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The effect of selected functional additives and heat treatment on nitrosamine content in pasteurized pork ham

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Abstract

The influence of pasteurization and sodium chloride, sodium ascorbate, polyphosphates and sodium nitrite coupled with pasteurization on nitrosamine contents in pork was studied. Nitrosamines: dimethylonitrosamine (DMNA) and diethylonitrosamine (DENA) were extracted from raw material, distilled, condensed in an evaporator under lowered pressure and analyzed chromatographically. An inhibitory effect of NaCl and sodium ascorbate on volatile nitrosamines (DMNA and DENA) was seen. Adding solutions of polyphosphates to the meat caused a slight increase in nitrosamine contents, higher than noted with sodium chloride. The effect of these compounds on nitrosamine formation depended on the presence of polyphosphates and sodium nitrite in the brine. If the brine contained nitrites, the adverse effect of sodium ascorbate and NaCl on nitrosamine formation was weaker. Moreover, a strong inhibitory effect of pasteurization on DMNA and DENA formation was observed.

Keywords: Nitrosamines; Dimethylonitrosamine (DMNA); Diethylonitrosamine (DENA); Additives; Pasteurization

1. Introduction

Nitrosamines are chemical substances with strong toxic, mutagenic, neuro- and nephrotoxic and carcinogenic effects. They are formed mainly in soil, but also in fodder, raw food materials (Rywotycki, 1997) and food products (Lijinsky & Reuber, 1982; Low, 1974; Mirvish, 1975; Rywotycki, 1998a,b; 2001) from primary, secondary and tertiary amines and amides, and are also products of the biotransformation of some pesticides and other precursors. Dimethylonitrosamine (DMNA) and diethylonitrosamine (DENA) have the strongest toxic activity.

Investigations have shown that many food products are contaminated with nitroso compounds, as the result of processes in which they form in slightly acidic environments by reaction of sodium nitrite and nitrogen oxides with such precursors as: proteins, peptides, amino acids and amines (Miśkiewicz, 1997).

The influence of some functional additives on nitrosamine formation in meat and meat products has been described (Rywotycki, 1997; 1998a,b; 2001; Smyk & Rywotycki, 1984). The present study examines the influence of heating of meat products on their contents of nitrosamines. Eisenbrand, Jancowski, and Preussmann (1977) stated that an increase in nitrosamine content in some meat products is a result of heat treatment.

Holland, Wood, and Randall (1981) found mean contents of diethylonitrosamine (DENA) in raw and steamed frankfurters of 2.6 and 3.4 μg/kg, respectively, and of nitrosomorpholine of 1.8 and 3.6 μg/kg.

For example, in raw bacon only trace amounts of nitrosamines can be detected whereas in fried bacon considerably greater contents are found (Sen, Donaldson, Iyengar, & Panalaks, 1973a). The formation of nitrosamines increases with time and temperature of frying. Most probably N_2O_3, which originates in cured meat, forms adducts with the unsaturated lipids. These decompose at elevated temperature and liberate nitrogen oxides which react with the free amines present in the environment (Liu, Conboy, & Hotchkiss, 1988).

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Skrypec, Gray, Mandagere, Booren, Pearson, and Cuppet (1985) suggest that nitrosopirolidine may originate from bacon frying due to formation of pseudo-nitroso derivatives of unsaturated lipids. The authors also observed that frying in a nitrogen atmosphere caused decreased formation of nitrosamines.

At the temperature usually used for cooking and baking some nitrosamines volatize or decompose whereas nonvolatile nitroso compounds increase in concentrations (Sen, Donaldson, Iyengar, & Panalaks, 1973b; Sen & Kubashi, 1987; Tricker, Perkins, Massey, & McWeeny, 1985), and the Nitrite Safety Council (1980) declared that usual methods of thermal processing, like baking, frying or microwave heating do not cause nitrosamine formation in frankfurters.

On canned minced lamb Szumilak and Gudaszewski (1985) found that the concentration of volatile nitrosamines increased with increasing temperature and time and the temperature of pasteurization had a strong influence on nitrosamine formation.

Decarboxylation of nitrosamine acids may also occur during heat treatment. The meat content of nitrosopirolidine increases from about 1.5 μg to 15 μg/kg (Belitz, & Grosch, 1992) during frying.

The present investigations were aimed at determining the influence of pasteurization and the frequently used functional additives: sodium chloride, sodium nitrite, polyphosphates and sodium ascorbate on nitrosamine formation in pork.

2. Material and methods

Muscles from gilts and hogs for ham production provided the test materials. The muscles were divided into eight groups, each in 21 replications. A representative sample (c.a. 1 kg) was collected from each group, ground in a mincer with 2 mm mesh, homogenized and the nitrosamine content determined. These were the control samples marked: A, B, C, D, E, F, G, H and I and did not contain 20% water addition or any functional additives, neither were they pasteurized. Duplicate tests were performed on groups formulated as follows:

A—raw meat,
A_1—pasteurized meat,
B_1—meat injected with brine containing only NaCl;
B_2—meat injected with brine containing only NaCl and then pasteurized;
C_1—meat injected with brine containing NaCl and sodium ascorbate;
C_2—meat injected with brine containing NaCl and sodium ascorbate and then pasteurized;
D_1—meat injected with brine containing NaCl and polyphosphates;
D_2—meat injected with brine containing NaCl and polyphosphates and then pasteurized;
E_1—meat injected with brine containing NaCl, sodium ascorbate and polyphosphates;
E_2—meat injected with brine containing NaCl, sodium ascorbate, polyphosphates and then pasteurized;
F_1—meat injected with brine containing NaCl and sodium nitrite;
F_2—meat injected with brine containing NaCl and sodium nitrite and then pasteurized;
G_1—meat injected with brine containing NaCl, sodium ascorbate and sodium nitrite;
G_2—meat injected with brine containing NaCl, sodium ascorbate, sodium nitrite and then pasteurized;
H_1—meat injected with brine containing NaCl, polyphosphates and sodium nitrite;
H_2—meat injected with brine containing NaCl, polyphosphates, sodium nitrite and then pasteurized;
I_1—meat injected with brine containing NaCl, sodium ascorbate, polyphosphates and sodium nitrite;
I_2—meat injected with brine containing NaCl, sodium ascorbate, polyphosphates, sodium nitrite and then pasteurized;
I_3—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10μg DENA + 10μg DMNA placed in the geometric centre of the can;
I_4—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10μg DENA + 10μg DMNA placed in the geometric centre of the can and pasteurized;
I_5—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10 μg DENA + 10μg DMNA placed by the can wall; and
I_6—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10 μg DENA + 10μg DMNA placed by the can wall and pasteurized.

The muscles were injected with 20% brine composed of 16 kg of table salt, 0.08 kg of sodium nitrite, 0.225 kg of sodium ascorbate, 1.5 kg of almine and 82.195 kg of water. Depending on the sample any component eliminated from the brine was replaced with water to make a total volume injected of 100 kg. The muscles were massaged in 40/20 min cycles for a total of 8 h.

After massage was complete representative samples were collected, ground in a mincer with 2 mm mesh, homogenized, and their nitrosamine contents determined.

The pasteurized canned meat was produced according to regulations described by Polish Standard No. 91/80-16/07, for both raw material selection and the process itself. Only the functional additives varied. The canned product was produced in 199 × 142 × 65 mm cans with 1365g (3lbs) of product. The cans were filled and then heated in an open boiler, so that the centre temperature would reach at least 72 °C and pasteurization time value was about 80 min. The pasteurization was calculated

assuming a z value of 10 °C (Ball & Olson, 1957; Wojciechowski, Szczepaniak, Morawiak, & Pinik, 1976).

Lethality was calculated every minute to ensure the most precise computations (Takacs, Wirtg, & Leistner, 1969; Wirth & Takacs, 1971). The limit of integration was from 55 °C during the temperature increase and to 55^0C during cooling (Reichert, 1977). The extent of heating was determined in the critical zone using using an electric thermometer with thermo-electric Cu-CuNi sensor. After pasteurization representative amounts of materials were sampled.

The contents of nitrosamines (dimethylonitrosamine—DMNA and diethylonitrosamine—DENA) in meat were assessed by Pancholy' s method (Pancholy, 1976) adapted for nitrosamine determination in meat and its products (Scanlan, 1973; Scanlan & Ryes, 1985). The contents of DMNA and DENA were determined using a Varian 3400 gas chromatograph coupled to a mass spectrometer (Finnigan MAT ITD. 800). The samples were separated on a 0.2-μm and 25-m long Hewlett-Packard capillary column. The samples were dissolved in chloroform and 0.5 μg of solution was

Table 1
The contents (mean $\bar{x}$ standard deviation of 21 samples) of pork processed in the presence of various ingredients

Sample	DMNA			DENA		
	Content (μg/kg)		Variance [%]	Content (μg/kg)		Variance [%]
	$\bar{x}$	$\pm s$	Z%	$\bar{x}$	$\pm s$	Z%
A—pork	12.09	1.07	8.9	11.81	0.60	5.1
A_1—pasteurized pork ham	7.72	0.62	8.0	7.59	0.39	5.1
B—pork	13.09	0.79	6.0	12.71	0.49	3.8
B_1—salted pork	9.55	0.55	5.7	8.96	0.45	5.0
B_2—pasteurized pork ham	3.78	0.24	6.3	3.48	0.40	11.6
C—pork	11.59	1.16	10.0	12.36	1.36	11.0
C_1—salted pork with added sodium ascorbate	7.35	0.76	10.4	7.58	1.30	17.2
C_2—pasteurized pork ham	2.75	0.41	14.8	2.84	0.57	20.0
D—pork	12.96	3.10	23.9	12.80	1.12	8.7
D_1—salted pork with added polyphosphates	11.33	2.33	20.6	11.72	1.38	11.8
D_2—pasteurized pork ham	4.32	1.24	28.6	4.68	0.61	13.1
E—pork	15.19	2.45	16.1	14.86	0.84	5.6
E_1—salted pork with added sodium ascorbate and polyphosphates	11.46	1.91	16.7	11.34	0.76	6.7
E_2—pasteurized pork ham	5.75	1.14	19.9	5.58	0.35	6.3
F—pork	13.44	1.63	12.1	13.93	2.41	17.3
F_1—salted pork with added sodium nitrite	16.98	2.48	14.6	16.74	1.24	7.9
F_2—pasteurized pork ham	8.64	1.64	19.0	8.86	1.66	18.8
G—pork	14.34	2.69	18.7	14.37	1.11	7.7
G_1—salted pork with added sodium ascorbate and sodium nitrite	12.90	2.66	20.6	12.56	1.27	10.1
G_2—pasteurized pork ham	5.09	1.01	19.7	4.85	0.54	11.1
H—pork	14.93	2.40	16.1	15.03	1.41	9.4
H_1—salted pork with added polyphosphates and sodium nitrite	18.56	2.23	12.0	19.16	1.97	10.2
H_2—pasteurized pork ham	11.38	1.45	12.7	11.48	0.66	5.8
I—pork	15.22	1.69	11.1	14.08	1.34	9.5
I_1—salted pork with added sodium ascorbate polyphosphates and sodium nitrite	16.85	2.77	16.4	15.49	1.55	10.0
I_2—pasteurized pork ham	11.05	1.20	10.9	10.40	0.96	9.3
I_3—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10 μg DENA + 10 μg DMNA in geometric centre of can	26.85	2.77	16.4	25.49	1.55	10.0
I_4—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10μg DENA + 10μg DMNA in geomteric centre of can and pasteurized	19.72	2.53	15.6	18.12	2.26	9.4
I_5—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10 μg DENA + 10μg DMNA by the can wall	26.85	2.77	16.4	25.49	1.55	10.0
I_6—salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10 μg DENA + 10μg DMNA by the can wall and pasteurized	17.77	2.42	15.1	17.18	2.17	9.0

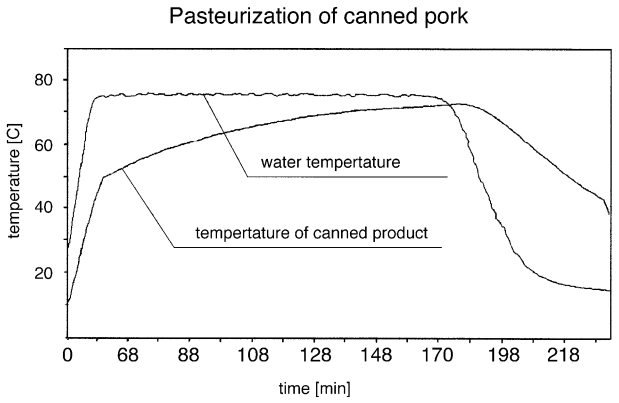

Fig. 1. Pasteurization of canned pork.

injected. A temperature gradient was applied (50–150 °C, 10 °C/min) with helium as carrier gas. The injector temperature was set at 180°C and the carrier gas pressure at 10 psi. The volatiles were identified by comparing their mass spectra with standards and by comparison of retention times with standards.

Quantitative and qualitative analysis was conducted by comparison with N-nitrosamine standard solution chromatograms.

3. Results and discussion

Analyses carried out at various times of the year on pork loins and hog joints found considerable quantities of nitrosamines (DMNA and DENA). This is a potential health hazard as these kinds of meat are popular. Average contents of nitrosamines in the test samples are presented in Table 1 (A–I_6).

The canned meat was produced from raw material with functional additives usually used for such meat processing to determine which of these, combined with heat treatment inhibits nitrosamine formation.

In the meat used for production of the uncured product an average of 12.09 μg/kg of dimethylonitrosamine and 11.81μg/kg diethylonitrosamine were found (Table 1). Pasteurization of this meat decreased the amounts of: DMNA to 7.72 μg/kg and DENA to 7.59 μg/kg, i.e. by 36.1 and 35.7%, respectively. Generally, pasteurization decreased the concentrations of the nitrosamines (Table 1).

In I control samples there were 15.22 μg DMNA and 14.08 μg DENA/kg of meat (Table 1). The pork injected with 20% brine containing NaCl, sodium ascorbate, polyphosphates and sodium nitrite had mean quantities of 16.85 μg DMNA and 15.49 μg DENA/kg of meat. So the amounts were bigger by respectively: 10.71 and 10.01%. The ham produced from this meat had 11.05 μg DMNA and 10.40 μg DENA/kg. In comparison to meat injected with brine, nitrosamine levels decreased by 34.42% DMNA and 32.86% DENA.

In samples I_3 and I_5 portions of salted pork with added sodium ascorbate, polyphosphates and sodium nitrite + 10 μg DENA + 10 μg DMNA were wrapped in aluminum foil and placed in the geometric center of the can (I_3) and by the can wall (I_5). After pasteurization the samples placed by the can wall had lower contents of nitrosamines than those from the geometric center of the can (Table 1). This is presumably because of the higher heat treatment experienced by the meat at the can wall (Fig. 1).

In addition to pasteurization the results clearly reveal a destructive effect of sodium ascorbate and a slightly lesser effect of NaCl on the formation of the nitrosamines (DMNA and DENA) and a catalyzing effect of polyphosphates, and that the magnitude of the effect of these compounds depends on the presence of nitrite in the brine. If the brine contains nitrites, the destructive effect of sodium ascorbate and NaCl on nitrosamine formation is less (Table 1).

These results support Hilldrum's (1975) theory regarding the inhibitory effect of chloride ion on the formation of the volatile nitrosamines (DMNA and DENA) at pH values higher than 4.0 and are consistent with the observations of Szumilak and Gudaszewski (1985) and Mirna, Spiegelalder, and Eisenbrand (1979) concerning the inhibitory effect of sodium ascorbate on nitrosamine formation in meat.

From the results it may be concluded that meat curing with polyphosphates and sodium nitrite increases the level of short chain nitrosamines, i.e. DMNA and DENA but the content of these nitrosamines can be diminished through the introduction of sodium ascorbate into the brine.

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