Paper No. : 11
Paper Title: Food Analysis and Quality Control
Module- 22: Chemical Preservatives in Foods

22.1 Introduction

Food safety has become an increasing and an important concern in the world. Today's consumer demands for foods that is ready to eat, fresh-tasting, nutrient and vitamin rich, and minimally-processed and preserved. Preservatives play an important role in ensuring the quality, stability and shelf-life of food. A preservative is defines as any substance which is capable of inhibiting, retarding, or arresting, the growth of micro-organisms, of any deterioration of food due to micro-organisms. The overall mechanism of action of preservatives is supposed to be by interfering with the cell membrane, enzyme systems and metal ion chelation mechanisms. An ideal preservative would be effective at low concentrations against all possible micro-organism, be non-toxic and compatible with other constituent of the preparation and be stable for the shelf-life of the preparation. Preservatives can be natural or chemical. In this module we will deal with the various chemical preservatives which are generally used in foods.

22.2 Weak organic acids

Weak organic acids includes acetic acid, benzoic acid, lactic acid, propionic acid and sorbic acid. These are organic compounds and which do not completely dissociated in water. Exceptions to these solubility characteristics exist in the presence of other substituents that affect the polarity of the compound and thus changing their solubility. The mechanism of action of the preservative action of organic acid include the acidification of the cell cytoplasm following the diffusion uncharged protonated aicds along the membrane and thereby disrupting membrane function and also nutrient transport which also contribute towards the anti microbial activity.

22.2.1 Acetic acid

Acetic acid in the form of vinegar is generally used for preservation of vegetables as pickles. It has antimicrobial activity which increases at low pH. Its calcium, potassium and sodium salts are used in bread and bakery products as it prevents ropiness and growth of moulds. These acids are also used in preparation of ketchups and mayonnaise.

22.2.2 Benzoic acid

Sodium salt of benzoic acid is most commonly used as it is more soluble than its free acid form. It is used in acid foods like fruit juices, carbonated beverages, pickles, sauerkraut and tomato sauces. It optimum activity lies in the pH range of 2.5-4. It is more active against yeast and bacteria.

22.2.3 Lactic acid

Lactic acid is also used in a wide range of food applications such as bakery products, beverages, meat products, confectionery, dairy products, salads, dressings, ready meals, etc. Potassium and sodium salts of

lactic acid improve water binding capacity and improves flavor. It makes an excellent acidification agent for many dairy products and acid regulator in juices and soft drinks.

22.2.4 Propionic acid

Sodium and calcium salts of propionic acid has antimicrobial activity against moulds and some bacteria .As it has a three unit carbon compound structure the inability of microbes to metabolize it gives the toxic effect of it on microbes. It is used in bakery field more extensively.

22.2.5 Sorbic acid

Sorbic acid is a straight chain trans-trans unsaturated fatty acid. They are most effective at low pH. It is basically used in foods such as cheese, baked products, fruit juices, salad dressings, tomato products, cottage cheese, carbonated beverages wines and pickles. Its antimicrobial property is due to the in ability of moulds to metabolize its conjugated unsaturated structure.

22.3 Metal chelators

Chelators that can be used as food additives include the naturally occurring acid citric acid, and the disodium and calcium salts of ethylenediamine- tetraacetic acid (EDTA).They both have metal chelating effect. Metal ions are essential for every cellular systems so interfering with the metal ions will cause disruption of cellular activities. There are many metallo enzymes which require zinc, magnesium or calcium which are required for cellular metabolism. Metal ion chelation leads to lower bioavialbilty of the important metals which also disrupts various essential biochemical reactions and the cell thus loose homeostatis leading to cell inactivation and even cellular death.

22.3.1 Citric acid

It is used in biscuits, jams, tinned fruits, alcoholic drinks, cheese and dried soup. It has many uses like it prevents the discoloration of food, increases the anti-oxidant effect of other substances and regulates pH in jams and jellies. It is added to ice-cream as an emulsifying agent to keep fats from separating and to caramel to prevent sucrose crystallization.

22.3.2 Ethylenediaminetetraacetate (EDTA)

It is an aminopolycarboxylic acid and a colorless, water-soluble solid. EDTA is added to some food as a preservative or stabilizer to prevent catalytic oxidative discolorations, which is catalyzed by metal ions. In soft drinks containing ascorbic acid and sodium benzoate, it mitigates the formation of benzene which is a health hazard.

22.4 Curing agents

Curing salts produce the basic color and flavor of products such as bacon, ham and have been used throughout history. These additives are used to preserve meat and give them desire color and flavor and discourage the growth of microbes and prevent toxin formation. Nitrate and nitrites are used generally as curing agents. Nitrite when added to meat converts into nitric oxide and combines with myoglobin to

form nitroslymyoglobin which is heat stable pigment. Nitrite curing inhibits growth of microbes such as *Clostridium* and *Steptococcus* and lowers the temperature required to kill *C.botulinum* and thus help in decreasing the chances of botulism. In bacteria, nitric oxide reacts with ferredoxin enzyme and destroys the cells as they not able to synthesize ATP and die due to lack of energy.

22.5 Parabens

Methyl, ethyl, propyl and heptyl esters of parahydroxy benzoic acids are generally termed as parabens. They are relatively ineffective against bacteria but are effective against moulds and yeast. The effective pH for its activity is 7.Parabens is colorless, odorless and tasteless except methyl paraben. They are non-volatile and nonhygroscopic. They differ from benzoic acid as they have antimicrobial activity in both acid and alkaline medium. Research has shown various possible modes of action of parabens. Parabens are found to be effective by disrupting the cytoplasmic membranes and leakage of intracellular RNA. Workers have also showed that parabens act by depleting the amino acid uptake of cells.They are used in fruit cakes, pastries and fruit fillings. In soft drinks methyl and propyl parabens can be used. Under FDA regulation, Methylparaben and Propylparaben are generally recognized as safe (GRAS) when used as chemical preservatives in foods, with a use limit of 0.1% for each.

22.6 Epoxides

Epoxides are cyclic ether that destroys all forms of micro-organisms and also there spores and sometimes even viruses. Epoxides are generally used in gaseous forms to achieve intimate contact with the microbes. Ethylene and propylene oxides are generally used and there use is limited to dry items like nuts and spices. Epoxides are also used as fumigants to destroy insects in grains, cocoa powder and packaging materials. Epoxides are alkylating agents they act by altering the functions of enzymes as they tend to react with groups (-SH, $-NH_2$,- OH) in cellular macromolecules. Treatment with epoxides is a suitable treatment for reducing microbe load on the spices and powders as high temperature treatment will deteriorate the volatile and flavor compounds of spices.

22.7 Sulphites

Sulphur dioxide and sulphites are used both as antimicrobial and as antioxidant substance. Sulphur dioxide is used as a gas and is used by bubbling through liquids directly. Instead of sulphur dioxide a number of sulphites are used which liberate sulphur dioxide when dissolved in water. The most common of which is potassium metabisulphite. In solution the free forms SO_2 and undissociated H_2SO_3 are responsible for the antibacterial activity while SO_3^{2-} is responsible for the antioxidant property. Sulphites are used in wines as an antioxidant as well as antiseptic or bacteriostatic. The antimicrobial activity of sulphurous acid is supposed to be due to the reaction of bisulphite with acetaldehyde in the cell, reduction of disulphide linkages in enzymes and formation of bisulphite addition compounds that interfere with

respiration. In aqueous solution sulphur dioxide and sulphites form sulphurous acid and ions of bisulphate and sulphites; these prevent the growth of yeasts and moulds. The sulphites are used in treatment of fruits and vegetables before and after drying and also to prevent enzymatic browning. In both these cases the sulfite bounds to a carbonyl intermediate group (quinnones) and prevent them from polymerizing to form a brown pigment. The reactionis dependent upon sulfite acting as a nucleophile .Sulphites are also used used to control the growth of microorganisms in soft fruits, lemon juices, beverages, sausages, pickles, and sea foods like fresh shrimp.

22.8 Hydrogen peroxide

Hydrogen peroxide is an oxidizing agent and is greatly used for bleaching purposes. Due to its oxidizing property it oxidizes the thiol groups of enzymes and protein causing metabolic inhibition of microbes. Foods such as wheat flour, crude soy lecithin, edible oil, egg white etc are bleached using hydrogen peroxide. In milk hydrogen peroxide is used as antimicrobial agent along with enzyme catalase.

22.9 Antioxidative agents

These slow or stop the breakdown of fats and oils in food that occurs in the presence of oxygen leading to rancidity. There are three types of antioxidants: True antioxidants such as Butylated hydroxytoluene (BHT) and Butylated hydroxyanisole (BHA) block chain reactions by reacting with free radicals. BHA and BHT are used in bakery products, cereals, fats and oils.

2.1 Various food and respective preservatives

The wide range of foods having wide ranges of preservation problems uses different preservatives for better product stability and shelf life. Here we will discuss various food groups and the preservatives used in them.

Foods groups	Preservative used
BAKERY	
Pre-packed, sliced bread and rye bread. Partially baked, pre-packed bread	Calcium propionate, Sodium propionate.
Cakes, muffins, pikelets and crumpets	Sorbates.
Biscuits	Sodium benzoates, sodium diacetate, citric acid, sulphites.
Fruit cakes, pastries and fruit fillings	Parabens
BEVERAGES	
Non alcoholic flavored drinks	Sorbates
Fruit juices	Citric acid, benzoic acids, sorbates
Carbonated beverages	Phosphoric acid, benzoic acids
Wines	Sorbic acid , sorbates, sulphites

Beer	Potassium methabisulphite
FRUIT (JAMS, MARAMALADES, FRUIT PREPARATIONS)	
Fruit based pie-fillings	Sulfites
Dried fruit	Sorbic acid, sorbates, sulphites
Candied fruit	Sulfites
Jams, marmalades and other fruit spreads	Sulfites, benzoates
DAIRY PRODUCTS	
Raw milk	Hydrogen peroxide
Cheese	Sorbates , sorbic acid
Ripened cheese	Sodium nitrate
MEAT, POULTRY, FISH	
Processed meat and poultry	Nitrates, nitrites, lactates ,acetates and diacetates
Pre-packed preparations of fresh minced meat	Lactates and acetates
Crustaceans and cephalopods (fresh, frozen, deep frozen, cooked)	Sulphites
Fish	Acetic acid, Propyl-ρ-hydroxy Benzoate
Dry sausage, semi-dry sausage	Nitrates
Bacon	Potassium nitrite
Solid cut meat; Solid cut poultry meat	Potassium lactate
OTHER FOODS	
Pickles	Acetic acid
Liquid soups & broths (not canned)	Sorbates and benzoates
Liquid egg (white, yolk, whole egg)	Sorbates and benzoates
Sauces, Ketchup	Benzoic acid
Dehydrated, processed and frozen potatoes	Sulphites
Ice-cream	Citric acid
Emulsions	Sorbates, citric acid
Processed mushrooms (including frozen)	Sulphites
Salad dressings	Lactic acid, acetic acid

References

Principles of Food Chemistry, John M. deMan, Aspen Publishers, 3rd ed. 1999.

Foods Facts and Principles, N.Shakuntala Manay and M. Shadasharanswamy, New Age International, 3rd ed. 2011.

Organic Acids and Food Preservation, Maria M. Theron, J. F. Rykers Lues CRC press ,1st ed. 2010.
Antimicrobials in Food, P. Michael Davidson, John N. Sofos, A. Larry Branen, CRC Press, 3rd ed. 2005

S. Brul and P. Coote.(1999). Preservative agents in foods mode of action and microbial resistance mechanisms. *International Journal of Food Microbiology* 50 , 1–17.

S.P. Anand and N. Sati (2013) Artificial Preservatives and their harmful effects: Looking toward nature for safer alternatives. *International Journal of Pharmaceutical Sciences Review* 4(7); 2496-2501.

Santos AL, Sodre CL, Valle RS, Silva BA, Abi-Chacra EA, Silva LV, Souza-Goncalves AL, Sangenito LS, Goncalves DS, Souza LO, Palmeira VF, d'Avila-Levy CM, Kneipp LF, Kellett A, McCann M, Branquinha MH.(2012). Antimicrobial action of chelating agents: repercussions on the microorganism development, virulence and pathogenesis. *Current Medicinal Chemistry,* 19, (17):2715-37.