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# Foodstuff authentication from spectral data: Toward a species-independent discrimination between fresh and frozen–thawed fish samples

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ABSTRACT

The substitution of fresh fish with frozen–thawed fish is a typical fraud that can damage consumers for several reasons. In fact, not only the quality of thawed meat can be negatively affected during freezing, but also safety issues can arise, as thawed meat is more susceptible to microbial growth. Though several strategies have been proposed for fresh fish authentication, their classification ability is strongly affected by the fish species being considered.

In this paper, we propose three different strategies based on latent variable modeling techniques in order to develop a multi-species classifier of the fresh/frozen–thawed status of fish samples using near-infrared spectra. Whereas the first two strategies model the information related to the species and to the fish together (either jointly or sequentially), the third strategy aims at explicitly separating them to improve the classification performance.

The proposed strategies were validated over a database of more than 1200 samples of several different species, with near-infrared spectra collected with two different instruments. The overall classification accuracies ranged between 80% and 91%, according to the strategy and the instrument used. We believe that this study can contribute to the development of a species-independent approach to foodstuff classification.

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## 1. Introduction

The substitution of fresh fish with frozen–thawed fish is a typical fraud that not only damages consumers from an economical point of view, but can also cause safety issues (Pavlov, 2007). In fact, although freezing is one of the most widely used methods to extend the shelf life of seafood, it can affect the overall organoleptic properties of the product, and thawed meat is characterized by a higher susceptibility to microbial growth. Furthermore, fish authentication is important for correct product labeling (Martinez et al., 2003), as promoted by recent regulatory actions (Uddin, 2010; European Parliament Legislative Resolution, 2011).

Several methods have been proposed for the identification of the fresh/frozen–thawed substitution fraud (e.g., eye lens evaluation, measurements of dielectric properties, erythrocytes lysis, hematocrit evaluation, muscles histology, enzymatic methods, etc.; Uddin, 2010). The classification ability of the majority of these systems is strongly affected by the species under investigation, the integrity of the product (whole fish or fillet) or by its shelf life (Uddin, 2010). For example, the use of methods based on changes in dielectric properties, while being accurate on intact fish, provides poor results when applied on fillets (Duflos et al., 2002). Enzymatic assays were found to be useful in fillets, but not applicable to all species (Duflos et al., 2002). Recently, Bozzetta et al. (2012) proposed muscles histology as a simple method for the evaluation of the fresh/frozen–thawed status. Despite the good classification results obtained on a wide range of species (more than 35 different species), the method requires time for sample processing (e.g., fixation and coloration) and the use of several reagents.

As an alternative to the abovementioned techniques, more rapid analytical technologies have been developed. Among them (Nott et al., 1999; Karoui et al., 2006; Vidaček et al., 2008; Fernández-Segovia et al., 2012; Leduc et al., 2012), near-infrared spectroscopy (NIRS) has been suggested by the promising results obtained on some species (Uddin, 2010; Sivertsen et al., 2011; Fasolato et al., 2012; Zhu et al., 2012; Kimiya et al., 2013; Ottavian et al., 2013). NIRS is a well consolidated analytical technology and plenty of applications can be found in the field of seafood authentication (Cozzolino and Murray, 2012). To the authors' knowledge, there are currently no NIRS application to multi-species databases, i.e. so far the fresh/frozen–thawed authentication problem has been solved only analyzing single species separately.

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In this paper, we propose and compare three alternative strategies based on latent variable modeling techniques (Geladi and Kowalski, 1986; Trygg and Wold, 2002; Barker and Rayens, 2003) in order to develop a multi-species classifier of the fresh/frozen–thawed status of fish samples. While the first two strategies model the information on the species and on the fish status fresh/frozen–thawed together (either jointly or sequentially), the third strategy aims at explicitly separating them to improve the classification performance. A thorough validation of the proposed strategies is carried out using two NIR instruments exploring different spectral regions, on a total of more than 1200 samples.

## 2. Materials and methods

### 2.1. Available dataset

The number of samples available for model calibration and model validation (per species, class and instrument; see also Section 2.2) is given in Tables 1 and 2. The fresh/frozen–thawed classification models were built considering only the samples of the four species indicated in Table 1 (independently on the strategy used; Section 2.3). For model validation, instead, two datasets were considered, namely V1 and V2 (Table 2). The V1 spectra were collected at the same time of the calibration samples, whereas the V2 spectra were collected at a different time.

For each species, the $N$ spectra considered were collected into an $\mathbf{X}_{sub}$ $[N \times M]$ matrix, where $M$ is the number of wavelengths ($M$ = 401 for FOSS spectra and 421 for UNITY spectra) and subscript $_{sub}$ refers to the initial letter of the species Latin name. As an example, swordfish (*Xiphias gladius L*) FOSS samples were collected into $\mathbf{X}_{xg}$ $[260 \times 401]$. Superscript $^{*}$ is used to identify the species which were used only for model validation (Table 2).

### 2.2. NIR analysis

For details about the origin, freezing, thawing and storage of the samples, the reader is referred to the references wherein they were originally presented (Fasolato et al., 2008, 2010a,b, 2012; Ottavian et al., 2012). As for the NIR analysis, the epaxial white muscles of fresh and frozen–thawed samples were minced using a Retsch Grindomix (Retsch GmbH, Hann, Germany) at 4000 rpm for 10 s. Two aliquots per sample were scanned in small ring cups in reflectance mode with two different instruments: a FOSS NIRSystem 5000 (FOSS NIRSystem Inc., Silver Spring, MD, USA) at 2 nm intervals from 1100 to 2500 nm; and a UNITY Scientific SpectraStar 2500TW (Unity Scientific, Columbia, MD, USA) at 1 nm intervals from 680 to 2500 nm. For each aliquot, a mean spectrum was obtained by averaging multiple scans. Then, the spectrum of the sample was obtained by averaging those of the two aliquots. Reflectance ($R$) values were converted into absorbance ($A$) values through $A = \log(1/R)$.

The analysis of the UNITY spectra was limited to the region between 680 and 1100 nm due to the noise characterizing the wavelength region above 1900 nm and considering that the NIR regions explored by the two instruments partially overlap. This was done in order to explore two different spectral regions with the available instruments.

**Table 1**
Available dataset in terms of number of samples per species, per class and per NIR instrument: calibration samples.

| Species | Symbol | Number of samples | | FOSS | UNITY |
|---|---|---|---|---|---|
| Gilthead sea bream (*Sparus aurata*) (Fasolato et al., 2010b) | $\mathbf{X}_{sa}$ | Fresh<br>Frozen–thawed | 53<br>53 | ✓ | ✓ |
| Red mullet (*Mullus barbatus*) (Fasolato et al., 2010a) | $\mathbf{X}_{mb}$ | Fresh<br>Frozen–thawed | 53<br>53 | ✓ | ✓ |
| Sole (*Solea vulgaris*) (Fasolato et al., 2008) | $\mathbf{X}_{sv}$ | Fresh<br>Frozen–thawed | 71<br>17 | ✓ | - |
| Swordfish (*Xiphias gladius L*) (Fasolato et al., 2012) | $\mathbf{X}_{xg}$ | Fresh<br>Frozen–thawed | 101<br>74 | ✓ | ✓[a] |

[a] Only 53 fresh and 53 frozen–thawed samples were available.

**Table 2**
Available dataset in terms of number of samples per species, per class and per NIR instrument: validation sets V1 and V2 samples.

| Validation set | Species | Symbol | Number of samples | | FOSS | UNITY |
|---|---|---|---|---|---|---|
| V1 | Gilthead sea bream (*Sparus aurata*) (Fasolato et al., 2010b) | $\mathbf{X}_{sa}$ | Fresh<br>Frozen–thawed | 27<br>27 | ✓ | ✓ |
| | Red mullet (*Mullus barbatus*) (Fasolato et al., 2010a) | $\mathbf{X}_{mb}$ | Fresh<br>Frozen–thawed | 27<br>27 | ✓ | ✓ |
| | Sole (*Solea vulgaris*) (Fasolato et al., 2008) | $\mathbf{X}_{sv}$ | Fresh<br>Frozen–thawed | 35<br>8 | ✓ | - |
| | Swordfish (*Xiphias gladius L*) (Fasolato et al., 2012) | $\mathbf{X}_{xg}$ | Fresh<br>Frozen–thawed | 50<br>35 | ✓ | ✓[a] |
| V2 | Gilthead sea bream (*Sparus aurata*) (Fasolato et al., 2010b) | $\mathbf{X}_{sa}$ | Fresh<br>Frozen–thawed | 71<br>71 | ✓ | ✓ |
| | Red mullet (*Mullus barbatus*) (Fasolato et al., 2010a) | $\mathbf{X}_{mb}$ | Fresh<br>Frozen–thawed | 71<br>71 | ✓ | ✓ |
| | Swordfish (*Xiphias gladius L*) (Fasolato et al., 2010a) | $\mathbf{X}_{xg}$ | Fresh<br>Frozen–thawed | 71<br>71 | ✓ | ✓ |
| | European sea bass (*Dicentrarchus labrax*) (Ottavian et al., 2012) | $\mathbf{X}^{*}_{dl}$ | Fresh<br>Frozen–thawed | –<br>38 | ✓ | - |
| | Different species[b] | $\mathbf{X}^{*}_{mix}$ | Fresh<br>Frozen–thawed | –<br>66 | ✓ | - |
| | Carp/tench (Cyprinus carpio/ Tinca tinca) | $\mathbf{X}^{*}_{cct}$ | Fresh<br>Frozen–thawed | 15 | - | ✓ |

[a] Only 27 fresh and 27 frozen–thawed samples were available.
[b] Among the species included in $\mathbf{X}_{mix}$: *Sarda sarda*, *Pollachius virens*, *Scorpaena scrofa*, *Pangasius spp.*, *Scomber scombrus*, *Gadus macrocephalus*, *Hippoglossus hippoglossus*, etc.

### 2.3. Statistical analysis

Principal component analysis (PCA; Jackson, 1991) was applied as an exploratory tool to reveal the internal correlation structure of the available datasets. This preliminary analysis was intended to identify the major sources of variability of the data (sample species, sample status, etc.).

After the preliminary analysis, three alternative strategies were developed for sample classification, with the aim of developing a classifier for the fresh/frozen–thawed status of the samples independently from their species. A schematic of the three strategies is given in Fig. 1, while details on the modeling techniques are presented in the following subsections.

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