Production of Benzene from Ascorbic Acid and Sodium Benzoate

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Recently, a great deal of attention has focused on the presence of benzene in certain bottled and canned soft drinks and fruit drinks. In some of these products, benzene has been found at levels higher than the maximum amounts permitted for water supplies (set at 10 parts per billion [ppb] by the World Health Organization [WHO], 5 ppb by the U.S., and 1 ppb by European regulations). In reality, this issue originated in the early 1990s, when beverage industry representatives met with Food and Drug Administration (FDA) representatives to discuss their discovery of this problem. At that time, it was decided that the beverage industry would handle the situation through notification of producers and reformulation, and no public notice of the issue was made. In recent years, new companies have entered the beverage manufacturing industry, and their unawareness of the benzene problem and the reformulations required may have contributed to the current situation. Because of the mechanisms by which benzene is formed in these beverages, concern has been raised regarding the possibility of products such as pie fillings also having benzene contamination.

Production of Benzene

Benzene production in soft drinks and fruit drinks has been linked to the presence of ascorbic acid (vitamin C) and sodium benzoate ingredients in the products. A metal catalyzed hydroxyl radical reaction (1) involving these two compounds results in the formation of benzene. Ascorbic acid may be a component of foods or beverages through natural occurrence or through addition as a vitamin supplement or an antioxidant. Sodium benzoate may also occur naturally and is a commonly used food preservative (antimicrobial agent).

A number of factors may impact the formation of benzene in foods (1, 2). These include:

- Formulations containing ascorbic acid and sodium benzoate show increased benzene formation upon exposure to heat and/or light.
- Other chemicals, such as erythorbic acid (an isomer of ascorbic acid), EDTA, oxygen, and sweeteners (e.g., high fructose corn syrup), influence benzene formation.
  - Sweeteners may inhibit the reaction since the problem is most noticeable in diet drinks.
  - EDTA appears to inhibit the reaction.
  - Like ascorbic acid, erythorbic acid may lead to benzene formation.
  - Removal of oxygen through CO_2 or N_2 sparge may inhibit benzene formation.
- At low concentrations of ascorbic acid, increasing levels of ascorbic acid result in increased benzene production. At higher levels of ascorbic acid (i.e., above the level of benzoic acid in the product), however, benzene production decreases (likely through competitive action of the ascorbic acid as a hydroxyl radical scavenger in the reaction).
- Metals (e.g., iron and copper) likely present in the water used to prepare the products serve as catalysts in the production of benzene.
- In experimental mixtures, the maximum amount of benzene was produced at pH 2. Production dropped sharply as the pH increased from pH 3 to pH 5, and no benzene was detected at pH 7.
- Citric acid in place of ascorbic acid also forms benzene, although not as readily.
- Solutions of ascorbic acid with benzoic acid anhydride, acetophenone, and benzaldehyde also form benzene after 24-hour exposure to light.

Regulatory Status

Based on FDA regulations, sodium benzoate is used in the baking industry as an antimicrobial agent and as a flavoring agent and adjuvant (21 CFR 184.1733) at levels not to exceed good manufacturing practice (current usage levels being ≤0.1 percent in food). Ascorbic acid is allowed as a dough conditioner in flour and whole-wheat flour (≤200 parts per million [ppm]; 21CFR 137.105 and 21CFR 137.200). In artificially sweetened fruit jelly (21CFR150.141) and artificially sweetened fruit preserves and jams, ascorbic acid and/or sodium benzoate (as well as certain other agents) can be used singly or in combination as preservatives, provided that the amount not exceed 0.1 percent by weight of the finished food.

Health Concerns

The U.S. Department of Health and Human Services (DHHS) has classified benzene as A1, a confirmed human carcinogen. Consumption of foods containing high levels of benzene can result in symptoms such as vomiting, irritation of the stomach, dizziness, sleepiness, convulsions, rapid or irregular heartbeat, and death. Longer-term exposure impacts the blood through damage to the bone marrow causing a decrease in red blood cells, leading to anemia. The immune system may also be affected, increasing the chances of infection, and leukemia may also occur (3).

Benzene Content of Foods:

Benzene is a ubiquitous substance in our industrial environment. It is present in the air from tobacco smoke, motor vehicle exhaust, industrial emissions, and automobile service stations as well as in products such as glues, paints, furniture wax, and detergents. Benzene may even be present in certain food packaging materials (4). Many food items have been determined to contain benzene—one source (5) estimated our daily intake of benzene from foods to be 250 μg whereas another source (6) provided an estimate of 5 μg.

In response to the initial concerns regarding benzene formation in beverages, a 1992 survey (7) measured the benzene content of various fruit juices, fruit drinks, and soft drinks, and levels ranging from 0.018 to 3.83 ppb were found. In this study, however, samples were stored under refrigeration, and this may have influenced the results based on the understanding that exposure to heat increases the amount of benzene produced.

Another study (8) examined more than 50 foods, including some that had previously been reported to contain naturally occurring benzene as well as others containing benzoates and ascorbates, either naturally occurring or added. This study found that, with the exception of liquid smoke products, foods that had previously been reported to contain naturally occurring benzene actually had very little (≤2 ppb). Foods containing naturally occurring benzoates and ascorbic acid also contained little or no benzene (≤1 ppb). Foods with added benzoates and ascorbates (e.g., imitation strawberry preserves, taco sauce, and duck sauce) had levels that ranged from <1 to 38 ppb.

Two studies related to FDA's monitoring of the nation's food supply through the Total Diet Program also provided information regarding benzene content of foods. The earlier study (4) measured the content of 60 volatile organic compounds (VOCs; include benzene) in 234 different food items. While detailed results were not provided, benzene was found in 28 of the 234 items with levels ranging from 9.49–283 ppb (average = 50.3 ppb). Sauerkraut had the highest level, and a table with limited details showed cake doughnuts to contain 11 ppb benzene. The authors of this article found that VOC content of a food was positively correlated with fat content of the food (i.e., higher fat foods had higher levels of VOCs). The other FDA study (6) also looked at VOC content of 70 different types of food items. Benzene was found in all products except American cheese and vanilla ice cream, and levels ranging from 1–190 ppb were measured. In this study, fresh and frozen apple pies were tested, and in 4 occurrences, benzene levels ranging from 2–11 ppb were found.

Implications for Pie Fillings

Based on the information provided above, it is likely that a variety of factors will influence the possible presence of benzene in products such as pie fillings that contain both ascorbic acid and sodium benzoate.

- Sweeteners present in pie fillings would tend to reduce benzene formation.
- Baking of a pie (exposure to heat) would tend to increase possible benzene formation.
- pH levels of pie fillings or fruits used in them (see Table I) would, with some exceptions, be in the range consistent with reduced levels of benzene production (pH 3 to pH 5).
- Fat levels of pie fillings tend to be relatively low, which would correlate with a reduced benzene content.
- Relative amounts of ascorbic acid and sodium benzoate used would impact potential benzene formation, with higher relative amounts of ascorbic acid leading to reduced benzene content.
- Use of lemon juice/citric acid as a pretreatment of the fruit in a filling or to modify the pH may have an effect.
- Certain packaging materials may also contribute to benzene content of a product, independent of ingredients present in the product.

Other than Reference 6 information on apple pies (probably included crust and filling), no additional sources were located through this literature search that provided actual levels of benzene in pies/fillings. Analysis of benzene requires a certain level of expertise, and a limited Internet check of food testing labs indicated that benzene is a substance that is not routinely determined in food products. Thus, the number of testing labs that perform this analysis may be limited, and the costs may be somewhat expensive.

References

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TABLE I

pH Values [a]

Product/Ingredient	pH Value Range
Pie Fillings	
Fruit	3.0 – 5.0
Cream	5.8 – 6.3
Lemon	3.0 – 4.0
Fruits/Vegetables	
Apples	2.9 – 3.3
Apricots	3.6 – 4.0
Bananas	4.5 – 4.7
Blackberries	3.2 – 3.6
Cherries	3.0 – 4.0
Dates	6.2 – 6.4
Gooseberries	2.8 – 3.0
Jams/Jellies	3.1 –3.3
Lemons	2.2 – 2.4
Peaches	3.4 – 3.6
Pumpkin	4.8 – 5.2
Raspberries	3.2 – 3.6
Rhubarb	3.1 – 3.2
Squash	5.0 – 5.4
Strawberries	3.0 – 3.5
Sweet Potatoes	5.3 – 5.6

[a] From Reference 9