# Formaldehyde Permeation Through Nafion™ Polymer



Perma Pure does not possess analyzers and calibration standards for the wide range of possible samples that might be submitted to our dryers, so we often must rely on the research of customers and academics to provide information about new applications. For many chemicals, we must rely on principles of operation and the chemistry of the compounds to determine their likely behavior in our dryers. The Merck Index indicates that formaldehyde is highly soluble in water and that it is highly reactive. Taking that information into account, we have the following comments.

1. Nafion™ polymer is a super-acid catalyst. We expect aldehydes that are susceptible to acid catalysis to undergo ancid-catalyzed enolization to form a dienol when exposed to Nafion™ polymer. In this case, that reaction would be: $HCHO + H_2O$ –> HO-CH-OHWith higher aldehydes we expect this reaction to occur, but with formaldehyde we have previously had reports that it does not occur because having hydrogen rather than a hydrocarbon chain attached to the central carbon means that there is little opportunity for charge sharing so that the initial step of acid-catalyzed enolization (breaking of the carbon-oxygen double bond) cannot occur.The circumstances creating an opportunity for this acid-catalyzed enolizaation would likely be elevated temperature, elevated water concentration, and presence of enabling compounds in the sample stream.For this reason, the concentration of water in the sample stream may affect the loss of formaldehyde by participating in its acid hydrolysis.

2. We have considerable data that shows that certain highly water-soluble gases (notably hydrogen chloride, chlorine, and nitric acid) are lost when the ratio of the dry purge gas to the sample is low, but that at higher ratios, the losses disappear. In conversation with DuPont, we have concluded (without proof, but with considerable experience) that the following process occurs.
    1. We know from DuPont that permeation of water through a Nafion™ tubing membrane (in this case the walls of our tubing) occurs in three steps:
        1. First the water binds to an active site (an exposed sulfonic acid group) on the surface of the tubing wall,

    2. Second the water permeates through the wall by being transferred rapidly from sulfonic acid to adjoining sulfonic acid within the ionic channels formed within the Nafion™ tubing,
    3. Third the water pervaporates from a bound solid state directly into the vapor phase in the surrounding gas.
2. We know that the rate limiting step can vary depending upon the temperature of the system, the thickness of the tubing wall, and the concentration of water on either side of the wall.
3. We and DuPont speculate that after the water molecule initially binds to the exposed sulfonic acid site, highly water-soluble gases may bind to the water molecule while it is still exposed on the surface of the tubing.
4. We continue to speculate that once bound to the water molecule, these highly water-soluble gases may remain bound to the water molecule and permeate along with it through the Nafion™ tubing, subsequently released from the external surface.
5. We speculate that if the purge gas flow rate is increased sufficiently to drive the reactions to the point where the initial binding of the water is the rate limiting step, then once bound the water immediately penetrates into the Nafion™ tubing, preventing the water-soluble gas from binding to it.
6. We know from considerable test data that losses of hydrogen chloride are common when the ratio of purge flow to sample flow is 5:1 or less, but when the purge gas flow is increased to a ratio of 10:1 or more, the losses disappear. We believe the processes described above account for these results.

If formaldehyde behaves in similar fashion, then the ratio of purge gas flow to sample flow will affect its losses. Likewise if formaldehyde can undergo acid catalysis to limited degree depending upon the exact circumstances (temperature, water concentration, etc.), then the water concentration in the sample gas may very well affect its losses by participating in the chemical conversion of the formaldehyde into some other compound or by serving as a binding site on the surface of the Nafion™ tubing to draw the formaldehyde through the Nafion™ tubing.

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