

# Nitrosamines in cured meat products

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Since Ender and his co-workers (1964) demonstrated that fish meal treated with nitrite was carcinogenic to sheep as a result of the presence of nitrosodimethylamine, many foods have been analysed for nitrosamines. Particular attention has been paid to cured meat products because both components of the nitrosamine reaction, nitrite and secondary amines or their precursors, are present in them. Several reports published prior to 1970 indicated that nitrosamines had been found in a few meat samples; however, the analytical methodology utilised is under question at present. Contaminating materials that can be mistaken for nitrosamines in the detection procedures have been demonstrated in both natural products and the solvents used in the analysis. A survey of the analytical techniques of that period and the difficulties inherent in the analysis of nitrosamines was presented at the IARC Conference on *N*-Nitroso Compounds in Heidelberg in 1971 (Wasserman, 1972).

In the last few years, however, research has intensified and nitrosamines have been reported in several types of meat products. The use of selective gas chromatography detectors and improved isolation methodology, combined with confirmation of the presence and structure of nitrosamines, has led to greater assurance in the findings. Reported herein is a compilation of recent information on the presence of nitrosamines, confirmed by mass spectrometry, and the conditions affecting their formation in meat products.

## NITROSAMINES IN MEAT PRODUCTS

### Ham

Fazio *et al.* (1971) examined 5 samples of ham, using a potassium chloride alkali flame-ionisation

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detector in a gas chromatograph. Of these, only one sample could be shown by mass spectrometry to contain as much as 5 µg/kg nitrosodimethylamine (NDMA). A modification of the method of Howard *et al.* (1970), utilising a rubidium sulfate salt alkali flame-ionisation detector, was used by Fiddler *et al.* (1971) in studying 10 samples of ham that included American fresh cured as well as canned hams, and Danish and Polish products. None of the hams was found to contain any NDMA at confirmable levels above 25 µg/kg. A coupled gas chromatography-mass spectrometry (GC-MS) system was used by Telling *et al.* (1971) to examine nitrite-cured cooked ham. The mass spectrometer, set at a resolution of 15 000, was used in the peak matching mode to detect NO<sup>+</sup> ions produced from nitrosamines. None was detected in any of the samples. (These workers also failed to detect nitrosamines in fresh pork or beef.)

### Sausage

Sen (1972) examined 36 samples of commercially smoked sausage and salamis, finding five samples with NDMA ranging from 10 to 80 µg/kg. The analytical procedures included oxidation of the nitrosamine to nitramine, followed by gas chromatographic analysis using the electron-capture detector, and GC-MS analysis of the sample isolated by thin-layer chromatography.

NDMA was found in 3 samples of frankfurters out of 40 studied (Wasserman *et al.*, 1972). Two positive samples, separated by 20 negative samples, came from one producer whose product contained high concentrations of sodium nitrite (> 150 mg/kg).

Crosby *et al.* (1972), using gas chromatography with a Coulson electrolytic-conductivity detector and mass spectrometry, found a trace (1–4 µg/kg) of NDMA in one Hungarian salami out of 6 varieties of salami tested for the presence of this nitrosamine and nitrosodiethylamine (NDEA).

PROCESSING FACTORS  
AFFECTING NITROSAMINE FORMATION

A variety of sausage products (bologna, frankfurters, pepperoni, salami, thuringer, etc.) were examined by Fazio *et al.* (1971), who found that none of the 18 samples contained a sufficient quantity of NDMA to be confirmed by mass spectrometry.

Bard (1973), reporting on a study sponsored by the American Meat Institute, found none of 14 volatile nitrosamines analysed for in 9 samples of wieners before heating, after heating in boiling water, or after pan frying.

### Bacon

Recent reports indicate that nitrosopyrrolidine (NPy) has been found in almost all samples of bacon tested after frying. Crosby *et al.* (1972) analysed 24 samples of various types of bacon for four nitrosamines: NDMA, NDEA, NPy and nitrosopiperidine (NPip). Traces of NDMA (less than 4 µg/kg) were found in 13 samples, less than 1 µg/kg NDEA in one sample, up to 40 µg/kg NPy in 13 samples and less than 1 µg/kg NPip in one sample of bacon. In only two samples of bacon was there more than 4 µg/kg nitrosamine, and in both cases the nitrosamine was identified as nitrosopyrrolidine.

Eight samples of bacon were analysed for 14 nitrosamines, but only nitrosopyrrolidine, in amounts ranging from 10 to 108 µg/kg, was found (Fazio *et al.*, 1973). Although the raw bacon did not contain any nitrosamines, the rendered fat contained more nitrosopyrrolidine than the edible portion. Sen *et al.* (1973) detected either NDMA or NPy in 8 samples out of 16 tested, but only performed mass spectrometric confirmatory tests for NPy on one sample and for NDMA on another. Negative results were obtained by Telling *et al.* (1971) on an unspecified number of English and Danish bacon samples tested for several nitrosamines. A sensitive method of analysis (Alliston *et al.*, 1972), in which the nitrosamine was reduced to amine electrochemically, derivatised with heptafluorobutanoyl chloride and detected with the electron-capture detector of the gas chromatograph, revealed trace amounts of NPy in both samples of fried bacon tested and 1.5 µg/kg in one sample of raw bacon. The bacon samples did not contain any of the other six nitrosamines investigated in this study.

### Frankfurters

Fiddler *et al.* (1972a) found that processing with concentrations of 1500 mg/kg sodium nitrite or greater consistently produced frankfurters containing approximately 10 µg/kg NDMA; this did not occur when 156 mg/kg sodium nitrite, the concentration legally permitted in the USA, was used. In addition, increasing the processing time from 2 to 4 hours produced more NDMA. In another study (Fiddler *et al.*, 1972b), 1700–17 000 mg/kg sodium nitrate were found to have little effect on NDMA formation, and increasing concentrations of sodium ascorbate (NaAsc) (from 550 to 5500 mg/kg) reduced the amount of NDMA formed in frankfurters prepared with 1500 mg/kg sodium nitrite. Sodium erythorbate (NaEry), an isomer of NaAsc, was also effective in inhibiting NDMA formation in frankfurters (Fiddler *et al.*, 1973a). Similar results were obtained in a model system in comparing the effects of the two isomers on the nitrosation of dimethylamine (Table 1) (Fiddler *et al.*, 1973b). Glucono-delta-lactone (GDL), in the absence of either reductant, increased the amount of NDMA formed. A similar result was reported by van Logten *et al.* (1972), who found that a greater concentration of nitrosamines was produced in meat prepared with 1% GDL and 0.5% sodium nitrite, as compared with meat prepared with 0.5% sodium nitrite alone.

Table 1. Effect of NaAsc and NaEry on NDMA formation in a model system containing dimethylamine, sodium nitrite and other cure components<sup>a</sup>

Cure component	NDMA formed (µg/litre)		
	No reductant added	NaAsc added	NaEry added
None	63	39	28
Sodium chloride	59	35	27
Sodium nitrate	59	32	37
GDL	117	32	33
SAPP	58	28	27
STPP	43	27	25
AscH	38	—	—
Sodium nitrate + GDL	101	28	31
Sodium chloride + STPP	49	31	30
Sodium chloride + SAPP + STPP	55	30	31

<sup>a</sup> GDL = glucono-delta-lactone; SAPP = sodium acid pyrophosphate; STPP = sodium tripolyphosphate; AscH = ascorbic acid; NaAsc = sodium ascorbate; NaEry = sodium erythorbate; NDMA = nitrosodimethylamine.

Table 2. Effect of frying conditions on nitrosopyrrolidine (NPy) formation in bacon

Temperature (°F)	Frying conditions		NPy (µg/kg) <sup>a</sup>	
	Time (min)	Degree of cooking	Storage time at 35°F (weeks)	
			0	2
210	105	Medium well	0	0
275	30	Medium well	8	5
350	6	Medium well	10 <sup>b</sup>	6
400	4	Medium well	17 <sup>b</sup>	7
210	10	Raw	0	0
275	10	Very light	0	0
350	10	Well	15	7
400	10	Burned	19 <sup>b</sup>	16 <sup>b</sup>

<sup>a</sup> Uncorrected.

<sup>b</sup> Confirmed by mass spectrometry.

### Bacon

Fiddler *et al.* (1973c) found that the amount of nitrosopyrrolidine formed in bacon was primarily dependent on the frying temperature and not on the duration of frying (Table 2). The largest amounts of NPy were formed at about 365°F by decarboxylation of nitrosoproline in a model system.

A study of other cooking methods, including microwave heating, baking, broiling and a "baconer", showed that the smallest amount of

NPy was formed by microwave heating. Herring (1973) reported a similar finding, using bacon prepared with concentrations of sodium nitrite varying from 30 to 170 mg/kg. Increasing the concentration of NaAsc from 0 to 2000 mg/kg in bacon prepared with 170 mg/kg sodium nitrite was also found to reduce or inhibit the formation of NPy during frying (Table 3).

Further studies on the effect of NaAsc on nitrosamine formation may lead to a process that will permit the use of sodium nitrite in the curing of meat products without giving rise to a possible public health hazard.

Table 3. Effect of ascorbate and storage on concentrations of nitrosopyrrolidine (NPy) in fried bacon <sup>a</sup>

Samples	NaAsc (mg/kg)	NPy (µg/kg)		
		storage period (weeks)		
		0	1	6
A	0	0	5	10
	500	0	0	0
	2000	0	0	0
B	0	13	11	5
	500	5	0	0
	2000	0	0	0

<sup>a</sup> Source: Herring, 1973. The bacon was prepared with 170 mg/kg sodium nitrite.

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