

Using the ASAP Series Analyzers to Acquire Nitrogen Micropore Isotherms With Minimum Error

The Micromeritics ASAP analyzer is a highly versatile gas adsorption instrument that offers a number of specialized optional analysis capabilities (in addition to the standard capabilities), one of which is an ultra-low pressure measurement capability. This micropore option is capable of producing sorption data covering nearly seven decades of pressure range. To collect optimum isotherm data in the low-pressure range, it is important to understand the science of the measurement and the effects caused by interfering phenomena.

A nitrogen isotherm measured on a microporous material held at a temperature of 77 K permits the pore size distribution and the volume of the micropores and mesopores to be estimated. This information is indicative of the performance of the material when used for many real-world adsorption tasks such as solvent recovery, odor control, water purification, atmospheric gas separations, moisture removal, and catalytic applications. In addition, the isotherm itself may be of interest in that the adsorption loading versus pressure relationship can predict the performance of the material in cryopumping and gettering applications. The sum total of the nitrogen isotherm data and the interpretations derived are also useful in research activities directed toward synthesis of engineered microporous materials having specific properties; it may supply evidence that the desired structure was or was not achieved.

As with most things that are valuable, 77 K nitrogen isotherms of good quality taken on microporous materials are not produced effortlessly but, instead, require insight and care to produce. While relatively little thought and preparation are necessary for satisfactory nitrogen BET work, the typical experimenter will find that he needs to control details of the experiment to produce good nitrogen micropore isotherms. Many experimenters will find that cryogenic argon isotherms of microporous materials are as useful as nitrogen isotherms. In addition, argon isotherms require less precise control and are less affected by non-ideal conditions than are nitrogen isotherms. Therefore, those who choose to measure nitrogen isotherms must learn to use techniques that are not usually required for other measurements.

The physical reasons for this extra care are:

1. Nitrogen is intensely adsorbed at 77 K by microporous materials. The unique properties of the nitrogen molecule cause it to adsorb even more strongly than several common gases such as argon, oxygen, and carbon monoxide which have higher boiling points. The result is that nitrogen pressures over the microporous sample tend to be extremely low at low fractions of the maximum adsorption loading. Equilibrium nitrogen pressures range from only a fraction of a millitorr to several millitorr, depending upon the material. The proportion of nitrogen adsorbed and bound to the sample may exceed that remaining in the gas phase by a ratio of more than a million to one.
 2. Hydrogen, neon, and helium do not usually adsorb on microporous materials at 77 K to any degree remotely comparable to that of nitrogen. Therefore, any traces of these three gases usually remain in the gas phase above the sample material and continue to exert essentially their full partial pressure. Nitrogen, on the other hand, will be selectively removed and exert a partial pressure millions of times less than it would in the absence of the adsorbing sample. Argon, oxygen, and carbon monoxide, although adsorbed somewhat, will behave similarly in that the pressure they exert is about one to three decades greater in proportion to the quantity present as compared to nitrogen.
 3. It is very difficult to obtain — and even more difficult to maintain — nitrogen gas purity better than a few parts-per-million (ppm) relative to unwanted hydrogen, helium, neon, argon, oxygen, and carbon monoxide. Residual air in the gas regulator and the delivery lines (especially the high pressure side of the regulator), small leaks from other gas sources through shared manifolds and associated seals, and absorption or adsorption of other gases onto or into surfaces followed by later release into the nitrogen all conspire against maintaining parts-per-million purity of the nitrogen. Interestingly, many other common impurity gases and vapors such as light hydrocarbons, water, and carbon dioxide that can be troublesome in other types of vacuum systems cause little or no problem here because, in small quantities, they either freeze out or readily adsorb onto the sample indistinguishably from the nitrogen.
 4. The rubber-like polymers used as seals which make the seals so reliable and long-lasting in practical adsorption instruments also (slightly) permit gases to dissolve into them or to permeate completely through them. Helium and hydrogen typically exhibit the greatest ability to move into and through these seals. The result is that all real-world valves and O-rings imperfectly isolate gases and permit a small degree of mixing either by (1) storing and releasing into the nitrogen a gas that was in earlier use, or (2) by flowing through the seal rubber from one chamber to another that holds a different gas. If, in individual seals, the surface finish of the rubber, the polymer type, and its porosity differ, then the magnitude of the effect may be quite different from one otherwise identical seal to another. Of all solid materials, only metals exhibit high resistance to gas solution or permeation, but even some of these are permeated readily by hydrogen. Glasses and organic materials, especially polymeric ones, are among the most permeable.
 5. The low equilibrium pressures of nitrogen over microporous materials lead to long time intervals for equilibrium following each added increment of nitrogen. These long intervals allow the accumulation to significant levels of the less-adsorbed gases even if the rates of entry to the manifold are small. It is not unusual for 60 hours to pass while acquiring an isotherm consisting of dozens of equilibrium data points. Much of this time may elapse while nitrogen pressures are still below 100 millitorr. An intrusion rate of only 0.01 millitorr per minute of a non-adsorbed gas could contribute an added 36 millitorr of (non-nitrogen) pressure and falsely skew the isotherm pressure axis upwards from the true
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nitrogen-only values. As a percentage of the total pressure reading, the harm done is usually greatest below 10 millitorr where the non-adsorbed gases may contribute several times as much pressure as the nitrogen if precautions are not taken.

6. Any isotherm measured using the ASAP analyzer at significant pressures requires that the free space above the sample be accurately known to permit computation of the amount of gas adsorbed as compared to that which remains in the gas phase and exerts pressure. Measurement of this free space using helium expansion from a known initial volume is the best way of obtaining an accurate number. Unfortunately, this means that the very seals, valves, and manifolds which soon will have to contain pure nitrogen will be exposed to helium at relatively high pressure and that some helium will inevitably remain behind and is likely to slowly re-emerge for hours or days afterward. Equally significant, this also requires that a pressurized source of helium be connected to the instrument manifold and that this helium will constantly permeate its associated inlet valve causing a constant small inflow of helium into the upper portion of the manifold.
7. The solid material of the sample and the glass of the sample tube are prone to dissolve helium and other gases in much the same manner as do the rubber polymers of the seals. How much gas may be dissolved depends upon a number of factors including the nature of the sample, the pressure of the gas, how long the exposure lasts, and the temperatures involved. Usually, the sample is the greater offender as compared to the sample tube, but the sample tube can contribute measurable amounts of outgassing from this source under some conditions.

In spite of the challenges that the above phenomena present, the knowledgeable operator can take steps to minimize the effects upon the isotherm data and produce quite good results. The following measures have been shown to be effective.

1. When doing nitrogen micropore work, never have helium or any of the other five gases connected to the ASAP analyzer. Instead, valve off the gas source at the regulator and leave a vacuum in the inlet lines. Be sure that significant air pressure does not leak into the line since air contains sufficient argon and oxygen to be troublesome.
 2. Use "entered" free-space values for all nitrogen micropore tests. For all the sample tubes you will be using, obtain and record these values all at one time using helium free-space measurements on the empty tubes.
 3. If the ASAP manifold has been exposed to helium, air, or to any of the other five gases mentioned, subject the entire manifold system to an extended pump-down before attempting nitrogen micropore tests. A few hours may be sufficient, but overnight is better. Plug and evacuate the sample port if it is not to be used for some time. When the ASAP analyzer is not to be used for some time, always leave it pumping on the entire manifold.
 4. Any sample or any sample tube that has been exposed to helium should be baked out under vacuum for some hours before attempting nitrogen micropore tests. Preferably, this is done using the ASAP sample port in manual mode using a heating mantle from the nearby outgassing station. Do not break the seal; just start the automatic analysis after removing the heating mantle.
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5. Any sample that has been exposed to room temperature air or any of the six gases mentioned should also be baked out in place on the sample port as instructed above prior to running.
6. Any unused gas inlets on the ASAP should be plugged and evacuated. Do the same with the calibration volume. Never allow a manifold valve to unnecessarily have a non-nitrogen gas pressure on the other side.
7. If it is necessary to backfill a prepared sample, always use pure nitrogen as the backfill gas and minimize the amount of time that it is exposed to any other gases.
8. Thoroughly purge the regulator of residual air after installing a new tank of nitrogen. Use only re-search grade purity gas of under 3 ppm combined content of argon, helium, oxygen, hydrogen, neon, and carbon monoxide. Purge and evacuate all gas lines. Use only metal lines, never plastic or rubber lines.

The ASAP gas dosing procedure limits the progressive accumulation of less-adsorbed or non-adsorbed gases by removing at intervals the accumulated gases in the upper portion of the manifold. Because the amount removed is proportional to pressure and the first removal may not occur until after one or more data points have been taken, it is not unusual to see data wherein the pressure (usually at pressures below 5 millitorr) rises initially and then falls back even though the gas volume adsorbed increases smoothly. While this looks odd, it is a clear warning that impure gases are encroaching and are falsely increasing the pressure axis values. It is far preferable to see this irregularity and to take warning than it is to produce a smooth curve of pressures lying far above the correct values and to have no means of detecting the fact that the data are flawed and misleading.

Micromeritics also offers a TranSeal™ for sample tubes that allows preparation of the sample on the ASAP analyzer degas rack followed by sealing under vacuum or pure nitrogen without breaking the seal prior to the beginning of analysis of the sample. A simple twist of a collar on the stopper allows the valve at the top to be opened when the analysis pump-down is at the properly low vacuum level. These simple accessories can be quite valuable due to the improved ease of obtaining quality data.

The most significant effect on micropore performance occurs if one adds the Unsaturated Hydrocarbons Option for protection against unsaturated hydrocarbons and other aggressive solvents. The Kalrez® seals used are several times more permeable to helium and other gases than are the standard nitrile rubber seals. In addition, individual seals appear to vary more than does nitrile rubber. This is a typical engineering dilemma in that the measures necessary to provide an improved level of performance in one area actually reduce the performance in another facet of the product. While the Kalrez seals do not preclude the running of good nitrogen micropore analyses, they require stricter adherence to the stray gas preventive measures previously listed than do the standard seals.

Adding the chemisorption analysis option to the ASAP has little or no direct effect upon the nitrogen micropore performance. However, the nature of the work that is done and the increased number and wider variety of gases connected to the instrument can increase the odds for unwanted gases to intrude. In addition, vapors and reaction products could possibly contaminate the instrument manifold and increase the outgassing rate.