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THE USE OF QUALITATIVE AND QUANTITATIVE METHODS IN ANALYTICAL CHEMISTRY TO DETERMINE THE CONTENT OF NITRATES IN COOKED MEATS

Nitrates are present almost in every food product but their amount should not exceed the limiting concentrations. Complex toxicological and hygienic studies have established acceptable daily dose intake of NO^3: 320 mg or 4 - 5 mg per 1 kg of body weight.

An excess of levels in the human body can adversely affect health. In digestive tract the nitrates transform partially into more toxic nitrites causing toxic effect. The nitrites in blood can cause methemoglobinemia, as well as hypoxia (tissue oxygen starvation) which develops due to the disturbed transportation of oxygen in blood. Products boiling and broth draining can reduce nitrate levels. Soaking of products slightly affects the nitrate content. It is useful to eat products rich with vitamin C, as far as it reduces the nitrate content in food.

There are several methods of quantitative analysis to determine the nitrate content:

- Photometric methods are based on the conversion of nitrate to nitrite, followed by the formation of colored solutions. The intensity of the red color of solutions containing nitrites is measured with photoelectric-color measurement device at a wavelength of 538 nm;
- Chromatographic methods (the method of gas chromatography, gas-liquid and ion chromatography). The method is based on different sorption of anions by adsorbent;
- Electrochemical methods: voltammetric methods are based on the detection of current-voltage curves (voltammogram); potentiometric methods provides application of ion selective electrodes (based on determining the relationship between the balanced electrode potential and thermodynamic activity of ions involved in electrochemical reactions);
- Special devices, such as nitrate-tester SOEKS NUC-019-1 is used for assessment (rapid test) of quantitative nitrate content in products.

For qualitative and quantitative determination of nitrate content in cooked meats, it is necessary to draw extract from samples for their further analysis. A preliminary study is conducted for this purpose. After the shell is removed, samples are crushed twice in a meat grinder with lattice holes (diameter of 3 to 4 mm). Samples are extracted with water and received solutions are with precipitated proteins. The next step is the filtration of our solutions. The analysis of the filtrate should be conducted not later than 24 h after sampling. Samples of raw products are immediately analyzed after grinding. The qualitative determination of nitrate is conducted using fractional technique with the help of following qualitative reactions.

1. The reaction with copper and sulfuric acid. A concentrated sulfuric acid and a copper metallic piece are added to a nitrate solution. The content of the test tube is heated. The emission of brown gas (NO_2) indicates the presence of nitrate in the reaction.

$$2NO_3^- + 8H^+ + 3Cu = 3Cu^{++} + 4H_2O + 2NO$$

$$2NO + O_2\ (air) = 2NO_2\uparrow$$

2. The reaction with iron (II) sulfate. A small amount of a nitrate test solution is continuously stirred and added to a solution of $FeSO_4$. Then, the concentrated H_2SO_4 is gently added into the tube, flowing down the walls so that the liquid could not mix at once. A brown ring appears on the verge of layers of H_2SO_4 and $FeSO_4$ solution. The reaction of NO with $FeSO_4$ gives weak complex relationship forming a brown compound [Fe (NO)] SO_4.

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

3. Nitrate reduction to ammonia when interacting with metallic zinc in the presence of alkali. A concentrated solution of alkali and a small amount of zinc dust are added to test tube with solution. The tube is closed (not too tightly) with a cotton wad (a thickness of about 1 cm) to avoid alkali splashing. A wet piece of phenolphthalein indicator or litmus paper is placed above the wad. In these conditions NO_3 ion is reduced to NH_3 which, in its turn, causes redness of phenolphthalein indicator or changes the color of litmus paper into blue.

The reaction is given in the equation:

$$NaNO_3 + 4Zn + 7NaOH = NH_3\uparrow + 4Na_2ZnO_2 + 2H_2O$$

4. The reaction with manganese (II) chloride ($MnCl_2$). Heated nitrate test solution with dual volume of saturated $MnCl_2$solution in concentrated HCl becomes dark brown, due to the formation of complex ions $[MnCl_6]^{2-}$:

$$3MnCl_2 + 12HCl + 2HNO_3 = 3H_2[MnCl_6] + 3H_2O + 2NO\uparrow$$

5. Reduction of NO_3- to NO_2-. The action of metallic zinc in the presence of acetic acid:

$$NO_3^- + Zn + 2CH_3COOH = NO_2^- + Zn^{2+} + 2CH_3COO^- + H_2O$$

6. MICROCRYSTALOSCOPIC reaction. The drop of the nitrate test solution is added with a drop of 10% solution of organic base "Nitron" ($C_{20}H_{16}N_4$) in 5% acetic acid. Sediment of a special cluster of needles of sour-nitrogen "Nitron" $C_{20}H_{16}N_4 \cdot HNO_3$ is formed.

7. The reaction of diphenylamine. 5 - 6 drops of diphenylamine in concentrated H_2SO_4 are placed on thoroughly washed and dried laboratory glass. Nitrate test solution is added with the a clean glass rod and stirred with the diphenylamine compound. Due to the oxidation of diphenylamine by nitric acid and in the presence of NO_3- an intensive blue color appears.

Recently, for the qualitative determination of nitrate content in foodstuffs the indicator paper "Indam" is used. It displays different colors depending on the content of nitrates in samples. Its colors are similar to those which are formed in the reaction of diphenylamine. By the attached indicator scale we can set approximate quantity of nitrate in samples. Thus, the indicator paper "Indam" can be used in practice for rapid assessment of nitrate content in samples. For examination of the nitrates concentration in samples of sausage products reaction with diphenylamine was used. Sensitivity of the

reaction is 0,001 mg per 1 ml. Nitrate content was determined comparing the color of the test solution extracts with a standard scale. The results are presented in the table. There were selected 4 different sausages of Ukrainian producers for our assessment: "Salami" - the manufacturer of LLC "Barcom" ("Rodynni kovbasky"), "Likarska" - TD "Myasna gilidiia", "Likarska" - factory of "Singurivski kovbasy" and "Zolote telia "- TD "Myasna gildiia".

Table

The results of the assessment of nitrates content in sausage products

Results of the laboratory research				Standard scale	
Trade mark	Kind of sausage	Solution color	Nitrates concentration	Solution color	Nitrates concentration
LLC "Barcom"	«Salami»	Light - blue	> 0,001 mg/dm^3	Light – blue	> 0,001 mg/dm^3
TD " Myasna gilidiia "	«Likarska», «Zolote telia»	Light – blue	> 0,001 mg/dm^3	Blue	> 1 mg/dm^3
"Singurivski kovbasy" factory	«Likarska»	Light – blue	> 0,001 mg/dm^3	Blue	>100 mg/dm^3

The table shows, that nitrate content in selected samples of domestically produced sausages is less than 1 mg / dm^3. This result corresponds to the normative values which are regulated by GOST 8558.2 - 78 "Meat products and a method of determining nitrate ". Taking into consideration the properties of nitrates and their possibility to participate in the synthesis of carcinogenic nitrosamines, the amount of nitrate in the products is strictly limited. Considering the potential danger of nitrate and complexity of regulation of nitrosopigments formation reactions, the use of salts of nitric acid in pickling meat (forcemeat) is currently not allowed. At the same time, the probability of converting nitrite to nitrate is not excluded; it causes the need to control salt content of nitric acid in meat products. Thus, for rapid assessment of nitrate levels in sausages, except the indicator paper "Indam", a high-quality reaction with diphenylamine, which is quite sensitive and effective, can be applied.