

Nitrites

10.1

Synonyms

German: Nitrite. *French:* Nitrites. *Italian:* Nitriti. *Spanish:* Nitritos. *Russian:* Нитриты.

10.2

History

Nitrates were used in food preservation for centuries (Binkerd and Kolari 1975) before it was eventually realized in 1899 that basically the active agent is not nitrate but the nitrite formed microbiologically from it (Kisskalt 1899). Because the conversion of nitrate to nitrite is a largely uncontrolled process, there has since been increasing preference for the direct use of nitrite. Initially nitrite was used alone but in most countries is now employed only in admixture with common salt in fixed and often legally stipulated ratios. In view of the toxicological properties of the nitrosamines formed under certain conditions by nitrite and those of the nitrite itself, the continued use of nitrites in food preservation is now undergoing critical examination (Walker 1990).

10.8

Regulatory Status

Nitrites (E 249 - E 250) are permitted in a number of countries for curing fish products.

In virtually all countries nitrites are permitted as curing agents and preservatives for meat products. Owing to the toxicity of pure nitrite, a number of countries permit the use of nitrite only in admixture with common salt; in the Federal Republic of Germany only nitrite curing salt may be employed in the manufacture of meat and sausage products. Nitrite curing salt is a mixture of sodium nitrite and common salt which contains at most 0.5% and at least 0.4% sodium nitrite.

10.9

Antimicrobial Action

10.9.1

General Criteria of Action

The antimicrobial action of nitrites is based on the nitrous acid they release and the oxides of nitrogen produced from the nitrous acid. These attach to the amino groups of the dehydrogenase system of the microorganism cell and thus cause an inhibitory action (Quastel and Woolridge 1927). Nitrites also have a specific inhibitory action on bacterial enzymes, which catalyze glucose degradation (Woods et al. 1981, Woods and Wood 1982). There are other points of attack for the nitrite in the bacterial metabolism through which the inhibition of growth can be explained, e.g. reactions with hemoprotein, such as cytochromes and SH enzymes (Castellani and Niven 1955, Roberts et al. 1990).

The action of nitrites increases with a falling pH value, in other words with the acid content of the medium. Whilst 4000 ppm nitrite are required to inhibit *Staphylococcus aureus* at pH 6.9, this minimum inhibitory concentration falls to 400 ppm at pH 5.8 and to 80 ppm at pH 5.05 (Castellani and Niven 1955). An addition of acidulants, glucono delta lactone or inoculation with acid-forming lactobacilli will therefore have a beneficial effect on the action of nitrite.

The nitrite concentrations of 80–160 mg/kg, which are usual in meat technology, are not adequate in the culture medium test to inhibit bacteria reliably. Apparently, an adequate action for practical conditions is obtained only by the combination of nitrite with common salt (Baird-Parker and Baillie 1973), an a_w value reduced by this and other factors, a sufficiently low pH value, a low redox potential and storage temperature, the heating and the low microbe count of foodstuff to be preserved (McLean et al. 1968, Leistner et al. 1973, Ala-Huikko et al. 1977, Lee et al. 1978, Lechowich et al. 1978).

One main point of practical interest in food preservation is the inhibitory action of nitrites on clostridia and thus on the formation of botulinum toxin. This action is increased approximately tenfold as is that against spores of *Clostridium botulinum* (Roberts and Smart 1974) if the nitrite has been heated together with the culture medium (Perigo effect) (Perigo et al. 1967, Perigo and Roberts 1968, Riha and Solberg 1975a, Riha and Solberg 1975b). The minimum inhibitory concentration of the nitrite is then in the range of 50–200 mg/kg, according to the pH value (Hustad et al. 1973, Baird-Parker and Baillie 1973, Leistner et al. 1973, Grever 1973). The causes of the Perigo effect have still not been completely clarified. Model experiments suggest that reaction products of the nitrite with the contents of meat, which may form upon heating, have an antibacterial action far higher than that of the nitrite itself. Such possible reaction products are nitrosothiols and the reaction products of the nitrite with sulfur-containing compounds and Fe^{2+} of the Roussin's salt type (Mirna and Coretti 1974, Tompkin 1993), although these are rather susceptible to heat (Mirna and Coretti 1974, Moran et al. 1975). Consequently, con-

sideration has now been given to the possibility that other reaction products of nitrite with substances contained in meat might also be responsible for the increased action of the nitrite in heated meat products, e.g. S-nitrosocysteine, complexes of cysteine with Fe^{2+} and oxides of nitrogen (Moran et al. 1975) or reaction products of the nitrite with sugars, amino sugars, sugar aldehydes and other carbonyl compounds (Mirna and Coretti 1976).

10.9.2

Spectrum of Action

The growth of fungi and yeasts is not affected by nitrites, whose action is almost exclusively antibacterial.

10.10

Fields of Use

Nitrite is added to meat products, especially sausages and cured meats, not only to obtain the desired cured color and the specific cured flavor but also to improve the keeping properties against bacterial spoilage. In the context of this book, only the latter effect is of interest. The addition of nitrite to meat products prevents not only the development of pathogenic and toxic microorganisms but also the formation of enterotoxins and other bacteriotoxins. Nitrite thus acts as a preventive against food poisoning. The desired antibacterial action is obtained in practice by concentrations of 50 to 160 mg/kg in the food to be preserved. A reduction in this applied concentration of nitrite, which would be desirable for toxicological reasons, can be justified only if equally multifunctional replacement substances are found. No such substances have yet been discovered.

Of the many products tested, sorbic acid and sorbates are the most suitable (Tóth 1983, Lück 1984). Under the production conditions for pickled goods, i.e. the usual a_w and pH values, the inhibitory effect of sorbic acid and sorbates on pathogenic and toxic microorganisms is in some cases even superior to that of nitrites (see chapter 19). However the pickling color and flavor resulting from the chemical effect of nitrite are not obtained with sorbic acid and sorbates. For this reason sorbates have not so far become established in the sector.

The other main alternatives to nitrite are the Wisconsin process, in which *Pediococcus acidilacticus* is added as a protective culture together with sucrose (Tanaka et al. 1985), the use of nitrite-free curing systems based on dinitrosylferrohemochrome or protoporphyrin IX (Smith and Burge 1987, O'Boyle et al. 1990, Shahidi and Pegg 1992) or the use of monascus pigments (Fink-Gremmels et al. 1991, Wirth 1991, Leistner 1994). Some of these methods produce an attractive color but in most cases the antimicrobial effect of nitrite is not achieved, or there are technical problems, or the products have not undergone full toxicological testing.

Nitrite is a highly reactive chemical and therefore converted in meat relatively rapidly (Woolford et al. 1976, Woolford and Cassens 1977). Part of it is oxidized to nitrate or converted to oxides of nitrogen, part is linked to myoglobin or other protein, part is bound to amino acids, such as tryptophan or tyrosine (Woolford et al. 1976), and part reacts with SH compounds. Lipids and carbohydrates, too, as well as many other food constituents, are possible reaction partners with nitrite (Greenland 1978).

While dry curing and pickle-curing is carried out mainly with nitrate, nitrite is employed to a greater extent for sausages and other products prepared from comminuted meat. Frequently, nitrite curing is also cheaper than that with nitrate because the curing process is more rapid. Nitrite is also used for rapid curing, including artery pumping, spray pumping, ultrasound curing, and curing under vacuum.

10.11

Other Effects

Nitrite attaches itself to the muscle color myoglobin to form nitrosomyoglobin, which is resistant to boiling. This process provides the red color of pickled meat.

Table 14. Inhibitory action of nitrite on bacteria (Castellani and Niven 1955)

Name of the bacteria	Minimum inhibitory concentration of nitrite in ppm after heating under	
	anaerobic conditions	aerobic conditions
<i>Streptococcus mitis</i>	40	4000
<i>Streptococcus lactis</i>	6000	10000
<i>Streptococcus liquefaciens</i>	800	6000
<i>Streptococcus faecalis</i>	4000	6000
<i>Streptococcus salivarius</i>	80	4000
<i>Streptococcus pyogenes</i>	2	20
<i>Lactobacillus casei</i>	4000	8000
<i>Lactobacillus arabinosus</i>	8000	25000
<i>Pediococcus cerevisiae</i>	8000	25000
<i>Bacillus megatherium</i>	80	4000
<i>Escherichia coli</i>	2000	4000
<i>Aerobacter aerogenes</i>	2000	4000
<i>Proteus vulgaris</i>	400	4000
<i>Salmonella typhosa</i>	800	2000
<i>Salmonella typhimurium</i>	2000	4000
<i>Shigella flexneri</i>	100	2000

In addition, nitrite is involved in producing the desired flavor of cured meat products (Tóth 1983) and protects the fat attached to the meat from oxidative spoilage. These “side effects” are regarded in food technology as being at least as beneficial as the preservative effect.