

Furan: Mechanisms of Formation and Levels in Food

Don S. Forsyth, Adam Becalski, Valerie Casey, Steve Seaman, Karen Pepper and Samuel Ben Rejeb, Food Research Division, Bureau of Chemical Safety, Food Directorate, Health Canada

Background

- Late March, 2004- Health Canada informed of US FDA investigation of furan in canned and bottled food commodities
- Furan has been shown to be carcinogenic in mice and rats, classified as “possibly carcinogenic to humans” (Group 2B) by IARC in 1995
- Although furan is used in industrial processes the likely source was considered to be formation during food processing
- April, 2004- Health Canada commenced method development for study of mechanism(s) of formation and survey of Canadian food products

Furans in Foods

- Furan derivatives have been reported in a wide variety of foods and are a significant flavour and odour component in coffee, cocoa, and various cooked meat products
- Furan has been found in coffee, canned beef, sodium caseinate, soy and rapeseed protein and caramel



Possible Mechanisms of Formation

- Thermal degradation of carbohydrates (Maillard reaction)
- Thermal oxidation of lipid
- Decomposition of ascorbic acid or its derivatives



Effect of Canned Beef Formulation and Processing Time on Furan Levels (Persson and von Sydow 1974)

| Formulation | Processing Time (min at 121°C) | Furan (ng/g) |
|--|-----------------------------------|-----------------|
| 79.3% beef, 20% H ₂ O, 0.7% NaCl | 15 | 930 |
| | 30 | 750 |
| | 45 | 760 |
| | 60 | 960 |
| | 75 | 870 |
| 66.3% beef, 13% fat, 20% H ₂ O, 0.7% NaCl | 30 | 3700 |
| 74.3% beef, 5% carbohydrate, 20% H ₂ O, 0.7% NaCl | 30 | 670 |
| 61.3% beef, 13% fat, 5% carbohydrate, 20% H ₂ O, 0.7% NaCl | 15 | 2800 |
| | 30 | 3900 |
| | 45 | 3700 |
| | 60 | 980 |
| | 75 | 1400 |

Analytical Methods

Two methods were used:

1. Static Headspace Analysis

- Mechanism(s) of formation and food survey

2. MicroExtraction Technique (MET)- A SPME related method developed at Health Canada

- Food survey

Both methods are based on isotope dilution (d_4 -furan) gas chromatography-mass spectrometry

Mechanism of Formation Studies

- 10 mg of test compound was added to a 1.5 mL vial containing 0.5 mL water
- Vials were heated 30 min at $118 \pm 1^{\circ}\text{C}$
- Cooled to 4°C
- D₄-furan added

Formation of furan from ascorbic acid and derivatives

| Reagents | Furan (ng/g) ^a | SD |
|---|---------------------------|------|
| Ascorbic acid | 35 | 11.9 |
| Ascorbic acid + Fe ⁺³ | 38 | 9.6 |
| Sodium ascorbate | 3.4 | 0.7 |
| Sodium ascorbate + Fe ⁺³ | 29 | 8.5 |
| Dehydroascorbic acid | 338 | 44.5 |
| Dehydroascorbic acid + Fe ⁺³ | 381 | 99 |
| Isoascorbic acid | 379 | 101 |
| Sodium isoascorbate | 15 | 0.8 |
| Sodium isoascorbate + Fe ⁺³ | 144 | 3.7 |
| Ascorbyl palmitate | 6.8 | 0.7 |
| Ascorbyl palmitate + Fe ⁺³ | 4.3 | 0.4 |

^aConcentration of furan in 0.5 mL of reaction mixture

Reagent – 10 mg

Fe⁺³ – 100 µg

Each value is an average of 4 experiments



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Formation of furan from fatty acids

| Reagents | Furan (ng/g) ^a | N ^b | SD |
|----------------------------------|---------------------------|----------------|-----|
| Linoleic | 125 | 4 | 26 |
| Linoleic + Fe ⁺³ | 498 | 4 | 185 |
| Linolenic | 625 | 4 | 96 |
| Linolenic + Fe ⁺³ | 985 | 3 | 2 |
| Trilinoleate | 78 | 4 | 16 |
| Trilinoleate + Fe ⁺³ | 136 | 4 | 20 |
| Trilinolenate | 570 | 4 | 96 |
| Trilinolenate + Fe ⁺³ | 463 | 4 | 4 |

^aConcentration of furan in 0.5 mL of reaction mixture

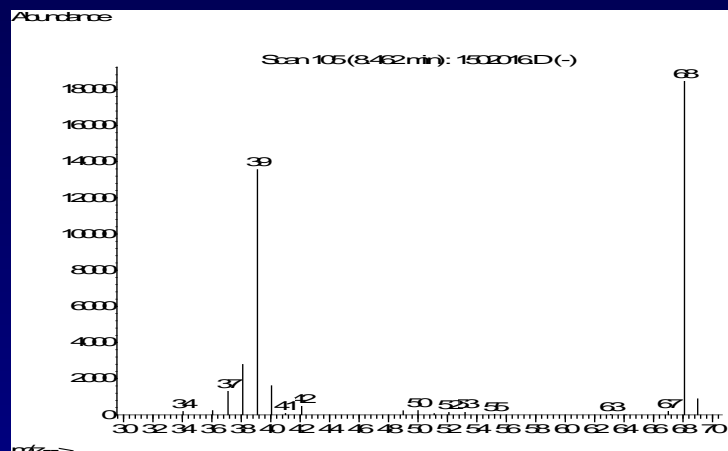
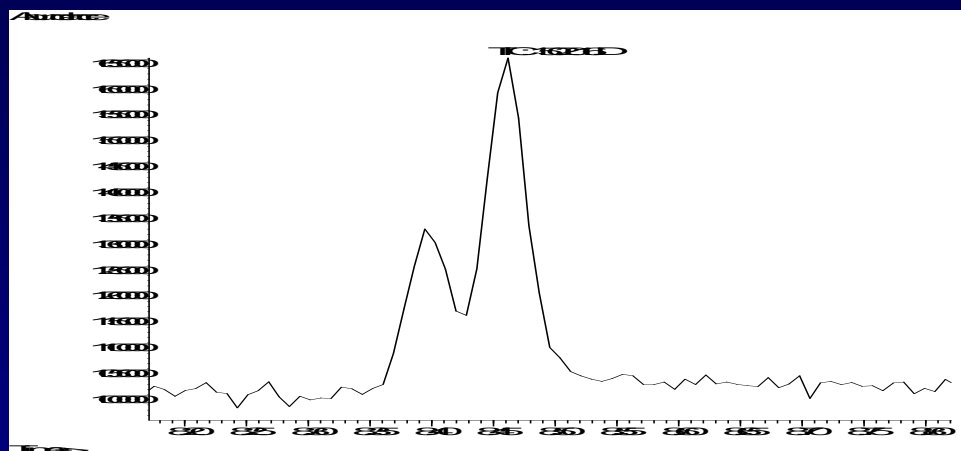
Reagent – 10 mg

Fe⁺³ – 100 µg

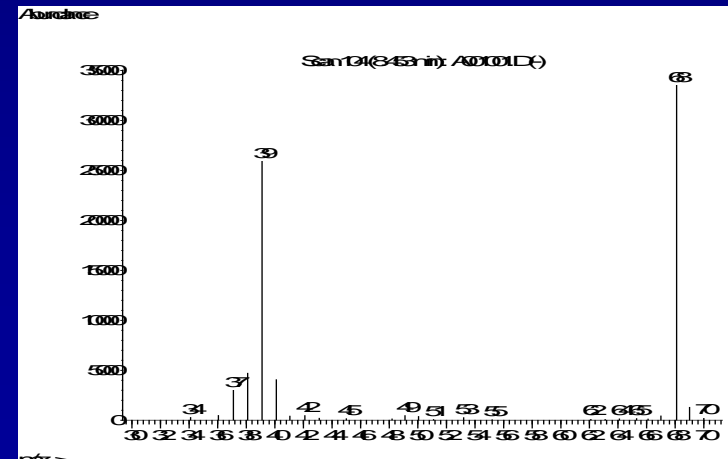
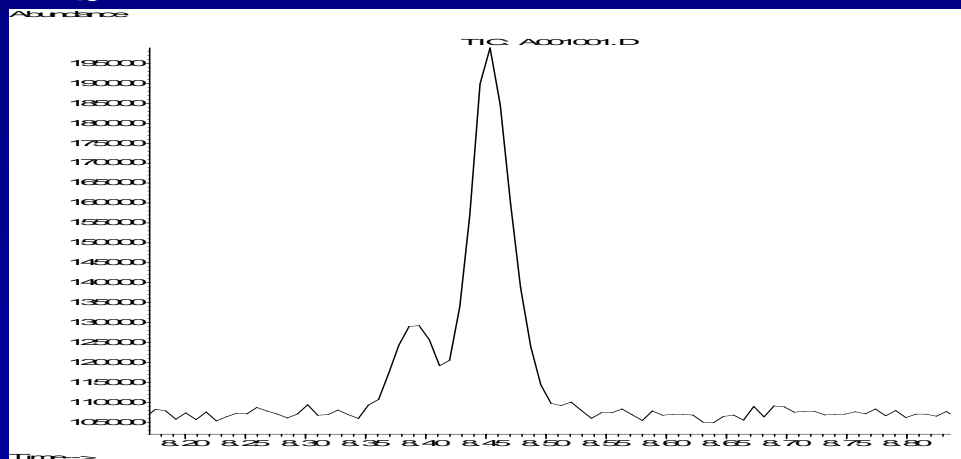
^b number of experiments

Chromatograms of: a) linolenic acid reaction and b) furan standard (1 ppm native, 0.25 ppm d₄)

a



b



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Conclusions

Two pathways of furan formation were identified in the model systems:

1. Polyunsaturated fatty acids (linoleic, linolenic) via peroxidation and ring closure
2. Decomposition of ascorbic acid derivatives particularly dehydroascorbic acid and isoascorbic acid



Preliminary Survey Results

Furan in Baby Foods

| Sample | Furan Concentration (ng/g) | |
|-----------------------|----------------------------|------------------------|
| | MET ^a | Headspace ^a |
| Beef with Broth | 6 | 6 |
| Banana | 7 | 8 |
| Carrot | 54 | 56 |
| Vegetable and Chicken | 18 | 19 |
| Apple Sauce | 5 | 5 |
| Mixed Vegetable | 146 | 154 |
| Alphabet Beef | 62 | 66 |
| Beef Stroganoff | 98 | 103 |
| Chicken and Stars | 25 | 26 |

^aAverage of two determinations



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Furan in Adult Foods

| Sample | Furan Concentration (ng/g) | |
|----------------------|----------------------------|------------------------|
| | MET ^a | Headspace ^a |
| Soups | 35-117 | 34-117 |
| Chili | 152-227 | 157-236 |
| Stew | 82 | 83 |
| Bean products | 14 | 14 |
| Canned luncheon meat | 7-31 | 4-28 |
| Coffee, fresh brewed | 14-52 | 14-51 |

^aAverage of two determinations

Next Steps?

- Further studies on mechanism(s) of formation using model systems and precursor fortified food matrices
- Losses of furan during food processing and cooking
- Further surveys of canned and bottled products
- Participate in round robin method validation study
- Update health risk assessment as new data becomes available



Thank-you !



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