

CHANGES IN THE CONTENTS OF SULFHYDRYL GROUPS AND PROTEIN-
BOUND NITRITES IN RAW DRIED SAUSAGES

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Summary

Followed are the changes in the content of free sulfhydryl groups and protein-bound nitrite during the ripening of raw dried sausages, produced with different salting mixtures. At product pH of 5,0 - 5,9 and NaNO_2/SH molar ratio 1:2,5 and 1:5 only a negligible part of total SH groups bind nitrite. The contents of the free sulfhydryl groups and the protein-bound nitrite are significantly influenced by the composition of the salting mixture, but do not affect the nitrosopigment stability against oxidation.

MODIFICATIONS DANS LA TENEUR EN GROUPES SULFHYDRIQUES ET EN NITRITE,
LIÉ AUX PROTEINES, CHEZ LES SAUCISSONS SECS

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Résumé

On a observé les modifications en groupes sulfhydriques libres et en nitrite, lié aux protéines, lors du séchage des saucissons secs, préparés à l'aide de différents mélanges de salaison. A un pH du produit de 5,0 - 5,9 et à un rapport moléculaire NaNO_2/SH de 1:2,5 et de 1:5 il n'y avait qu'une partie insignifiante de groupes-SH disponibles qui liait du nitrite. La teneur en groupes sulfhydriques libres et en nitrite, lié aux protéines, était influencée considérablement par la composition du mélange de salaison, mais elle n'influait pas sur la stabilité du nitrosopigment à l'oxydation.

VERÄNDERUNGEN IM GEHALT AN SH-GRUPPEN UND AN MIT EIWISS VERBUNDENEM NITRIT IN ROHWÜRSTEN

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Zusammenfassung

Es wurden die Veränderungen im Gehalt an freien SH-Gruppen und an mit Eiweiss verbundenem Nitrit bei der Trocknung von mit verschiedenen Pökelmischungen vorbereiteten Rohwürsten beobachtet. Bei einem pH-Wert von 5,0-5,9 und NaNO_2/SH - Molverhältnis 1:2,5 und 1:5 wird Nitrit nur von einem unwesentlichen Teil der vorhandenen SH-Gruppen verbunden. Der Gehalt an freien SH-Gruppen und an mit Eiweiss verbundenem Nitrit wird wesentlich von der Zusammensetzung der Pökelmischung beeinflusst, aber er übt keinen Einfluss auf die Stabilität des Nitrosopigmentes gegen Oxydation aus.

ИЗМЕНЕНИЯ В СОДЕРЖАНИИ СУЛЬФИДРИЛЬНЫХ ГРУПП И СВЯЗАННОГО С БЕЛКОМ НИТРИТА В СЫРО-ВЯЛЕННЫХ КОЛБАСАХ

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Резюме

Рассмотрены изменения в содержании свободных сульфгидрильных групп и протеин-связанного нитрита при сушке сыро-вяленых колбас, приготовляемых с использованием различных солевых смесей. При pH продукта 5,0 - 5,9 и NaNO_2/SH мольном соотношении 1:2,5 и 1:5 только незначительная часть имеющихся в наличии SH - групп связана с нитритом. Содержание свободных сульфгидрильных групп и протеин-связанного нитрита зависят в значительной мере от состава солевых смесей, но не оказывает влияние на стабильность нитрозопигмента против окисления.

CHANGES IN THE CONTENTS OF SULFHYDRYL GROUPS AND PROTEIN-BOUND NITRITES IN RAW DRIED SAUSAGES

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In recent times it is believed, that the sulfhydryl groups in meat play a vital role in the formation of nitroso-myoglobin. Möhler /1974/ offers as a possible mechanism, the direct reduction of metmyoglobin-nitrite in nitrosomyoglobin by way of the protein SH groups as electron donors. The inhibition of this reaction however, is only partial with the use of alkylating reagents, even when they are in excess to the thiol groups. Olzman /1974/ believes, that the established degree of inhibition predisposes the presence of a small quantity of free SH groups, which act as an end electron donor in an electron transport chain, whose limiting stage is the ascorbate-dehydroascorbate redox system. Another possible mechanism is the offered by Mirna & Hofmann /1969/, that by a reaction of sulfhydryl groups and nitrite in meat are formed nitrosothiols as a form of "activated" nitrite, which facilitates the transport of nitric oxide on the myoglobin.

The possible participation of the sulfhydryl groups in the formation and stability of nitrosopigment directed us to follow their changes during the process of ripening of raw dried sausages, produced with different salting mixtures as well as the protein-bound nitrites.

Methods and Materials

1. The investigations were made on "Panagiurska Loukanka" a type of dry sausage, whose recipe and technology were described previously by Nestorov et al. /1975/. The following salting mixtures were used:

- Test A: 400 mg/kg potassium nitrate
- Test B: 250 mg/kg potassium nitrate + 120 mg/kg sodium nitrite
- Test C: 120 mg/kg sodium nitrite
- Test D: 120 mg/kg sodium nitrite + 500 mg/kg sodium isoascorbate

2. The total content of sulfhydryl groups was established after the method of Sedlak /1968/ with the exception, that after the addition of the absolute methanol the investigated suspension was immediately filtered and the filtrate was measured at 412 nm. The measurement of the quantity of protein bound nitrite was made after the modified by Olzman & Krol /1972/ method "b" of Mirna /1970/. The results were calculated on the bases of 100 g dry matter. The protein content was 32-33% in the dry matter.

Results and Discussion

The changes in the content of sulfhydryl groups in the different tests is presented on Fig. 1. After a decrease during the first three days is observed a tendency for rising towards the tenth day with its maximum. Later the quantity of the sulfhydryl groups decreases faster with minimal quantities in the ready product of tests A and B to two times lower than same of tests C and D.

The quantity of protein-bound nitrite increases significantly during the first three to six days of drying, with maximal values for tests A and B established two to three days later than the other test groups. On the 13-14th day the concentration of the bound nitrite is at its minimum for all four tests, the absolute value in the samples produced with the addition of nitrate is twice as big from the tests where for the salting was used only nitrite. In the ready product the nitric oxide containing SH groups are 1,6-1,8% and 0,5-0,6% from the established total SH groups, respectively.

Depending on the quantity of the added nitrite and/or nitrate, the protein-bound nitrite /excluding the nitroso-myoglobin/ is 5-10% during the first period of drying and decreases to 2,0-2,3% in the ready product /Tabel 1/. These data confirm the values established by Mirna /1970/ for "Rest-NO" in raw dried sausages after a five days period of ripening, as well as the differences in the protein-bound nitrite content depending on the type of salting mixture.

In our earlier work /Nestorov et al., 1975/ we demonstrated, that of highest importance for colour formation in the Loukanka sausage are the first 7-8 days from the beginning of drying. During this period is observed a fast decrease of free nitrites and an intensive formation of nitrosomyoglobin. The established maximum content of protein-bound nitrite during the period, makes possible the supposition for its participation in the process of colour formation in the Loukanka sausage, inspite of the fact, that in the present study there are no direct proofs for this.

The obtained results show, that only a negligible part /0,3-2,6%/ of the present SH groups bind nitrite under the conditions of the experiment /pH 5,0-5,9 and NaNO₂/SH molar ratio 1:2.5 in tests A and B, and 1:5 in tests C and D/. Maximal contents of the thiol groups, established towards the 10th day of ripening, as well as the observed decrease in the concentration of same during the following period, could hardly be explained only by their interaction with nitrite /Krilova, 1966/. These changes most probably are due to the denaturation of the proteins during drying and the following oxidation of the sulfhydryl groups.

G1:4

The reduction capacity of the SH-containing compounds present in excess in the product during the period of drying, can not protect the nitrosopigment from oxidation, which at least in a negligible degree occurs after the 10th day /Nestorov et al. 1975/. At the same time we could not established whether there is a correlation between the stability of the pigment /after illuminating of a fresh cut with a standart light/ from the concentration of the SH groups and from the quantity of protein-bound nitrite. Most probably the sulfhydryl groups containing compounds and their interaction with nitrite play an important role only in the first period of the formation of nitrosopigment and the reduction of the nitrites.

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Fig.1 ○—○ Test A x—x Test B
 ○—○ Test C x—x Test D

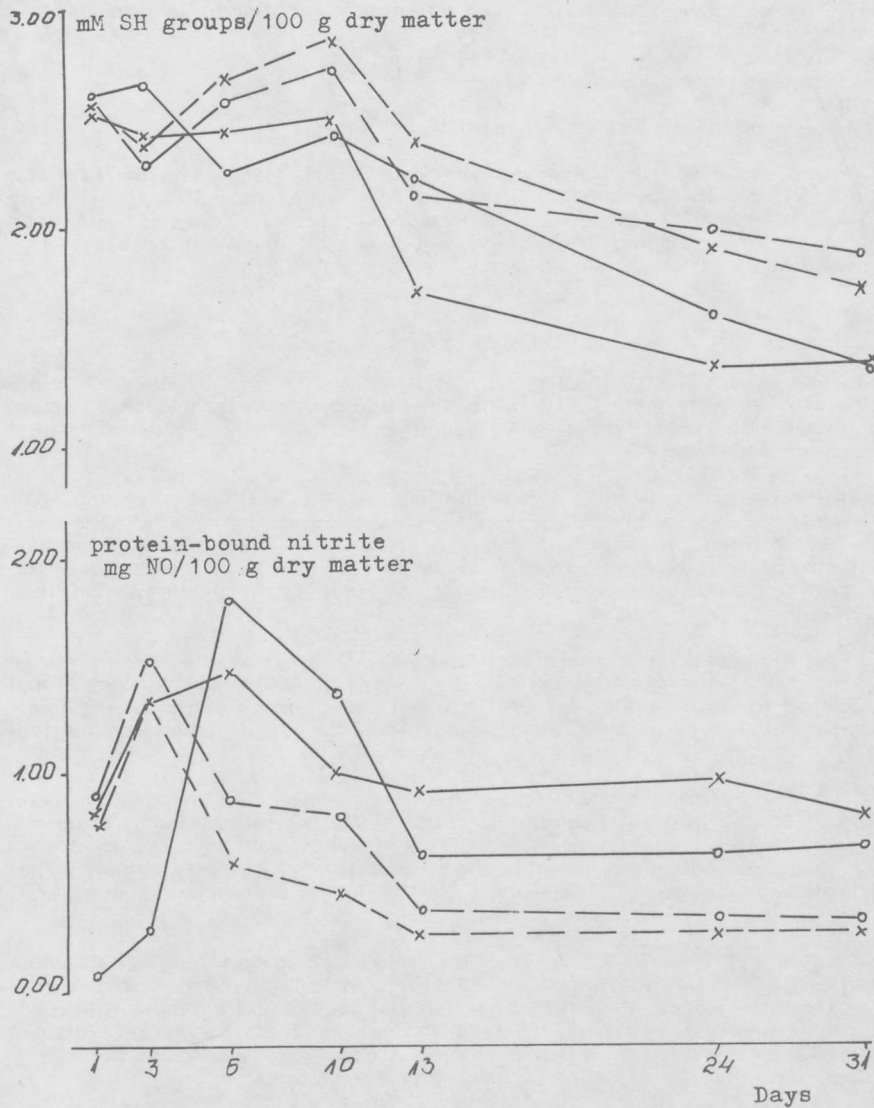


Table 1.

Test	Added nitrate and/or nitrite mg NO/100 g dry matter	Day	Protein-bound nitrite	
			% of the added nitrite	% of the total SH groups
A	31,6	3rd	0,85	0,34
		6th	5,69	2,67
		13th	1,90	0,90
		24th	1,90	1,26
		31st	2,09	1,68
B	34,9	3rd	3,78	1,81
		6th	4,21	2,03
		13th	2,58	1,75
		24th	2,75	2,22
		31st	2,15	1,82
C	13,4	3rd	11,46	2,25
		6th	6,52	1,11
		13th	2,70	0,56
		24th	2,47	0,71
		31st	2,32	0,57
D	13,4	3rd	9,89	1,83
		6th	4,27	0,70
		13th	1,87	0,35
		24th	1,87	0,44
		31st	1,87	0,44