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

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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

The use of CO₂ 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 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 CO₂ 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 NH₃ 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).

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 ($B^{\text{aq}}$) and its conjugated acid ($BH^+$). In addition, the Henry coefficient ($H$) describes the volatilization of the base from a liquid ($B^{\text{aq}}$) to the headspace ($B^{\text{gas}}$) 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 versa. To conclude a small example. Considering 2.28 mg/m³ 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 CO₂) and describes the relationship between TVB-N values and sensorial odour measurements.