

Sample Preparation on the ASAP 2010 Surface Area Analyzer

Regardless of how well designed a surface area instrument may be, the BET surface area it measures will be consistent and repeatable only if the sample surface has first been cleared of bound gases and vapors, which accumulate due to atmospheric exposure. These gases and vapors (contaminants), if not removed, alter the BET result by blocking access of nitrogen to pores or by lowering the strength of the interaction of the nitrogen with the surface, causing less adsorption to occur at a given pressure. The ASAP 2010 and the ASAP 2010 Chemi provide, respectively, vacuum/heat and flowing-gas/heat sample preparation.

Gases and vapors may be bound to a surface by weak bonds of physical adsorption (physisorption) or by stronger bonds of chemical adsorption (chemisorption). Thermal agitation, even at a constant temperature, is constantly increasing and decreasing the vibrational energy of these bound molecules in a random manner. If enough energy is instantaneously transferred to a gas molecule, it may attain “escape velocity” such that it breaks loose from the forces that bind it to the solid surface, allowing it to re-enter the gas phase above the sample. Only while these molecules are in the gas phase is it possible to remove them, either by pumping them away with a vacuum or entraining them in a flow of some gas that cannot bind itself to the sample surface.

When cleaning a surface, the rate limiting step is almost always the liberation from the surface, and no increased quality of vacuum or purity of the non-adsorbing gas can in any way affect this liberation rate. The only way to increase the liberation rate is to raise the sample temperature to cause the thermal agitation to become more energetic. Of course, if the liberated molecules are not efficiently and promptly removed, the reverse process of re-adsorption will increase until at some pressure, there will be an exact balance between departing and arriving gas molecules on the surface. Fortunately, the pressure at which this balance occurs increases exponentially with increasing temperature so that relatively small increases in temperature can more than compensate for less than perfect vacuum or purity levels of the purging gas flowing over the sample.

Practical engineering issues place limits on our ability to benefit from the highest levels of vacuum or purge gas purity when we look at some of the compromises that must be made in a real-world gas adsorption analyzer.

- Sample tube stems need to be small enough in diameter to keep gas measurement errors low, even though this impedes the vacuum quality.
- Leak-tight gas valves must have relatively small passageways, which further limit vacuum conductance.

- Filter frits at the sample port are necessary to minimize the likelihood of pulling sample particles into the manifold.
- Polymer O-rings and valve plungers must be used to ensure reliable sealing for routine use. These polymers absorb gases (such as air, water vapor, CO₂, and hydrocarbons) that were previously used in the manifold. They may also emit volatile plasticizers or monomers.

Since all of these can prevent attaining ultimate vacuum (of which better vacuum pumps are capable) or add impurities to the gas stream, using expensive, purer grades of gases is unjustified.

While limits to the cleanliness levels that can be economically reached in a productive, commercial gas adsorption analyzer do exist, there are many design features that can markedly improve the performance. The ASAP 2010 design incorporates a number of these well-proven concepts, beginning with separate vacuum systems for sample preparation and analysis, which help immeasurably by keeping the relatively “dirty” and higher temperature process of initial sample cleaning isolated from the cleaner and lower temperature operations involved in sample analysis. The sample may be forcefully stripped of contaminants at as high a temperature as is required to dislodge and remove them from the system with only moderate vacuum. Should deposition of viscous contaminants in the degassing manifold occur, recovery is greatly speeded and simplified due to the simple design and lower cost components used there. Once a sample is cleaned, it can be moved to the analysis section and is not likely to challenge the vacuum capability. Vacuum measurement is as close to the sample port entrance as possible to give a realistic measurement. These measurements are corrected for thermal transpiration when static, equilibrated data are taken.

All manifolds are formed in monolithic stainless steel blocks to ensure minimal retention of contaminants, ease of cleaning, rapid pumpdown, and corrosion resistance. Two manifold sections are created in this analysis manifold; an upper section is for gas entry, and a lower section serves as the equilibrating manifold. During sample equilibrations, the upper section is continuously evacuated to serve as a guard volume so that diffusion of various analysis gases, such as helium or air, through their valve seats will not lead to their accumulation in the analysis gas. This is especially crucial when low equilibrium pressures are to be measured on microporous materials where hundreds of standard cubic centimeters of nitrogen may be adsorbed at a pressure of approximately one micrometer Hg. One micrometer Hg additive partial pressure (amounting to less than one part per million) of non-adsorbable helium would cause a 100% equilibrium pressure error.

Summary

Surface area analyzers that use flowing gas or moderate vacuum to remove contaminants from the sample, such as the ASAP 2010 Series, are as effective as those that use higher levels of vacuum because of the practical difficulty of achieving the highest vacuum at the sample, the diminishing level of returns, and the time limits and handling restrictions. The ASAP 2010 Series features separate vacuum systems to keep the sample from being contaminated by vapors driven from the degas samples. The constant interruptions caused by sharing a single vacuum source are also avoided, leading to a high level of instrument productivity. A good, well-designed vacuum system ensures a properly cleaned sample, and a clean sample provides accurate data. The ASAP 2010 Series surface area analyzers provide both.