APPLICATION NOTE 167

The Principles and Theory of the Isothermal Jacket for Free Space Control in Gas Adsorption

Introduction

It has been 55 years since the first commercially available transportable static-volumetric gas adsorption instrument was invented by Dr. Clyde Orr and Mr. Warren Hendrix at the Georgia Institute of Technology (Georgia Tech). Of course, this is the invention which began Micromeritics Instrument Corporation in 1962. Since that time, significant and numerous advances have taken place as the "State-of-the-Art" has progressed.

This paper is a review of what Micromeritics engineers and researchers have learned about how to optimize instrument performance through improvements in freespace control.

Freespace, when used in this context is the volume of the sample holder (sample tube) below the valve which connects it to the dosing manifold of a gas adsorption instrument which is not displaced by the sample. It is important in a volumetric system to precisely know this volume and for this volume to remain stable throughout an analysis, despite evaporating cryogen. It is measured at room temperature and then after the Dewar is raised, at the liquid cryogen temperature. This latter measurement is known as cold freespace. Changes in cold freespace can contribute significantly to gas inventory calculation errors in even the most sophisticated instruments.

Micromeritics first introduced and patented the Isothermal Jacket for temperature control of cold freespace in the mid 1980's. The following is a product bulletin which describes the significant advantages of this device taken from that time.

1987 Isothermal Jacket Product Bulletin

The BET* technique for surface area and other models for pore size distribution evaluation employing low temperature gas adsorption requires precise measurement of gas quantities. Accurate gas quantity measurement is possible only if pressure, volume, and temperature are accurately known in all parts of the measurement system. Since adsorption onto the material being tested must occur at cryogenic temperature and practical considerations dictate that the remainder of the system be at or near room temperature, it becomes imperative, especially in the space connecting the sample at low temperature to the remainder of the system, that temperature stability be maintained. This most critical interconnecting space presents a special challenge because of its large temperature gradient and the fact that cryogenic fluid evaporation will change the size of the zone if not properly controlled.

If, as illustrated below, a sample is simply immersed in a bath of liquid nitrogen (LN_2) and connected by tubing to other thermostated components, the gradient zone increases in length as the LN_2 evaporates and its level falls. This gives rise to an increasing volume within the tubing of uncertain temperature distribution–one segment of the connecting tubing being exposed to the ambient air and the remainder coming more and more under the influence of the evaporated but still chilled nitrogen gas.

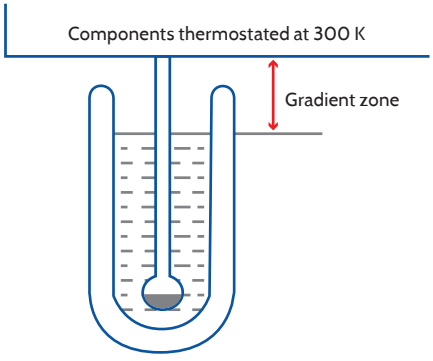

Illustration 1

*Brunauer, S.; Emmett, P.H.; and Teller, E. "The Adsorption of Gases in Multimolecular Layers" J. Am. Chem. Soc. 60, 309-19 (1938)

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Some instrument manufacturers attempt to rectify this situation by causing the LN_2 Dewar to rise as the liquid level falls. This indeed fixes the volume immersed but the length of tubing exposed to ambient conditions has to be greater initially and the connecting tube length contacted by chilled nitrogen gas of intermediate temperature thereafter increases as exposure to the ambient environment decreases as shown by Illustration 2. Because of this shift, the temperature distribution between the gradient extremes still changes and only partial compensation for evaporation is achieved.

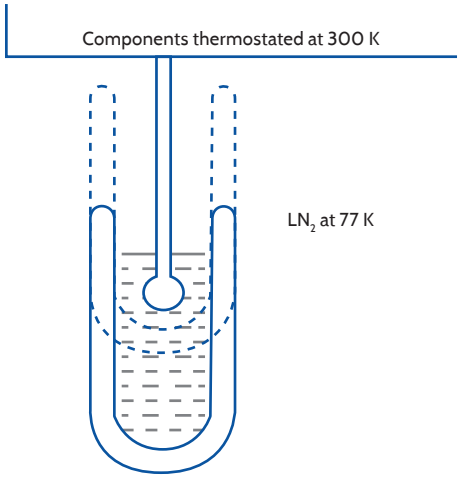


Illustration 2

In the mid 1980's, Micromeritics had for a decade employed the classical procedure of transferring fresh LN_2 from a large storage reservoir to the sample Dewar as evaporation proceeds in order to hold the liquid level fixed and the gradient constant, Illustration 3. This provides excellent stability but requires a somewhat involved LN_2 transferring mechanism.

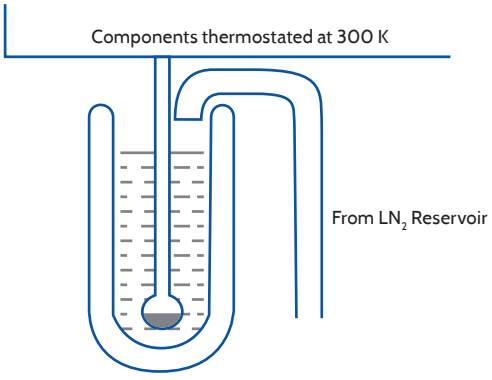


Illustration 3

Now (in 1987) Micromeritics has developed a very simple device described as an Isothermal Jacket® for which a patent is pending and which also provides excellent stability. The new device consists basically of a material having interconnecting pores encased in an impervious outer shell which simply fits around the tube connecting the sample space with other system components. As long as the lower end of this composite is submerged in LN_2, the porous material remains saturated with LN_2 throughout its entire length, evaporation taking place only from its upper exposed end. The level of LN_2 about the connecting tube thus remains constant until only a very little LN_2 remains in the Dewar. The Dewar can be replenished with LN_2 just before depletion or at other convenient times, to provide temperature constancy for as long as needed. Use does not degrade the jacket and there is nothing to wear out. The Isothermal Jacket, Illustration 4, is truly a unique solution to what has long been a control problem.

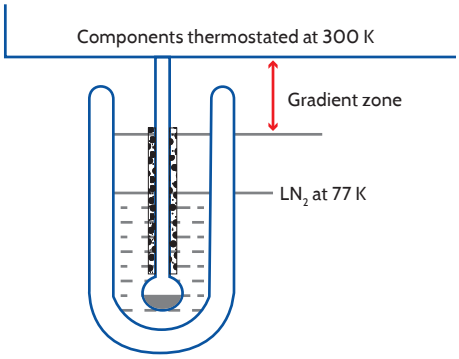


Illustration 4

Duplicate measurement systems, one corresponding to Illustration 4 and one to Illustration 1, and consisting of a pressure transducer, a bulb immersed in a 1-liter Dewar of LN_2, and connecting tubing serve to illustrate the stability provided by an Isothermal Jacket.

When the tubing within the Dewar was surrounded with a Jacket (Illustration 4) and the system partially filled with helium, the pressure held between 357.78 and 357.85 mmHg over an 8-hr period. During this time the LN_2 level fell 150 mm. The experiment without the Jacket (Illustration 1) resulted in the pressure changing very nearly linearly from to 373.34 mmHg during the same period. 359.19

What follows is a study performed some years later to demonstrate very clearly the direct effect in performance of different freespace control systems.

In gas adsorption studies of powder and granules such as adsorbents and catalysts for the purpose of evaluating their surface area and pore structure, ever-present requirements are maintaining the sample at constant temperature, typically that of the cryogen liquid nitrogen (LN_2), and maintaining other conditions fixed so that gas pressures about the sample can be accurately assessed. A problem arises because the LN_2, even when contained in the highest

quality Dewar, evaporates and its level decreases with time. Because of this level change, if no means of compensation is provided, a segment of any access channel leading to the sample from instrumentation at laboratory temperature is exposed to a changing temperature environment, meaning the gas pressure about the sample is also changing.

At least three means of providing compensation for LN_2 evaporation have been devised. These include (1) frequently replacing the lost LN_2 in small increments, (2) raising the Dewar as the LN_2 level decreases, and (3) providing a special wick about the access channel to confine evaporation to one fixed point on the channel. The first requires a means for pumping LN_2 into the Dewar each time the level drops an increment and a means for sensing the LN_2 level in small increments. The second requires starting with the sample immersed only minimally in the Dewar contents and then raising the Dewar mechanically in response to the LN_2 level decrease. It also requires a sensor to track the LN_2 level. The third is passive and is called an isothermal jacket; it depends only on the natural surface tension of the LN_2. The Isothermal Jacket is patented.

This report gives the results obtained with the three-enumerated means of control using a simple experimental arrangement of a sample bulb with a valve for admitting a gas, a transducer to follow the gas pressure as a function of time, and a Dewar to contain the LN_2.

1. An LN_2 pump and level detector were added when performing the level control experiment.

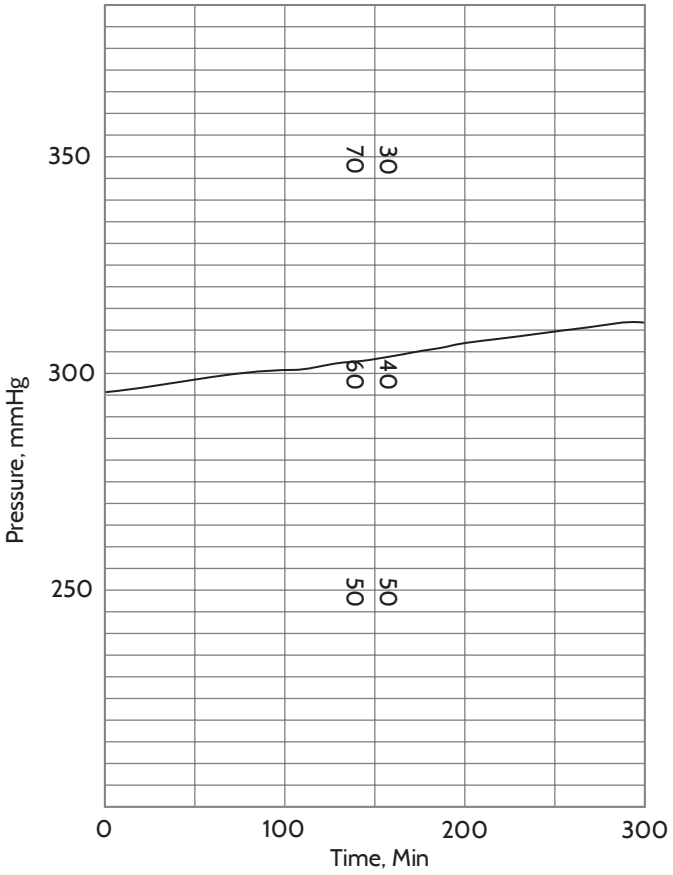
2. A motorized mechanical jack and the same LN_2 level detector were used in the rising Dewar test, but the experimental arrangement remained otherwise identical.

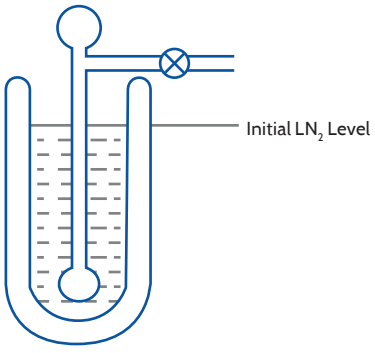
3. An isothermal jacket was merely slipped about the tube joining the sample bulb and pressure transducer when performing the third test.

The experimental system was purposely constructed to magnify equally deficiencies in the performance of the three techniques. Toward that end, the tube connecting the sample bulb, which would be immersed in LN_2, and the pressure transducer at ambient temperature was 20 cm long and 9 mm in internal diameter. A wide-mouth, 1-liter Dewar was employed as the LN_2 reservoir.

Four tests were performed. All tests were begun with the sample bulb immersed in LN_2 and with nitrogen gas at a pressure of approximately 300 mmHg in the sample tube. The pressure change with time was followed on a chart recorder. The experimental set-ups are diagrammed below and a representative recording is shown beside it.

The first test was made with no compensation at all.



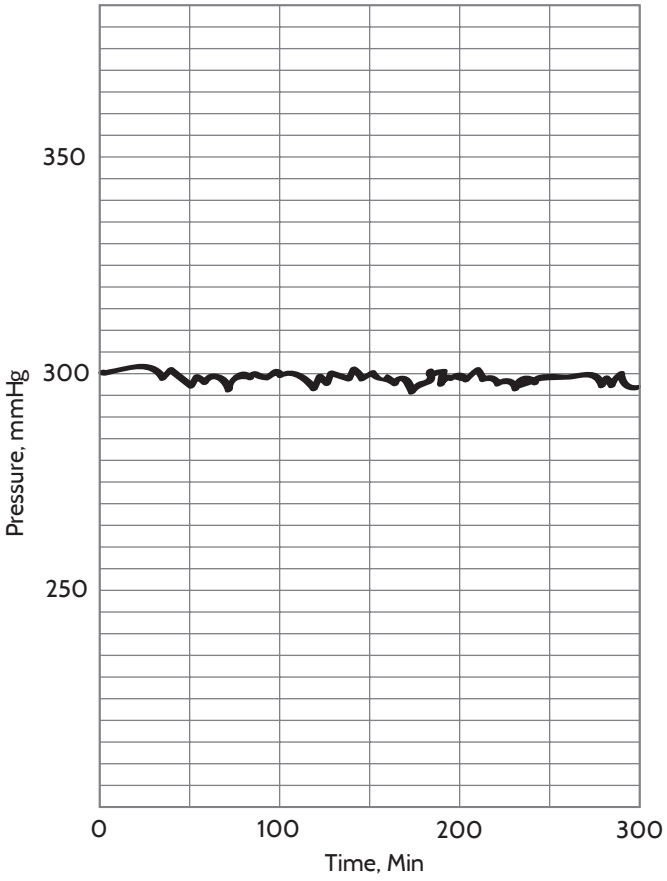


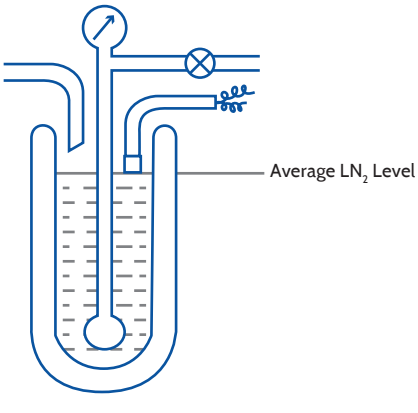
Test 1. No Control

Without compensation for LN_2 level decrease, the pressure in the system would be expected to increase with time because more of the stem leading to the sample bulb and its gas content are exposed to ambient temperature influences. This behavior is exactly what the recording to the right of the diagram shows.

Level control added to the system, as diagrammed below, would be expected to maintain stable conditions within narrow limits. As shown by the accompanying pressure-time recording,

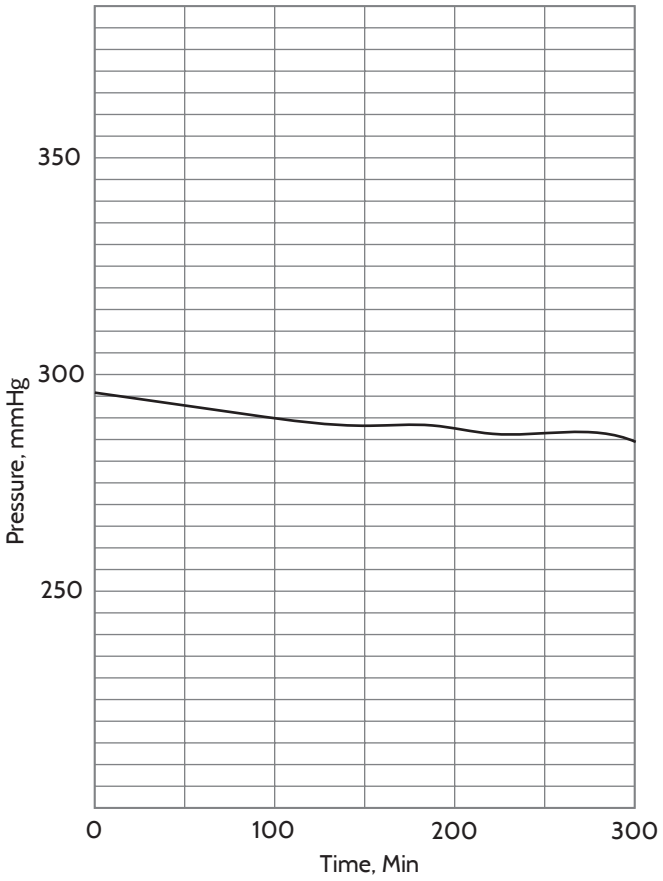
it does this with minor fluctuations arising due to LN_2 surface disturbances as each increment of new liquid is added. This system accomplishes its intended goal and is attractive for very long analysis time situations. If the time is too long however, ice extracted from the water vapor in the ambient atmosphere will build up choking off access to the entire system. It also requires somewhat expensive peripheral equipment.

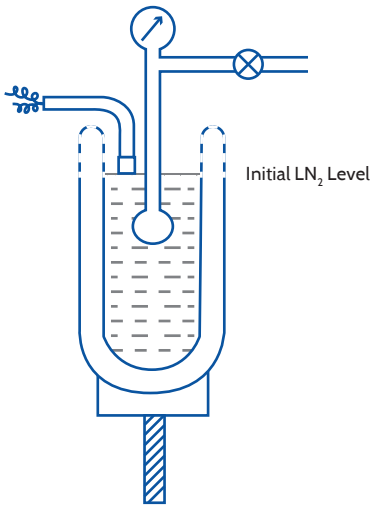




Test 2. LN_2 Level Control

Raising the Dewar to compensate for evaporation, as shown by the next diagram, inserts more of the stem leading to the sample and the gas contained in the stem into the expanding cold vapor zone deeper and deeper within the Dewar. This would be expected to produce a decrease in gas pressure, as indeed it does as is revealed by the companion recording.



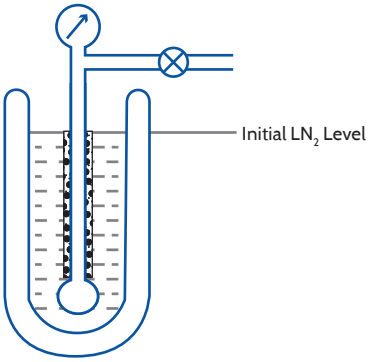


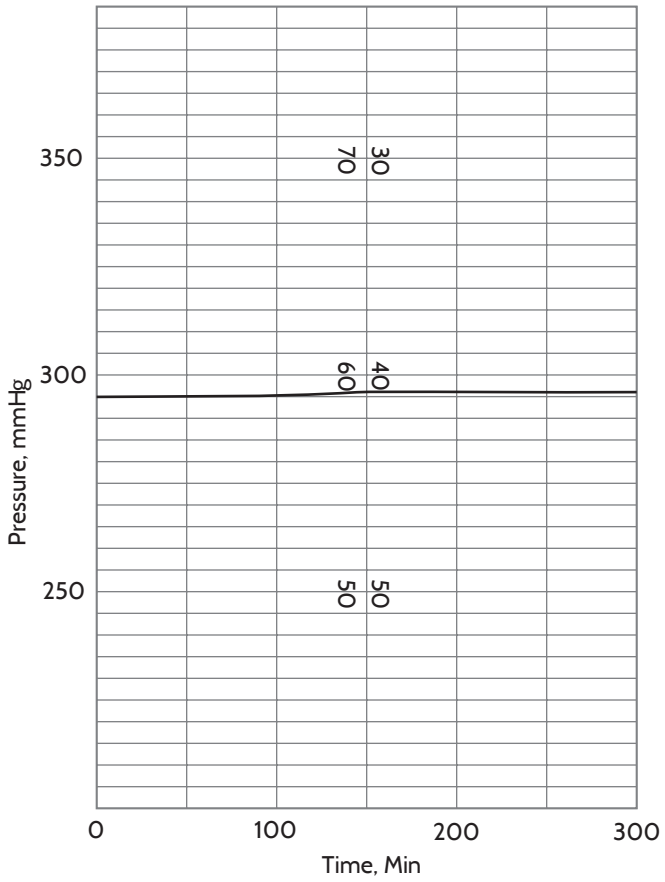
Test 3. Rising Dewar

Of course, this effect can be mitigated by making the stem of small internal diameter so that less gas is contained therein and by inserting some kind of filling rod to take up much of the remaining volume. A small diameter stem creates difficulties in getting a sample in and out of the sample space; a close-fitting filler rod decreases the rate at which a sample can be evacuated when that step is required by an analytical procedure and it provides an added heat conduction path from the cold zone to the warm zone. As with level control, peripheral equipment adds to the initial expense and maintenance costs. Examining the recording for no control and the recording for the rising Dewar suggests that using a small diameter connecting stem from the sample bulb and no compensation would each produce about equally satisfactory results.

The final diagram and companion recording pertains to the Isothermal Jacket system. A bit of explanation is in order here. Isothermal Jackets are tubes of about 2.5 cm outside diameter and up to 18 cm in length.

Their inside diameter ranges from 1.25 to 0.5 cm. Their outer shell is a thin nearly impervious layer inside which is a porous layer. They are designed to fit snugly about the stem of a sample tube. When their lower extremity is inserted in a cryogenic fluid such as LN_2, the LN_2 rises by capillary action to the upper extremity to which evaporation is now largely restricted. The jacket thus bathes the stem in LN_2 and continues to do so until the level in the LN_2 bath falls below the lower extremity. Since the stem leading from the sample bulb is surrounded over a fixed length by LN_2 regardless of the LN_2 level in the Dewar, no change in gas pressure inside the stem would be expected until the Dewar is nearly empty. The recording shows this is indeed the case.





Test 4. Isothermal Jacket

In summary, this investigation has shown that stable conditions are achieved only when the liquid nitrogen level about the stem is maintained constant and that this situation is achieved by just two techniques–level control and Isothermal Jackets. The Isothermal Jacket, being inexpensive, reusable, and simple to use in addition to providing the best stabilization clearly is the obvious choice.

Through 55 years of product development, and having tried many different approaches, Micromeritics has learned that Isothermal Jackets are the best option for our users. They are simple, inexpensive devices which require no maintenance, will work with a wide range of cryogens, require no electronic circuits to control, are guaranteed for the life of the instrument against failure and provide the most stable freespace and thus the highest quality data collection.