Effects of Temperature on Nafion™ Tubing Gas Dryers

Maximum Operating Temperature

Nafion™ polymer ionomer tolerates relatively high temperatures; its melting point is over 200°C. The Chemours Company, the manufacturer of the ionomer, lists a maximum operating temperature for its membranes of 190°C. When Perma Pure produces tubing from this material, we list a maximum operating temperature of 120°C. This lower temperature is conservatively assigned because The Chemours Company membranes are bonded to reinforcing materials and are used with liquids while Perma Pure gas dryers are used with gases and are not reinforced. We are concerned about pressure tolerance at higher temperatures due to softening of the material, but Nafion™ tubing will presumably tolerate temperatures in excess of this specification.

Minimum Operating Temperature

Nafion™ tubing dryers absorb water on the internal surface of Nafion™ tubing, then perevaporate it into a surrounding dry purge gas (typically air). When the water is absorbed as water vapor then released as water vapor, there is no net change in phase and consequently no net energy is consumed. If water is present as a liquid rather than as a vapor within the tubing, it will still be absorbed as a liquid then released as a vapor, but now there is a change of phase from liquid to gas, requiring an input of energy.
If liquid water is permitted to enter the dryer, the transformation of the liquid into water vapor will draw heat from the dryer, cooling it. As the dryer cools, it condenses more water. As it absorbs this additional liquid water, it will cool more rapidly. Soon the dryer is cold and wet, and the dryer is then functioning as a condenser rather than as a permeable membrane. At this point the dryer has failed, and it must be removed from service and dried before it can again function properly. To prevent this failure, liquid water must not be permitted to enter the dryer during operation. The minimum operating temperature of the dryer is therefore limited by the sample dew point. As the gas sample passes through the dryer, water is removed and the sample dew point becomes progressively lower down the length of the dryer. The minimum operating temperature is the dew point of the sample at that point in the dryer, and is a temperature gradient, higher at the sample inlet and lower at the sample outlet.

Rate of Water Absorption

Nafion™ polymer is mostly an inert fluorocarbon polymer. Scattered through the fluorocarbon matrix are ionic channels consisting of sulfonic acid groups (hence the name ionomer). These ionic channels extend from the internal surface of the tubing to the external surface. The sulfonic acid groups very readily bind water in a reversible reaction as water-of-hydration. Once bound to the sulfonic acid groups at the internal surface of the tubing, water molecules very quickly pass along the ionic channel to the external surface of the tubing, where the water perevaporates (assuming the water vapor pressure at the external surface is lower than at the internal surface). This binding of water as water-of-hydration follows First Order reaction kinetics, so the rate of reaction is proportional to temperature. An elevated operating temperature will increase the initial rate of water removal, and the dryer will come to a final equilibrium dew point faster. For Nafion™ tubing dryers, the initial rate of water absorption roughly doubles for each 10°C increase in operating temperature.

Final Equilibrium Sample Dew Point

Nafion™ tubing functions essentially as a permeable membrane to water, with water transport driven by the partial pressure gradient of water vapor across the membrane. As water is removed from the sample, the gradient is reduced. Given sufficient residence time of the sample within the tubing (a long enough tube), the sample will come to a final equilibrium dew point. This final equilibrium dew point is limited by the dew point of the purge gas or by the residual water in the walls of the tubing, whichever is higher.

Some water is strongly bound to the sulfonic acid groups within Nafion™ tubing and always remains within the tubing regardless of the water content of the sample or the purge gas. When the dew point of the purge gas is sufficiently low, this residual water in the tubing wall determines the final equilibrium sample dew point that may be reached. When the water content of the sample is reduced sufficiently so that it matches the residual water within the tubing, there is no longer a gradient and drying stops. At 20°C, the residual water bound to the sulfonic acid corresponds to a sample dew point of -45°C (about 75 ppm of water).

The amount of residual water bound within the tubing is proportional to temperature. The final equilibrium dew point achievable rises about 1°C for each 1°C increase in operating temperature of the dryer at its outlet end.

The sulfonic acid groups within Nafion™ polymer are stabilized by the presence of the fluorocarbon matrix surrounding them as well as the other sulfonic acid groups within the ionic channels. The sulfonic acid will very easily donate a proton (function as an acid), and Nafion™ polymer is considered to be a superacid. The Hammett scale rates the strength of acids on an increasing number scale. Nafion™ polymer is rated 11-13, while concentrated sulfuric acid is rated 11. Nafion™ polymer therefore functions very effectively as a strong acid catalyst and is used commercially for this purpose.

Nafion™ Polymer Reactivity

Nafion™ tubing dryers are intended to remove water while minimizing all other changes to the sample. Most inorganic compounds are unaffected by acid catalysis within the working temperature range of Nafion™ tubing dryers, but some organic compounds undergo unwanted chemical reactions when exposed to Nafion™ tubing at elevated temperatures. For this reason it is desirable to avoid operating the dryer at temperatures higher than necessary. Normally operating temperatures below 100°C present no problems while temperatures above 120°C are much more likely to present problems. Operating temperatures within the range of 100° to 120°C should be selected only as necessary, and higher temperatures should not be used unless strictly necessary.

Conclusions

Based on the information provided above, Perma Pure recommends that its dryers be operated with an inlet sample operating temperature above the initial sample dew point and with a cool outlet temperature. In practice this means operating at ambient temperature with samples that are non-condensing at ambient. With samples that have dew points above ambient, the sample inlet end of the dryer should be heated to a temperature about 10°C above the sample dew point while the sample outlet should remain at ambient (the purge gas will function as a coolant) so that a temperature gradient is established down the length of the dryer. Sampling systems from Perma Pure of the GASS™ family of products provide proper temperature control to optimize operating conditions for any samples needing a heated dryer.