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Module – 12: Preservation of foods by chemical methods – the ideal chemical preservatives

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Component-I (A) - Module Structure:

Structure of Module/Syllabus of a module (Define Topic of module and its subtopic)	
Preservation of foods by chemical methods – the ideal chemical preservatives	Introduction, An ideal antimicrobial preservative and added preservatives; Organic acid and their salts: Propionates, Benzoates, Sorbates, Acetates; Nitrites and Nitrates, Sulfur Dioxide and Sulphites, Ethylene and Propylene oxides, Sugars and Salts, Alcohol, Formaldehyde,Woodsomke,Spices and other condiments, Other food additives, Antibiotics.

Component-II - Description of Module

	Description of Module
Subject Name	Food Technology
Paper Name	Food Microbiology
Module Name	Preservation of foods by chemical methods – the ideal chemical preservatives
Module Id	FT/FM/12
Pre-requisites	Types of food preservation methods, Biological and chemical nature of food, types of food
Objectives	To study about types chemical preservatives and their properties as preservative
Keywords	Chemical preservatives, Perishable foods, Sorbates, Alcohol, Antibiotics, Shelf-life

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1. Introduction

Food preservation includes a variety of methods that allow food to be kept for extended periods of time without losing its nutritional quality and avoiding the growth of unwanted microorganisms. In general, there are three basic objectives for the preservation of foods: a) Prevention of contamination of food from damaging agents (microbes, insects etc., b) Hinder or prevention of growth of microbes in the food and c) Delay of enzymic spoilage such as self-decomposition of the food by naturally occurring own enzymes.

Hence, our purpose is to select the appropriate food preservation procedures which effectively manage the microbial content of foods with affecting the nutritional qualities of food. To achieve this objective, there are several chemicals (synthetic or artificial) and natural compounds are available which may be added. A food additive is a substance or mixture of substances, in addition to the basic food stuff present in food as a result of any aspect of production processing, storage or packaging such as vitamins, mold inhibitors, bactericides, emulsifiers, minerals, food coloring, synthetic flavors and sweeteners etc. Those food additives which are specifically added to prevent the deterioration or decomposition of food have been referred to as chemical preservatives (intentional additives). Some chemicals that get into food accidentally are referred to as 'unintentional additives' like the unavoidable residues of agricultural chemicals like weedicides, pesticides, antibiotics etc.

Nowadays, a number of conventional methods of food preservation are used at the household level that can be categorized as chemical methods such as sugar, salt, brine, vinegar; spices and wood-smoke are generally regarded as safe and natural preservatives. Mainly, salting, sugaring and wood smoking are all methods of curing foods. Most of chemical preservatives may inhibit microorganisms by interfering with their cell membranes, their enzyme activity or alteration in their genetic mechanisms. Other kind of preservatives may be used as antioxidants to hinder the oxidation of unsaturated fats, as neutralizers of acidity, as stabilizers to prevent physical changes in food and as coatings or wrappers to keep out microbes, prevent loss of water or delay undesirable microbial enzymatic and chemical reactions in food.

2. An ideal antimicrobial preservative and added preservatives

In general, preservatives are substances which prolong the shelf-life of foodstuffs by protecting from microorganism attack. As per list, the preservatives are one of the 26 major additives categories that are used in the food processing and have been evaluated many times and confirmed to be safe by the food regulatory authorities like Scientific Committee on Food (SCF) and the European Food Safety Authority (EFSA) at maximum levels. Preservatives, both naturally occurring and synthetically made, According to the Canadian Food Inspection Agency (CFIA), preservatives are grouped into classes (I-IV), with each class having similar microbiological or chemical activity.

Class I: Curing preservatives in cheeses and meats

Class II: Antimicrobials (which inhibit the activity or growth of microorganisms)

Class III: Antifungals (which inhibit the activity or growth of yeast and mold) and

Class IV: Antioxidants and its synergists (which are used to prevent the oxidation of vitamins, minerals and lipids of foods and ant browning agents which prevent both enzymatic and non-enzymatic browning of foodstuffs).

An ideal antimicrobial preservative should have following attributes:

- Demonstrate broad spectrum of microbial activity, so that wide range of microbes can be killed or destroyed.
- It should be non-toxic to handlers and consumers.
- The cost of production should be low (economical)
- It is expected that it should not affect organoleptic properties of food to be preserved and should not be inactivated by food.
- Preservative should not promote the growth of resistant strains and
- It should kill microbes effectively rather than inhibit multiplication.

There are certain factors that influence the effectiveness of chemical preservatives in killing microorganisms or inhibiting their growth and activity like concentration of the chemical, kind, number, age, temperature, duration, and other chemical and physical characteristics of the substrate in which the organism is found (intrinsic and extrinsic parameters etc.) must be taken into consideration while applying them. Antimicrobial preservatives used in food can be categorized in four groups:

1) Natural organic acids and their salts, vinegars, sodium chloride, sugars, spices and their oils, woods smoke, carbon dioxide, and nitrogen. Such added preservatives were not defined as such by law.
2) Substances having generally recognized as safe (GRAS) status for addition to food such as propionic acid and its salts, sorbic acid and their salts, benzoic acid and benzoates and their derivatives, sulfur dioxide and sulfites etc. However, some restriction on the use of few on them must take into consideration during their application, table 2.1).
3) Certain chemicals considered to be food additives, which are not listed in the first two groups. Though, they can be used only when proved safe in clinical trials for humans or animals and later on they can then fall into group 4.
4) Chemicals proved safe and approved by the Food and Drug Administration (FDA) from time to time.

Keeping in view of public health safety, all additive and preservatives must have to be approved for use in foods before they can be used. Specifically, expert organizations like the Scientific Committee for Food, the European Food Safety Authority and the Joint FAO/WHO Food Additives Committee have examined the safety concern of each preservative and made some guidelines and recommendations on their use including maximum levels. These recommendations are taken up by governments both nationally and internationally level so that foods can be preserved commendably along with ensuring that food is safe to consumption.

Table 2.1: Common type of food preservatives and kind of food products they are used in with their maximum permissible limits.

Food Preservative		Type of food products	Maximum Permissible limit*
Type of preservative	Example		
Antimicrobial	Benzoates and sorbates	Pickles, fruit juices, jams, cheese	200 ppm
	Propionates	Bakery products, cheese, fruits	0.32%
	Sulfites and sulfur dioxide	Dry fruits, fruits, molasses, wine fried or frozen potatoes and prevent discoloration in fresh shrimp and lobster.	200-300 ppm
	Nitrites and nitrates	Meat products	100-120ppm
Antioxidants	BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene)	Baked foods and snacks, meats, breakfast cereals, potato products.	100 ppm for meat products; 50 ppm for breakfast cereals and potato products.
	Tert-Butylhydroquinone	Baked foods and snacks, meats	100 ppm
Antienzymatic	Erythorbic acid (iso-ascorbic acid) and citric acid.	Soft drinks, juices, wine, and cured meats.	200-350 ppm

*please note that the permissible limits for use of food preservatives vary depending on the food product, from country to country.

2.1 Organic acid and their salts

Preservatives are intensely added in food to inhibit or kill microorganisms. The classification of preservative is based on various other criteria: such as their chemical composition and nature, their mode of action, specificity, effectiveness and legality. Generally, organic acids (i.e. lactic, acetic, propionic, sorbic, benzoic, citric, caprylic, fumaric, malic acids etc.) and their salts may be added to or developed in food by the process

of microbial fermentation. It has been demonstrated that undissociated form of organic acids penetrates cell membrane more easily than dissociates form. Organic acids inhibitory to food borne pathogens such as *Bacillus, Campylobacter jejuni, Escherichia coli, Clostridium, Listeria monocytogenes, Salmonella, Pseudomonas, Staphylococcus aureus*. For example, citric acid is applied as a substitute for fruit flavors and for preservation of drinks, jams, jellies etc.

2.1.1 Propionates

Propionic acid is a short-chain fatty acid like some other fatty acids. In general, up to 1% propionic acid is naturally produced in Swiss cheese by *Propionibacterium freudenreichii*. It most effective in undissociated form as compare to dissociated. However, activity of propionic acid depends on pH of substance to be preserved. It is used to inhibit molds (mainly) and to inhibit yeasts and bacteria, for example sodium or calcium propionate is used most widely in the inhibition of mold growth and rope development in baked goods and for mold prevention in many cheese food and spreads. In bread, 0.1 to 5% concentration propionates are added to prevent *Bacillus subtilis* growth, which is responsible for ropiness. Propionates are s used for preservation of baked foods, cheese etc.

2.1.2 Benzoates

The sodium salt of benzoic acid has been used extensively as antifungal agent in food. It is very effective against *Talaromyces, Pichia* 0.1% level, pH 3.6 to 4.0 and reduces *E.coli* by 3 to 5 log in 7 days at 8^{o}C. Their effective range of pH 3.0 to 8.0. Benzoates are most effective against yeast and molds at pH 5.0-6.0. It has been used into jams, jellies, carbonated beverage, margarine, fruit salads, pickles, fruit juices etc. Though, the mechanism of action of the benzoates is still not clear, it is known, however, that the effectiveness of the benzoic acid esters increases with an increase in the chain length of the ester group. They are more effective against fungi (molds and yeasts) and to gram positive bacteria. They may interfere with function of cell membrane and have permeabilizing effect and induce potassium efflux related to porin expression in outer membrane of *E. coli*.

2.1.3 Sorbates

Sorbic acid is a chemical compound (occurs naturally), first isolated in the berries of the Rowan tree. It shouldn't be confused with asorbic acid or vitamin C. Salts of sorbic acid such as the calcium sorbate, sodium sorbate, or potassium sorbate, is used as a direct antimicrobial additive in food and as a spray, dip or coating on packaging materials. Sorbic acid and its salts prevent the growth of mold, yeast but less effective against bacteria. In addition, Sorbate preservatives:

- Are very effective inhibitors of most common microorganism types that can attack foods and responsible for spoilage.

- It is s a naturally occurring polyunsaturated fatty acid, which is completely metabolized in human system.
- Do not affect taste, color, texture or flavour of foods.
- Are very effective over a wide range of pH. When used at the pH levels of most mildly acidic food products (pH 5.5-6.0).
- Sorbates are the most effective preservatives against a wider spectrum of food spoilage microorganisms than benzoates or propionates. In general, sorbate efficacy increases with greater acidity. Above pH 4.0, usually sorbates are more effective than sodium benzoate and sodium or calcium propionate. Sorbates are at their optimum effectiveness used below pH 6.0 and are comparatively ineffective at pH 7.0 and above.

Sorbate and its salts widely used in preservation of fruit cocktails, dried fruits, pickles, cheeses, cheese products, baked goods, beverages, syrups, fruit juices, jams, jellies etc.

2.1.4 Acetates

Acetic acid is a primary component of vinegar. It is in the form of vinegar may be used in mayonnaise, pickles, catsup, pickled sausages and pigs' feet. Acetic acid is more effective against yeasts and bacteria than against molds. The derivatives of acetic acid are monochloroacetic acid, peracetic acid, dehydroacetic acid and sodium diacetate, have been recommended as chemical preservatives. Sodium acetate is the sodium salt of acetic acid. Sodium acetate is used for preservation of mainly acidified food, refrigerated food and meat products food and it controls pH. It has been proved that 0.1% concentration of sodium acetate in bread, pH 5.1, and shelf life 6 days at 30^{o}C, inhibits *Bacillus subtilis* growth and 1% concentration of sodium acetate increases shelf life of catfish by 6 days at 4^{o}C.

2.2 Nitrites and Nitrates

Such chemical compounds occur naturally in the environment and are considered important plant nutrients. Nitrites and nitrates can also be applied to some food products as a preservative. In general, combinations of these various salts have been used in curing solutions for meat. Though, nitrates and nitrites have been used to preserve food for hundreds of years but there is concern that they may be linked to some kind of cancers. Normally, nitrite decomposes to nitric acid and forms nitrosomyoglobin with heme pigments in meats and a stable red color is given to meat. Further, nitrites can react with secondary and tertiary amines to form nitrosamines amines to form nitrosamines (known to be carcinogenic). They have shown the inhibitory potential to *Clostridium botulinum* and used for preservation of bacon, ham. As nitrates have only a limited effect on little number of organisms and hence, would not be considered a good chemical food preservative.

2.3 Sulfur dioxide and sulfites

In past, the Egyptians and Romans burned sulfur to form sulfur dioxide as a means of sanitizing their wine-making equipment and storage vessels. They were basically used as disinfectants, but nowadays sulfur dioxide and sulfites are used in the wine industry to sanitize equipment and to reduce the normal flora of the grape must. Salts of SO_2 such as potassium sulfite and sodium sulfite are commonly used for preservation of vegetables and fruits by controlling spoilage and fermentative fungi (yeasts and molds) in wine, malolactic and acetic acid bacteria. In aqueous solutions, sulfur dioxide and various sulfites form sulfurous acid, which is the most active antimicrobial compound.

Sulfites are inorganic salts that have antioxidant and preservative properties. Several compounds capable of producing sulfite, called sulfiting agents, that can be used to prevent enzymatic and nonenzymatic browning, control growth of microbial cells and act as bleaching agents, antioxidants or reducing agents. Sulfites are used on fruits and vegetable to prevent unpleasant browning and on lobster to prevent melanosis or "black spot", in wines to suppress bacterial growth and to bleach certain food starches and cherries. Beside food applications, sulfites are used in pharmaceuticals to maintain the stability and potency of some medications. Though, sulfite treatment levels in foods vary widely by application and residual levels do not usually exceed several hundred parts per million (ppm) but may approach 1000 ppm in certain fruit and vegetable products. At pH 4.0, it is 500 times more active as well as effective and used to inhibit *E. coli*, yeasts and mold like *Aspergillus* sp.

2.4 Ethylene and propylene oxide

Ethylene oxide exists as gas, kills all microorganisms. Propylene oxide can also kills many microorganism, is not as effective as that of ethylene oxide. They are thought to acts as an alkylating agent and employed as fumigant in warehouses and applied to dried fruits, eggs, dried yeast, cereals, spices etc. Hydroxyl ethyl group blocks reactive groups within microbial proteins and inhibits them. Ethylene oxide is used as gaseous sterilant (500 to 700 mg/L) and used for flexible and semirigid containers. Destruction of *Clostridium botulinum, Cl. sporogenes, Bacillus coagulans, B. stearothermophilus* and *Deinococcus radiodurans* occurs by ethylene and propylene oxide gases. However, propylene oxide is permitted only as packaging fumigant for cocoa, gums, dried fruits, spices and starch.

2.5 Sugar and salt

Salt is one of the world's ancient food preservatives, used since antiquity to preserve meat and fish. The food products that are treated with salt can remain in good condition for several years, as it dehydrates the food and the microbes present in the food. Hence, microbes can't contribute to decomposition or spoilage. It also keeps food dry enough to prevent the growth of mold and yeast. It causes high osmotic pressure, which leads plasmolysis of cells; the percentage of salt needed to inhibit growth or harm the cells is varying with the kind

of microorganism. Generally, NaCl is used in brines and curing solutions or is applied directly to the food and it has been reported to have its other following actions:

- Salt may ionizes to yield the chlorine ion, which is detrimental to microbes present in food.
- It can create anaerobic environment by reduces the solubility of oxygen in the moisture and
- Salt may interferes with the action of proteolytic enzymes.

Like salt, sugar (glucose or sucrose) removes moisture from food and owe their usefulness as preservatives to their ability to make water unavailable to microorganisms and to their osmotic effect checking the growth microbes that contribute to spoilage or decomposition. There is sufficient evidence that sugar has been used as a preservative for thousands of years (the ancient Egyptians were even known to preserve food in jars of honey). Typically, foods preserved in sugar are sweet and may be stored in sugary syrup such as honey or cooked in sugar until they crystallize. Sweetened condensed milk, fruits in syrups, jellies and candies are examples of some of food preserved by use of sugars.

2.6 Alcohol

It is a perfect antiseptic as it kills microbes and used to preserve fruits. Although, the fruit won't keep all their qualities as their sugar and flavor will dissolve in alcohol. Therefore, sugar must be added to the preserve. Generally, the fruits are preserved in flavorless spirit in large corked jars or sealed with a glass lid and a rubber band. The most commonly used alcohol is ethanol, a coagulant and denaturizer of cell proteins. The most effective germicidal concentrations of ethanol is in between 70 and 95%. Vanilla and lemon extracts (flavoring extracts) are preserved by their content of alcohol.

2.7 Formaldehyde

It is also known as methanal, which is a colorless gas but with a pungent and irritating smell. It is extremely reactive and readily soluble in H_2O. Pure formaldehyde is not commercially available while formalin (about 40% formaldehyde) is the most commonly used formaldehyde-containing solution. Formaldehyde is used as a food preservative illegally since it can prolong the shelf-life of a food by protecting against deterioration caused by microbes. In 2007, high level of formaldehyde (1200 mg/kg) detected in the concerned noodle fish is likely to be added deliberately as a preservative after the fish was caught, during transportation or storage. The texture of noodle fish adulterated with formaldehyde is likely to be stiff subsequently formaldehyde would react with the fish protein and result in muscle toughness and reduce its deliciousness. Hence, the addition of formaldehyde to food is not permitted, except as a minor constituent of woods smoke because this compound is very effective against wide range of microorganisms such as molds, bacteria and viruses can be used where its poisonous nature and irritating smell are not objectionable.

2.8 Woodsomke

It is one of the ancient food preservation methods that perhaps arose after the development of cooking with fire. Simply, smoking is used to increase the shelf life of perishable food items and adding desired flavors to them. It is achieved by exposing the food to smoke released from burning plant materials (wood). Woods smoke contains a several number of volatile compounds, which may have bacteriostatic and bactericidal effect i.e. formaldehyde, aliphatic acids, primary and secondary alcohols, ketones, acetaldehyde, other aldehydes, waxes, resins, catechol, methyl, pyrogallol and its methyl ester etc. Normally, wood smoke is much more effective against vegetative cells than against bacterial spores and the temperature varies with the kind of wood employed. Mostly, this method is applied for the preservation meats and fish that have undergone curing and mainly for cooking or flavoring of some fruits as well as vegetables (i.e. paprika, cheeses, spices) and ingredients for making drinks (i. e. malt) and tea leaves are also smoked.

2.9 Spices and other condiment

Spices and condiments are defined as "Vegetable products or mixtures, free from extraneous matter, used for flavoring, seasoning or imparting aroma in foods. Though, spices and other condiments do not have any noticeable bacteriostatic effect but may help other agents in preventing or suppressing the microbial growth in food. Generally, the inhibitory spectrum of spices varies with the kind of spice and the microorganism being tested (for example: mustard flour and the volatile oil of mustard are very effective against yeast *Saccharomyces cerevisiae* but are not as effective as cinnamon and cloves against most bacteria). It has been proved that the essential oils of spices are more bacteriostatic than the corresponding ground spices. For example cinnamon (containing cinnamic aldehyde) and clove (containing eugenol) usually are much more inhibitory than are other spices.

2.10 Other food additives

The purpose of use of additives in food is to improve the keeping quality of a food by making it last longer on the shelf or in the fridge. Some commonly used other food additives are as follows:

- Halogens are added to water for washing food (washing butter), equipment, for cooling and for addition to some products (bromine is used as a food additive in flour and some fruit-flavored soft drinks. Unluckily, bromine can have an adverse impact on your thyroid gland). Normally, water for drinking may be chlorinated by the direct addition of chlorine, or hypochlorites or chloramines may be used. Such halogens kill microbes by oxidation, injury to cell membranes, or direct combination with cell proteins.
- Wrappers of fruits impregnated with iodine have been employed to increase the keeping time of fruits.

- Iodophors (combinations of iodine with non-ionic wetting agents and acid) are being used in the decontamination of dairy utensils.

2.11 Antibiotics

Antibiotics are secondary metabolites produced by microorganisms that inhibit or kill a wide spectrum of other microorganisms. In general, antibiotics are used in the feed of cattle's or in treating their disease them. Occasionally if cattle's and poultry are fed on antibiotics, residues may be found in milk. According to the Food and Drug Administration, that milk from such infected animals should not be used for human consumption for at least three days following the treatment of the animal with the antibiotic. However, most of the better-known antibiotics have been tested on raw food, mainly proteinaceous ones i.e. meats, fish, and poultry, in an attempt to lengthen the storage time at chilling temperatures as shelf life increases two to three times, due to reduced growth of the microorganisms. Antibiotic Aureomycin (chlortetracycline) has been found superior to other antibiotics tested because of its broad spectrum of activity. Another antbiotic Terramycin (oxytetracycline) is almost as good for increasing the time of preservation of food. Both Chlorotetracycline (Aureomycin) and Oxytetracycline (Terramycin) have been used in the cooling water for dressed poultry. Likewise, antibiotics are added in packing of raw fish and shell fish and later its cooking of destroy the antibiotic residues, making them safe for human consumption.

Sometimes developed preservatives such as lactic acid, alcohol, bacteriocins (Nisin, a polycyclic antibacterial peptide with 34 amino acid residues used as a food preservative produced by *Lactoccous lactis*) etc. could be produced in food by microbes.

3. Summary

Home and commercial scale food preservation is a very practical approach for making the best of available food. Several methods of food preservation are available nowadays. Chemical food preservation has been experienced ever since man first began to store food for later use. In general, food storage raised the problem of spoilage mainly caused by microbes (bacteria, fungi and yeasts), making food inedible or unsafe for consumption because microbial activity could lead to potentially fatal food poisoning. From ancient times, a wide variety of chemicals have been employed to prevent microbial spoilage in food and their use times from well before the point when the existence of microorganisms was first suspected. Such chemicals range from naturally occurring substances like salt, sugar, saltpeter and spices to recent food additives (benzoates, sorbates and sulfites etc.). Some oldest food preservatives like salt and sugar, which dehydrates living microbial cells and causing death or inhibiting their growth. It is true that about six times as much sugar as salt needs to be used to accomplish the desired effect and both need to be used in relatively large quantities to be effective. Hence, this obviously confines their use as they will impart a strong flavor to the food

(especially in the case of salt) and therefore, employed where their tastes will compliment those of the foods (e.g. salt is used for meats and sugar for fruit). Alternatively, there are many herbs and spices contain chemicals which can kill or inhibit microorganisms and these have also been used as preservatives such as garlic, onion, allspice and oregano are particularly effective in killing of bacterial cells. Eventually, the criteria for successful food preservation is to prevent contamination by disease causing (pathogenic) organisms or toxicity through chemical and maintenance of optimum qualities like organoleptic properties, color, flavor, texture and the nutritive value of the foods.