A case study: shelf-life of smoked herring fillets by volatile compounds analysis.

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ABSTRACT.

Two different products of vacuum packed cold smoked herrings were analyzed at time intervals in order to evaluate the efficiency of the processing and product stability. Microbiological total counts, lactic acid bacteria, total coliforms, pH, water activity, water content, salt content (WPS) were determined. Differences in hygienic conditions and salt content were found. Principal components analysis (PCA) of volatile compounds determined by GC-MS analysis allowed the differentiation of the processing.
1 Introduction

The more widespread smoked herrings marketed in Italy are beheaded with skin, vacuum packaged, silver and golden types; less frequent are skinned fillets, softer and with a milder taste, vacuum packaged, which meet more with the liking of the modern consumer. The cold smoked herring is at the limit of the group of the lightly preserved seafood (Huss, 1994), comprising products with low salt level (<6% NaCl-Water Phase Salt WPS), preservatives or smoke, pH value >5, mainly vacuum packaged, requiring refrigeration temperatures and typically consumed as ready-to-eat without heat treatment.

The process must allow the survival of an adequate number of spoilage organisms, which have the important role to compete with the growth and toxin formation of C. botulinum type E and non-proteolytic types B and F (FDA, 2001a).

The control measures of potential hazards are based mainly on salt control (nitrite addition is not allowed by EC regulation in these products), on control of exposition to temperatures that favour C. botulinum throughout the processing steps, on maintenance at refrigeration temperatures of the final products. With regard to this, US HACCP regulations suggest a critical limit for vacuum packaged cold smoked products of at least 3.5 % NaCl –WPS at ≤ 4.4°C, allowing for short time periods temperatures up to 10°C (FDA, 2001b).

The purpose of this investigation was to answer an importer’s request, that was to verify the established shelf-life of smoked vacuum packed herring fillets of a new producer (product A). With this aim traditional analytical techniques and SPME headspace-gas chromatography-mass spectrometry were applied comparing product A to a traditional one (B) on the furnished packets.

2 Materials and Methods

A total of 18 packets of smoked herring fillets, peeled and vacuum packed of two different producers were compared (10 of producer A, 8 of B). The packages were stored at 0-2°C for the whole period of the trial. Analyses were performed as described in Bernardi et al., 2009. Water activity (aW), water content, NaCl–WPS were performed in quadruplicate. The enumeration of Total Psychrotrophic Count (TPC), Lactic Acid Bacteria (LAB), total coliforms, pH and SPME GC-MS analyses were performed at time intervals in duplicate. Volatile compounds were tentatively identified by matching mass spectral data with the Wiley and NIST reference libraries of standard compounds. The identification was confirmed by comparison of the retention times and mass spectra (MS) with available authentic standards (AS). Semi-quantification of the compounds was based on arbitrary units of peak area counts divided by 105.

3 Statistical analysis

Principal component analysis (PCA) and statistical analysis were performed by the SPSS package version 9.0 (SPSS Italia, Bologna).
4 Results and discussion

WPS rate was amply above the 3.5 % NaCl-WPS; in product B, salt content was more variable; $a_w$ was similar in both, but more variable in product A, allowing to consider safe both products.

Product A had at the arrival ($27^{th}$ days from production) a very high TPC (5.74 Log CFU/g), afterwards TPC decreased and LAB counts overcame 7 Log CFU/g, but without causing detectable olfactory deterioration of flavour.

Product B showed lower TPC and LAB than A (<3.70 and 5.78 Log CFU/g, respectively at $9^{th}$ days). Total coliforms were under the limit of detection (<2 Log CFU/g) both in A and B (table n.1).

In product B forty-five peaks were determined and identified by GC-MS. Particularly, in product B benzaldehyde and furfural and small quantities of propionaldehyde and hexanal were present, while absent in A. Phenol was present in both, without significant differences. Acetic acid was found more in product B. Dimethyl sulfoxide and dimethyl sulphide were more represented in A than in B. As a whole, product B showed an aromatic profile more complex and rich in qualitatively superior compounds, while product A showed a very little articulate profile. In figure n. 1 the analysed samples and the identified variables (volatile compounds) are represented in the space described by the two principal components, the first component explaining 78.3% variability among data, the second component explaining 9.2% variability. Samples are clearly distinguished in two groups, coinciding with A and B productions. The second component allows to distinguish product A on $27^{th}$ day from the subsequent samples.

On the “best before” date, product A had an initial softening with presence of fluid material in the pack, without other sensorial changes; product B maintained a better firmness, also for a lesser water content. The bacterial count at the first sampling of A was high, indicating bad hygienic condition, while the product B was hygienically better at about the same storage time.

Product A had a higher salt content; this was a negative aspect, not only from a nutritional point of view, but also for the consumer’s present preferences; its WPS ratio allowed the same stability of the product B although a higher water content. WPS more than 6% puts both products at the limit between lightly preserved and semi-preserved seafood (Huss, 1994).

The obtained results allowed to assume a different processing technology: brine salting for A, due to the high water level and the uniform salt content of the fillets, while for B a dry salting process with purging was probable, because of a considerably lower water content and a higher variability in the salt concentration (Coefficient of Variation 13.8%).

In the verified conditions, the shelf life of product A is to be stated up to 4 weeks instead a “best before” date of 45 days; microbiological parameters of B were stable for the whole period of the trail. The exclusive presence in the product B of benzaldehyde and furfural, aldehydes known for giving a strong taste of smoke, confirmed the perception of a more typical aroma of the herring B.

The clear finding of dimethyl sulfoxide and dimethyl sulphide only in the product A, well match with the microbial condition of A; these sulphur compounds may be the expression of bacterial activity besides of ripening (Triqui, 1995).
Table 1. Conservation parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m</td>
<td>M</td>
</tr>
<tr>
<td>aw</td>
<td>0.923</td>
<td>0.966</td>
</tr>
<tr>
<td>Water content %</td>
<td>72.25</td>
<td>75.18</td>
</tr>
<tr>
<td>Salt %</td>
<td>5.25</td>
<td>5.59</td>
</tr>
<tr>
<td>WPS %</td>
<td>6.57</td>
<td>6.92</td>
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Microbiological analyses

<table>
<thead>
<tr>
<th>day</th>
<th>A</th>
<th>B</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>27</td>
<td>45</td>
</tr>
<tr>
<td>TPC (Log CFU/g)</td>
<td>5.74</td>
<td>&lt;4.70</td>
</tr>
<tr>
<td>LAB (Log CFU/g)</td>
<td>6.78</td>
<td>7.63</td>
</tr>
<tr>
<td>Coliforms (Log CFU/g)</td>
<td>&lt;2.00</td>
<td>&lt;2.00</td>
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</tbody>
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Legend:
m = minimum value
M = maximum value
CV = coefficient of variation
TPC = Total Psychrotrophic Count
LAB = Lactic Acid Bacteria

5 Conclusions

The results related to the study of the volatile fraction confirmed what deduced by the more traditional analyses: in spite of the close outward likeness between the two products, their processing technologies were very different, resulting in distinct products as regards shelf life and quality. The reported case is an example of the result of the delocalization, due to economical reasons, of food processing in countries applying less advanced or less consolidated technologies or procedures with inferior process standard.
Figure 1. Biplot of principal component scores and factor loadings from principal component analysis applied to volatile compounds of product A (scores L) and product B (scores D).

Volatile compounds identified in smoked herring (Clupea harengus) by GC-MS: 1) 2-pentene; 2) heptane; 3) dimethyl sulphide; 4) methyl-cyclo-hexan; 5) propanal; 6) furan; 7) propanone; 8) methyl acetate; 9) 2-methyl-furan; 10) ethyl acetate; 11) 2-butanol; 12) 3-methyl-butanal; 13) ethanol; 14) benzene; 15) 2-ethyl-furan; 16) branched hydrocarbon; 17) 2-pentanone; 18) chloroform; 20) hexanal; 21) p-xylene; 22) cyclopentanone; 23) 2-methyl-cyclo-pentanone; 24) 3-methyl-cyclo-pentanone; 25) pyrazine; 26) cyclohexanone; 27) acetoin; 28) 2-methyl-2cyclopentanone; 29) 3-furaldehyde; 30) acetic acid; 31) 2-furaldehyde; 32) acetyl-furan; 33) benzenaldehyde; 34) propanoic acid; 35) dimethylsulfoxide; 36) 5-metil 2-furaldehyde; 38) gamma-butyrolactone; 39) butanoic acid; 40) 3,4-dimethyl-3-penten-2-one; 41) 5-metil-2(5H)-furanone 44) 2-pyranone; 45) 2-methoxy-phenol; 46) guaiacol; 47) phenol; 50) 2-furanone.


References


