Pigments and colours

Quality of food is generally based on colour, flavour, texture and nutritive value.

Colour is one of the most important quality attributes of a food.

The colour of a food is due to natural pigments present, except in cases where colourants have been added.

Therefore an understanding of such pigment systems is essential.

Plant pigments

E.g. chlorophyll, anthocyanin, betanin, flavonoids, carotenoids etc.
Chlorophylls

Structure of chlorophyll consists of a porphyrin nucleus chelating a magnesium atom and a phytol tail.

Porphyrin nucleus is made up of four pyrrole rings (tetrapyrrole). Pyrroles are cyclic compounds.

Pyrrole rings are connected through methylene bridges.

Phytol tail is a 20 carbon alcohol with an isoprenoid structure.
Chlorophyll structure

Algae and cyanobacteria contain chlorophyll $c$ and $d$
Chlorophylls

Chlorophylls are of several types. Chlorophyll a and chlorophyll b are the most important in plants.

Chlorophyll derivatives:

Chlorophyll (bright green) → Pheophytin (olive brown)
- Mg

Chlorophyll (bright green) → Chlorophyllide (bright green)
- phytol

Chlorophyllide (bright green) → Pheophorbide (brown)
- Mg
Deterioration of chlorophylls

- Chlorophylls are deteriorated due to processing and subsequent storage.
- Green vegetables develop dull olive-brown colour pheophytin upon heat processing and storage.
- Chlorophylls of dehydrated products packed in clear containers are photo-oxidized into pheophytin so the product develops dull brown colour during storage.
- Green vegetables undergo colour changes upon freezing and subsequent storage. Time and temperature of blanching before freezing affect the colour deterioration.
- Immediately after blanching the colour becomes brighter due to disappearance of air pockets in the tissues of raw vegetables, which hide the true colour.
Addition of CuCl$_2$ can prevent the degradation of chlorophyll in green pepper. Rapid chelating ability of the Copper complex (Copper phylloquinone) and its high heat and acid stability prevents chlorophyll degradation.

Vegetables turn olive green after 10 min cooking in boiling water. Acids are naturally present in all vegetables. Chlorophyll, which is protected by walls, are damaged during cooking allowing acidic compounds to come into contact with chlorophyll, which changes the colour.

Longer a vegetable is cooked, more chlorophyll molecules will be altered and most of the green colour will be lost. Cooking green vegetables for 5-7 min. will protect chlorophyll from acidic damage.
Deterioration of chlorophylls

- Canned peas, green beans and asparagus are more yellowish than their frozen counterparts. It is due to the intense heat used in the canning process and the longer cooking time required to ensure product sterility. The combined effect results not only losing its Mg atom but also structural changes in the molecule.

- Upon γ-irradiation and storage, chlorophylls of green vegetables are converted to pheophytin (olive brown).

- Blanched cucumbers develop off colour upon fermentation in acetic brine due to phophorbide formation.
Preservation of green colour of chlorophylls

Several methods have been proposed to preserve the green colour of fruits and vegetables.

1. **Use of chlorophyllase enzyme:**

   The chlorophyllase enzyme converts chlorophyll in to chlorophyllide (green). However the heat stability of chlorophyllide is not so high.

2. **Use of alkalizing agents:**
   
   E.g. Ca(OH)$_2$, Mg(OH)$_2$, NaHCO$_3$
Preservation of green colour ....

Alkaline pH converts chlorophyll into chlorophyllin, an attractive green colour molecule. However, alkali treated green vegetables also develop off colours upon storage. Bad effects of alkali treatment include destruction of vitamin C and weakening the texture of vegetable foods.

3. High temperature short time treatment (HTST):

This treatment produces a very attractive product immediately after processing, but develops off colours upon storage.
Preservation of green colour ....

4. **Controlled Atmospheric (CA) Storage:**

   In this method the carbon dioxide concentration of storage atmosphere is increased. When asparagus is stored under these conditions, increased retention of chlorophyll has been observed.

5. **Treatment Combinations:**

   Combination of HTST and alkalizing agents

   Combination of alkalizing agents, chlorophyllase enzyme and HTST

   Treatment combinations too produce attractive products, but off-colour develops upon storage.
These colour changes are due mainly to acetic acid formed during storage.

The stability of chlorophyll in plant products can be maintained by employing several methods such as,

- Using high quality raw materials
- Careful handling of products
- Using combined treatments
- Employing optimum storage conditions
Anthocyanins

- Common in plant kingdom:
- Several fruits, vegetables and flowers have them
- E.g. grapes, strawberries, apples, roses
- Water-soluble pigments located in cell sap
- Intensely colored – red, orange, blue, purple

Structure:

- All anthocyanins are derived from flavylium cation
- Twenty anthocyanins are known, but about six are important in foods.
  e.g. pelargonidin, cyanidin, delphinidin, pheonidin, petunidin and malvidin
Flavilium cation structure
Anthocyanins

- Distinctive colours of fruits, vegetables and flowers are produced by a combination of 4-6 pigments.
- In blueberries about 15 pigments are involved.
- Anthocyanin molecules are glucosides. Five types of sugar have been found as a component of the anthocyanin molecule.
- They are glucose, galactose, arabinose, xylose and rhamnose.
Anthocyanidins are derived from anthocyanidins by adding sugars. R groups contain a combination of H, OH or OCH$_3$ in different types of anthocyanidins.
Stability of anthocyanins in foods

- The flavylium nucleus is highly reactive
- The reactions involve decolorization of the pigment which is undesirable in fruit and vegetable technology.
  Destruction is greater at higher pH values but the pigment is fairly stable at acidic medium.
- Anthocyanins show a range of colours with changes in pH [red in acid (vinegar); blue in alkali (baking soda)]
- Sulphiting of fruits is an important process for bulk storage of fruits. Addition of suphites or SO₂ results in rapid bleaching of the pigment.
- The reaction is S-addition. Colour is regenerated when the product is boiled or acidified.
Stability of anthocyanins in foods

- Destruction of anthocyanin is high in the presence of ascorbic acid although the mechanism is not clear.
- Enzymes capable of hydrolyzing glycosidic linkages (glycosidases) can also decolourize anthocyanins.
Flavonoids

- Flavonoids are polyphenolic, secondary metabolites. Many plants contain flavonoid pigments.

- Approximately 400 flavonoids are known.

- Chemical structure is similar to anthocyanins but relatively more stable to heat and oxidation than anthocyanins.

- Flavonoids – Flavonol
  Flavanone

- **Flavonols:** found in tea and asparagus.
  E.g. quercetin, myricetin, rutin

- Flavonols form complexes with metal ions like iron and tin.
Flavonoids

- Tin complex is yellow in colour - desirable in canned asparagus.
- Iron complex is undesirable – dark colour
- Flavanones: found mainly in citrus plants
- Derivatives are very sweet and can be used in making synthetic sweeteners.

E.g. Neohesperidin dihydrochalcone – 2000 times sweeter than sucrose.
Tannins

• Form yellow to brown colour.

• Tannins are a complex mixture of gallic acid, ellagic acid and glucose

• Different forms of tannins available. E.g.

  **Tannic acid**  –  9 mol. gallic acid and 1 mol. glucose

  **Condensed tannins**  –  Dimers of catechin

  **Hydrolyzable tannins**  –  Polymers of gallic acid and ellagic acid
Betanins

• Group of compounds similar to anthocyanins in visual appearance.
• Found in beet, cactus fruits, amaranthus and flowers such as bougainvilla.
• About 70 betanins are known. Betanins are of two colours.
  - Betaxanthin – yellow colour
  - Betacyanin – red colour
• Betanins are subjected to thermal degradation but sufficient pigment is available even after canning.
• Isolated beet pigment is a potential food colourant.
Carotenoids

• Lipid soluble pigments responsible for red, yellow, orange colours of plant and animal products.
• Found in carrots, tomatoes, yellow/orange-coloured fruits, green leafy vegetables, red palm oil, butter, egg-yolk, algae etc. E.g.
  • β-carotene — dark green leaves, yellow fruits
  • Violaxanthin - in variety of plants, spinach
  • Neoxanthin - in spinach
  • Lutein - dark green leaves, pea, broccoli
  • Zeaxanthin - dark green leaves, maize
  • Lycopene — tomato, water melon,
  • Capsanthin – red bell pepper, chillie
  • Fucoxanthin — brown algae
  • Astaxanthin - green algae, krill, shrimp
Carotenoids

- Fucoxanthin, lutein, violoxanthin and neoxanthin are produced in large amounts.
- β-carotene and others are produced in smaller amounts but they occur widely.