Application of near infrared and mid-infrared spectroscopy to assess freshness in sea bream (*Sparus auratus* L.) and salmon (*Salmo salar* L.) during ice storage

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Introduction

Fish is an extremely perishable food commodity. Rapid, post-mortem modification of fish muscle can have a significant impact on fish quality and consumer acceptance and, as a consequence, on the aquaculture industry. Storage in ice is fairly effective and widely used as a fish preservation method. Nevertheless, a progressive deterioration in sensory and other properties still occurs, mainly due to changes in lipids and proteins.[1] Although a variety of biochemical, physical, and microbiological methods have been used to assess fish freshness, sensory evaluation is still the most satisfactory. However, this approach is costly and time-consuming, and not readily available in all situations.[2] The aim of the work presented here was to evaluate the applicability of near infrared (NIR) and mid-infrared (MIR) spectroscopies as rapid and inexpensive tools for the assessment of sea bream and salmon freshness during ice storage, in comparison with traditional chemical indexes.

Materials and Methods

Aquacultured, ungutted sea bream (*Sparus auratus* L.) and gutted salmon (*Salmo salar* L.) were obtained 4 days after slaughter, packaged in polystyrene boxes and covered with a layer of flake ice. The samples were stored in ice (replaced daily) in a cold room (+4°C) either whole or as fillets, for up to 21 and 17 days respectively.

Samples were analysed at regular intervals with both chemical methods and spectroscopic techniques. The muscle portion of whole or filleted samples was minced with a Waring Blendor (Torrington, CT, USA) laboratory homogeniser prior to analysis. Total volatile basic nitrogen content (TVB-N) was determined according to the official method of the European Community;[3] thiobarbituric acid reactive substances (TBArs) were analysed according to Tsironi et al.;[4] trimethylamine level (TMA) was analysed according to AOAC Official Method 971.14.[5]

NIR spectroscopy was performed using an FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen, Germany) equipped with an integrating sphere (12500–3750 cm^{-1}). MIR spectra were collected with an FT-IR spectrometer (Vertex 70, Bruker Optics, Ettlingen, Germany) fitted with a germanium crystal attenuated total reflectance (ATR) cell (4000–700 cm^{-1}). The spectral data were standardised with different pretreatments, including standard normal variate (SNV) correction, extended multiplicative scatter correction (EMSC), and first derivative calculation; data were processed with principal component analysis (PCA) using The Unscrambler 9.8 (Camo Software AS, Oslo, Norway).

Results and Discussion

TVB-N, TBArs and TMA increased over time, reflecting the progressive spoilage of samples. Similar values of each parameter except TBArs were reached in salmon and sea bream, both in whole and filleted samples (Figures 1 and 2). TBArs is widely used for assessing the degree of lipid oxidation in fish,[2] and reached maximum values in whole samples of sea bream, probably due to ungutting of fish; whole gutted salmon presented much lower levels.

Reference paper as:
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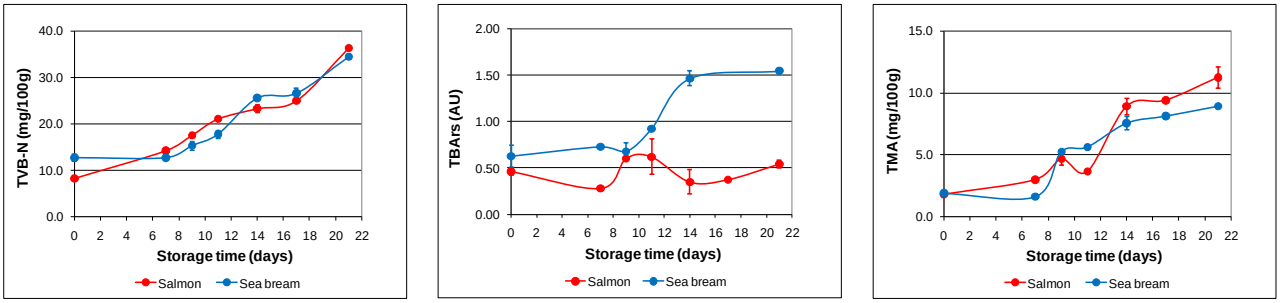

Figure 1. Evolution of freshness chemical indices in whole salmon and sea bream stored in ice.

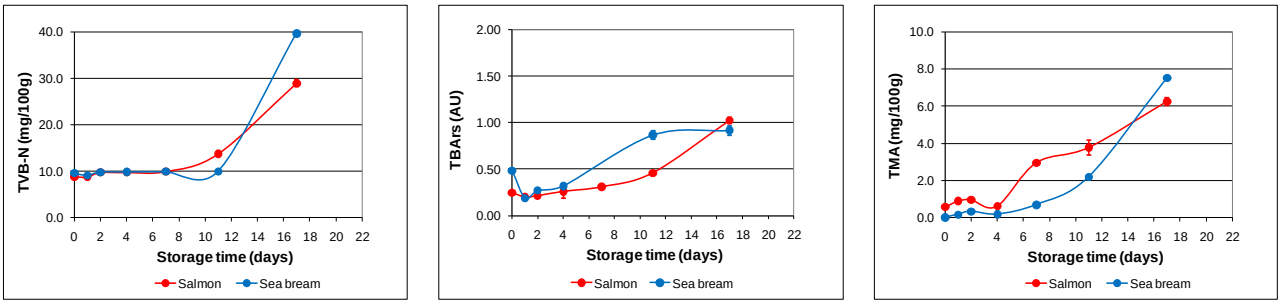

Figure 2. Evolution of freshness chemical indices in salmon and sea bream fillets stored in ice.

TVB-N is mainly produced by bacterial decomposition of fish flesh, and freshly caught fish typically contains 5 to 20 mg.100 g^{-1}, whereas levels of 30–35 mg.100 g^{-1} are generally regarded as the limit of acceptability for iced-stored fish.[6] TVB-N values reached or exceeded the upper limit of acceptability only after 17 days of storage in both whole and filleted samples.

TMA is produced by the decomposition of trimethylamine oxide (TMAO) caused by bacterial spoilage,[2] thus its level is a function of the initial content in TMAO and is variable in different fish species. TMA levels were initially low, both for whole and filleted samples of salmon and sea bream. The level of 5 mg.100g^{-1} indicates incipient spoilage[7] and was reached after 12 and 14 days in ice for whole and filleted samples, respectively, with no difference between the two species.

MIR and NIR spectral data collected from fish muscle were preprocessed (SNV, EMSC and first derivative). PCA was then performed to examine spectra evolution as a function of storage time in ice. PCA score plots discriminated samples according to storage time, corroborating the chemical parameter evolution. In particular, the PCA applied to sea bream NIR spectra showed a good discrimination of whole fish and fillet samples based on storage time, principally related to molecular modifications of lipids and water (e.g. Figure 3).

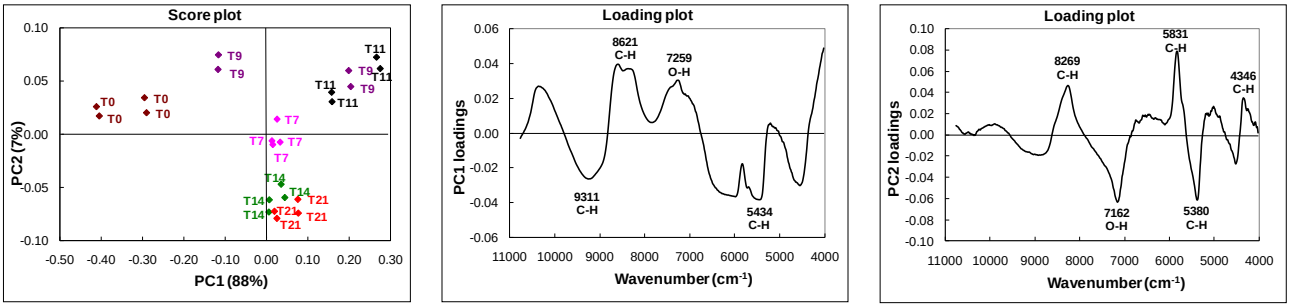

Figure 3. Results of PCA applied on NIR spectra of whole sea bream, after EMSC pretreatment.

PCA results from salmon NIR spectra were less clear, but a good distinction of the oldest samples was observed (particularly for fillets; Figure 4). These results agreed with TBARs data, and revealed a minor lipid oxidation for whole salmon.

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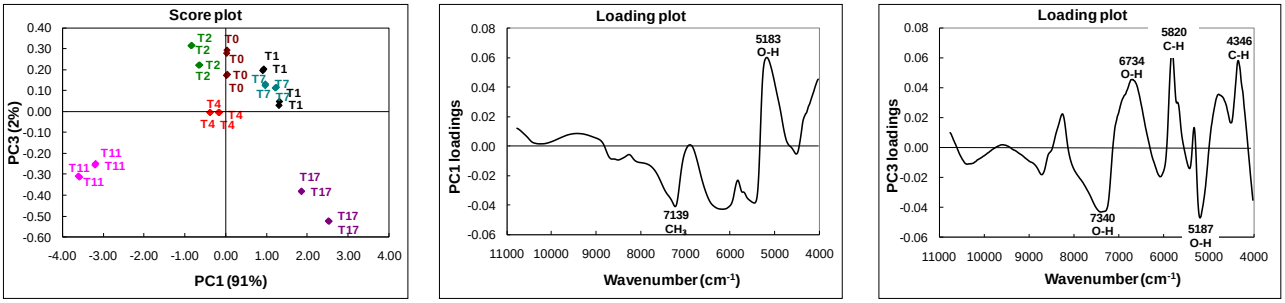

Figure 4. Results of PCA applied on NIR spectra of salmon fillets, after SNV correction.

MIR analysis gave good results for both fish species and in particular for fillets (Figures 5 and 6). In this case sample discrimination was mainly related to amine groups and thus to protein degradation.

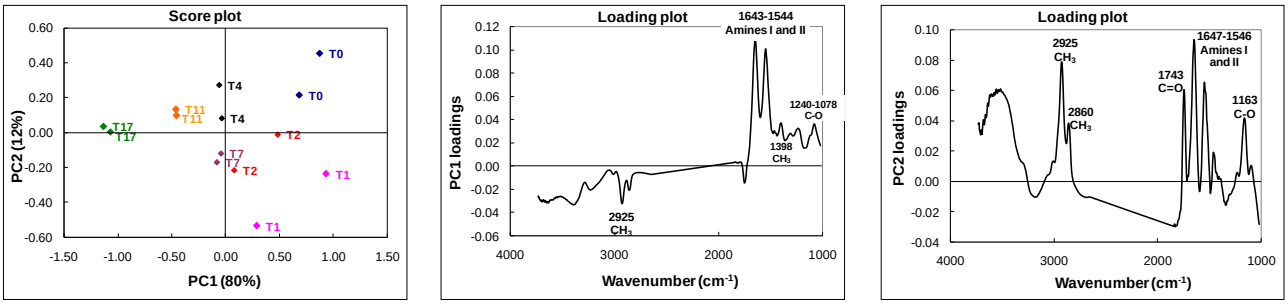

Figure 5. Results of PCA applied on MIR spectra of sea bream fillets, after SNV correction.

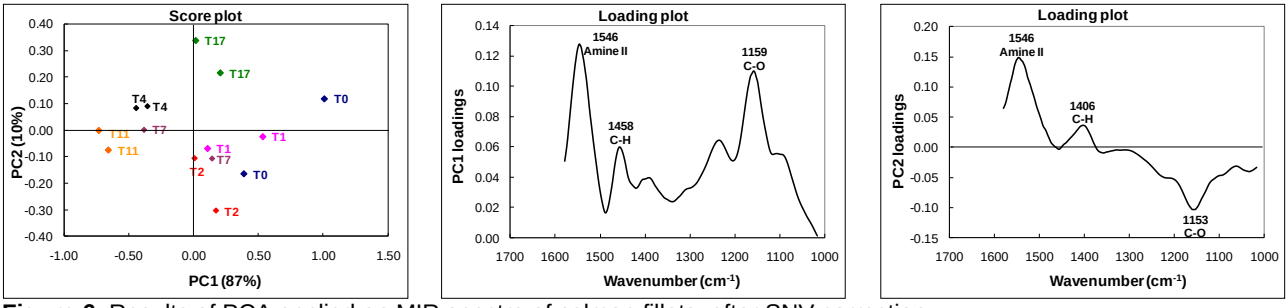

Figure 6. Results of PCA applied on MIR spectra of salmon fillets, after SNV correction.

Conclusion

The PCA analysis of NIR and MIR spectra of salmon and sea bream, both as whole fish and fillets, reflected the evolution of the chemical parameters observed during storage in ice. Sample discrimination was mainly ascribed to lipid oxidation and protein degradation.

Vibrational spectroscopy is thus a useful tool for rapid, easy, and low-cost evaluations of fish freshness, and meets the needs of the fish sector for developing analytical methods that can be applied in online monitoring systems.

Acknowledgements

Authors are grateful to Dr. Andrea Gaudenzi for his technical assistance and to the "Italian Society for NIR Spectroscopy (SISNIR)" for financially supporting the participation to the 15th International Conference on NIR Spectroscopy (NIR 2011).

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