UNIVERSITEIT GENT

FACULTY OF BIOSCIENCE ENGINEERING

Volatilization of microbiologically produced amines (trimethylamine, dimethylamine and ammonia) in Modified Atmosphere Packed grey shrimp (*Crangon crangon*)

Bert Noseda[1], Joke Goethals, Ilse Van Bree[1], Peter Ragaert[1], Herman Van Langenhove[2], Jo Dewulf[2] and Frank Devlieghere[1]

[1]Laboratory of Food Microbiology and Food Preservation, Member of Food2know, Ghent University, Belgium
[2] Laboratory of Environmental Organic Chemistry and Technology, Ghent University, Belgium

Introduction and Objective

The microbiological production of volatile bases in fishery products is since decades a well known spoilage phenomenon. Limit values for the total volatile basic nitrogen content (TVB-N) and the trimethylamine nitrogen content (TMA-N) for fish stored under ice correspond well with microbiological growth and sensory data. Yet, this correlation between, microbiological growth, TVB-N and TMA-N limit values and sensory rejection data appears to be vague for fishery products stored under different modified atmosphere packaging (MAP) conditions. The aim of this study was to investigate the effect of the pH of the shrimp matrix and the effect of the shrimp matrix itself on the volatilization of these metabolites.

Results

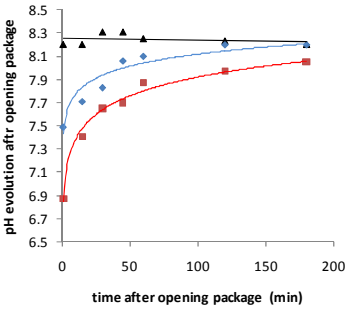

Figure 1

The use of CO_2 in MA packed products results in a pH drop of the product because of the formation of carbonic acid in the water phase of the product. **Figure 1** describes the pH evolution of grey shrimp packed with CO_2 in function of time after opening the package (t=0min). The shrimp were packed under three different MAP conditions and stored at 4°C resulting in three different concentrations of dissolved CO_2 in the product: ▲ 0ppm, ♦ 600ppm, ■ 1200ppm. Once the package was opened and left to stand at 20°C, the carbon dioxide diffuses into the atmosphere resulting into an increase in pH over time.

Figure 2 A, B and **C** describe measured headspace concentrations of TMA, DMA and NH_3 at different pH levels, after introduction of 5.0 mg N of the respective base / 50 g water (+) or mixed shrimp (●) in a closed system. The data were obtained using Selective Ion Flow Tube Mass Spectrometry (SIFT-MS).

Figure 2 A, **B** and **C** depict the importance of pH on the volatilization of TVB-N components. The higher the pH, the more free bases are released and the more base is found in the headspace of a closed system. Minor pH deviations cause a major effect on volatilization of the bases. The dataset was fitted to an exponential regression resulting in good correlations (R^2>0.9).

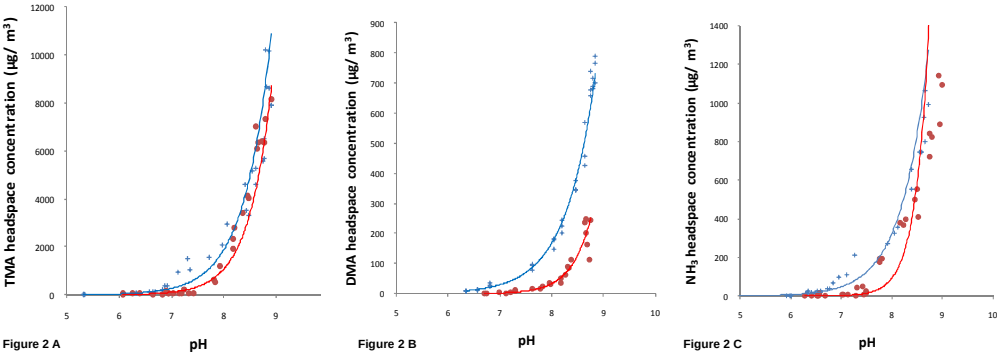

Figure 2 A Figure 2 B Figure 2 C

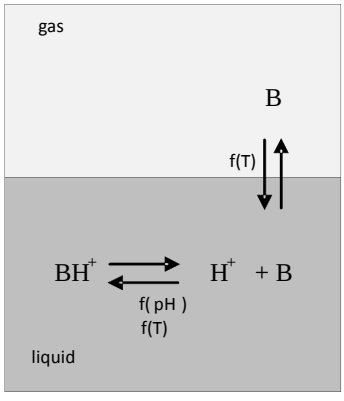

Figure 3

The pH of the shrimp product will eventually, next to the TVB-N content, be decisive whether a product will be unacceptable based on the presence of off-odorous bases. When considering a base in an aqueous solution, inside a closed two-phase gas-liquid system, the Henderson-Hasselbalch equation describes the relationship between pH and the dissociation of the base (B^{liquid}) and its conjugated acid (BH^+). In addition, the Henry coefficient (H) describes the volatilization of the base from a liquid (B^{liquid}) to the headspace (B^{gas}) at a certain temperature T. **Figure 3** depicts schematically the equilibration reaction for bases in a closed gas-liquid system.

The coinciding Henderson Hasselbalch equilibrium and equilibration constants H' for TMA, DMA and ammonia in the shrimp matrix were in this research determined allowing a calculation of the headspace concentration of the volatile bases in the headspace of a closed system, given the pH, the temperature and the quantity of amines present in the product (mg N/100g) and vice verse. To conclude a small example. Considering 2.28 mg/m^3 the limit of acceptability as headspace TMA concentration (Noseda et al.,2010). This headspace concentration correlates with 15.7 mg TMA-N/100g shrimp at pH 8.0, 49.4 mg TMA-N/100g shrimp at pH 7.5 and 155.5 mg TMA-N/100g shrimp at pH 7.

Conclusion

This research therefore provides important insights for the interpretation of TVB-N values in MAP grey shrimp products, where pH is a variable parameter (due to the use of CO_2) and describes the relationship between TVB-N values and sensorial odour measurements.

Noseda,B., Ragaert,P., Pauwels, D., Anthierens, T., Van Langenhove, H., Dewulf,J. and Devlieghere F. (2010) Validation of Selective Ion Flow Tube Mass Spectrometry for Fast Quantification of Volatile Bases on Atlantic Cod (Gadus morhua). Journal of Agricultural and Food Chemistry,58,5213-5219.