

SAFETY AND STABILITY OF ARTIFICIAL SWEETENERS IN DAIRY FOODS

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Introduction

Sweeteners can be divided into two main groups: bulk and intense sweeteners. Simple sugars such as glucose, fructose, sucrose and maltose; sugar alcohols such as sorbitol, maltitol and lactitol; starch and starch hydrolysates such as glucose syrups; and high-fructose corn syrups, all belong to the class of bulk sweeteners. They confer body and texture to foods. Intense sweeteners form a very heterogeneous chemical group. Some are naturally occurring molecules extracted from plant material (glycyrrhizin, steviosides, thaumatin), whereas others are artificial compounds obtained by organic synthesis (aspartame, acesulfame-K, sucralose, saccharin, cyclamate, etc.). Unlike bulk sweeteners, they are generally not metabolized by the body and are excreted unchanged. For this reason, and due to the fact that they are used at very low levels in foods, they are also referred to as nonnutritive or noncaloric sweeteners (Prodolliet, 1996). These low calorie artificial sweeteners are used to aid in the management of diabetes and dental caries, weight control and create a variety of good tasting foods and beverages (www.caloriecontrol.org, 2004).

According to a notification amending the PFA rules, 1955 and issued by the Ministry of Health and Family Welfare on June 25, 2004, the use of artificial sweeteners has been allowed in food items as per the limits prescribed. Present notification permits the use of four artificial sweeteners like saccharin, aspartame, acesulfame-k and sucralose in combination, within prescribed limits. Use of artificial sweeteners has been allowed for the first time in sweets like halwa, khoya, burfi, rasogolla, gulabjamun and other milk products. Quantitative information on the sweeteners degradation/decomposition in dairy systems would help to establish any excess required to compensate for processing and storage losses. Degradation and hydrolysis of these sweeteners during prolonged heat treatment has been of concern due to the formation of some potentially toxic metabolites.

Stability of sweeteners

Long-term storage and heat stability are important factors for the use of intense sweeteners in many food products and beverages. The sweeteners have been found to have different response behaviour towards heat and pH. Sweeteners are highly sensitive to extreme conditions of pH and temperature and consequently break down to their respective moieties.

Acesulfame potassium (acesulfame K): It is approved for use in a wide range of products, including tabletop sweeteners, desserts, puddings, baked goods, candies and soft drinks. Acesulfame potassium occurs as a colorless to white-colored, odorless crystalline powder with an intensely sweet taste. It dissolves readily in water, even at room temperature. The approximate sweetening power is 200 times that of sucrose. Acceptable daily intake (ADI) is 15 mg/kg body weight/day. It blends well with other sweeteners and is synergistic with aspartame and sodium cyclamate but less so with saccharin.

Stability: In aqueous media, acesulfame-K is distinguished by very good stability. After several months of storage at room temperature, virtually no change in acesulfame-K concentration was found in the pH range common for beverages. Prolonged continuous exposure to 30°C did not cause losses exceeding 10%, the threshold for recognition of sweetener's difference (Hoppe and Gassmann, 1985). Even at temperatures of 40°C, the threshold for detection of sweetness differences was exceeded after several months, only for products having pH 3.0 or less (Von Rymon Lipinski, 1988 and 2004). Acesulfame-K containing beverages can be pasteurized under normal pasteurization conditions, without loss of sweetness. Sterilization is possible without losses under the normal conditions (i.e., temperatures around 100°C for products having lower pH levels and 121°C for products around and greater than 4.0 pH). In baked foods, no indication of decomposition of acesulfame-K was found, even

when biscuits with low water content were baked at high oven temperatures for short periods. This corresponds to the observation that acesulfame-K decomposes at temperatures well above 200°C.

Decomposition: Acesulfame-K is a derivative of oxathizin. Decomposition of acesulfame-K occurs only under extreme conditions of pH. In acidic conditions (pH 2.5), acesulfame-K breaks down to acetone, carbondioxide, ammonium hydrogen sulphate, amidosulphate, acetoamide and acetoamide N-sulfonic acid, while it decomposes to acetoacetic acid and acetoacetamide N-sulfonic acid in alkaline conditions (pH 3-10.5) (Arpe, 1978).

Aspartame: It occurs as off-white, almost odorless crystalline powder with an intensely sweet taste nearly 200 times that of sucrose (www.nutrasweet.com, 2005). It is slightly soluble in water and sparingly soluble in alcohol but insoluble in fats or oils. ADI of 50 mg/kg body weight/day. Aspartame has a sweet taste with minimal bitterness. Its onset of sweetness may be slightly slower than sucrose, and the sweetness may linger. Studies have demonstrated that the taste profile of aspartame closely resembles that of sucrose. It enhances various food and beverage flavors, especially fruit flavors. Aspartame is non cariogenic and helps in production of sugar free frozen desserts (Jana et al, 1994). Although aspartame may hydrolyze with excessive heat, it can withstand the heat processing used for dairy products and juices, aseptic processing, and other processes in which high-temperature, short time and ultra-high-temperatures are used.

Stability: Under dry conditions, the stability of aspartame was excellent. However, it was affected by extremely high temperatures that were not typical for the production of dry food products. At 25°C, the maximum stability was observed at pH 4.3. Aspartame functioned very well over a broad range of pH conditions, but was most stable in the weak acidic range in which most foods existed, i.e. between pH 3.0 and 5.0. Since, aspartame had lower free moisture; the shelf-life stability of aspartame exceeded the predictable shelf-life stability of these products (Beck, 1978). Fellows *et al.* (1991) observed that 60% of the original aspartame remained after 6 months at 21.1°C. Based on the tests, shelf-life estimates for the fruit preparations in yoghurt were 1.5 months at 32.2°C, 4-6 months at 21.1°C and >6 months at 4.4°C.

Keller *et al.* (1991) evaluated three commercial yoghurt cultures and strains of *L. bulgaricus* and *S. thermophilus*, for their effect on aspartame degradation during and after fermentation. The rate of aspartame loss was related to growth of organisms. Aspartame degradation rates were correlated to metabolic rate of the culture. As the rate decreased, loss of aspartame decreased. Results indicated that aspartame remained stable in yogurt, provided it was added after fermentation. Microbial content has been shown to affect the degradation rate of aspartame in some but not in all food products. Higher levels of initial microbial population and subsequent increase in population over time resulted in higher rates of aspartame degradation.

The major problem with aspartame is that, at the inherent pH of milk (6.6), the rate of aspartame degradation is extremely rapid, even under refrigeration. This degradation is accompanied by sweetness loss, which reduces the sensory shelf life of the product (Tsoubeli and Labuza, 1991). Aspartame degradation is minimal in the pH range of 4-5 (Bell and Labuza, 1991), which is below the pH of protein stabilization. Processing of milk at UHT is necessary as inherent dairy microorganisms can degrade aspartame.

Prodollet and Bruelhart (1993) detected aspartame and its degradation products: diketopiperazine, aspartylphenylalanine and phenylalanine in commercial products viz. tabletop sweeteners, candy, cream, yoghurt, powdered beverages and cola samples. Leonard and Theodore (1994) observed the kinetics of aspartame degradation in low to intermediate moisture systems, by incorporating aspartame into agar/micro crystalline cellulose model systems, prepared at pH 3.0, 5.0 and 7.0, equilibrated after freeze-drying to three water activities (0.34, 0.56 and 0.66) and stored at 25°C to 45°C. Aspartame was most stable at pH 5.0 and became less stable as pH decreased or increased. They also evaluated the stability of aspartame in commercially sterilized skim milk beverages. The pH and storage temperature appeared to be the two most important factors. The half-lives were 1 to 4 days at 30°C and 24 to 58 days at 4°C. Decreasing the pH from 6.7 to 6.4 doubled the stability of aspartame. Physico-chemical properties and the storage stability of low-fat lassi and

flavoured dairy drink using aspartame and fat replacers gave significant decrease in pH and increase in acidity and viscosity at 25°C than at 8°C. Aspartame losses were more in flavoured dairy drink than in lassi (Kumar, 2000).

Decomposition: Aspartame is a dipeptide composed of two amino acids, L-aspartic acid and the methyl ester of L-phenylalanine. In liquids and extreme conditions of moisture, temperature, and pH (<3.0 and >6.0), the ester bond is hydrolyzed, forming the dipeptide, aspartylphenylalanine, and methanol. Ultimately, aspartylphenylalanine is hydrolyzed to its individual amino acids, aspartate and phenylalanine. Methanol is hydrolyzed by the cyclization of aspartame to form its diketopiperazine. Other products formed include phenylalanine aspartic acid from diketopiperazine and β -aspartylphenylalanine (Mazur, 1974).

Saccharin: It occurs as a white crystalline odorless powder, or has a faint aromatic odor. It is slightly soluble in water, sparingly soluble in alcohol. It is about 500 times as sweet as sucrose. ADI is 15 mg/kg body weight/day. Saccharin is stable under the normal range of conditions employed in food formulations. It is commercially available in three forms: acid saccharin, sodium saccharin and calcium saccharin. Sodium saccharin is the most commonly used form because of its high solubility and stability. It is freely soluble in water and sparingly soluble in alcohol. It has a metallic aftertaste that is detectable above concentrations of 0.1% in solution. Calcium saccharin, however, might be chosen for a "sodium-free" product. In its bulk form, saccharin and its salts have been shown to be stable for several years (Nabors, 2001). Saccharin is the foundation for many low-calorie and sugar-free products around the world. It is used in table top sweeteners, baked goods, jams, chewing gum, canned fruit, candy, dessert toppings and salad dressings.

Stability: In its bulk form, saccharin and its salts show no detectable decomposition over long periods. They are also highly stable in aqueous solutions over a wide pH range. DeGarmo *et al.* (1952) studied the stability of saccharin in aqueous solutions. They found that saccharin solutions buffered at pH's ranging from 3.3 – 8.0, were essentially unchanged after heating for 1 hour at 150°C. Recent work using high performance liquid chromatographic techniques has confirmed their findings (PMC Specialties Group, 2004). Only under severe conditions of high temperature, high and low pH, over extended period does saccharin hydrolyze to a measurable extent.

Decomposition: Saccharin is a derivative of isothiazol. DeGarmo *et al.* (1952) showed that only under severe conditions of high temperature, high and low pH over an extended period does, saccharin hydrolyze to a measurable extent. The only hydrolysis products are 2-sulfobenzoic acid and 2-sulfamoylbenzoic acid.

Sucralose: It occurs as anhydrous, white, crystalline, orthorhombic needle-like crystals with an intensely sweet taste. It is a chlorinated sucrose derivative that is 500 to 600 times sweeter than sucrose. It has no calories and is exceptionally stable (Lawson, 2000). ADI is 5 mg/kg body weight/day. Sucralose is the only non-caloric sweetener made from sugar. Its unique combination of sugar-like taste and excellent stability allow sucralose to be used as a replacement for sugar in virtually every type of food and beverage, including in home cooking and baking. Sucralose is not used for energy in the body and does not break down as it passes rapidly through the body. The sweetest of the currently approved sweeteners, it has a clean, quickly perceptible sweet taste. The solubility and aqueous stability of the sweetener allow it to be provided as a liquid concentrate for industrial use. Studies in model food systems, demonstrate that sucralose can be used in dry food applications, with no expectation of discoloration when food products are handled in normal food distribution systems. The actual use level varies with the sweetness level desired and the other ingredients and flavor system used in the specific formulation.

Stability: Solubility was measured in a thermostatically controlled jacketed glass vessel. The temperature range studied was 20°C - 60°C. Sucralose is freely soluble in water and ethanol. As the temperature increases, so does the solubility of sucralose in each of the solvents. The data

demonstrated that sucralose is easy to use in food operations (Jenner and Smithson, 1989). Dry neat sucralose was sealed in glass vials, stored at 75°F, 86°F, 104°F and 122°F, and monitored for the development of colour. The time to first discolouration was 18 months at 75°F, 3 months at 86°F, 3 weeks at 104°F and less than 1 week at 122°F. However, dry neat sucralose had sufficient shelf life if the product was properly packaged, stored, and handled at appropriate temperatures.

Simple aqueous solutions were evaluated for stability of sucralose over various pHs, temperatures and times. After 1 hour of storage at 100°C, there was 2% loss at pH 5.0, a 3% loss at pH 7.0, and a 4% loss of sucralose at pH 3.0 (Anonymous, 1987). The stability of sucralose solutions stored at 30°C for up to 1 year at pH 3.0, 4.0, 6.0 and 7.5 showed no measurable loss of sucralose after 1 year of storage at pH 4.0, 6.0 and 7.5. At pH 3.0, there was less than 4% loss of sucralose after 1 year of storage (Mulligan *et al*, 1988). These data revealed that sucralose withstands heat processing conditions typical of most food processes, but under extreme conditions would slowly break down to its component moieties.

Decomposition: Sucralose is a chlorinated disaccharide. Under conditions of low pH and high temperature, sucralose breaks down slowly into its component moieties, 4-chlorogalactose and 1, 6-dichlorofructose. However, in extreme cases of high pH, 3, 6-anhydro-β-D-fructofuranosyl-4-chloro-4-deoxy-α-D-galacto pyranoside is formed (Goldsmith and Merkel, 2004).

Conclusion:

Artificial sweeteners can be used to expand markets for existing low-calorie products, such as jams and jellies, chewing gum, and carbonated soft drinks. Development and approval of a variety of safe, low-calorie sweeteners and other low-calorie ingredients will help to meet this consumer demand. The ideal sweetener should be stable in both acidic and basic conditions and over a wide range of temperatures. Long-term storage and heat stability are important factors for the use of intense sweeteners in many food products and beverages.

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