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DVS Application Note 47

Determination of True Density by Dynamic Vapour Sorption

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The versatility and impact of Dynamic Vapour Sorption (DVS) for the true density measurements of solid powder materials have been investigated. True density measurements on different amounts of Lactose and Avicel (microcrystalline cellulose) samples were successfully determined using DVS and a gas Pycnometer for comparison.

Introduction

True density is a fundamental parameter required for characterising many solid materials and slurries including: monitoring of structural rearrangement and porosity of carbon and ceramics after calcination, monitoring the composition of pharmaceutical active and excipient ingredients, determination of the reproducibility when blending building materials and determination of the crystallinity of plastic films and polymers as well as pigmented coatings [1-2]. True density has historically been determined by liquid displacement using for example, kerosene or naptha. However, gas rather than liquid, is the preferred medium since it is cleaner, faster and more amenable to automation, and does not require the rigorous thermostatting associated with liquid techniques [3].

Based on the gas displacement technique, the DVS powder density method measures the weight of the sample in two gases of known density. The most accurate results are obtained when the gas is moisture-free, non-reactive and behaves as ideally as possible. For this reason, helium is chosen for most applications. However, other inert gases such as nitrogen may be used as well. The measurement and calibration are fully automated and the internal temperature control of the DVS allows measurements to be performed isothermally, thus making it independent of room temperature fluctuations.

This application note outlines how DVS instruments can be used to measure the true density of different amounts of Lactose (Sigma Aldrich) and Avicel (PH 101, FMC Corporation). The density values obtained from the DVS instruments are compared against those obtained by a gas Pycnometer for the same materials.

Theory

For the DVS calculations, the Force of Buoyancy given by Equation 1 may be used to determine the density of a particular material:

Force of Buoyancy = Weight of Fluid Displaced = $\rho_{fluid} V g$ (1)

The difference between the force of buoyancy in two different gases can be calculated using Equation 2 :

$$F1 - F2 = (\rho 1 - \rho 2) V g \quad (2)$$

where, F1 is the buoyancy force exerted by Gas 1; F2 is the buoyancy force exerted by Gas 2; ρ1 is the density of Gas 1; ρ2 is the density of Gas 2; V is the volume; and g is the gravitational acceleration.

Equation 2 provides the required sample volume to be used in Equation 3 :

$$\rho = M / V \quad (3)$$

where, M is the mass of the sample.

The working equation of a gas Pycnometer is based on the Ideal Gas Law:

$$PV = nRT \quad (4)$$

At constant temperature, PV is constant. With known values of weight of the sample, volume of the sample chamber, volume of gas reservoir and change in pressure, the volume of the sample is translated into the absolute density using Equation 5 :

$$P1V1=P2(V1+V2) \quad (5)$$

where, V1 is the volume of Empty Sample Chamber – Volume of Filled Sample Chamber; V2 = Volume of the gas reservoir; V2 is the volume of the gas reservoir; and P1 and P2 are the gas pressures in the sample chamber and reservoir, respectively.

Method

A schematic of the DVS-Advantage instrument is shown in Figure 1. The instrument measures the uptake and loss of vapour gravimetrically using the SMS UltraBalance. There are two confirgurations of the SMS UltraBalance: (1) one gram capacity with a mass resolution of at least 0.1 µg and (2) four gram capacity with a mass resolution of at least 1.0 µg. The desired partial pressure of the vapour surrounding the sample is obtained by mixing the saturated and dry carrier gas streams using electronic mass flow controllers. The DVS-Advantage instrument has the unique capability to actively measure and control the concentration of water and a wide range of organic vapours. This is accomplished by utilising a proprietary optical sensor which is specifically tuned for a wide range of solvents. This technology allows the instrument to measure and control organic vapour concentrations in real time. The DVS-Intrinsic instrument has similar balance configurations (1 gram or 4 gram capacity), but is designed for water vapour only.

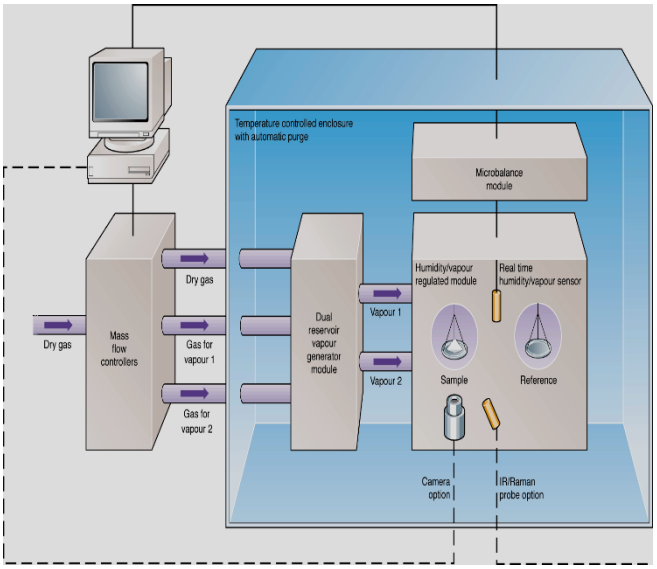

Figure 1. Schematic overview of the SMS DVS-Advantage instrument.

The sample density wizard provides step by step instructions of how to perform an experiment to calculate the bulk density of a sample. The experiment is based on Archimedes principle i.e. the net upward buoyancy force is equal to the magnitude of the weight of fluid displaced by the body. Therefore, it is necessary to use weight of the sample in two different gases with significantly different densities e.g. Air and Helium. Pycnometer measurements were performed using a helium Micromeritics AccuPyc II 1340.

Results

The DVS wizard will display a sample density report as shown in Figure 2, where the densities of the material in Air and Helium are reported.

Sample Density Report:	
Sample:	Lactose
Target Temperature (°C):	25.0
Total Flow Rate (sccm):	200
Gas # 1	
Air:	
Density (g/cm^3):	0.001161
Sample Mass (mg):	80.5145
Gas # 2	
Helium:	
Density (g/cm^3):	0.0001636
Volume of Solid (cm^3):	0.0516342490
Density of Solid in Air (g/cm^3):	1.5593235398

Figure 2. Sample output of the Powder Density calculation in the DVS Advantage control software.

For Lactose sample masses of less than 20mg, neither the DVS nor the Pycnometer gave consistent readings. However, for sample masses of Lactose greater than 20mg, the DVS and Pycnometer results (Figure 3) were similar and in good agreement with the density value provided by SigmaAldrich (1.52 gcm^{-3}).

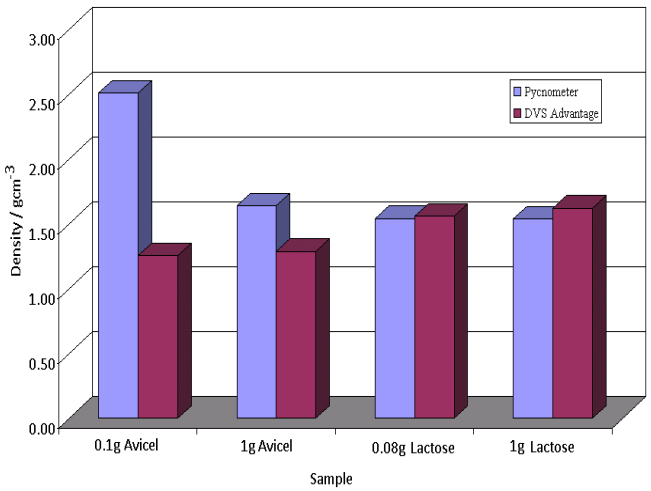

Figure 3. Comparison between powder density measurements obtained from the DVS Advantage and the Micromeritics AccuPyc Pycnometer.

For Avicel samples, Figure 3 shows that the DVS powder density results were consistent for different masses of Avicel and in good agreement with the reported value by FMC Corporation (1.40 gcm^{-3}) [4]. However, the Pycnometer showed inconsistent results for different masses of Avicel. This could be due to the sensitivity of the cellulose powder to atmospheric moisture and the absence of a drying stage during the measurements with the Pycnometer, whereas the DVS allows for a drying period by requiring a stable mass reading.

Conclusion

The DVS Advantage powder density measurements offer reliable and convenient methods for studying different sample sizes using a range of gases. The internal temperature control (5 - 60 ºC) allows measurements to be performed isothermally and independent of room temperature. In addition the DVS methods offer in-situ conditioning of the samples before the density measurements.

References

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