LAST MINUTE

Formation of Semicarbazide (SEM) from Natural Compounds in Food by Heat Treatment

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SEM has long been considered a characteristic metabolite of the antibiotic nitrofurazone which belongs to the group of nitrofurans. Nitrofurans have been widely used in veterinary practice as antibacterial agents in the treatment of pigs, poultry, fishes and shrimps. However, nitrofurans have been banned in the European Union since 1993/1995. As these drugs are listed in Annex IV of the Council Regulation 2377/90 no maximum residue limit (MRL) has been assigned.

Studies have proven that nitrofurazone is rapidly metabolised in animals. Thus it is not detectable even if the animals are analysed immediately after treatment. In contrast, the tissue bound metabolite SEM is detectable for several weeks after application and is therefore used as the marker residue of nitrofurazone in official residue control. In 2001 SEM was found by European Community Laboratories mainly in fishery and aquaculture products originating from South-East Asian countries. Later on the nitrofurazone metabolite was also detected in covered poultry imported from Brazil, as well as in carrageenan, in egg powder and in lysozyme.

Recently, there has been concern that SEM in food may originate from other sources, in particular in the case of processed or composite food products [1]. Studies confirmed that SEM is formed as a consequence of the thermal degradation of azodicarbonamide (ADC). ADC is not only used as a flour additive but also as a blowing agent in plastic gaskets of packaging materials and it was shown that SEM migrates from the gaskets into the food [2]. Further investigations revealed the natural presence of SEM in algae and shrimps as well as its formation from natural precursors upon hypochlorite treatment, e.g. in carrageenan [3]. However, positive detection of SEM in dried egg products and lysozyme gave rise to suspicions of further sources of SEM. Initially, a contamination during a processing step of dried egg products, i.e. chromatography on a carrageenan resin column, was discussed. Thereby, the carrageenan was considered to be the origin of the contamination of the processed egg products. But a determination of SEM in dried egg products that have been obtained by a chromatography on a carrageenan-free resin column gave reasons to search for further sources. Finally, the warm storage, a common practice in the processing of dried egg products (which is performed for microbiological reasons), was supposed to be the origin of positive SEM findings.

In order to study the formation of SEM during heat treatment, dried albumen as well as similar products, i.e. egg powder, whey powder and carrageenan were analysed after warm storage. The samples were kept in an aluminium foil covered beaker and in an open or a closed plastic tube, respectively, and stored in a drying oven at 70–80°C. SEM was determined by HPLC-MS/MS after acid hydrolysis of the sample and derivatisation with 2-nitrobenzaldehyde [3].

It was shown that a significant formation of SEM could occur in dried egg products and in whey powder during warm storage. No formation was observed for carrageenan. After one week about

100 μg/kg have been analysed in the dried albumen stored in the beaker. In this sample SEM values increased rapidly during the first three weeks and raised slowly about 300 μg/kg after five weeks storage. SEM formation in egg and whey powder was less pronounced. After one week 3 μg/kg SEM were analysed in egg powder and 5 μg/kg in whey powder stored in a beaker. Concentrations increased during five weeks storage to 10 μg/kg and 20 μg/kg, respectively.

Generally, SEM formation occurred to a lower degree when the samples were stored in a closed plastic tube. For all matrices the formation was lower by a factor of 10 compared to storage in an aluminium covered beaker. After three days storage of dried albumen the content of SEM had risen to 1 μg/kg in the closed plastic tube, to 15 μg/kg in the aluminium foil covered beaker and to 25 μg/kg in the open plastic tube, respectively. This observation may imply a dependency of SEM formation on the availability of oxygen. However, storage of dried albumen in a closed plastic tube under nitrogen atmosphere for four weeks lead to results comparable to a four-week storage in a closed plastic tube under normal atmosphere. Further tests on storage under nitrogen atmosphere and at different temperatures are currently carried out.

From this study it has to be concluded that positive findings of SEM in dried egg products could be caused by warm storage and not only by the illicit use of nitrofurazone in livestock breeding or by a contamination with ADC.

References

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[3] Hoenicke K., Gatermann R., Hartig L., Mandix M., Otte S. (2004): Food Add. Cont., **21**: 515–525.