## MANUFACTURE OF MEAT PRODUCTS WITHOUT ADDED NITRITE OR NITRATE – QUALITY AND SAFETY ASPECTS

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#### Abstract

There is increasing interest in meat products processed with less or no additives. This applies particularly to 'organic' meat products. The use of nitrite in the processing of organic meats has been discussed controversially for many years. It is a synthetic chemical with toxicological concern but because of its effect on appearance and flavour of meat products, marketing of nitrite-free sausages and hams proved to be difficult. Moreover, nitrite contributes to the safety and shelf life of several meat products. However, this (antimicrobial) effect of nitrite strongly depends on the type of product and may be compensated, in most products, by adapting the processing conditions (e.g. by lowering the ripening temperatures for raw sausages; increasing the  $F_0$  values for shelf-stable cooked sausages). The inhibitory effect of nitrite on oxidative deterioration of fats may be – within limits - compensated for by selection of the raw material and by limiting the access of oxygen. In dry sausages and raw hams with long aging times, an acceptable red colour which has been shown to consist of zinc protoporphyrin IX ("Parma Ham Pigment") is obtained without curing agents. This paper summarizes data of recent studies, in particular on the effect of nitrite on product safety and stability, and gives recommendations on the safe processing of meats with little or no nitrite added.

Key words: nitrite; curing; meat products; safety; quality

#### Introduction

The use of curing agents (nitrite, nitrate) in meat processing has been a controversial issue since the 1970s because toxicological concerns must be weighted against the benefits of curing agents to appearance, flavour, stability and safety of meat products. The last few years saw an increasing demand for meats with less additives. The "organic" meat sector (meat produced and processed according to Regulation (EC) 2092/91 as amended by Regulation (EC) 780/2006) grew rapidly in Germany and other countries, and even many manufacturers of "conventional" meat products look for possibilities to reduce the list of additives to these products. The Regulation (EC) 780/2006 only permits the use of nitrite and nitrate at reduced input levels and only if "no technological alternative giving the same sanitary guarantees and/or allowing to maintain the specific features of the product is available".

This paper discusses the role of curing agents in the manufacture of several meat products, and alternatives to their use.

**Curing agents and colour of meat products.** The mechanism of curing colour formation is well known and has been recently summarized by Honikel (2008). Since consumers associate pink colour of meat product with "freshness", marketing of greyish meats is difficult (Hamm, 2007). Recent discussion focused on the following two alternatives:

(1) In situ-formation of zinc protoporphyrin IX: During ripening of raw meats salted without nitrite,  $Fe^{2+}$  ions in the porphyrin ring are slowly replaced by  $Zn^{2+}$  ions, and the resulting reddish colour is reasonably stable (Wakamatsu *et al.*, 2004). This explains the red colour of raw hams with extended ripening times. However, this alternative is, at present, not applicable to cooked meats and raw meat products with short ripening times.

(2) In situ-formation of nitrite from nitrate occurring naturally in components of plant origin: Some vegetables (e.g. celery) tend to accumulate nitrate even under conditions of limited nitrogen supply during cultivation. They could be added, in a dried form, to sausage mixtures. If these are pre-incubated at elevated temperatures (around 40 °C) in the presence of a suitable nitrate-reducing starter culture, small amounts of nitrite are formed that are sufficient for the formation of a pink colour during heating of the sausages (Fischer *et al.*, 2005; Sebranek&Bacus, 2007). This method makes use of the fact that current food legislation normally does not require labelling of added enzymes, microbial starter cultures and compounds formed by these *in situ*. However, use of this method without proper labelling may mislead the consumer, especially buyers of organic meats.

**Curing agents and flavour of meat products**. The known effect of nitrite on the flavour of cured meats is mainly due to its ability to bind to  $Fe^{2+}$ . In this form, iron can no longer initiate oxidative changes of polyunsaturated fatty acids present in lipids. Attempts to replace this effect of nitrite by use of synthetic antioxidants had little if any success. To minimise undesired changes (in particular, rancid or warmed-over flavours), it is advisable to (i) use pork from animals fed a diet rich in tocopherol and poor in polyunsaturated fatty acids, (ii) exclude oxygen during the preparation and filling of the sausage mix as far as possible (Klettner & Troeger, 2000), (iii) use spices with high antioxidative capacity (e.g. rosemary), and (iv) limit the "best before" date of the products. The levels of nitrite formed *in situ* from "natural" nitrate from vegetables (see above) may also bring about an acceptable level of curing flavour (Fischer *et al.*, 2005).

Antimicrobial effects of curing agents: general remarks. European legislation on food additives (Directive 2006/52/EC) classifies curing agents as preservatives, i.e. as compounds inhibiting micro-organisms. This decision is mainly based on an expert opinion published by the European Food Safety Authority (EFSA, 2003) and focusing on the effect of nitrite on *Clostridium botulinum*. Indeed, nitrite has been shown in model systems and challenge studies (predominantly with products related to cooked hams or luncheon meat) to contribute to the inhibition of *Clostridium botulinum*. Nitrite also affects undesired Gram-negative bacteria in the early stages of sausage fermentation (Hechelmann *et al.*, 1974; Sanz *et al.*, 1997) and possibly *Listeria monocytogenes* (Duffy *et al.*, 1994). However, Grever & Ruiter (2001) and the EFSA (2003) pointed out that the antimicrobial effect of nitrite depends on many factors such as the pH and the levels and forms of iron in the product. For a comprehensive risk assessment, the probabilities of process failure and of non-detection of unsafe products during distribution and consumption, as well as epidemiological data and industrial experience must be taken into account.

Nitrite and product safety: some recent studies. Recent data of Stegeman et al (2006; see Table 1) confirm that use of nitrite at levels above 50 mg NaNO<sub>2</sub>/kg delays growth of *Clostridium botulinum* in pasteurised Bologna-type sausages at 15 °C.

Table 1

# Growth of *Clostridium botulinum* (inoculation level: ca. 100 spores/g; mixture of proteolytic and non-proteolytic strains) in canned Bologna-type sausages (boterhamworst) cooked to P<sub>70</sub>=55 minutes and stored at 15 °C. No growth was observed at 10 °C or below. Data from Stegeman *et al.* (2006)

Batch	Water activity	NaNO2 added (mg/kg)	Weeks until growth of clostridia
1		0	2–4
2	0.973 <u>+</u> 0.02	54	8–12
3		108	8–12
4		0	6–8
5	0.970 <u>+</u> 0.03	54	>12
6		108	>12

Using the approach of Hauschild (1982), Lücke & Hechelmann (1986; see Lücke & Roberts, 1993) calculated the probability of toxin formation during unrefrigerated storage of canned sausages heated to  $F_0$  values of 0.3–0.4. This mimics the situation in traditional home-scale canning of meats which was identified as a major risk factor for botulism (see Lücke, 2003). The results (Table 2) show a marked effect of nitrite only for Bologna-type, not for liver sausages. They also indicate that the effect of nitrite may be compensated for by reducing the water activity. Alternatively, the heat treatment should be intensified by

increasing the  $F_0$  value by about 0.6–0.8 units (resulting in a reduction of P by 3–4 units, assuming a  $D_{121}$  value of 0.2 for spores of proteolytic *C. botulinum* strains).

#### Table 2

Probability (P) of formation of botulinum toxin from a single spore present in sausage mixtures heated at 99 °C to about  $F_0 = 0.34$  and stored at 21 °C for 3 months. Data from Lücke & Hechelmann, 1986, quoted by Lücke & Roberts, 1993

Product	Water activity	NaNO <sub>2</sub> added (mg/kg)	log <sub>10</sub> P
	0.972	~80	-6.8
Bologna-type		0	-6.1
sausage	0.979–0.982	~80	-6.9
		0	-3.9
	0.972	~80	-5.2
I ivon coucogo		0	-5.3
Liver sausage	0.979–0.982	~80	-2.5
		0	-2.2

Nitrite had only a small effect on growth of *Listeria monocytogenes* on cooked sliced meat products (Table 3). The effect of water activity was much more marked.

Table 3

# Effect of water activity and nitrite on the growth of *Listeria monocytogenes* on cooked meat products. Data from Stegeman et al (2007)

Product	Water	NaNO <sub>2</sub> added	Doublings of <i>Listeria monocytogenes</i> at 7 °C	
Product	activity	(mg/kg)	within 14 days	within 21 days
Bologna-type	0.965	79	<1	<1
sausage	0.905	40	<1	~1.3
Cooked how	0.973	79	11–12	11–12
Cooked ham		40	12–13	12–13

Nitrite and spoilage by micro-organisms. We determined the shelf life of six batches of cooked sliced vacuum-packed bologna-type sausages at 8 °C that had been prepared by one manufacturer without nitrite and with 80 mg NaNO<sub>2</sub>/kg, respectively (Lücke *et al.*, 2007). The products were spoiled by recontaminants (lactic acid bacteria, *Brochothrix thermosphacta*; see Borch *et al.*, 1996). Judged by sensory evaluation, by pH decrease and by microbiological data, the vacuum-packed sausages analysed had a shelf life of about 5–10 days at 8 °C after being sliced without the usual precautions taken to avoid recontamination. Spoilage indicators were off-odours and aromas described as "sour" and "rancid". In uncured sausages, these deviations were more pronounced and observed some days earlier, as also found by Graubaum *et al.* (2003), but this effect may be due to differences in the slicing process leading to higher initial counts of spoilage bacteria. Since "rancidity" was observed in both cured and uncured sausages, it was rather due to short-chain fatty acids formed by *Br. thermosphacta* than to fat oxidation.

Psychrotrophic *Enterobacteriaceae* in the recontaminant flora were found to cause pink spots on a greyish product, probably by reducing traces of nitrate present in uncured sausages. This deviation will further reduce shelf life and acceptability.

### Conclusions

It is difficult to compensate for the effect of curing agents on colour and flavour of meat products. On the other hand, the effect of curing agents on product safety and shelf life differs considerably according to the type of product. Under practical conditions, added nitrate has no antimicrobial effect, so it is difficult to understand why it is categorised legally as "preservative". Whether and how the manufacture of cooked meats should be modified if nitrite is omitted or if its ingoing level is reduced to 50 mg NaNO<sub>2</sub>/kg or less may be summarised as follows (see also Lücke and Roberts, 1993; Lücke, 2003):

**Perishable cooked meats not cooked in sealed containers** are normally spoiled by recontaminants and may be expected to be stored under refrigeration. Thus, maintenance of the chill chain becomes even more important but no specific measures are necessary to compensate for any antimicrobial effect of nitrite.

Meat products pasteurised in sealed containers are often stored under insufficient refrigeration. Irrespective of nitrite addition, sausages containing liver or blood should be cooked to  $F_0$  values above 1.5. Other sausages prepared without nitrite should be cooked to  $F_0$  values above 1.0. Alternatively, the formulation should be modified to attain a water activity below 0.96 (for liver and blood sausages) or below 0.97 (for other products) and the products should be cooked to  $F_0$  values above 0.4.

From literature data (see e.g. Lücke, 2003; Hummerjohann, 2004), the following recommendations for the safe manufacture of raw meat products can be derived:

**Raw sausages** without added nitrite should be fermented at 18 °C or below (such as traditional varieties prepared with saltpetre). At fermentation temperatures between 18 and 22 °C, use of appropriate starter cultures and sugars is necessary to ascertain a rapid pH decrease. Undried fermented sausages without nitrite addition should not be produced.

**Raw hams** can be safely produced by keeping the temperature of the meat below 5 °C until sufficient salt has penetrated into all parts of it to attain a water activity below 0.96. This is essential, irrespective of the use of curing agents.

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