

Code of Practice C: Peroxides

1. Several commonly-used organic solvents containing the ether linkage are susceptible to peroxidation by atmospheric oxygen. Serious accidents have occurred in the past due to the explosion of these peroxide-containing solutions during distillation. These solvents include diethyl ether and other dialkyl ethers, 1,4-dioxane, tetrahydrofuran, triethyl orthoformate, monoglyme ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$), diglyme ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$), 2-methoxyethanol, 2-methoxyethyl acetate, 2-butoxyethanol and propionaldehyde. Peroxide in diisopropyl ether is particularly dangerous because of its tendency to separate as a solid on the neck and upper parts of bottles. Other classes of compound, including alcohols and alkenes (particularly dienes, homoallylic polyenes and chloroalkenes) are also susceptible to autoxidation reactions that lead to the formation of explosive products. In many cases, commercial materials that are susceptible to autoxidation are supplied with stabilisers to decrease the rate at which dangerous levels of peroxides accumulate.

Use only peroxide-free solvents.

Wherever possible, avoid evaporating ether-based solvents to dryness.

2. Testing for Peroxides

Ethers obtained from the Central Store should be tested for peroxide before use. They should be retested at fortnightly intervals thereafter. Particular care and attention should be paid to any other materials described above in Part 1, in particular any material that does not contain a stabiliser or has been stored for a lengthy period of time.

- (a) Test papers for peroxides are available from the Chemistry Stores.
- (b) To a sample of the ether add an equal volume of 2% KI solution and one drop of hydrochloric acid (2 mol dm^{-3}). A brown coloration of iodine in the ether layer (blue when starch is added) indicates the presence of peroxide.

3. Emergencies

- (a) In the event that a solvent contains high levels of peroxides, do not allow the solvent to evaporate. If the solvent is miscible with water, add at least 5 parts water to 1 part solvent and seek the advice of your supervisor, the Safety and Research Technician, or the Departmental Safety Coordinator.
- (b) In the event that an explosion has occurred, evacuate uninjured personnel from the vicinity, switch off any equipment involved and deploy the emergency measures outlined in Section B (summon first aid for minor injuries, dial 9999 for major injuries and then notify the University on 43333).