

Like other chemicals, solvents will degrade over time. Solvent deterioration is dependent on several factors' elapsed time since purification, shipping and storage conditions, individual solvent properties and the presence or absence of stabilizers. Most Honeywell Burdick & Jackson solvents are inherently stable and relatively inert. However, several solvents require chemical stabilizers to prevent or slow degradation. Certain less stable solvents are also available without additives because no suitable preservative exists that will not interfere with a specific analytical method. All these solvents require special handling to minimize degradation problems. Elevated levels of some solvent degradation products may even present safety hazards. Contact Honeywell Burdick & Jackson's customer service at 800-368-0050 with questions about solvent degradation and appropriate solvent selection for a particular application. Additional safety, storage and handling information can be found in Material Safety Data Sheets (MSDS).

Handling Less Stable Solvents

It is best to avoid less stable solvents when developing methods. Unfortunately, some procedures require their use. Most solvent manufacturers recommend using a product within one year. This timetable begins on the date of solvent manufacture and not when the consumer purchases or receives it. As a general guideline, purchase solvents in quantities which will be used within three to six months. The "date of receipt" and "internal expiration date" should be recorded in the time line log on every B&J solvent label. This simple but important notation aids stock rotation and inventory control. When using solvents near your internal expiration date, test the solvent for degradation products (such as acid in chlorinated solvents and peroxides in ethers) and for suitability in your particular application. All solvents should be stored in a controlled environment. Keep unopened containers in a vented, approved flammable liquid storage cabinet at room temperature and minimize exposure to light, heat and oxygen. Outdoor storage sheds, where extreme temperatures may occur, should be avoided. Repeated or rapid temperature variations may lead to package breathing or leakage. This breathing exposes the solvent to air which can accelerate degradation as well as contaminate the solvent. Once opened, an unstabilized solvent should be blanketed with clean argon or nitrogen and tightly recapped. These solvents should be monitored regularly for evidence of degradation. To avoid solvent waste, the appropriate container size is important. If solvent consumption is very low, 1L bottles should be used so that opened

containers are not on hand for long periods of time. For example, if tetrahydrofuran is used at a rate of approximately 1L per week, a case of twelve 1L bottles may be a wiser purchase than a case of four 4L bottles. Smaller bottles will be used more quickly, thereby minimizing the potential for peroxide problems and solvent waste.

Chlorinated Solvents

Chlorinated solvents such as chloroform and dichloromethane degrade at varying rates. Susceptibility to degradation depends on the solvent type and storage conditions. Light, heat or oxygen can initiate free radical formation resulting in phosgene, hydrochloric acid and other degradation products. To improve solvent stability and increase shelf life, solvent manufacturers add preservatives to chlorinated solvents.

Chloroform

Pure chloroform is unstable and rapidly generates free radical degradation products. Although many additives can inhibit this decomposition process, alcohols and olefins are the most successful and widely used preservatives. Olefins act as free radical scavengers and remove decomposition products such as hydrochloric acid.

Alcohols inhibit free radical formation, but they must be present at higher levels (up to 1%) to be effective. Although amylene is the most common additive, chloroform is also available with amylene and ethanol. Because ethanol will increase mobile phase polarity and therefore affect the analysis, methods that use chloroform should state whether or not ethanol is included as a preservative.

Chloroform Testing Verify chloroform integrity prior to use by testing an aqueous extract for free chloride using an AgNO₃ solution.

Dichloromethane (Methylene Chloride)

Dichloromethane is more stable than chloroform, but still requires a preservative. Amylene, cyclohexene and other olefins, as well as hydrocarbons like cyclohexane, are commonly used as scavengers of decomposition products. B&J has determined that either cyclohexene or amylene effectively stabilizes dichloromethane. As each stabilizer scavenges free radicals, by-products are formed. Low levels of scavenging by-products generated in cyclohexene-preserved material have retention times in capillary gas chromatography methods which may interfere with target analytes. Consequently, B&J offers dichloromethane preserved with amylene for these applications. The scavenging by-products of amylene-preserved material elute near the solvent front and before any reportable analytes. Some suppliers have offered dichloromethane preserved with only methanol. Aqueous extractions remove the methanol stabilizer and result in an unpreserved dichloromethane layer. Under these conditions, analyte degradation could occur prior to sample processing and yield inaccurate analytical results.

Ethers

Light, heat or oxygen cause ethers to form free radicals that generate peroxides. Peroxide formation raises several concerns. Their explosive nature makes safety the most serious issue when handling peroxide-containing solvent. Also, peroxides in any solution can react with analytes or degrade column packing materials when used in liquid chromatography mobile phases. To minimize peroxide-related problems, purchase ethers in quantities small enough to ensure their use within 30 days after opening. As an added safety precaution, test the solvent for peroxides prior to use. Ether Testing Many peroxide testing procedures are available, but simply shaking a 1:1 (v/v) mixture of an ether sample with 10% aqueous potassium iodide solution will detect peroxides. A colorless or faint yellow solution indicates

low-level peroxide contamination, but a dark yellow or brown color indicates significant peroxide levels. Solvent manufacturers employ several procedures to minimize ether degradation. One method is to eliminate one or more of the sources leading to free radical formation. Manufacturers blanket the solvent with inert gas during bottling to remove oxygen and use amber bottles to shield the solvent from UV light. These packaging techniques protect the solvent until the bottle is opened. Another method to extend solvent shelf life involves adding stabilizers.

Ethyl Ether (Diethyl Ether)

This solvent will readily form reactive and hazardous peroxides. At levels of 100 ppm or greater, peroxides pose an explosion hazard. This dangerous situation may easily occur if the solvent is concentrated by evaporation. At lower levels, peroxides can react with sample components, causing loss of analytes and generation of artifacts. Several effective preservatives have been developed. A common one for ethyl ether is butylated hydroxytoluene (BHT). Because this preservative interferes with electron capture GC analyses and contains an aromatic functional group which absorbs strongly around 280 nm, it cannot be used in B&J Brand Ethyl Ether. For methods using either EC or UV detectors, B&J Brand Ethyl Ether can be purchased with no added preservatives or with ethanol as a stabilizer. Ethanol must be present at high levels (2%) to be effective. As with ethanol-preserved chloroform, solvent polarity is increased by the addition of ethanol.

Tetrahydrofuran (THF)

Tetrahydrofuran is a cyclic ether also capable of forming peroxides. Consequently, solvent manufacturers sometimes add butylated hydroxytoluene (BHT) to inhibit peroxide formation. Because this very effective stabilizer is a strong UV absorber, BHT-preserved THF has limited utility in LC methods using UV detection. Therefore, we also offer THF packaged under nitrogen without any stabilizers. Increased UV absorbance is a common chromatographic symptom of peroxide formation in THF. Less common is a chemical reaction between peroxides and analytes. A chromatographic analysis was performed successfully, then set aside for several weeks. The method was restarted using THF that had been left on the instrument. The chromatogram now showed a second peak. Troubleshooting revealed that the peroxide level in the THF was greater than 80 ppm. Replacing the degraded solvent with a fresh bottle of THF solved the problem.

Methyl t-Butyl Ether (MTBE)

Added preservatives are not necessary since MTBE does not tend to form peroxides. The postulated mechanism for peroxide formation in ethers involves initial formation of a hydroperoxide, the insertion of oxygen between the carbon alpha to the ether oxygen and a secondary or tertiary carbon-hydrogen bond. In MTBE, one of the -carbons has three methyl groups and no hydrogens attached; the other is a methyl group with only primary hydrogens. Therefore, peroxide formation in MTBE is typically not significant.

Ketones

Chromatographers ordinarily find ketones such as acetone and methyl ethyl ketone stable and easy to use. New applications and lower detection limits, however, have created conditions in which solvent degradation effects may be important. Methyl ketones will degrade over time through an acid- or base-catalyzed condensation of the ketone with its enol tautomer, always present at trace levels. Low levels of dimerized ketone do not generally affect analyses, but excessively high levels indicate the solvent has undergone extensive degradation. For applications with exceptionally high purity requirements, purchase no more solvent than will be consumed in the lab within a few months.

Water

High purity water and water with added buffers readily grow bacteria in HPLC reservoirs. Ghost peaks in gradients result from bacterial by-products and dead bacteria. Use a bacteriostat or change the aqueous portion of the mobile phase daily to minimize bacterial contamination. Water stored in unclean containers, either plastic or regular lab glassware, can leach contaminants from the container. When exposed to air after opening, water can also absorb organic contaminants. Water used in liquid chromatography methods should be purchased as HPLC grade or generated in the laboratory using a commercial water purification apparatus designed to produce HPLC grade water. The simplest way to avoid water problems is to make certain the mobile phase reservoirs are properly maintained.

Hydrocarbon Solvents

Hexane and other hydrocarbon solvents are normally assumed to be stable, so their degradation is seldom considered a potential source of chromatographic artifacts. In rare instances, solvent degradation can cause spurious peaks or increased baseline noise. Degradation occurs when hydroperoxides are formed by the auto-oxidation of hydrocarbons in the presence of dissolved oxygen. Branched or cyclic hydrocarbon isomers will degrade faster due to the formation of a more stable hydroperoxide. Because the hydrocarbon is attacked by oxygen in a free radical chain reaction, little oxygen is required. This process is similar to the free radical reactions other solvents undergo. Hydrocarbons protected from air in a sealed system such as the Honeywell Burdick & Jackson Stainless Steel Pressure Dispense System (SSPDS) show little degradation.

Honeywell Burdick & Jackson

101 Columbia Road
Morristown NJ, 07962
Toll Free in U.S.

Technical Service: 1-800-368-0050
Customer Service: 1-800-322-2766

www.honeywell.com/burdickandjackson



Responsible Care®
Good Chemistry at Work

Burdick & Jackson is a registered
trademark of Honeywell International, Inc.

© 2008 Honeywell International Inc.

Honeywell