







Cured meat products without direct addition of nitrate or nitrite: what are the issues?

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Abstract

The growing popularity of food products marketed in the United States as "natural" and "organic" has resulted in a proliferation of marketing efforts to meet consumer demands for these foods. Because natural and organic foods are not permitted to use chemical preservatives, the traditional curing agents used for cured meats, nitrate and/or nitrite, cannot be added to natural and organic processed meat products. However, alternative processes that utilize ingredients with high nitrate content, such as vegetable-based ingredients, and a nitrate-reducing starter culture can produce processed meats with very typical cured meat properties. Because it is not possible to analytically measure the amount of nitrite produced by this process, several potential issues deserve consideration. Regulations, for example, should permit labeling that accurately reflects the process and products, manufacturing procedures must be standardized to achieve product consistency, marketing efforts should clearly communicate the nature of these products to consumers, product quality must be maintained, and microbiological safety must be assured.

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1. Introduction

In many parts of the world, natural and organic foods have been experiencing an explosive market growth. Natural and organic processed meats have been a very significant part of that growth, and in the United States, have made up the fastest growing category of natural and organic foods (Mitchell, 2006; Organic Trade Association, 2006). Several studies have documented that consumer preferences for organic and natural foods are based on concerns about antibiotics, pesticides, hormones, genetic modifications in plants and animals, and chemical additives

that consumers associate with conventionally produced foods (Bourn & Prescott, 2002; Devcich, Pedersen, & Petrie, 2007; Dreezens, Martijn, Tenbult, Kok, & deVries, 2005; Saher, Lindeman, & Hursti, 2006; Siderer, Maquet, & Anklam, 2005; Winter & Davis, 2006). Consumers are willing to pay significant premiums for organic and natural foods. Premiums of 10-40% for organic foods over conventional products are common (Winter & Davis, 2006) but for meat and poultry, premiums may reach 200% (Bacus, 2006) or even more. In one such example, the average retail price for four brands of organic broilers in the Midwest during April and May, 2006 was \$3.19/lb. compared to \$1.29/lb. for conventionally produced broilers, a 247% difference (Husak, 2007). The large premiums that consumers are willing to pay for natural and organic foods have resulted in a rapid proliferation of new products and increased marketing by retailers (Petrak, 2005).

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In the US, natural and organic foods must be produced and processed according to United States Department of Agriculture (USDA) regulations that define these products. In most cases, natural and organic foods are very similar to conventional products and do not differ in the typical characteristics expected by consumers. However, in the case of processed meat products such as hams, bacon, frankfurters, bologna and others that are typically cured by addition of sodium/potassium nitrite or nitrate, the requirements for natural or organic labeling do not permit addition of nitrite or nitrate. Nitrite, added directly or derived from nitrate, is a unique, distinctive cured meat ingredient for which there is no substitute, consequently significant process and product changes are necessary to produce natural or organic processed meats that provide consumers with the properties expected of traditional cured meat products. These changes, combined with labeling requirements for these products, have resulted in a category of processed meats in the US that is confusing, and perhaps even misleading, to consumers. Further, because of the essential role that nitrite plays in cured meat quality and safety, changes in the products need to be carefully examined in light of the processing changes that are being introduced for manufacturing natural and organic processed meats. Consequently, several considerations including regulatory, manufacturing, marketing, quality and safety issues need to be addressed.

2. Background

2.1. Definitions of natural and organic processed meats

The requirements for processed meats such as hams, bacon, frankfurters and bologna to qualify as natural or organic in the US have resulted in unique approaches to the development of these products. This is because, while "natural" and "organic" are two separate and distinct categories of meat and poultry products in terms of USDA regulations and labels, neither of these product categories are permitted to be manufactured with added sodium (or potassium) nitrite or nitrate. However, the USDA permits the manufacture of uncured versions of typical cured meats according to the Code of Federal Regulations (2006), 9 CFR 319.2, which reads:

"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 products as commonly prepared with nitrate and nitrite: *And providing further*, That labeling for such products complies with the provisions of 317.17 (C) of this subchapter".

Thus, there is another category of processed meats, separate from "natural" and "organic", and that category is "uncured". The definitions of natural and organic require that "uncured" be included on the label for products labeled with a standardized cured product name (i.e., uncured bacon), but it is important to note that not all products labeled "uncured" are natural or organic.

Processed meats that are labeled "natural" must comply with the definition of the term provided by the USDA Food Standards and Labeling Policy Book (USDA, 2005). This definition requires that a natural 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 the product and its ingredients are not more than minimally processed".

The term "minimally processed" includes

"...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 those physical processes which do not fundamentally alter the raw product..., e.g. grinding meat...". (USDA, 2005).

The definition of natural has been controversial. For example, in the 2005 edition of the USDA Food Standards and Labeling Policy Book, a note was added indicating that sugar, sodium lactate (from a corn source) and natural flavorings from oleoresins or extractives are acceptable for "all natural" claims (USDA, 2005). However, because lactate is widely recognized as an antimicrobial ingredient, such use may conflict with the "no chemical preservatives" requirement for labeling of a product as natural. This was the basis for a petition submitted to the USDA in October, 2006 after which the Agency removed lactate from the guidance statement provided for natural claims. The USDA will, however, consider use of lactate for natural foods on a case-by-case basis for applications where the ingredient may function as a flavoring rather than a preservative. Further, the Agency is currently planning to initiate new rulemaking processes in the near future for the use of "natural" to clarify these uses as well as the use of natural claims relative to livestock production practices (O'Connor, 2006).

Products labeled as organic are much better defined and controlled in the US than the products labeled with natural claims because organic products are governed by the USDA Organic Foods Production Act (OFPA), first established in 1990 as part of the 1990 Farm Bill (Winter & Davis, 2006). The OFPA created a National Organic Standards Board, which established a National List of Allowed and Prohibited Substances, and developed National Organic Program Standards. The standards, implemented in 2002, specify methods, practices and substances that may be used for production, processing and handling of organic foods. Meat, for example, must be raised under

organic management and come from a USDA-certified farm. Ingredients used for processed products are clearly defined as permitted or prohibited in the OFPA National List. Organic products may be labeled as; (1) "100% organic" which must contain only organically produced ingredients; (2) "organic" which must contain at least 95% organically produced ingredients; or (3) "made with organic ingredients" which must have at least 70% organic ingredients. Products with less than 70% organic ingredients are not allowed to be labeled as organic and are permitted only to list those ingredients that are organic on the label. Those products that qualify for the "organic" and "100% organic" labeling are permitted to use the USDA organic seal as part of the label.

2.2. Definitions of cured and uncured processed meats

The term "cured" relative to processed meats is universally understood to mean the addition of nitrite or nitrate with salt and other ingredients to meat for improved preservation (Pegg & Shahidi, 2000). While several ingredients including sugar, spices, phosphates and others are typically included in cured meats, it is the addition of nitrite in one form or another that results in the distinctive characteristics of cured meat (Cassens, 1990). The typical color, flavor, shelf life and safety of ham, bacon, frankfurters, bologna and other cured products are so widely recognized by consumers that these product names are considered "standardized" and "traditional" by the USDA for product labeling and to not require any further clarification to communicate the expected product properties to consumers. On the other hand, products that are similar but made without nitrite or nitrate, must be clearly labeled as "uncured" as described earlier. This is because "uncured" versions of standardized products like ham, bacon, frankfurters and bologna are significantly different from the traditional products that they emulate. At the same time, there are a number of processed meats that are traditionally manufactured without nitrite or nitrate, and that are not labeled as uncured because the standardized product name effectively communicates that the product is not cured. Fresh sausage, such as pork sausage, for example, is not labeled as "uncured" because these products are standardized, traditional and the common name is clearly understood.

The advent of natural and organic processed meat products, both of which prohibit direct addition of nitrite or nitrate, but that also resemble traditional cured meat has made it necessary to require "uncured" as part of the traditional product name. However, because current meat processing technology has developed means by which nitrate and nitrite can be indirectly added to these products to achieve very typical cured meat properties, the labeling designations for these products as uncured is confusing and technically inaccurate. Further, because the indirect addition of nitrate and nitrite to natural and organic processed meats has not been thoroughly investigated in terms of nitrite chemistry and subsequent product properties, a

number of important questions remain to be answered, particularly in regard to quality and safety.

3. Review of conventional cured meat ingredients and processes

Conventionally – cured meat products are characterized by addition of nitrate and/or nitrite. While other ingredients, particularly sodium chloride, are essential parts of typical cured meat formulations, it is the nitrate/nitrite that provides the distinctive properties that are common to all cured meat products. The role of nitrate/nitrite is so commonly understood in the meat industry that the term "cure" is used as both a noun and a verb, meaning either nitrate/nitrite as chemical entities, or the addition of these ingredients to meat, respectively.

3.1. Nitrate

Numerous reviews of the history of meat curing have suggested that meat curing originally developed from use of salt contaminated with sodium or potassium nitrate (Binkerd & Kolari, 1975; Cassens, 1990; National Academy of Sciences, 1982; Pegg & Shahidi, 2000; Pierson & Smoot, 1982; Sebranek, 1979).

While it is not clear when saltpeter (potassium nitrate) was first recognized as a curing agent, it is clear that nitrate, either as saltpeter or as a contaminant of sodium chloride, was used to cure meat for centuries before research chemists began to unravel the chemistry of meat curing. In the late 1800s, it was discovered that nitrate was converted to nitrite by nitrate-reducing bacteria, and that nitrite was the true curing agent. The first half of the 20th century brought a gradual shift from nitrate to nitrite as the primary curing agent for cured meats as the advantages of faster curing time for increased production capacity became more important, and as nitrite chemistry became better understood. By the early 1970s, relatively little nitrate was being used for cured meats (Binkerd & Kolari, 1975). The late 1960s and early 1970s also brought a watershed event for the cured meat industry when it became obvious that nitrite could result in formation of carcinogenic n-nitrosamines in cured meat. Subsequent research demonstrated that a significant factor in nitrosamine formation was residual nitrite concentration, and consequently, nitrate was eliminated from most curing processes to achieve better control over residual nitrite concentrations (Pegg & Shahidi, 2000). Today, nitrate is rarely used and then only in a few specialty products such as dry cured hams and dry sausage where long, slow curing processes necessitate a long-term reservoir for nitrite that can be slowly released over the course of the process.

3.2. Nitrite

The chemistry of nitrite in cured meat is an extremely complex mixture of interactive chemical reactions involving several different reactants. Nitrite is a highly reactive compound that can function as an oxidizing, reducing or a nitrosylating agent, and can be converted to a variety of related compounds in meat including nitrous acid, nitric oxide and nitrate (Honikel, 2004). To further complicate understanding of nitrite chemistry, it has become clear that the formation of nitric oxide (NO) from nitrite is a necessary prerequisite for most meat curing reactions (Møller & Skibsted, 2002). Fortunately, fundamental research on nitric oxide has become one of the most active research areas in biology because nitric oxide has been found to play crucial roles in several physiological functions in living organisms. Fundamental research on nitric oxide in biological systems since the early 1990s has facilitated better understanding of nitrite and nitric oxide in cured meat (Møller & Skibsted, 2002; Stamler & Meissner, 2001).

The most effective way to consider nitrite chemistry in cured meat is to consider the practical effects of the addition of nitrite to meat. The first and most obvious effect is that of cured color development. Close examination of the chemical reactions involved with color development immediately make it obvious that the chemistry of nitrite in meat is a phenomenally complex event. For example, nitrite does not act directly as a nitrosylating (transfer of nitric oxide) agent in meat but first forms intermediates such as N₂O₃ (Honikel, 2004)in the mildly acidic conditions typical of postmortem muscle, and NOCl (Fox, Sebranek, & Phillips, 1994; Møller & Skibsted, 2002; Sebranek & Fox, 1985, 1991) in the presence of salt.

Formation of NO from the intermediates is facilitated by reductants such as ascorbate, and the NO will react with the iron of both myoglobin (Fe⁺²) and metmyoglobin (Fe⁺³) to form cured meat pigments and cured color. These reactions demonstrate two of the most important factors governing nitrite reactions in conventionally cured meat products; namely pH and reductants. However, several other nitrite reactions are involved in cured meats and contribute to nitric oxide production. For example, when nitrite is added to comminuted meat, the meat quickly turns brown due to metmyoglobin formation because nitrite acts as a strong heme pigment oxidant and is, in turn, reduced to NO. The NO reacts with metmyoglobin and subsequent reduction reactions convert the oxidized heme to reduced nitric oxide myoglobin for typical cured color following cooking. Further, nitrite can also react with sulfhydryl groups on proteins to release nitric oxide in an oxidation-reduction reaction that results in a disulfide (Pegg & Shahidi, 2000).

In addition to the above reactions of nitrite in meat, all of which affect the rate and/or extent of cured color development, nitrite plays a key role in cured meat as a bacteriostatic and bacteriocidal agent. Nitrite is strongly inhibitory to anaerobic bacteria, most importantly *Clostridium botulinum* and contributes to control of other micro organisms such as *Listeria monocytogenes*. The effects of nitrite and the likely inhibitory mechanism differs in different bacterial species (Tompkin, 2005). The effectiveness of nitrite as an

antibotulinal agent is dependent on several environmental factors including pH, sodium chloride concentration, reductants and iron content among others (Tompkin, 2005). While the means by which nitrite achieves microbial inhibition is not clear and many mechanisms have been proposed, all of the factors that impact nitrite inhibitory effects are also important to the known reactions that generate nitric oxide for cured color. Thus, the reaction sequences involving nitric oxide are probably an important part of the antimicrobial role of nitrite in cured meat. For example, some researchers have suggested that nitrous acid (HNO₂) and/or nitric oxide (NO) may be responsible for the inhibitory effects of nitrite (Tompkin, 2005). Because it appears that nitrite reactivity is key to microbial inhibition (one indicator of this is the strong dependence on pH), there has been some question whether ingoing or residual nitrite is most critical to antimicrobial effects. Tompkin (2005) concluded that residual nitrite at the time of product temperature abuse is critical to antibotulinal effects and that depletion of residual nitrite during product storage will reach some point at which inhibitory effects are also depleted.

The nitrite reaction sequences involved with cured color development probably also play a key role in the strong anti-oxidant function of nitrite in cured meat, because proposed mechanisms for the antioxidant effect of nitrite include reaction with heme proteins and metals, and formation of nitroso- and nitrosyl-compounds that have antioxidant properties (Pegg & Shahidi, 2000). It is likely that these proposed mechanisms are dependent upon the same initial reactions of nitrite that form nitric oxide for cured color.

Nitrite is also responsible for the production of characteristic cured meat flavor, though this is probably the least well understood aspect of nitrite chemistry (Pegg & Shahidi, 2000). It is easy to distinguish cooked, cured ham from fresh roast pork on the basis of flavor but the chemical identity of distinguishing flavor components in cured meat has eluded numerous researchers. Some of the flavor difference may be due to the suppression of lipid oxidation by nitrite but other antioxidants do not produce cured meat flavor. If nitrite does, in fact, form some volatile flavor factors, this would represent yet another reaction product of nitrite in cured meat.

In addition to the nitrite reactions which result in cured meat color, microbial inhibition, antioxidant effects and flavor, it has been demonstrated that addition of nitrite to meat results in formation of nitrate and nitrogen gas as well as reaction with carbohydrates and lipids (Honikel, 2004; Pegg & Shahidi, 2000).

The point of this brief discussion of nitrite chemistry and the functions of nitrite in cured meat is to emphasize that nitrite is a highly reactive ingredient when combined with meat, and results in a complex mixture of reaction products. Because nitrite, particularly as nitric oxide, so readily reacts with a wide variety of substrates, reaction kinetics could be an important determinant of how nitrite

is proportioned among the various competitive substrates and reaction products. A slow formation of nitrite (such as from nitrate) in meat might be significantly different in terms of nitrite reaction products than the direct, one-time addition of a full load of nitrite. If, for example, the fastest-reacting substrates consumed a greater share of the nitrite during slow nitrite formation than in the case where nitrite is added directly, then the end products of the more reactive substrates might achieve greater final concentration.

3.3. Past and current safety issues associated with nitrite

Issues that have been raised concerning the safety of using nitrate and nitrite for cured meat have included chemical toxicity, formation of carcinogens in food or after ingestion, and reproductive and developmental toxicity. None of these issues represent relevant concerns for nitrate or nitrite in light at the current regulated levels of use in processed meats. While nitrite is recognized as a potentially toxic compound, and there have been cases where nitrite was mistakenly substituted for other compounds in food or drink at concentrations great enough to induce toxicity symptoms, the normally controlled use of nitrite in processed meats represents no toxicity risk.

However, the issue of carcinogenic nitrosamines formed from nitrite in cured meat was a very serious concern in the 1970s. Fortunately, changes in manufacturing practices and reduced levels of nitrite used in curing solved the problem of nitrosamine formation in cured meat. Yet, a background concern about nitrite has lingered, and in the 1990s, a series of epidemiological studies reported that consumption of cured meat was related to childhood leukemia and brain cancer (Peters et al., 1994; Preston-Martin & Lijinsky, 1994; Preston-Martin et al., 1996; Sarasua & Savitz, 1994). Further, in 1998, nitrite was proposed as a developmental and reproductive toxicant under California's Proposition 65 (Safe Drinking Water and Toxic Enforcement Act). Fortunately, both issues (nitrite as a carcinogen and as a developmental/reproductive toxicant) have been largely resolved by subsequent studies and careful scientific review (Milkowski, 2006).

The issue of ingested nitrate and nitrite first arose in the 1970s when it was recognized that carcinogenic nitrosamines could be formed in the stomach following ingestion. Subsequent work has shown that less than 5% of the nitrite and nitrate typically ingested comes from cured meat, the rest coming from vegetables and saliva (Archer, 2002; Cassens, 1997a; Milkowski, 2006). Nevertheless, in 2006, the International Agency for Research on Cancer (IARC) concluded that "Ingested nitrate or nitrite under conditions that result in endogenous nitrosation is probably carcinogenic to humans" (Coughlin, 2006). While the IARC report is still in progress, the conclusions are likely to ramp up questions and concerns about nitrite as a food additive. In light of the anticipated challenges to nitrite in cured meat, it is imperative that as much information as possible

is developed for all processed meat applications where nitrite and/or nitrate have a role.

3.4. Current US regulations on nitrite and nitrate

Current regulations on use of nitrite and nitrate in the United States vary depending on the method of curing used and the product that is cured. For comminuted products, the maximum ingoing concentration of sodium or potassium nitrite is 156 parts per million (ppm) or 0.25 oz. per 100 lbs. (7 g/45.4 kg), based on the green weight of the meat block (USDA, 1995). Maximum ingoing nitrate for these products is 1718 ppm. Sodium and potassium nitrite and nitrate are limited to the same amount despite the greater molecular weight of the potassium salts, which means that less nitrite or nitrate will be included when the potassium salt is used. For immersion cured, and massaged or pumped products, maximum ingoing sodium or potassium nitrite and nitrate concentrations are 200 ppm and 700 ppm, respectively, again based on the green weight of the meat block. Dry cured products are limited to 625 ppm and 2187 ppm of nitrite and nitrate respectively. If nitrite and nitrate are both used for a single product, the ingoing limits remain the same for each but the combination must not result in more than 200 ppm of analytically measured nitrite, calculated as sodium nitrite in the finished product.

Bacon is an exception to the general limits for curing agents because of the potential for nitrosomine formation. For pumped and/or massaged bacon without the skin, 120 ppm of sodium nitrite or 148 ppm of potassium nitrite is required along with 550 ppm of sodium ascorbate or sodium erythorbate which is also required. It is important to note that this is a specifically required amount whereas other nitrite limits are maximum amounts. To accommodate variation in pumping procedures and brine drainage from pumped products, the regulations for pumped and/ or massaged bacon permit $\pm 20\%$ of the target concentrations at the time of injecting or massaging. For example, sodium nitrite concentrations within the range of 96-144 ppm are acceptable. Nitrate is not permitted for any bacon curing method. There are two exceptions to these regulations for pumped and/or massaged bacon: first, 100 ppm of sodium nitrite (or 123 ppm of potassium nitrite) with an "appropriate partial quality control program" is permitted and, second, 40-80 ppm of sodium nitrite or 49-99 ppm of potassium nitrite is permitted if sugar and a lactic acid starter culture are included. Immersion cured bacon is limited to 120 ppm of sodium nitrite or 148 ppm of potassium nitrite while dry cured bacon is limited to 200 ppm or 246 ppm, respectively. For bellies cured with the skin on, nitrite and reductant concentrations must be reduced by 10%, based on the assumption that skin comprises approximately 10% of the belly weight.

It is important to note that the regulations also require a minimum of 120 ppm of ingoing nitrite for all cured "Keep Refrigerated" products "unless safety is assured by some other preservation process, such as thermal processing, pH or moisture control". The establishment of minimum ingoing nitrite concentration is considered critical to subsequent product safety. This is a significant consideration for natural and organic cured meat products.

On the other hand, for cured products that are processed to ensure shelf stability (stored at ambient temperature and do not require refrigeration), there is no minimum ingoing nitrite level. The USDA Processing Inspector's Calculations Handbook (USDA, 1995) suggests that, for shelf-stable products, "...40 ppm nitrite is useful in that it has some preservative effect. This amount has also been shown to be sufficient for color-fixing purposes...".

4. Ingredients used for natural and organic cured meats

Because of the negative perceptions of nitrite-cured meat held by some consumers, the "uncured" natural and organic versions of typical cured meats have enjoyed wide-spread market acceptance. A survey of 56 commercial "uncured" meat products including bacon, ham, frankfurters, bologna, braunschweiger, salami, Polish sausage, Andouille sausage and snack sticks showed that most of these products demonstrated typical cured meat color and appearance (Sindelar, 2006b). Review of the product ingredient statements showed that sea salt, evaporated cane juice, raw sugar or turbinado sugar, lactic acid starter culture, natural spices or natural flavorings, and celery juice or celery juice concentrate were used in many of the products.

Analyses of samples of four selected commercial brands each of natural or organic bacon, hams and frankfurters showed that all samples except one sample of bacon contained residual nitrite at concentrations ranging from 0.9 ppm to 9.2 ppm. Residual nitrate was found in all products at concentrations of 6.8 ppm to 44.4 ppm (Sindelar, 2006a). Residual nitrite was lower in most of the natural or organic products at the time of sampling than in comparable commercial products made with conventional addition of nitrite. Other cured meat properties including instrumental color, cured pigment concentration, lipid oxidation and sensory properties were, in general, similar for the natural or organic products relative to the conventionally cured products but greater variation in the natural and organic products was obvious. Most notable was low color values, low cured pigment content and low sensory scores for those products that contained little or no residual nitrite. It is important to note that because these were commercial products selected at retail, the time of manufacture and storage history of each was unknown. Nevertheless, these results suggest that: (1) there is wide variation among the natural and organic processed meats that simulate conventionally cured products; and (2) a large majority of natural and organic processed meats demonstrate typical cured meat properties, including cured color, flavor and significant concentrations of residual nitrite and nitrate. Thus, it is clear that nitrite and nitrate are being introduced to these products indirectly as components of other ingredients.

4.1. Unique ingredients in natural and organic processed meats

The most common ingredient observed in review of the product labels of natural and organic processed meats was sea salt. Sea salt is derived directly from evaporation of sea water, unrefined without addition of free-flow additives and retains the natural trace minerals characteristic of the source (Heinerman & Anderson, 2001; Kuhnlein, 1980). Several varieties of sea salt are available and differ depending on the geographical origin of the water used and the mineral content (Saltworks, 2006). While sea salt has been suggested as a likely source of nitrate, limited analytical information suggested that nitrate content of sea salt is relatively low. Herrador, Sayago, Rosales, and Asuero (2005) reported that Mediterranean sea salt contained 1.1 ppm of nitrate and 1.2 ppm of nitrite. Cantoni, Berretta, and Bianchi (1978) analyzed 10 samples each of 3 grades of sea salt and found nitrate and nitrite concentrations of 0.3-1.7 ppm and 0–0.45 ppm, respectively.

The second most common ingredient observed in natural and organic processed meat ingredient lists was raw sugar, most often shown as turbinado sugar. Turbinado sugar is a raw sugar obtained from evaporation of sugar cane juice followed by centrifugation to remove surface molasses. Remaining molasses gives turbinado sugar a light brown color and flavor similar to brown sugar. While it seems possible that raw sugar could include nitrate, there appears to be no evidence of significant nitrate or nitrite concentrations in raw sugar.

Natural flavorings or spices, and celery juice or celery juice concentrate were frequently listed as ingredients, and because these are plant/vegetable products, the potential contribution of nitrate from these sources is very significant. Vegetables are well-known as a source of nitrate with concentrations as high as 1500–2800 ppm (National Academy of Sciences, 1981) in celery, lettuce and beets. Vegetable juices and vegetable powders are commercially available and may be used as ingredients in natural and organic foods. Analysis of some commercially available vegetable juices showed that carrot, celery, beet and spinach juice contained 171 ppm, 2114 ppm, 2273 ppm and 3227 ppm of nitrate respectively (Sebranek, 2006). After 10 days of storage at room temperature, nitrate levels in these juices declined by 14-22%. Nitrite was not detected initially but concentrations of 128–189 ppm of nitrite were found after 10 days at room temperature, probably resulting from bacterial reduction of nitrate. Analysis of commercial celery juice powder indicated a nitrate content of 27,462 ppm or about 2.75%, reflecting the increased concentration following drying (Sindelar, 2006a). Clearly, vegetable products offer the greatest potential to introduce natural sources of nitrate into processed meats. Juices and powders have advantages in supplying nitrate in

concentrated form. Celery juice and celery powder appear to be highly compatible with processed meat products because of very little vegetable pigment (as opposed to beets, for example) and a mild flavor profile similar to raw celery that does not detract greatly from finished product flavor.

A critical ingredient for processed meats with natural nitrate sources is a nitrate-reducing bacterial culture if typical cured meat properties are the final objective. The necessity of bacterial reduction of nitrate to nitrite for meat curing has long been recognized, and nitrate-reducing cultures have been commercially available for several years. Most applications of these cultures have been for dry sausage where a long-term reservoir of nitrite during drying is desirable and where subtle flavor contributions from the culture are considered important (Olesen, Meyer, & Stahnke, 2004). The lactic acid starter cultures used for fermented sausage, primarily Lactobacillus plantarum and Pediococcus acidilactici, do not reduce nitrate. However, cultures of coagulase-negative cocci such as Kocuria (formerly Micrococcus) varians, Staphylococcus xylosus, Staph*ylococcus carnosus* and others will reduce nitrate to nitrite. These organisms can achieve nitrate reduction at 15–20 °C but are much more effective at temperatures over 30 °C (Casaburi, Blaiotta, Mauriello, Pepe, & Villani, 2005). The typical recommended holding temperature for commercial nitrate-reducing cultures is 38–42 °C to minimize the time necessary for adequate nitrite formation. Recent research has documented that time is a critical parameter in the development of typical cured meat properties from natural sources of nitrate. Sindelar (2006a) reported that holding time at 38 °C was more critical than the amount of naturally-added nitrate for development of cured meat properties in frankfurters and hams. Time appeared to be more critical for the small diameter frankfurters that reached internal temperature of 38 °C quickly than for the large diameter hams where internal temperature increased to 38 °C more slowly.

Sindelar, Cordray, Sebranek, Love, and Ahn (in press a) evaluated several quality characteristics of frankfurter-style cooked sausages manufactured with starter culture and either 0.2% or 0.4% celery juice powder, each held at 38 °C for either 30 min or 120 min. The products were evaluated during 90 days of refrigerated, vacuum-packaged storage and compared with conventionally processed products manufactured at the same time with added sodium nitrite. Color measurements (Hunter a^+ values reflectance ratios, cured pigment concentrations) indicated that treatments with short incubation time resulted in less cured color/redness than the nitrite-cured control though this difference was not always significant. Cured color/redness was comparable to the nitrite-cured control with the longer incubation time for the first 14 days following manufacturing but the difference became non-significant during extended storage. Residual nitrite following incubation was dramatically different with 5.6 ppm and 7.7 ppm found for the 0.2% and 0.4% celery powder levels, respectively,

after 30 min but 24.5 ppm and 46.0 ppm observed after 120 min. No differences were noted for lipid oxidation between any of the treatments and the control. The nitrite-cured control received the highest sensory scores though differences were not significant for all sensory properties.

A similar experiment with hams (Sindelar, Cordray, Sebranek, Love, & Ahn, in press b) was conducted using either 0.2% or 0.35% celery powder and incubation time of 0 min or 120 min. The treatment with no incubation time was included because the extended thermal process (3 hrs., 35 min.) used for hams relative to small diameter frankfurter-style sausage was expected to result in adequate nitrate reduction by the culture. Results showed that there were no treatment differences in objective color measurements or cured pigment concentrations and all products were similar in color properties to the nitrite-cured control. Residual nitrite, following the 120 minute incubation for the 0.2% and 0.35% celery juice powder additions, was 19.5 ppm and 36.1 ppm, respectively. The residual nitrite was significantly less for the hams with celery juice powder (21.0–36.0 ppm at day 0; 7.2–21.3 ppm after 90 days) relative to the nitrite-cured control (63.4 ppm at day 0: 34.1 ppm after 90 days). However, residual nitrite was greater in hams with a greater amount of added celery juice (27.7–36.0 ppm from 0.35% celery powder vs. 19.3– 21.0 ppm from 0.20% celery powder at day 0 compared with 11.7–21.3 ppm vs. 7.2–8.8 ppm, respectively, for each after 90 days). Sensory panel evaluation indicated that the greater celery powder treatment (0.35%) resulted in greater vegetable aroma and flavor with less ham aroma and flavor. The treatments with a low level of celery powder (0.2%) were similar to the nitrite-cured control for all sensory properties evaluated.

The authors concluded that the celery juice powder/starter culture treatment was an effective alternative to the direct addition of sodium nitrite to small-diameter, frankfurter-style cured sausage but that incubation time at 38 °C is an important factor for product quality. The celery juice powder/starter culture treatment was also effective for hams but in this case the amount of celery juice powder proved to be more critical. For large diameter products such as hams, it appears that the slow temperature increase that is part of a typical thermal process may provide enough time for the culture to achieve nitrate-to-nitrite reduction. Further, the delicate flavor profile of hams makes these products more susceptible to flavor contributed by vegetable products.

The authors also pointed out that the concentration of celery juice powder used (0.2%, 0.35% and 0.4% – total formulation weight basis) could provide, with 100% nitrate-to-nitrite conversion, maximum ingoing nitrite concentrations of 69 ppm, 120 ppm and 139 ppm (meat block basis), respectively, based on the initial nitrate concentration of 27,462 ppm in the celery powder. Because these nitrite concentrations are, at best, significantly less than the 156–200 ppm normally included in cured comminuted

products or injected products, it seems likely that product quality differences could occur in some circumstances. It is also worth noting that the actual amounts of nitrite formed from nitrate when natural nitrate sources are used could be a concern relative to microbiological safety. The shelf life of processed meats manufactured with natural nitrate sources in generally less than nitrite-cured products because less nitrite is present and other typical preservatives such as phosphates, lactate, curing accelerators and antioxidants are not included (Bacus, 2006).

Ingredients that might be considered as curing adjuncts for natural or organic processed meats include vinegar, lemon juice solids, and cherry powder. Acidulants such as vinegar have potential to accelerate nitrite reactions because of the impact of pH. However, reducing pH in these products is also a concern for reduced moisture retention because phosphates and many of the traditional water binders cannot be used for natural or organic products. Lemon juice solids or powder are typically significant sources of citric acid which could have similar pH effects as vinegar. Cherry powder, on the other hand, is high in ascorbic acid which functions as a strong nitrite reductant but does not have a large impact on product pH.

An evaluation of a cured pork product manufactured with a natural nitrate source (celery powder) and with or without 0.28% cherry powder showed that including the cherry powder reduced residual nitrite by about 50% (Baseler, 2007). Residual nitrite declined from 61 ppm to 32 ppm during 12 weeks of storage for a nitrite-cured control, 18–10 ppm for the celery powder treatment and 10–3 ppm for the celery powder/cherry powder treatment. Addition of cherry powder did not alter the product pH. Other product properties (color, lipid oxidation) were not consistently different though the nitrite-cured treatment showed greater redness (Hunter a^* values) after about 4 weeks of storage.

Natural antioxidants such as rosemary may be used to provide flavor protection and to retard lipid oxidation in processed meats. However, these compounds do not contribute directly to nitrate/nitrite reactions in meat systems. Further, it appears that the nitrite generated from natural nitrate sources as reported by Sindelar et al. (in press a, in press b) was sufficient to provide strong antioxidant effects as typically observed in nitrite-cured meats. Past research has shown that as little as 50 ppm added nitrite has a highly significant effect on lipid oxidation (Morrissey & Techivangana, 1985). Thus, relatively small amounts of nitrite formed from nitrate probably provide an important antioxidant role in natural and organic processed meats.

4.2. Processes for naturally-cured meats

Most processors that utilize "natural curing" are following processing procedures that are, in general, similar to those processes that include chemical nitrites and nitrates. Naturally-cured products typically utilize natural sources of nitrate, but some natural ingredients may also contain

nitrite. If sufficient nitrite is consistently available from a natural source, no changes in the normal process are required.

Naturally-cured meat products that utilize natural ingredients for a nitrate source need an ingredient that contains a relatively high natural nitrate content. The nitrate ion is much more available, more consistent in concentration and more stable than nitrite, and can be found in a wide variety of natural ingredients. When using a natural nitrate source, conversion of the nitrate to nitrite is required. Typically, this conversion is accomplished by specific microorganisms (with a nitrate reductase enzyme), as described earlier, that are also acceptable food ingredients. When using these microorganisms, the conversion process requires time, with the specific amount of time depending upon the temperature, the environment, and the concentration of the reactants, namely the microorganisms and the naturally-occurring nitrate. The conversion time can be decreased by increasing the reactant concentrations with the amount of starter culture the most critical.

In all natural curing processes, good distribution of both the nitrate source and the starter culture is essential to achieve uniform curing. The natural nitrate source, if dry, is usually either blended with the dry seasoning component for comminuted products, or added directly to curing brines. The starter culture commonly is diluted first with good quality water (i.e. distilled, or low in chlorine or other bacteriocidal chemicals) prior to the addition to comminuted products (the USDA permits a maximum 0.5% combined water and starter culture without labeling the added water) or may also be added directly to curing brines. Also, it is recommended that the starter culture should not be pre-blended with anything that might affect viability (i.e. spices, salt), and thus the nitrate-reducing activity of the culture. The naturally-occurring nitrate is soluble, but the starter culture is not soluble, being water-dispersible, therefore some agitation is recommended for brines to achieve optimal distribution of the culture in the meat product. With curing brines, the pH of the brine is critical to achieving optimal natural curing as well as final product texture, because the phosphates or other buffering agents typically used with nitrite-added products cannot be included for products labeled natural or organic. Generally, low pH brines (i.e. <5.5) are not desirable, thus the pH effect of any added natural ingredients should be considered. With comminuted meat products, the pH effect of directly-added ingredients is not as critical due to the buffering capacity of the meat. Liquid sources of naturally-occurring nitrates (vegetable juices) also are utilized but these ingredients pose some manufacturing issues. Typically, most of these liquids are not shelf stable, and are supplied in frozen form. Secondly, the added water that is a component of the juices must be considered.

For small diameter cooked sausage, formulation and processing are essentially the same as for nitrite-added products, except for the nitrate source and the culture, and a smokehouse process that includes an "incubation"

period of about 1 h at 42 °C to achieve nitrate reduction prior to a smoke-cook thermal process. For injected products, the physical injection of the brine with the culture is critical because the culture will not migrate significantly from injection sites. Consequently, good distribution by injection is necessary to avoid uncured spots. Increased injection percentage of brine is generally preferred to facilitate better distribution. For thermal processing, no "incubation" period is likely to be necessary for large diameter products due to the longer process time involved with relatively slow increase in internal temperature. As product diameter is decreased, the heat process may need to be adjusted to achieve optimal nitrate conversion. With injected bellies, for example, a short "incubation" period at 42-46 °C may be necessary prior to the usual heating cycle. Because bacon is not fully cooked, relatively high bacterial counts from the added culture will remain in the finished product. Fermented sausage products do not typically require any adjustments in processing because the fermentation step already incorporated into the process provides adequate nitrate conversion. Because most starter cultures, particularly in the US consist of lactic acidproducing bacteria only, it is imperative to confirm that the added starter culture is composed of a mixed culture including nitrate-reducing organisms as well as those included to ferment the added sugars. Many mixed starter cultures are available to accomplish both functions, or the nitrate-reducing culture can be added "on top" of a currently used acid-producing culture.

5. Current issues with natural and organic cured meats

5.1. Regulatory

The current US regulatory requirements concerning "organic" meat products are well defined, thus processors desiring to make such products must adhere to a fixed set of regulations outlining permitted ingredients. With "natural" meat products, however, the rules for permitted ingredients recently have become more confusing. The petition submitted to the USDA in October, 2006, suggested that the 2005 revisions to the agency's "natural" policy created inconsistencies by allowing foods carrying the "natural" label to contain synthetic ingredients and preservatives. Much of the concern expressed by the petitioner was the allowance of sodium and potassium lactates in "natural" products, since these ingredients would be considered "chemical preservatives". The petition to the USDA proposed that extensive rulemaking should be initiated for meat and poultry products labeled as "natural" in much the same way that had been done with products labeled as "organic". Currently, the USDA has begun the rulemaking process for new regulations on natural products with a public meeting in Washington in December, 2006, and a comment period that concluded in March, 2007.

The issue of lactates as "chemical preservatives" also raised the issue of other dual-function ingredients, whereas the ingredient may be considered as a natural ingredient for flavor and/or function, but can also have a dual function as a "natural" preservative. The issue of "natural preservative" vs. "chemical preservative" has not been defined, as yet. Many natural compounds that exist in the environment can serve to inhibit microorganisms, retard oxidation, and thus "preserve" the product and would be valuable ingredients in food products that are labeled as "natural". Until this issue of "natural" vs. "chemical" preservatives is resolved, the current US regulatory environment is retarding innovative product development and may compromise food safety as well.

5.2. Manufacturing

When manufacturing "natural" and "organic" meat products using natural ingredients, the inherent variability of natural ingredients must be considered. In the natural curing process, whereby naturally-occurring nitrates are converted by starter cultures to nitrites, the concentration of the nitrate in the source plus the nitrate-reducing activity of the starter culture will effect the degree of curing achieved. Typically, in products cured with direct addition of sodium nitrite in the US, the ingoing nitrite is limited to 156 ppm in most meat products and 120 ppm in injected bacon. In naturally-cured meat products, the ingoing nitrate level is most often between 40 ppm and 60 ppm, thus there is, at best, significantly less nitrite in these products than in the typical nitrite-cured products. Measurable residual nitrite concentrations in both types of cured products are often similar without major differences in color or color stability. However, product quality will be very dependent upon actual nitrite formation in the product during the nitrate reduction phase of the process. While reduced shelf-life has been observed in naturally-cured meats, a significant part of the change is probably due to the lack of other traditional ingredients that are not permitted in "natural" products (i.e. phosphate, ascorbate, erythorbate, citric acid, synthetic antioxidants) as well as reduced concentration of nitrite.

5.3. Marketing

The issue of consumer understanding of what is meant by "natural" meat products is difficult to define. Many consumers may not comprehend that natural ingredients often contain naturally-occurring chemicals virtually identical in chemical nature to those chemicals synthetically produced. One of the current concerns with "naturally-cured" meat and poultry products is that these products often contain residual nitrate and nitrite, even though labeled as "no nitrates or nitrites added". According to the US Code of Federal Regulations (2006) in 9 CFR 319.2, the processor has no choice but to label such products (i.e. "... to which nitrite or nitrate is permitted or required to be added...") as "uncured" and no "nitrates or nitrites added" even though the processor may be utilizing a natural curing process.

To provide the consumer with the most accurate information, more appropriate labeling would be to use a term such as "naturally-cured" and eliminate the "uncured" and "no nitrates or nitrites added" requirement that currently exists in the US.

5.4. Quality

The quality characteristics expected of traditional cured meats that are unique to these products include the reddish-pink color of cooked denatured nitrosylhemochrome, a flavor that is distinct from uncured products, and longterm flavor protection resulting from the strong antioxidant effect of nitrite on meat systems. The fixation of desirable color is the first and most obvious effect of nitrite when added to meat and is considered an essential function because color is a critical component affecting consumer retail purchases (Cornforth & Jayasingh, 2004). As little as 2–14 ppm of nitrite (depending on species) can induce pink coloration in cooked meats, though at these levels the color is often sporadic and likely to fade with time. Extensive research in the 1970s showed that 25–50 ppm of ingoing nitrite was adequate to develop relatively stable cured color (National Academy of Sciences, 1982). While there are indications that cured color may be less intense with 40-50 ppm of nitrite instead of 150-200 ppm depending on product type, 40–50 ppm is generally considered adequate for cured color development in most products. Thus, it would appear that cured color development can be achieved relatively easily in processed meat using natural sources of nitrate and a nitrate-reducing culture. A related question, however, concerns the long-term stability of the cured color formed in these products. One of the difficulties with assessing potential cured color intensity or stability with nitrate-based cures is that the absolute amount of nitrite formed from nitrate cannot be determined due to the reactive nature of nitrite in meat. Sindelar et al. (in press a) reported that for frankfurter-type sausages, products made with celery powder and culture had 9.3-31.9 ppm of residual nitrate remaining when 69 ppm of nitrate was added as part of the celery powder, and 12.2-81.4 ppm when 139 ppm was added. So, if 100% of the nitrate that was depleted was in fact reduced to nitrite. the ingoing nitrite concentrations ranged from 37 ppm to 127 ppm. This is sufficient nitrite to generate desirable cured meat color characteristics in most processed meat products. Similar results were observed for color with hams (Sindelar et al., in press b) where the residual nitrate concentrations suggested formation of nitrite in the range of 45-119 ppm. Thus, the quality of cured color in terms of intensity and stability is not likely to be a major issue in processed meats using natural sources of nitrate if appropriate processing procedures are followed to achieve nitrate reduction, and if adequate packaging (oxygen removal by vacuum or gas flushing and high oxygen-barrier films) is used (Møller et al., 2003).

Cured flavor is an important quality attribute of cured meats that is derived from addition of nitrite, though the chemical nature of the flavor has never been established. It is clear, however, that relatively low concentrations of nitrite result in significant cured flavor. Several researchers have reported acceptable cured meat flavor in products formulated with 40 ppm of ingoing nitrite (Pegg & Shahidi, 2000). In a series of reports, MacDonald, Gray, Stanley, and Usborne (1980), MacDonald, Gray, Kakuda, and Lee (1980) and MacDonald, Gray, and Gibbins (1980) concluded that addition of 50 ppm of nitrite to hams was sufficient to produce significant cured meat flavor and antioxidant protection. Thus, in addition to color, it appears that 40–50 ppm or more of ingoing nitrite will result in a significant flavor contribution to cured meat.

The third quality contribution of nitrite to cured meat is the often-overlooked, but highly effective role of nitrite as an antioxidant, and it is clear that nitrite is again effective at relatively low concentrations. Morrissey and Techivangana (1985), for example, using cooked, ground beef, pork, chicken and fish muscle, reported that 50 ppm of nitrite reduced TBA values by 50–64% for beef, pork and chicken, and about 35% for fish. Nitrite concentrations of 100 ppm resulted in TBA reductions of 57–72%, and 200 ppm reduced TBA values by 87-91%. There was a very clear relationship between saturated:unsaturated fat ratios and the TBA values, with more unsaturated fats resulting in greater TBA values regardless of the nitrite concentration. While nitrite is effective as an antioxidant at 50 ppm, it is more effective at greater concentrations up to 200 ppm. A point to note is that the antioxidant function of nitrite in cured meat, while highly effective, is not as unique as the color and flavor contributions. There are a number of other antioxidants including natural compounds that can protect meat lipids from oxidation and flavor deterioration.

If at least 50 ppm of nitrite is formed from nitrate during processing of meat products with natural nitrate sources, it appears that the typical quality characteristics expected of cured meat (color, flavor, flavor stability) will be achieved. A question that is more difficult to answer is the long-term stability of those quality characteristics. It is well recognized that when nitrite is fully depleted from cured meat, color fading and flavor changes typically occur. Some residual nitrite is essential to maintaining typical cured meat properties during extended product storage, and 5-15 ppm residual nitrite has been reported for commercial cured meats in the US (Cassens, 1997b). It is important to keep in mind that packaging and environmental conditions, particularly temperature and exposure to light, are critical to long-term cured meat quality, and become more critical when residual nitrite is reduced.

5.5. Safety

The safety of processed meats that simulate traditional cured meats by using natural sources of nitrate is a significant issue for two reasons; first, nitrite is a very effective antimicrobial agent, particularly for preventing toxin production by *C. botulinum* and second; residual nitrite concentration is a well-known risk factor in the potential formation of carcinogenic nitrosamines. In both cases, ingoing and residual nitrite concentrations must be carefully controlled to provide product safety.

The antimicrobial role of nitrite in cured meat has been well documented. While nitrite plays a key role in inhibition of C. botulinum, extensive research has demonstrated that pH, reductants (ascorbate and erythorbate), salt, phosphates and thermal processing are all highly interactive with nitrite for achieving inhibitory effects (Tompkin, 2005). It has been suggested that both the amount of added nitrite and the amount of nitrite present as residual nitrite at the time of temperature abuse are important to antibotulinal protection. Because ingoing nitrite is depleted over time in cured meat, the importance of ingoing nitrite is probably due to the increased residual nitrite that results. Christiansen (1980), in a review of botulinal inhibition by nitrite, concluded "that any change in nitrite usage which reduces the level of residual nitrite or increases the rate of nitrite depletion could increase the above mentioned (botulinal) theoretical risk".

The issue for processed meats that utilize natural sources of nitrate is that the true amount of nitrite formed is unknown and impossible to measure because nitrite reacts quickly with meat components. While the amount of detectable residual nitrite in these products is significant, it is often less than that found in nitrite-cured products (Sindelar et al., in press a, in press b) depending on processing conditions. On the other hand, the nitrite reactions means that there are variable pools of nitrite-modified compounds in cured meat that remain available as reactive sources of nitric oxide (Kanner & Juven, 1980; Møller & Skibsted, 2002). Consequently, the microbial safety of processed meats manufactured with natural sources of nitrate is very difficult to assess without microbiological challenge studies. This is a very significant current research need for effectively assessing the safety of these products.

The second potential safety issue that should be considered with these products is the implications of higher-thanusual nitrite concentrations. Sindelar et al. (in press a) found that a frankfurter-style sausage processed with 0.4% celery powder and an extended incubation time resulted in significantly more residual nitrite than a nitrite-cured control throughout 90 days of storage. Elevated residual nitrite in bacon is a potential risk for nitrosamine formation and actual ingoing nitrite concentrations need to be carefully controlled to avoid this potential problem. The nature of the time-temperature relationship for reduction of nitrate to nitrite by a starter culture makes the concentration of nitrite a variable entity. Further, vegetable products are recognized as extremely variable in nitrate content as a result of different environmental conditions that occur during plant growth (National Academy of Sciences, 1981). Consequently, more information is needed on the best means by which to control nitrite formation in

processed meats manufactured with natural sources of nitrate to assure that excess concentrations of nitrite do not become a safety issue.

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