

CHANGES IN RESIDUAL NITRITE IN SAUSAGE AND LUNCHEON MEAT PRODUCTS DURING STORAGE¹

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(Received for publication April 25, 1973)

ABSTRACT

Changes in residual nitrite content of 18 sausage products during storage for various lengths of time are reported. Most pre-packaged processed meats (storage temperature 5 ± 2 C) showed decreasing residual nitrite levels during storage. All dried meat products (storage temperature 24 ± 1 C) showed increasing residual nitrite levels during storage. Residual nitrite decreased with cooking for the three products evaluated.

Retention of cured meat color is presently dependent on use of nitrite in the curing process. It has been reported that approximately 20 ppm residual nitrite are sufficient to produce acceptable color and flavor in pork but sausage products were not included in this study (8). The residual nitrite level in cured meat products has been the basis for determining the desirable level of nitrite added for curing meat products. However, the desirable level of residual nitrite during refrigerated storage of cured sausage products has not been satisfactorily resolved. In addition, factors which influence the degree of retention of residual nitrite in cured sausage products have not been fully explained. Among factors which have been identified as influencing the level of residual nitrite in cured meat products are time and temperature of processing, pH, reducing activity of the system, storage time and temperature, and meat to water ratio (9, 11).

Kolari and Auman (9) reported that 20-25% of the nitrite has been estimated to disappear during mixing of raw meat mixtures. Nordin (10) noted that depletion of nitrite during storage of commercially canned hams has been observed in the industry but has not been reported. In a study of fresh ground ham, canned by a commercial technique, Nordin (10) found that nitrite was depleted at a rate independent

of the initial nitrite concentration. Unsterilized samples, held at room temperature showed a rate of depletion of nitrite that increased rapidly with time. For samples held at other temperatures (28 - 225 F) and for sterilized samples held at room temperature, the higher temperatures and lower pH resulted in a greater rate of depletion. Nordin (10) concluded that bacterial utilization of nitrite accounted for the more rapid depletion of nitrite in unsterilized samples held at room temperature. Kolari and Auman (9) reported that franks and bologna decreased in residual nitrite levels after 3 and 8 weeks storage, respectively, whereas meat loaves increased in residual nitrite after 5 weeks storage, then decreased. Liver sausage showed no appreciable change after 3 weeks storage. The presence or absence of ascorbate did not affect residual nitrite level during storage. Oldsman and Krol (11) concluded that the level of nitrite added, sodium chloride content, and vacuum chopping and canning had no effect on the rate of nitrite depletion.

Nitrate can be converted to nitrite by bacteria (4) and the nitrite is, in turn, converted to nitric oxide, which reacts with myoglobin and hemoglobin (2, 15). Nitrite was found to have significant bactericidal properties if the pH was in the range of 4.5 to 5.5, provided the bacterial population was not abnormally high (5, 12). Shank et al. (12) proposed that oxidation-reduction reactions of nitrite resulted in production of nitrite, nitric oxide, and nitrogen dioxide. Nitrite can be in equilibrium with nitrous acid in the presence of water. The equilibrium condition favors nitrous acid at pH 4.5 - 5.5, with nitrous acid having bactericidal properties. Nitrite has been shown to prevent growth of germinated spores of *Clostridium botulinum*. (5, 7). Castellani and Niven (3) and Tarr (13) showed that sodium nitrite had a bactericidal effect on selected bacteria. Thus, the level of residual nitrite in processed meats has importance in maintaining the shelf-life of processed meats.

This study was made to determine the changes in residual nitrite during the shelf-life storage and the effect of cooking on selected processed sausage products.

¹Paper No. 4034 of the Journal Series of the North Carolina State University Agricultural Experiment Station, Raleigh, N. C. This investigation was supported, in part, by Good Mark, Inc., Raleigh, N. C. The use of trade names in this publication does not imply endorsement by the North Carolina Agricultural Experiment Station of the products named, nor criticism of similar ones not mentioned.

²Present address: GoodMark, Inc., Raleigh, North Carolina.

TABLE 1. TYPE OF PACKAGING, INITIAL NITRITE AND NITRATE ADDED, FINISHED PRODUCT PH LEVELS, AND RESIDUAL NITRITE OF FRANKFURTERS STORED FOR VARIOUS TIMES AT 5 C

Product	Type packaging ¹	NO ₂ ² added (ppm)	NO ₃ ² added (ppm)	Storage time (days)	Initial pH	Residual ³ NO ₂ (ppm)
Frankfurters-10/lb all beef	Vacuum film	110	119	0	6.24 ± .14	27 ± 4a
				10		16 ± 2b
				20		13 ± 1bc
				31		11 ± 1c
Frankfurters-8/lb all meat	Vacuum film	116	124	0	6.07 ± .05	33 ± 1a
				10		12 ± 1b
				20		10 ± 0c
				31		9 ± 2c
Frankfurters-10/lb all meat	Vacuum film	116	124	0	5.91 ± .01	39 ± 2a
				9		20 ± 5b
				20		15 ± 3bc
				31		11 ± 1c
Frankfurters-12/lb all meat	Vacuum film	116	124	0	5.92 ± .03	42 ± 2a
				9		37 ± 2b
				20		31 ± 2c
				31		15 ± 2d
Frankfurters-14/lb all meat	Vacuum film	116	124	0	6.03 ± .03	25 ± 1a
				10		21 ± 1b
				20		17 ± 2c
				31		9 ± 1c

¹Vacuum film (21 in. Hg) consisted of a non-forming web (mylar, laminated to polyethylene) and a forming web (Saran coated mylar).

²Initial NO₂ and NO₃ values were calculated from the weighed amounts of NaNO₂ and NaNO₃ added to the emulsions during processing.

³Mean and standard deviation of 4 determinations. Any two means for a specific product were significantly different at the 0.05 level, when not having the same letter suffix.

MATERIALS AND METHODS

In the shelf-life storage experiments, various commercially processed meat products were selected from specific production lots and placed in a controlled temperature unit 48 h after processing. The beginning of the storage period was designated as day 0. All products were processed by standard commercial methods of manufacturing. The quantities of sodium nitrite and sodium nitrate initially added to each product were below the maximum allowed by federal regulations (14). The amounts of nitrate and nitrite added at the time of processing are shown in Tables 1, 2 and 3. These were determined by calculation of the quantities added during formulation. Sodium erythorbate was added to all products, except souse loaf, at a level of 0.05% based upon initial meat weight.

The products used in the shelf-life storage study, with days on which nitrite analysis were done in parenthesis, were: frankfurters (0, 9, 10, 20, 31); Polish and smoked sausage (0, 5, 8, 15); salami, spiced luncheon meat, and souse loaf (0, 10, 21, 30); pickle and pimento loaf (0, 7, 14, 20); bologna (0, 6, 12, 17); pickled hot sausage (0, 30, 64); pizza beef stick, chili beef stick, salami beef stick, spice beef jerky (0, 30, 60, 88). The prepackaged processed meats which are normally refrigerated were stored 5 ± 2 C and the dried and pickled sausage products were held at 24 ± 1 C. The storage times were selected to coincide with the estimated shelf-life of each product. Storage times and temperatures are listed for each product in Tables 1, 2, and 3. The pH measurements were made on samples from packages of products with similar treatments to those used for nitrite analysis.

The effect of cooking was determined on day 0 for smoked sausage, Polish sausage, and five frankfurter samples. Cooking refers to heating for serving and was accomplished 48 h

after processing. Frankfurters were cooked by heating tap water (1 pt.) to boiling (100 C), introducing 2 frankfurters, bringing the water to a second boil, turning off the heat source, covering and holding for 10 min. The frankfurters were removed, blotted of excess water, and prepared for analysis. Polish sausage was cooked by placing 5 sausages in cold tap water (1 pt.), heating to the boiling point (100 C), and maintaining the temperature for 10 min. The sausages were removed, blotted free of excess water, and prepared for analysis. Smoked sausages were split lengthwise, placed in a preheated (149 C) fry pan, cooked 2 min on each side, removed, and prepared for analysis.

Two packages of each product were sampled in duplicate for each nitrite determination. All shelf-life products were taken directly from the package and prepared for analysis. Each sample was homogenized for 1 min in a pint jar using a Sunbeam blender. The residual nitrite content of the samples was determined according to the A.O.A.C. method (1) which is not influenced by the presence of ascorbate.

RESULTS AND DISCUSSION

The range of residual nitrite at 0 days storage for frankfurters was 25-42 ppm (Table 1). This variation did not appear to be related to type or size of frankfurter. The residual nitrite content decreased significantly and steadily during storage but varied among types of frankfurters. In all instances there was a significant decrease in residual nitrite by storage day 9 or 10. The rate of decrease in nitrite was slightly different for each type of frankfurter but after 31 days storage the final range in residual ni-

trite levels (9-15 ppm) was relatively close.

Data in Table 2 indicate that Polish and smoked sausages, salami, and spiced luncheon meat showed similar initial residual nitrite levels to that of the frankfurters. However, there was a significant decrease by storage day 8 or 10 for these products. Also, the rates of decrease during storage for Polish and smoked sausages were similar to those for frankfurters.

Salami and spiced luncheon meat had rapid rates of decrease in residual nitrite, especially during the first 10 days of storage, but these products had relatively low levels of residual nitrite after 30 days storage. During the first 12 days of storage, the residual nitrite decrease for bologna was not significant but by storage day 17 the value showed a significant increase above the levels previously observed. The low variation (standard deviations) within samples suggested that the observed increase in residual nitrite in bologna was actual but there is no evident explanation for the difference in the rate of change in bologna as compared to salami and spiced luncheon meat.

No significant change was found in residual nitrite content of pickle and pimento loaf during the storage period (20 days) but the initial level was only 9 ppm. The reason(s) for the differences in rate of change for residual nitrite among those four luncheon loaves is not evident on the basis of data obtained in this study. Souse loaf increased from no detectable residual nitrite initially to 13 ppm after 10 days storage but the nitrite content was highly variable during the 30-day storage period. The only significant increase was between the initial and 10th day of storage. The reason for this result is not evident since a level of 83 ppm was added at the time of curing. It was postulated that all of the available nitrite was depleted during curing and processing with a subsequent conversion of the sodium nitrate to nitrite during storage. It can be noted that pickled hot sausage showed an increase in residual nitrite from 4 to 10 ppm during the 64 days of storage (Table 3). These three products (pickle and pimento loaf, souse loaf, and pickled hot sausage) were relatively low in initial nitrite levels and the high variability in all products indicates that the trends in residual

TABLE 2. INITIAL NITRITE AND NITRATE, RESIDUAL NITRITE, AND pH LEVELS OF SELECTED SAUSAGE PRODUCTS STORED FOR VARIOUS TIMES AT 5 C

Product	Type packaging ¹	NO ₂ ² added (ppm)	NO ₃ ² added (ppm)	Storage time (days)	Initial pH	Residual ³ NO ₂ (ppm)
Polish sausage	Overwrap film	128	139	0	5.90 ± .05	24 ± 2a
				5		22 ± 1a
				8		18 ± 0b
				15		16 ± 1c
Smoked sausage	Overwrap film	123	132	0	6.23 ± .02	30 ± 2a
				5		30 ± 2a
				8		26 ± 1b
				15		19 ± 2c
Salami, sliced	Vacuum film	126	136	0	6.81 ± .02	42 ± 10a
				10		12 ± 1b
				21		6 ± 1c
				30		6 ± 1c
Pickle and pimento loaf, sliced	Vacuum film	81	87	0	5.99 ± .01	9 ± 2a
				7		7 ± 1a
				14		8 ± 1a
				20		8 ± 1a
Bologna, sliced	Vacuum film	126	135	0	6.50 ± .02	20 ± 2a
				6		18 ± 1a
				12		17 ± 0a
				17		25 ± 3b
Spiced luncheon meat, sliced	Vacuum film	140	150	0	6.44 ± .18	39 ± 3a
				10		12 ± 1b
				21		11 ± 1b
				30		10 ± 2b
Souse loaf, unsliced	Overwrap film	83	89	0	4.24 ± .02	0
				10		13 ± 8b
				21		4 ± 2b
				30		7 ± 1b

¹Vacuum film (21 in. Hg) consisted of a non-forming web (saran coated mylar laminated to polyethylene and a forming web (saran coated polyvinyl chloride laminated to polyethylene). Overwrap film consisted of polyethylene.

²Initial NO₂ and NO₃ values were calculated from the weighed amounts of NaNO₂ and NaNO₃ added to the emulsions during processing.

³Mean and standard deviation of 4 determinations. Any two means for a specific product were significantly different at the 0.05 level, when not having the same letter suffix.

TABLE 3. INITIAL NITRITE AND NITRATE, RESIDUAL NITRITE, AND pH LEVELS OF BEEF STICK SAUSAGE STORED FOR VARIOUS TIMES AT 24 C

Product	Type packaging ¹	NO ₂ ² added (ppm)	NO ₃ ² added (ppm)	Storage time (days)	Initial pH	Residual ³ NO ₂ (ppm)
Pizza flavored beef stick (1 cm. dia.)	Non-vacuum film	125	135	0	5.00 ± .01	2 ± 1a
				30		10 ± 2b
				60		8 ± 0b
				88		15 ± 3c
Spice flavored beef stick (1 cm. dia.)	Non-vacuum film	101	109	0	4.54 ± .07	3 ± 1a
				30		5 ± 2ab
				60		7 ± 1b
				88		12 ± 1c
Chili flavored beef stick (1 cm. dia.)	Non-vacuum film	126	135	0	4.66 ± .11	3 ± 0a
				30		9 ± 2b
				60		10 ± 1b
				88		18 ± 1c
Salami flavored beef stick (1 cm. dia.)	Non-vacuum film	101	109	0	4.86 ± .01	4 ± 1a
				30		8 ± 1b
				60		10 ± 1b
				88		17 ± 3c
Beef jerky (1 cm. dia.)	Non-vacuum film	—	—	0	5.59 ± .01	4 ± 0a
				30		4 ± 1a
				60		11 ± 1b
				88		14 ± 1c
Pickled hot sausage	Bottled, glass jar	123	132	0	4.06 ± .04	5 ± 0a
				30		5 ± 1a
				64		10 ± 1b

¹Non-vacuum film was saran coated cellophane.

²Initial NO₂ and NO₃ values were calculated from the weighed amount of NaNO₂ and NaNO₃ added to the emulsions during processing.

³Mean and standard deviation of 4 determinations. Any two means for a specific product were significantly different at the 0.05 level, when not having the same letter suffix.

TABLE 4. EFFECT OF COOKING ON THE RESIDUAL NITRITE LEVEL OF SMOKED SAUSAGE, POLISH SAUSAGE, AND FRANKFURTERS AT 0 DAYS STORAGE (48 H AFTER PROCESSING)

Product	Before cooking, residual nitrite, (ppm) ¹	After cooking, residual nitrite, (ppm) ¹	Residual nitrite loss (%)
Smoked sausage	29 ± 2a	28 ± 2a	3.4
Polish sausage	24 ± 2a	16 ± 1b	25.0
Frankfurters			
All beef, 10/lb. (13.2 x 2.17 cm.)	27 ± 4a	22 ± 3a	18.5
All meat, 8/lb. (13.2 x 1.76 cm.)	33 ± 1a	27 ± 1b	15.0
All meat, 10/lb. (13.2 x 2.17 cm.)	39 ± 2a	23 ± 3b	41.0
All meat, 12/lb. (13.2 x 1.92 cm.)	42 ± 2a	30 ± 2b	28.6
All meat, 14/lb. (13.2 x 1.77 cm.)	25 ± 1a	19 ± 1b	24.0

¹Mean and standard deviation of 4 determinations. Any two means for a specific product were significantly different at the 0.05 level, when not having the same letter suffixes.

nitrite changes during storage may be of little consequence at low residual nitrite levels.

Without exception, all varieties of dried sausage products increased in residual nitrite content during the 88-day storage period (Table 3). The initial values for dried sausage and jerky were extremely low (2-4 ppm) and reached a final residual nitrite content of 12-18 ppm. Although the moisture level was not measured during storage, the moisture-proof film was sealed and it was not possible that these relatively dry (22% moisture) products could have lost sufficient moisture to cause the rate of increase observed. Olsman et al (11) reported that the rate constant for nitrite depletion was directly propor-

tional to the meat:water ratio based on studies of model systems; the greater the water content, the faster the depletion. It is possible that the meat:water ratio was the basis for an increase in residual nitrite in the dried products. However, further research is needed to establish the cause of the increase.

The highest residual nitrite value observed for any pre-packaged processed meat product was 42 ppm. All products (except bologna on storage day 17), that showed significant decreases in residual nitrite, had initial levels of 20 ppm or higher and were of relatively high pH (>5.9). With the exception of bologna and beef jerky samples, all samples which showed an increase in residual nitrite during storage

had initial nitrite levels of < 4 ppm and were relatively low in pH (< 5.0). The beef jerky had a pH of 5.59 but an initial residual nitrite level of 4 ppm. Even with these exceptions, the results suggest that low initial levels of nitrite and/or relatively low pH values and/or moisture levels are associated with an increase in residual nitrite during storage. Also, those products which increased in residual nitrite level during storage apparently developed conditions which favored conversion of nitrates to nitrites. The observed decreases in residual nitrite suggest that oxidation-reduction reactions occurred to convert the nitrite to nitrous oxide. The mechanism for these changes was not investigated in this study, and this indicates the need for further research on this problem.

Residual nitrite levels obtained by chemical analysis of the cooked frankfurters are in Table 4. The decrease in nitrite caused by cooking ranged from 3.4 to 41.0% and did not appear to be related to a common parameter such as emulsion type, product size, or quantity of nitrite added initially or present at the onset of the storage study.

ACKNOWLEDGMENT

The authors express their appreciation to Mr. Rodney Freeze for assistance with the analytical work of this investigation.

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