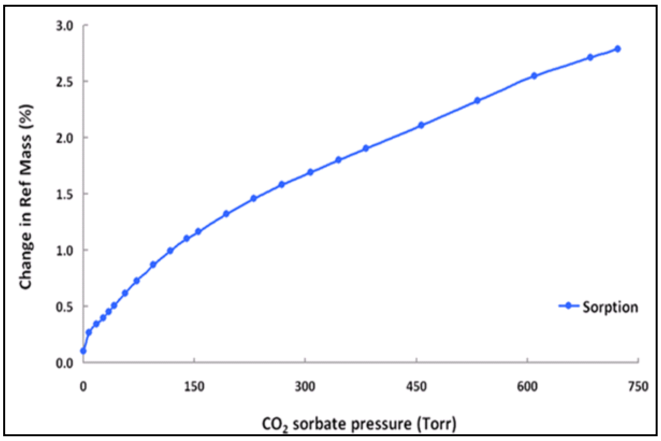

Figure 3. CO2 gas sorption on MOFs

3) SO_2 gas sorption on zeolites at 25°C

Figure 4 shows the sorption of SO_2 gas on three different zeolites. The sorption was found to be irreversible at 25°C and the uptakes are between30% to 35% of reference masses at low partial pressure, making these zeolites a very good candidate for SO_2 capture.

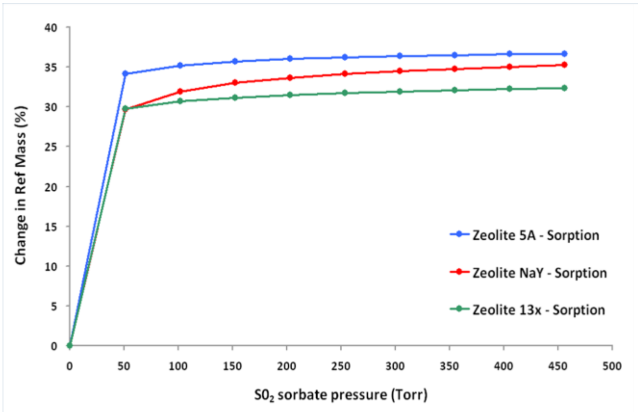

Figure 4. SO2 gas sorption on zeolites

4)Low vapour pressure adsorption of 2-hexanol on activated carbon

Normal static vacuum methods suffer from the effect of system leak rates for sorption at low pressures, resulting in the system pressure not equalling to the vapour partial pressure. Dynamic vacuum overcomes this problem by continuously bleeding the vapour into the system and continuously taking vapour out using the down-stream butterfly valve to control the pressure.

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The Figure 5 demonstrates low pressure measurement of 2-hexanol on activated carbon. Accurate measurements cannot be easily achieved at such low partial pressures in a volumetric system.

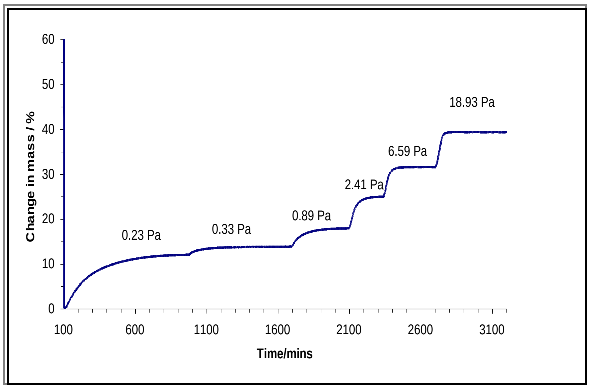

Figure 5. Low partial pressure adsorption of 2-hexanol on activated carbon

5) Separation of octane from water by activated carbon at 25°C

Co-adsorption has attached more and more interest for its application in filtration and separation. Figure 6 shows the co-adsorption of mixture of octane and water at different ratio. The activated carbon shows strong preference for sorption with octane, making it a potential useful agent for the separation of octane from water.

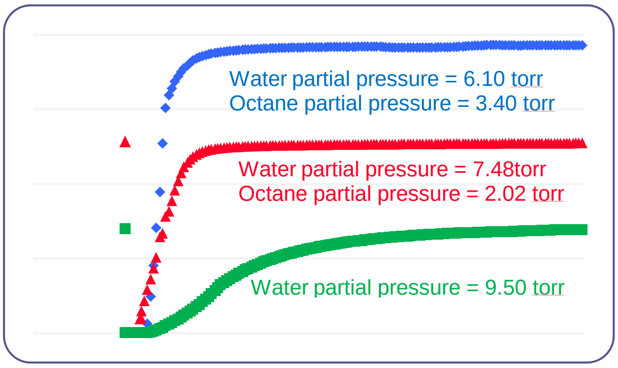

Figure 6. Co-adsorption of octane and water on active carbon

Conclusion

Dynamic and gravimetric vacuum sorption instrument offers a flexible research platform for studying adsorption processes under dynamic or static experimental conditions. In addition to what ambient flow sorption instruments can offer, such as activation energy, BET surface area, diffusion constants, micro/meso-pore size distributions, glass transition, etc. SMS DVS Vacuum instrument can also offer measurements on vapour pressure and heat of evaporation of solids, low pressure vapour/gas sorption and vacuum drying.

References

[1]Vapour Pressure Measurement of Pesticides using the DVS (App 48), Peng Miao and Majid Naderi

[2]Low Vapour Pressure Measurements of Solid State Pesticides using the DVS Vacuum Knudsen Method (to be published). Peng Miao etc.

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