Compounds Removed by Nafion® Dryers

Nafion is a copolymer of perfluoro-3,6-dioxa-4-methyl-7octene-sulfonic acid and Teflon® (polytetrafluoroethylene). This may seem confusing; in simpler terms Nafion contains a Teflon backbone with occasional side chains of another fluorocarbon added. The fluorocarbon side chain terminates in a sulfonic acid ($-SO_3H$).

With the exception of the sulfonic acid groups, all of Nafion is a fluorocarbon polymer. Like most fluoropolymers, it is chemically inert (extremely resistant to chemical attack). Its sulfonic acid groups are immobilized within the bulk fluorocarbon matrix and cannot be removed, but unlike the fluorocarbon matrix the sulfonic acid groups do participate in chemical reactions. The presence of sulfonic acid makes Nafion selectively permeable to compounds that bind to sulfonic acid.

Nafion can function as a cationic exchange resin when exposed to liquids. In the liquid phase, ionic compounds will dissociate into free ions that can interchange with the sulfonic acid group within Nafion, and the ions will permeate very readily through the polymer.

Perma Pure dryers are designed for use only with samples in the gas phase. Compounds do not dissociate into free ions in the gas phase until the temperature exceeds a thousand degrees. This temperature is far above the operating temperature range of the dryers. Consequently, Nafion does not permit ionic compounds to permeate in the gas phase unless they specifically complex with sulfonic acid. Very few gaseous compounds complex (bind) with the sulfonic acid, so Nafion is very selectively permeable to compounds in the gas phase.

Removal Mechanisms

Nafion removes compounds from a gas stream in three ways:

1. Compounds that bind to the sulfonic acid in Nafion will readily permeate through the polymer. These compounds are limited essentially to gases that function as bases (in an acid-base reaction). Not all but most bases contain an hydroxyl group (-OH). For this reason, the following compounds are all actively removed by Nafion:
   a. Water (H-OH)
   b. Alcohols (R-OH where R is any general organic group)
   c. Ammonia (forms ammonium hydroxide complex with water, $NH_3 + H_2O = NH_4\text{-}OH$)

   Primary amines ($R\text{-}NH_2$) and secondary amines (R1,R2-NH) are removed by the same mechanism as ammonia.

2. Nafion functions as an acid catalyst due to the strongly acid properties of the sulfonic acid group within the Nafion. As a strong acid catalyst, Nafion converts organic compounds susceptible to acid catalysis into other compounds. Strictly speaking the compound is not removed from the sample gas, but it is converted into another compound instead. Acid catalysis occurs with compounds that have:
   a. Double or triple bonds between carbon atoms or between carbon and other atoms.
   b. Steric stress in the molecule (structural stress that can be relieved by reorganization of the molecule).

Organic compounds that have single bonds between the carbons are described as simple hydrocarbons, or alkanes (methane, ethane, propane, butane, pentane, hexane, heptane, octane, etc.). These compounds do not undergo acid catalysis and are not removed.

Organic compounds that have double bonds between the carbons are called alkenes (ethylene, propylene, butylene, etc.). Compounds that have triple bonds between the carbons are called alkynes. Both alkenes and alkynes under go acid catalysis and may be transformed, depending upon the specifics of the compound.

Benzene rings are very stable organic structures. Even though it has double bonds between carbons within the ring structure, benzene does not undergo acid catalysis into another compound. This is confirmed by EPA Method TO-14, which specifically cites Nafion gas dryers for use with benzene, toluene, xylene, and various other organic compounds. When another group is attached to the benzene ring, the other group will determine whether acid catalysis will occur. For example, benzaldehyde is still an aldehyde, and will still undergo acid catalysis. The presence of a benzene ring will not cause a compound to undergo acid catalysis, but it will not protect it from undergoing acid catalysis if another active group is present that will undergo this reaction. Compounds containing a benzene ring are described as aromatic compounds, and as a class they are not removed by Nafion.

3. By a combination of methods #1 and #2 above, Nafion converts a compound into an alcohol, then removes it. Many organic compounds contain a carbonyl group (-C=O). This group will undergo acid catalysis to form an alcohol. The proper name for the reaction is acid-catalyzed enolization (enols are another name for alcohols). In this reaction the carbon doubly bonded to oxygen combines with water to form a diol, a carbon with two hydroxyl groups attached (C=O + H_2O yields HO-C-OH).

Aldehydes, ketones, and organic acids all contain a carbonyl group. All are removed by Nafion after undergoing acid-catalyzed enolization. These compounds are not merely converted into another compound, but actually permeate through the Nafion after converting into an alcohol.

Since the compounds removed by this process must first undergo acid-catalyzed enolization, the rate of removal of the compound depends upon how easily it will undergo acid catalysis. This depends upon the nature of the organic group R attached to the carbonyl group. For example, formaldehyde has only a hydrogen in the R group position. Since the hydrogen will not readily accept charge sharing, formaldehyde resists acid-catalyzed enolization, and little or no formaldehyde is removed by Nafion from a gas sample. Benzaldehyde, on the other hand, has a benzene ring in the R group position. A benzene ring will very readily accept charge sharing, so benzaldehyde undergoes acid-catalyzed enolization and subsequent removal by Nafion.

Other organic compounds that have double or triple bonds between carbon and another atom (oxygen or nitrogen) may also undergo acid catalysis and subsequent removal. Nitriles are an example of compounds with a multiple bond between carbon and nitrogen that are removed by Nafion. Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) are two examples of other compounds that are also removed by Nafion.

Summary

Nafion gas dryers directly remove water, alcohols, ammonia, amines, and other compounds that possess an hydroxyl group or convert to one under acid catalysis. Some compounds are not removed but are rendered unrecognizable by acid catalysis. Inorganic compounds in general are not removed (other than water and ammonia).

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