Vol. 13, No. 3

Using Hydrocarbon Vapors and Aggressive Adsorptives with Micromeritics' ASAP Series

Micromeritics ASAP 2000 series Accelerated Surface Area and Porosimetry instruments are suitable for use with a wide variety of gas and vapor adsorptives, including water and many hydrocarbon vapors, in addition to the array of traditional gaseous adsorptives. The adsorptives that are appropriate for use with a particular instrument and in a specific environment are dictated by several factors including chemical activity (corrosiveness), saturation pressure (or boiling temperature at atmospheric pressure), and the capability of the laboratory to manage and control any hazards associated with the adsorptive.

Nitrogen and argon continue to be the most widely used probe molecules in gas adsorption analyses. However, the use of adsorbents and molecular sieves in an increasing variety of applications has prompted the use of more specific probe molecules, the same molecular species that will be encountered in the application of the material. These small-scale laboratory experiments provide the analyst direct information on the performance of the adsorbent when interacting with a particular gas or vapor.

Vapor Adsorptives

Liquid vapors, particularly those from hydrocarbons and water, are sometimes used as adsorptives during the analysis of microporous and mesoporous materials by physical adsorption. A source of purified liquid must be available from which to obtain vapors. The purification process removes atmospheric gases or other contaminants that may be present in the liquid. Micromeritics provides an accessory for this purpose, which also serves as the vapor reservoir.

The less-aggressive, 'saturated' hydrocarbon vapors (those containing only carbon single bonds) typically are safe to use with the standard manifold, which is equipped with Buna-n (Nitrile) seals. However, unsaturated hydrocarbons (those containing double or triple carbon-carbon bonds) are more aggressive than saturated ones and the prudent use of these types of adsorptives require a special manifold incorporating the more-impervious and more chemically resistant Kalrez® seals. Appendix A provides details on differentiating between saturated and unsaturated hydrocarbons.

Vacuum Seals

All manifolds are not necessarily manufactured with the most chemically resistant seals available. This is because chemical resistant seals don't provide the best overall seal performance (there are some performance trade-offs). The performance specifications for vacuum sealing materials include permeability, which is related to absorption and adsorption that leads to outgassing and/or swelling, and chemical resistance and temperature range, both of which are related to decomposition and loss of mechanical properties. Comparisons of seal properties are provided in Appendix B.

Other Wetted Materials in the Gas Handling System

The other wetted material of primary concern is that of the manifold, which is stainless steel in the case of ASAP series instruments. Although stainless steel is known for high resistance to corrosion, analyses with corrosive gases and vapors such as NH_3, SO_2, and H_2S should be attempted only with great care. If water molecules are mixed with these gases, they become sufficiently corrosive to metals and, over an extended period of use, damage could occur.

Other Precautions

There also is another general warning: all hydrocarbons, CO_2 and possibly other adsorptives will dissolve in the vacuum pump oil to various extents. Accumulation over time will limit the vacuum-producing capabilities of the system. Overnight purging with nitrogen usually restores the lost vacuum performance.

Certain gases and vapors pose a hazard to laboratory personnel, for examples, H_2S and HCN. For this reason, Micromeritics does not recommend use of these hazardous adsorptives.

Conclusion

Because of the wide variety of gases and vapors that are of interest for physical and chemical adsorption studies, no single seal material can provide high chemical resistance and high sealing characteristics for all gases. The analyst must realize that maximum analytical performance and minimum need for maintenance will occur only when the wetted materials and adsorptives used in the instrument are compatible.

APPENDIX A. Types of Hydrocarbon Vapors

Saturated Hydrocarbons

Carbon can bond with hydrogen in a variety of ways to form different hydrocarbon molecules. Hydrocarbons are compounds that contain only hydrogen and carbon atoms. The simplest hydrocarbon is methane (CH_4) having only a single carbon atom. Other saturated hydrocarbons are: ethane (C_2H_6), propane (C_3H_6), butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), nonane (C_9H_{20}), and decane ($C_{10}H_{22}$). These and many more saturated hydrocarbons are members of the alkane series. The alkane series consists of hydrocarbons that have only a single covalent bond between the carbon atoms which form the backbone of the compound. The alkane series all have names which end in "ane." The general formula for the alkane series is:

$$C_nH_{2n+2}$$

where n is the number of carbon atoms.

Saturated hydrocarbons, without other functionality groups may be considered chemically inert to some extent. These saturated hydrocarbons sometimes are referred to as paraffins. This group of hydrocarbons is generally suitable for use with the standard ASAP instrument.

Unsaturated Hydrocarbons

When less than the full compliment of hydrogen atoms is present in a hydrocarbon chain or ring, the hydrocarbon is said to be unsaturated. Unsaturated hydrocarbons are characterized by having two adjacent carbon atoms linked by two or three bonds instead of only one. These "double" or "triple" bonds are more chemically reactive than single bonds. These may be broken and new atoms attached without disrupting the existing backbone of the hydrocarbon. Unsaturated hydrocarbons are grouped into the following series.

Hydrocarbons with one or more double bonds between the carbon atoms are referred to as the "alkene" series. All alkenes have a name ending in "ene." An example is ethylene (C_2H_4). The prefix "poly" means many. So polyethylene is many ethylenes linked together.

Alkenes are open chain unsaturated hydrocarbons in which a carbon-carbon bond is a double covalent bond. The general formula for the alkene series is:

$$C_nH_{2n}$$

Where, n=number of carbon atoms and n is greater than 1. They are very reactive organic compounds also known as "olefins." Examples of olefins are ethene, propene, penlene, etc.

"Alkynes" are open chain unsaturated hydrocarbons in which one triple covalent bond exists between any two carbon atoms. The general formula for the alkynes series is:

$$C_nH_{2n-2}$$

Where, n is the number of C-atoms and n is greater than 1. Alkynes are very reactive compounds. Examples of alkynes are ethyne, propyne, pentyne, etc.

Aromatic hydrocarbons consist of structured and multiple bonds. If the molecule contains several joined rings, it is called a polycylic aromatic hydrocarbon.

Aromatics:
Benzene (C_6H_6) and derivatives
Toluene ($C_6H_5CH_3$)
Benzaldehyde C_6H_5CHO
Ethene (Ethylene) C_2H_4
Ethyne (Acetylene) C_2H_2 aromatic hydrocarbon

Common Seal Materials Used in Gas Sorption Instruments

Chemical Group	Abbreviations	Trade Name or Common Name
Chloroprene	**CR**	Neoprene® (E.I. DuPont)
Fluorelastomer	**FKM**	VITON ® (Dupont Dow Elastomers)
Nitrile	**NBR**	Buna N
Perfluoroelastomer	**FFKM**	KALREZ ® (Dupont Dow Elastomers)
Polychlorotrifluoroethylene	**PCTE**	kel-F ® (3-M Company)
Polytetrafluoroethylene	**PTFE**	Teflon® (E.I. DuPont)

continued on page 10....

Hydrocarbons cont.

APPENDIX B. Vacuum Seals

The most common sealing materials used in gas sorption instruments are Viton®, Teflon®, Kalrez®, Buna-N, and Kel-F®. These are common names or trade names for different types of plastic materials, as illustrated in the table below. A material suitable for use in a gas sorption instrument must have mechanical properties allowing it to be machined and fabricated. It must have high tensile strength and retain its elastic and plastic properties over the range of operating temperatures and mechanical stresses to which it will be subjected. The valve seal material must be resistant to tear and abrasion as well as resistant to the chemical that will contact it—various gases, hydrocarbon vapors, water vapor, acids and alkali. To allow the achievement and maintenance of high vacuums, the material must have a low vapor pressure, low permeability, and acceptable surface and bulk desorption rates. Unfortunately, there is no known material that has excellent specifications for ALL of these variables under the range of conditions of use of a gas sorption instrument.

Gases or vapors that permeate the seal can have a softening and/or swelling effect on it. The magnitude of the effect depends on the particular seal material. Although a *slight* swelling of the seal may, in some circumstances, enhance the efficiency of the seal, the gas or vapor that permeated the seal will outgas when pressure is lowered or when another gas or vapor is used. Compared to Viton, Kalrez begins to permeate more quickly.

Kalrez has most of the same advantages as Viton but Kalrez has greater chemical and temperature resistance. Other than these considerations, Kalrez appears to be inferior to Viton in sealing efficiency. However Kalrez is considerably more expensive than Viton.

Under difficult conditions, there are no other elastomers which achieve the overall operational performance of Kalrez perfluoroelastomer seals. Kalrez combines the elasticity and sealing force of an elastomer with the chemical resistance and thermal stability of Teflon fluoroplastics.