

# BILDUNG UND STABILITÄT DES NITROSOPIGMENTES BEI ROHWÜRSTEN IN ABHÄNGIGKEIT VON DER ZUSAMMENSETZUNG DER PÖKELMISCHUNGEN

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## Zusammenfassung

Es wurden die Veränderungen des pH und der Menge des Nitroso-Pigmentes, sowie der Gesamtreduktionsaktivität und des Nitrit- und Nitratgehaltes von "Panagürska Lukanka" während des vollständigen technologischen Prozesses verfolgt.

Die Ergebnisse erlauben uns zu behaupten, dass durch die gemischte oder reine Nitritpökung ein Standardprodukt mit einem erheblich niedrigeren Restnitritgehalt erzeugt werden kann.

Die Beseitigung des einzigen Nachteils - nämlich der gesenkten Stabilität der Farbe - sollte man durch Zugaben von farbstoffstabilisierenden Mitteln erreichen.

# FORMATION ET STABILITE DU NITROSOPIGMENT DANS LES SAUCISSONS SECS EN FONCTION DE LA COMPOSITION DES MELANGES DE SALAISSON

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## Résumé

On a étudié les modifications du pH, de la quantité du nitrosopigment, de l'activité totale de réduction, ainsi que les changements dans les quantités du nitrite et du nitrate de la "Loukanka Panagurska" pendant le procès technique. On a déterminé de même la stabilité de la couleur du produit fini.

Les résultats obtenus nous permettent de déduire qu'avec la salaison au nitrite ou la salaison au nitrite-nitrate, on peut obtenir un produit standard contenant une quantité beaucoup plus faible de nitrites résiduels. L'élimination de l'unique inconvénient - la stabilité diminuée de la couleur, peut être évitée par l'adjonction des agents stabilisant la couleur.

# FORMATION AND STABILITY OF NITROSOPIGMENTS IN RAW-DRIED SAUSAGES DEPENDENT ON THE COMPOSITION OF THE SALTING MIXTURES

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## Summary

The changes in pH, quantity of nitrosopigment, total reduction activity, changes in nitrite and nitrate contents, were followed for the dry sausage "Panagiurska loukanka" during the whole technological process. The colour stability of the ready product was established as well.

The obtained results permit us the assessment, that mixed or purely nitrite salting could produce a standard product with considerably lower content of nitrites. The only disadvantage - lower colour stability, should be corrected by addition of colour stabilizing agents.

# ОБРАЗОВАНИЕ И СТАБИЛЬНОСТЬ НИТРОЗОПИГМЕНТА В СЫРОВЯЛЕННЫХ КОЛБАСАХ В ЗАВИСИМОСТИ ОТ СОСТАВА ПОСОЛОЧНОЙ СМЕСИ

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## Аннотация

Во время полного технологического процесса наблюдались изменения pH, количества нитрозопигмента, общей окислительно-восстановительной активности, содержания нитрита и нитрата в "Панагурской луканке". Определена и стабильность окраски готового продукта.

Полученные результаты позволяют сделать вывод, что при использовании посолочной смеси или чистого нитрита можно получить стандартный продукт с более низким содержанием остаточного нитрита. Устранение единственного недостатка - заниженной стабильности окраски - следует искать путем добавления веществ, стабилизирующих окраску продукта.

## FORMATION AND STABILITY OF NITROSOPIGMENTS IN RAW-DRIED SAUSAGES

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The use of nitrate in the formation of the characteristic colour of salted meat products has a century old history, but only at the end of last century, it was established that in reality the nitrite is the active substance. During the processing, the added nitrite and/or nitrate, are quickly transformed in compounds which act on the formation of colour and specific flavour of salted meat (Walters 1971, Wasserman and Talley 1972). Established is also the role of nitrite as a strong inhibitor of botulineforming pathogenic microorganisms (Ingram 1971).

The revision during the last years of legislature limiting nitrite use became imperative, after it was proved that the increase of free nitrite leads to a higher formation of *N*-nitrosamines having a cancerogenous action (Fiddler 1972). In spite of the fact that the opposite resolution (lower values for nitrite is a guideline, that there are no *N*-nitrosamines) has not been proved experimentally and is not sure, there should always exist precautions for nitrite to be minimized as far as possible. Very clear is the need for a revision of the nitrite use in all meat products, and alternatively following steps for measures limiting the quantities of used and remaining nitrites.

In the Bulgarian raw-dried sausage "Loukanka" in all its varieties, at present is used 100 mg/kg of Potassium nitrate, as a result of which, in the ready product are discovered from 70-240 mg/kg nitrite and 140-430 mg/kg nitrate (Dilova et al 1975). The present investigation has for object the study of the degree of reduction of these quantities nitrites added during the production of loukanka without changes in the quality of the ready product.

## Methods and Materials

1. The tests were made with the raw-dried sausage "Panagiurska Loukanka", the filling patty for which has the following formulation :

Beef of unified quality	60 kg
Pig red meat	20 kg
Fat	20 kg

NaCl	2.2 kg
Sugar	0.1 kg
Spices	0.7 kg

Along with the spices in the patty, for all varieties was added a starter culture from Strain P<sub>4</sub>. After filling the sausages were put into a chamber at a temperature of 13 - 15°C and a relative humidity of 75 - 82%. The air movement was maintained to 0.5 m/sec for the first two days, and to 0.05 - 0.1 m/sec for the rest of the period. Drying was completed at the 28 - 30 day.

The following salting mixtures were tested :

Alternative A : 1000 mg/kg of Potassium nitrate

Alternative B : 250 mg/kg of Potassium nitrate + Sodium isoascorbinate

Alternative C : 80 mg/kg Sodium nitrite

Alternative D : 80 mg/kg of Sodium nitrite + 500 mg/kg Sodium isoascorbinate

The sodium isoascorbinate was produced by Fizer.

2. The nitrites and nitrates in the investigated samples of sausages, were determined after the method of Grau and Mirna modified by Möhler (1964). The nitrosomyoglobine was determined after the method of Hornsley (1956) with a threefold extraction of the individual sample. Stability of colour we determined by the change in percentage of the nitrosopigment after 30 minutes of illumination from a distance of 25 cm with a fluorescent lamp (intensity 200 Chandelles). The reducing activity was determined after the method of Ando and Nogata (1970).

## Results and Discussion

Data for the changes of the mean data values of the investigated indexes during the drying of the product are expressed graphically on fig.1. The changes in the pH follow the pattern determined in our previous investigations (N.Dilova et al 1975) - a rapid decrease on the 4 - 5 day, decrease or stabilization to a permanent value, on the 10 - 12 day, followed by a well expressed, but slow increase of pH, to attain a value of 5.75 - 6.15 in the ready product.

The fast change of acidity in the patty of the loukanka sausages during the first days, determines the intensity of the process of splitting of the nitrites and the formation of the nitrosopigment.

We have established differences in the content of nitrosomyoglobine on the fourth day between the samples prepared with the different salting mixtures. To this moment the reduction of the nitrate in the samples from Alternative A, is effected to a satisfactory degree to ensure a good reddening of the product. During the period of the first 4 - 8 days, are encountered the highest values of nitrosopigment for the whole period of drying. The intensive process of nitrosomyoglobine formation is in conformity with an increased reduction activity (with the exception of altern.A) and is well influenced by the low pH value of the medium. After this maximum a tendency is observed for its percent reduction in the product, but very slowly and insignificant in value.

The free nitrites in the samples of altern.B, C, and D, decrease during the whole period of drying, while in the A altern. we observed a quick increase during the first 4 days, followed by a period of a lengthy but slight decrease. At the same time, the quantity of the added and formed nitrates (Möhler 1973) decreases, but with a variable speed.

Having in mind the lack of substantial differences in the content of nitrosomyoglobine between the different alternatives in our experiment, it is natural to inquire about the fate of the added during the salting, nitrates and nitrites. Data from table 1 represent what part of them is used for the formation of the brined red colour of the ready product. In connection with the formulation and quantity of the salting mixture, the part of it, which is bound with the pigments in the meat is from 2 to 15%. During the first days of the technological process, from 30 to 50% of the added nitrates and/or nitrites are discovered as nitrate, which relative part during the following weeks, decrease to 5 - 13%. The part of free nitrites, also decreases 2 - 4 times during the drying of the product.

What is the fate of the rest of the added nitrates and/or nitrites - to this moment and for this question, the experimental work which we have made, does not give an answer. After Mirna (1970), during the first five days of the ripening for the raw-dried sausage, about 15% of the added nitrite is bound with the proteins. As the sulfhydryl groups increase (as a result of protein denaturation during the drying process), and their interaction with nitrites, could

be explained the existing decrease of free nitrites in the filling patty. This supposition is confirmed by the results obtained lately in our laboratory (unpublished data).

For the influence of the salting mixture on the stability of colour of the ready product, we have an impression from the decrease of the percentage of nitrosopigment, following the standard illumination :

Altern.A	Altern.B	Altern.C	Altern.D
-40%	-48%	-58%	-30%

Our data confirm the findings of Wirth (1973), that with long storage of sausages, the use of nitrate ensures a more stable color in comparison to nitrite salting. In spite of this, it is clear that the advantage of the salting mixtures with nitrites is bigger along with the low content of free nitrites, which in turn ensures a stable red colour to the product. The lack of differences in the microflora of the samples from product produced after the different salting mixtures (Djevov et al, unpublished data) confirm the possibility for the change of nitrates with nitrite in the salting mixtures for loukanka type sausages.

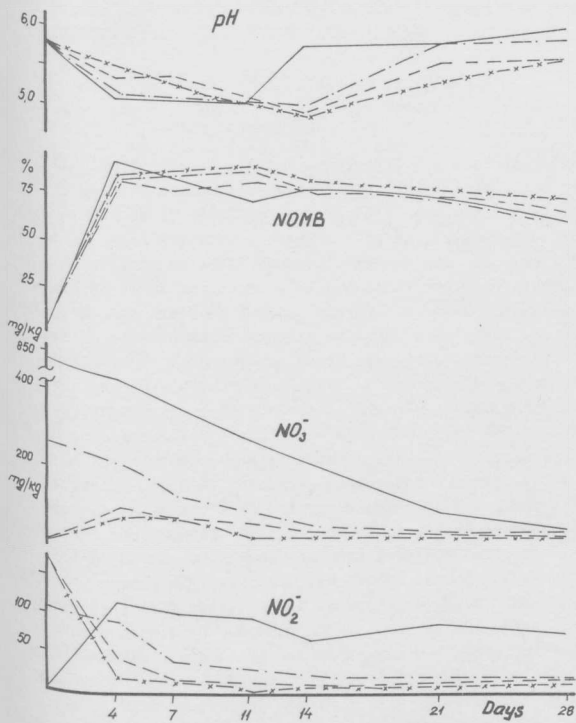


Figure 1

Change in pH value, nitrosomyoglobin, nitrates and nitrites in "Panagiurska Loukanka" during ripening. Data for NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> are evaluated as NO to dry matter. Altern.A(—), Altern.B(- - -), Altern.C(- · - · -), and Altern.D(- x -)

Table 1  
Balance of Nitrites, Nitrates and Nitrosomyoglobin (in mg NO/kg dry matter) during the ripening of "Panagiurska Loukanka"

Alternative	Added quantity nitrate and/or nitrite	Day	Free nitrate	Free nitrite	Nitroso myoglobin	Total
A	844 - 100%	4th	469-55.5%	101-11.9%	20.8-2.5%	590-69.9%
		10th	194-22.9%	84- 9.9%	17.7-2.2%	269-35.3%
		20th	70- 8.3%	78- 9.3%	14.4-1.7%	163-18.4%
		30th	47- 5.6%	63-7.5%	13.8-1.6%	124-13.8%
B	311 - 100%	4th	190-61.3%	78-25.2%	17.4-5.6%	288-92.1%
		10th	76-24.6%	27- 8.7%	18.0-5.9%	121-39.0%
		20th	26- 8.3%	15- 4.9%	12.7-4.1%	54-17.3%
		30th	25- 8.2%	14- 4.5%	10.6-3.4%	50-16.0%
C	149 - 100%	4th	70-47.4%	41-27.4%	17.1-11.5%	128-86.1%
		10th	46-30.7%	9- 5.8%	18.8-12.6%	73-49.1%
		20th	24-16.0%	10- 7.0%	14.1- 9.5%	49-32.6%
		30th	18-12.3%	10- 7.0%	10.1- 7.0%	39-26.0%
D	149 - 100%	4th	49-32.6%	12- 7.9%	19.3-13.0%	80-53.4%
		10th	26-17.7%	4- 2.9%	23.6-15.8%	59-39.4%
		20th	21-14.2%	8- 5.2%	16.7-11.2%	46-30.6%
		30th	14- 9.4%	7- 4.7%	14.6- 9.8%	36-23.9%

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