Nitrates/Nitrites and Preservative Replacements in Meat Products

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Objectives

- To review the basic functions and importance of nitrites and nitrates as curing agents in meat products
- To present and discuss the various types of “clean label” processed meat products and their regulatory requirements
- To discuss alternatives to replace conventional nitrates/nitrites and antimicrobial preservatives in clean label processed meat products in the context of the technical challenges involved
Agenda

- History of Meat Curing
- Nitrate and Nitrite – The Basics
- Nitrate and Nitrite in the Diet
- Nitrate and Nitrite Content of Foods
- Functions of Nitrate and Nitrite in Meat Products
- Alternative Curing Systems
- Alternative Antimicrobial Systems
- Labeling of Clean/Simple Label Processed Meat Products
One of the oldest forms of food preservation
Very likely discovered by accident via contamination of salt with saltpeter (potassium nitrate)
By 10th century, Romans were adding saltpeter intentionally to obtain distinctive color and flavor
First USDA regulations for nitrite and nitrite use in meat products established in 1925
Regulations last updated in 1970
Bacon-specific regulations established in 1978 (to minimize potential for nitrosamine formation)
Nitrate and Nitrite

- Ionic forms:
  - Nitrate – \( \text{NO}_3^- \)
  - Nitrite – \( \text{NO}_2^- \)

- Sodium or potassium salts
  - NaNO\(_3\) or KNO\(_3\)
  - NaNO\(_2\) or KNO\(_2\)
Sodium Nitrate

- **Source:**
  - Can be mined or synthesized
  - In meat products, functions as a source and reservoir of nitrite
Sodium Nitrite

- **Source:**
  - Commercially synthesized by treating sodium hydroxide with mixture of nitrogen dioxide and nitric oxide:
    \[2 \text{NaOH} + \text{NO}_2 + \text{NO} \rightarrow 2 \text{NaNO}_2 + \text{H}_2\text{O}\]

- By definition, cured meats must contain nitrite

- Important public health function due to proven track record of *C. botulinum* prevention, which has been further validated by recent research
Nitrate and Nitrite in the Diet

- Two major sources in the body:
  - **Endogenous** $\rightarrow$ L-arginine-NO synthase pathway
    - NO (nitric oxide) generated by conversion of L-arginine to L-citrulline by nitric oxide synthase (NOS) is oxidized in blood and tissues to form $\text{NO}_3^-$ and $\text{NO}_2^-$
  - **Exogenous** $\rightarrow$ Diet
Nitrate in the Diet

- Mean daily intake = 43–141 mg (WHO, 2007)
- Total (exogenous) intake sources
  - Plant foods: ≈80%
  - Drinking water: 10–15%
- Food intake sources
  - Various vegetables
    - Largest contributors of dietary intake of nitrate; ≈85–90%
    - E.g., lettuce, cabbage, spinach, beets, celery, radishes
Nitrite in the Diet

- Mean daily intake = 1.2–3.0 mg (WHO, 2007)
- Total intake sources
  - Saliva: ≈93%
  - Vegetables: ≈2%
  - Cured meats: ≈5%
- Enterosalivary circulation of dietary nitrite
  - Ingested nitrate is absorbed in small intestine, 25% of which is secreted in saliva, ≈20% of which is converted to nitrite by oral cavity bacteria
    - Therefore ≈5% of ingested nitrate becomes converted to nitrite
      » This amount accounts for ≈93% of total ingested nitrite
  - Nitrite in saliva may produce NO under acidic conditions (as in stomach) in sufficient amounts to protect against swallowed pathogens (Duncan et al. 1995)
Enterosalivary Circulation of Dietary Nitrate

EXOGENOUS NO$_3^-$

Food

Water

INGESTED NO$_3^-$

100%

SMALL INTESTINE

25%

65–70%

converted to NO$_2^-$

SALIVA

5%

20%

urine excretion

re-ingestion
Nitrite/nitrate concentrations of selected foods collected from five U.S. cities in 2009

<table>
<thead>
<tr>
<th></th>
<th>Nitrate (ppm)</th>
<th>Nitrite (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Broccoli</td>
<td>394</td>
<td>29–1140</td>
</tr>
<tr>
<td>Cabbage</td>
<td>418</td>
<td>37–1831</td>
</tr>
<tr>
<td>Celery</td>
<td>1495</td>
<td>20–4269</td>
</tr>
<tr>
<td>Lettuce</td>
<td>850</td>
<td>79–2171</td>
</tr>
<tr>
<td>Spinach</td>
<td>2797</td>
<td>65–8000</td>
</tr>
<tr>
<td>Cured, dried, uncooked sausage</td>
<td>113</td>
<td>0.1–2289</td>
</tr>
<tr>
<td>Cured, cooked sausage</td>
<td>32</td>
<td>0.8–541</td>
</tr>
<tr>
<td>Fermented, cooked sausage</td>
<td>46</td>
<td>1.8–320</td>
</tr>
<tr>
<td>Whole-muscle, brine cured, uncooked</td>
<td>14</td>
<td>3.5–32</td>
</tr>
<tr>
<td>Whole-muscle, brine cured, cooked</td>
<td>16</td>
<td>0.2–108</td>
</tr>
<tr>
<td>Whole-muscle, dry-cured, uncooked</td>
<td>106</td>
<td>0.4–1367</td>
</tr>
</tbody>
</table>

Maximum ingoing nitrite and nitrate limits (in ppm) for meat and poultry products

<table>
<thead>
<tr>
<th>Curing Agent</th>
<th>Immersion Pumped</th>
<th>Massaged or Pumped</th>
<th>Comminuted</th>
<th>Dry Cured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Nitrite</td>
<td>200</td>
<td>200</td>
<td>156</td>
<td>625</td>
</tr>
<tr>
<td>Potassium Nitrite</td>
<td>200</td>
<td>200</td>
<td>156</td>
<td>625</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>700</td>
<td>700</td>
<td>1718</td>
<td>2187</td>
</tr>
<tr>
<td>Potassium Nitrate</td>
<td>700</td>
<td>700</td>
<td>1718</td>
<td>2187</td>
</tr>
</tbody>
</table>

Potassium nitrate 5% = 5,000 ppm
Concerns About Nitrite

- **Toxicity**
  - Very reactive; toxic at very high doses
  - Lethal dose ≈ 1 g (14 mg/kg body weight)
    - Assuming 15 ppm residual nitrite, this would be equivalent to ingesting 1,086 56-g hot dogs (66.7 kg)
  - Concern for methemoglobinemia, primarily in infants (blue baby syndrome)

- **Nitrosamines and Cancer**
  - N-nitrosamines cancer-causing potential discovered during 1950s/1960s
  - Formed by reaction of nitrite with secondary amines near neutral pH and temperatures > 130°C
  - For more information, consult Sindelar & Milkowski (2012)
Functions of Nitrite

- Cured Color
- Cured Flavor
- Texture
- Antimicrobial
- Antioxidant

Organoleptic effects
1. Color

- Due to nitric oxide (NO) production from NO$\textsubscript{2}^-$

\[ \text{NO}_3^- \xrightarrow{\text{nitratreductase}} \text{NO}_2^- \xrightarrow{\text{cure accelerator}} \text{NO} \]

- <5 ppm NO$\textsubscript{2}^-$ required for this effect
- Promoted by acidic conditions
- Accelerated by reductants, salt, pigments (Fe)
Functions of Nitrite

- Interaction of NO with meat pigment myoglobin

\[ \text{Myoglobin} \rightarrow \text{Nitrosomyoglobin} \rightarrow \text{Nitrosylhemochrome} \]

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{Heat} \]

Nitrosylhemochrome (pink cured meat color)
Functions of Nitrite

2. Antimicrobial

• Inhibitory activity towards many microorganisms, including Clostridium botulinum

• Acts in synergism with salt and other antimicrobials, e.g., lactate, to control Listeria monocytogenes
Functions of Nitrite

3. Antioxidant

• Effective for preventing rancidity
  – Decreases rate of lipid oxidation
  – Eliminates “warmed-over flavor” in cooked meats
  – Interacts with heme iron
  – NO scavenges free radicals

• Antioxidant activity of NO$_2^-$ may play a role in cured flavor
Functions of Nitrite

4. **Flavor**
   - Cured flavor not clearly understood
   - Is it a specific flavor compound or *the absence* of other flavor compounds? Is it both?
     - Fewer flavor compounds have been isolated from cooked cured meats than from uncured cooked meats
     - Does antioxidant activity play a role?

5. **Texture**
   - Protein crosslinking of sulfur-containing amino acids by nitrite
Functions of Nitrite

No other known substance possesses all of nitrite’s unique properties
Functions of Nitrate

- Serves as nitrite precursor and/or reservoir
- Sometimes included in starter cultures as a cured color promoting agent
- Also available from natural sources, such as celery powder and swiss chard
  - “Natural” or “Alternative” curing
  - Requires conversion to nitrite
    - In-plant fermentation
    - Pre-converted
Nitrate/Nitrite Alternatives

- Health concerns over nitrite in the 1960s lead to development of truly uncured (nitrite-free) products in the 1970s
  - These provided inferior organoleptic, safety and shelf-life properties than their cured counterparts
- In response, in 1972 USDA established requirement that products “for which there is a standard and to which nitrate or nitrite is permitted or required to be added, may be prepared without nitrate or nitrite and labeled with such standard name when immediately preceded with the term ‘Uncured’…”
- 1979 amendment include statement “No Nitrate or Nitrite Added.”
Clean/Simple Label Alternatives in Processed Meats

- Elements to replace:
  - Curing system
    - Nitrate/nitrite, ascorbate/erythorbate
  - Antimicrobial system
    - Lactate/diacetate, benzoate, propionate, others
    - Any ingredient called by its chemical name
  - Other ingredients
    - Phosphates, binders (e.g., carrageenan, *modified* starches)
    - Any ingredient called by its chemical name

- This necessitates search for “natural” or simple-name versions of these ingredients or other ingredients with similar functionality
Alternative Curing Systems

- Three basic elements of an alternative curing system
  - Nitrate/nitrite source
  - Cure accelerator
  - Bacterial starter culture (not always necessary)
Alternative Curing Systems

1. Nitrate/nitrite source
   • Commercial vegetable juices and juice powders
     − Celery (most common); Swiss chard
     − Other sources (e.g., lettuce, spinach, beets) not yet exploited commercially for this purpose
1. Nitrate/nitrite source, cont.

- Types:
  - Regular
    » Commercial sources vary from 20,000–30,000 ppm NO\textsubscript{3}\textsuperscript{-}
    » Typically standardized to a specific NO\textsubscript{3}\textsuperscript{-} content
    » Require fermentation step during processing to convert NO\textsubscript{3}\textsuperscript{-} to NO\textsubscript{2}\textsuperscript{-}
  - Pre-converted
    » NO\textsubscript{3}\textsuperscript{-} converted to NO\textsubscript{2}\textsuperscript{-} by supplier
    » Typically standardized to specific NO\textsubscript{2}\textsuperscript{-} content (up to >15,000 ppm)
    » Eliminates the need for fermentation step
1. **Nitrate/nitrite source, cont.**
   - Should try to maximize usage level to increase ingoing NO$_2^-$ content
   - There’s no regulatory limit, but, in most cases, self-limiting at 0.3–0.4% due to strong celery flavor
     - Maximum level is formulation specific, with blander-tasting products tolerating less
     - Opportunity for flavor research??
1. Nitrate/nitrite source, cont.

- Concern
  - Does system generate enough nitrite to control *C. botulinum*, *C. perfringens* and *L. monocytogenes*?
    - E.g., pre-converted celery powder (22,500 ppm NaNO₂) at 0.4% would result in 90 ppm ingoing NaNO₂. Is that enough?
    - It has been estimated that at least 70 ppm is needed for adequate antilisterial activity (Glass et al., 2008)
    - Commercial alternatively-cured frankfurters, hams and bacon have been shown to have more potential for growth of *C. perfringens* (Jackson et al., 2011)
    - Effectiveness of nitrite is affected by of other factors (e.g., other antimicrobials, salt level, temperature, \( a_w \), etc.)
Alternative Curing Systems

2. Lactic acid starter culture

- Reduce NO$_3^-$ to NO$_2^-$ via production of nitrate reductase
- Commercially available strains
  - *Staphylococcus carnosus, S. utilis, S. vitulinus, Micrococcus varians*
- Requires fermentation step (1–2 h at ≈27–38°C) prior to cooking to allow for NO$_2^-$ formation
  - Conversion not 100% efficient; difficult to control [NO$_2^-$]
- Not necessary when using pre-converted NO$_2^-$ sources
3. Cure Accelerators

- Natural sources of ascorbic acid
- Types
  - Cherry powder
  - Acerola powder
  - Lemon juice powder (to lower pH)
Antimicrobial Systems

- **Conventional**
  - Nitrite
  - Lactate
  - Diacetate
  - Benzoate
  - Propionate

- **Simple Name and or Natural**
  - Cultured sugars
  - Vinegar / buffered vinegar
  - Lemon juice / lemon juice solids
  - Plant extracts (e.g., rosemary, oregano, sage)

- Much commercial development activity in this area
- Need to confirm antimicrobial effectiveness (safety and shelf-life) on case-by-case basis by use of microbial challenge studies
- Some commercial microbial growth predictive models incorporate simple name antimicrobials
1. Uncured Products

- “Any product, such as frankfurters and corned beef, for which there is a standard in this part and to which nitrate or nitrite is permitted or required to be added, may be prepared without nitrate or nitrite and labeled with such standard name when immediately preceded with the term “Uncured” in the same size and style of lettering as the rest of such standard name: Provided, That the product is found by the Administrator to be similar in size, flavor, consistency, and general appearance to such product as commonly prepared with nitrate and nitrite...” 9 CRF 319.2
1. Uncured Products, cont.

- Products “which contain no nitrate or nitrite shall bear the statement “**No Nitrate or Nitrite Added.**” This statement shall be adjacent to the product name in lettering of easily readable style and at least one-half the size of the product name.” 9 CFR 317.17(c)(1)

- These products must also bear the statement “**Not Preserved—Keep Refrigerated Below 40°F At All Times**” unless they have been thermally processed to $F_o$ of 3 or more; they have been fermented or pickled to pH of 4.6 or less; or they have been dried to a water activity of 0.92 or less.” 9 CFR 317.17(c)(2)
Labeling
2. “Natural” Products

- USDA-FSIS Food Standards and Labeling Policy Book:
  - The term “natural” may be used on labeling for meat products and poultry products, provided the applicant for such labeling demonstrates that: (1) the product does not contain any artificial flavor or flavoring, coloring ingredient, or chemical preservative (as defined in 21 CFR 101.22), or any other artificial or synthetic ingredient; and (2) the product and its ingredients are not more than minimally processed.
  - Therefore, sodium nitrate or nitrite are not allowed
    » Products must be labeled “uncured”
2. “Natural” Products, cont.

• USDA-FSIS Food Standards and Labeling Policy Book:
  – Minimal processing may include: (a) those traditional processes used to make food edible or to preserve it or to make it safe for human consumption, e.g., smoking, roasting, freezing, drying, and fermenting, or (b) those physical processes which do not fundamentally alter the raw product and/or which only separate a whole, intact food into component parts, e.g., grinding meat, separating eggs into albumen and yolk, and pressing fruits to produce juices.
Labeling

 UNCURED

 NO NATURALLY OCCURRING IN SEA SALT & CELERI POWDER

 NO NITRATES OR NITRITES ADDED EXCEPT FOR THOSE NATURALLY OCCURRING IN SEA SALT & CELERI POWDER

 NO ANTIBIOTICS USED ** • HUMANELY RAISED **

 VEGETARIAN GRAIN-FED DIET • GLUTEN & CASEIN FREE • NO FILLERS

 INGREDIENTS: BEEF ** • WATER • CONTAINS LESS THAN 2% OF THE FOLLOWING: SEA SALT, PAPRIKA, CONCENTRATED ONION, SPICES, NUTMEG OR CELERY POWDER, GLUTEN & CASEIN FREE

 Fully cooked. Best within 4 days of opening, may be frozen for up to 6 months.

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Labeling

3. Organic Products

- Governed by Organic Foods Production Act (1990) and managed by the National Organic Program (NOP)
  - Establishes prohibited practices, requirements and allowed substances
- Synthetic and non-organic substances that may be used are listed in the National List of Allowed and Prohibited Substances (7 CFR 205.605 and 606)
- Sodium nitrate or nitrite specifically prohibited
  - Products must, therefore, be labeled “uncured.”
Labeling

3. Organic Products, cont.

- Regulated by Organic Foods Production Act (1990):
  - “100% Organic”
    - Only organically-produced ingredients and processing aids
    - Water and salt are excluded
    - Can use USDA organic seal
  - “Organic”
    - 95%+ organically-produced ingredients, excluding water and salt
    - Can use USDA organic seal
  - “Made with Organic Ingredients”
    - 70+ organically-produced ingredients
    - Cannot use USDA organic seal
Labeling


Questions? Consumer Care 866-587-5655 or visit www.applegate.com

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*Except for those naturally occurring in sea salt and celery powder.
**Grass-fed Beef - The meat from cattle raised on grass and grains from their natural habitats with limited access to the environment that provides them with fresh vegetation and natural conditions, free from the use of antibiotics and synthetic growth hormones.

Heating Instructions: Grill: Place over medium heat and turn until browned. DO NOT Bring water to a boil, reduce heat, carefully add hot dogs. Simmer for about 5 minutes. For kids under 3 years, cut lengthwise, then slice.

Real food has a story. Visit us online and learn more about the people, places and practices behind our products.
References

References, cont.

Thank You