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THE INCIDENCE OF NITROSAMINES IN SOME MEAT PRODUCTS

Oșvat I. M.*, Camelia Bara*, Bara L.*, Bura Giani*

*University of Oradea, Faculty of Environmental Protection, Gen.Magheru st., no.26, 410048, Oradea, e-mail: <u>osvatm_bali@yahoo.com</u>

Abstract

In the present study there was examined the incidence of nitrosamines in Sibiu salami and Banat salami in cheese and smoked cheese in order to broaden the scope of knowledge concerning the tolerated doses of nitrosamines in foods consumed by humans and carcinogenic action explained by several mechanisms. Analyses were conducted during 2007 - 2011 on 6 samples of meat products – Sibiu salami and Banat salami, 6 samples of cheese and cottage cheese, time to analyze the presence of nitrosamines such as NDMA, NDEA, NPYR.

Key words: nitrates, nitrites, nitrosamines, meat products

INTRODUCTION

Nitrates, nitrites and nitrosamines are toxic products that contaminate or are formed in food products. Nitrosamines are the subject of numerous investigations, especially in food toxicology. In the specialty literature no reports of carcinogenic nitrosamine compounds in a wide range of food products are reported: meat products processed with nitrates and nitrites, cheese, some plant products, but also in animal and human body (BARNEA M., and col. 1979).

The occurrence of nitrosamines in food products of animal origin can be observed when some basic conditions are met. Nitrosamines are formed from secondary, tertiary and quaternary amines. So far there have been over 100 nitrosamines recorded, but in food, due to technological processes, there are mainly formed volatile nitrosamines, such as:

- N-dimethylnitrosamine(DMNA)
- N-diethylnitrosamine(DENA)
- N-dipropylnitrosamine(DPNA)
- N-dibutylnitrosamine (DBNA)

The precursors of nitrosamines are nitrates, nitrites and amines. Nitrates and nitrites enter the body with water, vegetables, fruits and meat preparations. Amines can be formed in food containing proteins, acids and phospholipids. A significant amount of secondary and tertiary amines that are interesting in the formation of nitrosamines are found in fish products (trimethylamine).

Intestinal microflora in the presence of nitrites has an important role in the process of nitrosating amines.

MATERIALS AND METHODS

Volatile nitrosamines (NDMA, NDEA, NPYR) were determined in 6 samples of meat products (Sibiu salami, Banat salami) and 6 samples of cheese (smoked cheese and cottage cheese).

For the determination of nitrosamines in the products mentioned there was imposed:

- Sample preparation by fine grinding;
- Preparation of samples for extraction, of the reagents for the equipment and the installations;
- Extraction of NA from samples in the solid phase;
- Execution of samples of chromatographic use;
- Sample purification by solid extraction;
- Confirmation or results by mass spectrometry;
- As reagents and materials there have been used:
- Dichloromethane, pentane, hexane, ethyl ether, ascorbic acid, ethyl alcohol reagents for analysis;
- paraffin oil, carborundum balls necessary for uniform boiling, carbon dioxide (compressed gas); filter cartridges with 3 ml volume, silica gel (0,200g), Chromabond HR-P (Macherey-Nagel Gmbh, Germany);
- Perfectly clean laboratory glassware usual: round-bottomed glass flasks of 250 ml and capture section with side lengthening for coupling to the vacuum pump, Dewar vessel for cooling cylinders, tubes, evaporator Heidolph for concentration of a Hamilton syringe of 1 and 10 micro liters;
- Samples of cromatographic use: dimetilnitozamina (NDMA), CAS no. 62-75-9; dietilnitrozamina (NDEA) CAS no 55-18-5; nitrozopirolidina (NPYR) CAS no. 930-55-2 (Sigma-Ajdrich Fine Chemicals).

As equipments for the processing, extraction and determining of the three volatile nitrosamines, there have been used:

- Plants for vacuum distilation of the samples;
- Vacuum pumps;

- gazcromatograf of high resoltuion - CARLO ERBA – Mega series, with specific NPD detector (detector for nitrogen and phophorus), capillary

column AGILENT DB – 5ms, length 30 m, interior diameter of 0,25 mm, film of 0,5 microns, gas carrier of Hydrogen, flow 1,8 ml/minute, detector temperature 265° C, with a temperature programme at the site of: 100°C, for 4 minutees at the inferior isotherm, 220° C at the high isotherm, for 4 minutes, warming speed of 20°C/minute;

- gaschromatography of high resolution FISSONS, detector MSD (mass spectrometry), the same type of column, temperature conditions, carrier gas – helium, flow of 1,8 ml/minute, transfer line 275°C, according to the data NI ST;



Gazcromatograf

- installation to prepair the samples by extracting in solid phase (SPE) with 12 places for the 12 SPE cartridges.

The determination of nitrosamines supported in the first phase their extraction from the samples.

For the extraction 50 g from the sample of analyzed, shredded product, passed through a fine site were introduced into a glass flask of 250 ml, that were dispersed in 75 ml of paraffin oil with 250 mg of ascorbic acid and 10-15 ml of distilled water. To the ascorbic acid there was added inhibitor of nitrosating reaction, and bidistilled water to assure a greater humidity of the analyzed product.

The glass flask thus prepared was coupled to a common air condenser. For condensation of volatile nitrosamines residues, the balloon was connected to a vacuum (1mmHg) in another flask and the flask was maintained at given temperatures in the Dewar vessel at temperatures given by carbonic snow mixed with ethylic alcohol to uniformization the cooled environment.

Cooling can be achieved with liquid nitrogen. Heating was provided by an electric water bath, and the distillation process was carried out for about an hour after the start of boiling. To ensure uniformity of boiling there were introduced a few carborundum balls and firebrick in their absence, into the extraction vessel.

After the distillation was considered as finished, the content of the flask of 50 ml, that represents the distillation with NA residues, has been subjected to a thawing process at the ordinary laboratory temperature (room temperature). After thawing, over this content there is added 5 ml of aqueous hydrochloric acid solution (1 ml of concentrated HCI + 9 ml of bi-distilled H_2O).

The environmental acidification took into acount the blocking of amines considered possibbly involved with NA. After the acidification, the content of the flask was extracted in three phases with 30 ml of dichloromethan.

All the three extracts were united and then concentrated in the evaporator Heidolph installation at a volume of 0,5 ml.

RESULTS AND DISCUSSIONS

The obtained results are presented in Table 1.

Table 1.

NDEA NPYR Produse Nr.probe NDMA micrograme/kg Micrograme/kg micrograme/kg Valori Valori Media Valori Media Media 3 0,08 0,100 0,03 0,04 0 Banat 0 Salami 0,120 0,05 0.04 0.1 Sibiu 3 0,07 0.113 0,07 0.085 0 0 Salami 0,140 0,10 0,09 0,13 3 0.015 0.03 Feta 0,02 0.03 0,01 0.04 0,02 0,05 cheese 0,04 0,03 0,02 0,04 3 0.085 0.049 0,015 Smoked 0,06 0,034 0,01 cheese 0,110 0,065 0,02 0,05 0.09 0,02

Mean content of NDMA, NDEA, NPYR in some meat and milk products

At the Banat salami and Sibiu salami there has been evidenced the presence of NDMA and NDEA; NPYR was absent. NDMA, at the Banat salami has been evidenced with $0,10 \mu g/kg$, and at the Sibiu salami of 0,113

 μ g/kg. NDEA at the Banat salami is evidenced in an average quantity of 0,04 μ g/kg, and at the Sibiu salami in an average quantity of 0,085 μ g/kg.

At the cheese samples there are evidenced all the three categories of nitrosamines (NDMA, NDEA, NPYR).

At the cottage cheese NDMA has an average value of 0,03 μ g/kg;; NDEA 0,015 μ g/kg; NPYR 0,04 μ g/kg, and at the smoked cheese NDMA is of 0,085 μ g/kg; NDEA 0,049 μ g/kg, NPYR 0,015 μ g/kg.

In all cases the maximum admitted value for nitrosamines has not been exceeded. (NA).

CONCLUSIONS

1. The analysis of nitrates in the water used for obtaining minced meat paste has values of 2,3 - 24,5 mg %. The average annual concentration of nitrites varies between 7,70-14,10 mg%, and the average value for the whole period is of 9,76 mg %.

The analysis of primary data evidenced the fact that 90% of the samples had a content of 10 mg % of nitrates. The maximum admitted limit at water is of 50 mg nitrates/l of water.

2. The avergae values of nitites in th study area is generally between the values admitted by the norms. Only a proportion of 2% of the samples there have been noticed maximum values 1,3 - 1,7 times greater that the values admitted by the norms concerning the sorts of salami, Parizian, Frankfurter, pastrami, that indicates the fact that manufacturers do not always work with procedures that eliminate this risk. There have been evidenced nitrites also in fresh meat products (mosaic salami), where the use of nitrites is forbidden.

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