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Effects of the smoking process on odour characteristics of smoked herring (Clupea harengus) and relationships with phenolic compound content

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Abstract: The relationship between smoking parameters and odour characteristics, evaluated by a trained sensory panel, were studied on smoked herring. In addition, a possible correlation between the content of 10 phenolic compounds and sensory perceptions was investigated. Five smoking techniques were applied, combining smoke production conditions, performed by pyrolysis of beech wood sawdust or by friction of beech wood log, with smoke deposition, either in a controlled kiln (traditional smoking) or by an electrostatic process. In the fifth smoking technique, a purified condensate of beech smokes was vaporised on fish fillets in the smokehouse. The time of smoking was 3 h for traditional smoking and the liquid smoke atomisation process and 12 min for the electrostatic method. The effects of three smoking temperatures (16, 24, 32 °C) were tested for both the traditional and the liquid smoke atomisation processes, as well as the effect of the position of the exhaust valve in the smokehouse in the case of the traditional method. Two different voltages were applied for the electrostatic process, 37 and 42 kV.

The results show a clear discrimination of the products since some odour characteristics are specifically related to the smoking process applied. All the studied parameters (smoke generation, deposition of smoked compounds, smoking temperature, exhaust valve opening in the smokehouse or voltage applied in the electrostatic tunnel) have an effect on the smell characteristics of smoke products, either on the odour intensity and/or on the kind of smoke note.

Multiple linear models were tested to find relationships between sensory properties and phenolic compounds. Although some compounds seem to be mainly involved in the "cold ash" note, the results illustrate the difficulty of reaching clear conclusions about a correlation between smoke odour and only 10 phenolic compounds. It is suggested that a better model could be found if other volatile compounds, besides the phenolic class, are taken into account.

Keywords: Herring; Smoking; Phenolic compounds; Sensory evaluation; Odour characteristics

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53 **1. Introduction**

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The production of smoked and salted fish is an important industry in France and represents 17% of the market share for aquatic product consumption (Girard & Paquotte, 2003). The increase in smoked fish consumption began in the 90's with the development of smoked salmon, now the most consumed smoked species before trout and herring. The smoking sector is of considerable economic importance for the seafood market. Each year 45000 tons of salmon are used in France to produce 18000 tons of smoked salmon, 15% of which is exported to Italy, Belgium and, to a lesser extent, Germany (OFIMER, 2004).

62 A recent European study on smoked salmon quality (Cardinal, Gunnlaugsdottir, Bjoernevik, 63 Ouisse, Vallet & Leroi, 2004) showed that the European market offers a large range of products 64 with different salt levels and different phenol contents (the criteria used until now as indicators 65 of smoking treatment intensity) and that sensory characteristics allow products to be classified in different groups. Moreover, the preference study, carried out in the same project with consumers 66 67 from various European countries, indicated that all consumers do not like the same kind of 68 products. Five classes of consumer with different preferences were identified (Anonymous, 69 2004). These preferences are related to specific sensory properties. For example, it appears that, 70 for the groups of consumers whose preferences are mainly explained by smoke odour or flavour, 71 not only is the intensity of smoking important but also the kind of smoke note. While some 72 people require a strong smoke odour and flavour, others want a specific "wood fire smoke" note. 73 The control of this smoke characteristic can be of real interest to processors who want to adapt 74 their products to consumer demand.

In the past, smoking parameters, such as the kind of generator, kind of wood, hygrometry or
temperature of the smokehouse and their effects on the deposit of compounds, have been studied
by different research teams (Daun, 1972; Girard, Talon, & Sirami, 1982; Girard, 1988). The

78 number of volatile compounds identified in a smoke, more than 400, explains the difficulty of 79 relating sensory perception to specific molecules (Maga, 1987; Cardinal, Berdagué, Dinel, 80 Knockaert & Vallet, 1997). Recent studies performed on phenolic compounds (Guillard & 81 Grondin, 2003; Sérot, Baron, Knockaert & Vallet, 2004) have shown that their deposition 82 depends on the smoking conditions and research conducted so far has suggested that phenolic 83 compounds play a key role in smoke perception. However, the relationship between these 84 compounds and sensory perception is not well detailed in the literature, especially for fish 85 products, although some authors cited by Maga (1987), such as Toth & Potthast (1984), have 86 evaluated the effect of some pure molecules in solution on sensory properties. More recently, the 87 study of Ojeda, Barcenas, Pérez-Elortondo, Albisu & Guillen (2002) has shown the difficulty to 88 associate molecules to specific terms for the description of smoke flavourings.

This study aims to investigate the effects of smoking processes on the odour of smoked product and to confirm the possible relation between phenolic compound content and sensory perception. It forms part of the same investigation as that carried out by Sérot et al. (2004). This previous work clearly indicated that the process applied affects the content of phenolic compounds, so knowledge about the effect of these compounds on sensory properties would allow the process to be adapted according to the target product.

95 For practical and cost reasons, herring fillets were used. Two smoke generation techniques were 96 tested, one based on the pyrolysis of sawdust sustained by air circulation (autocombustion) and 97 the second producing smoke by friction of wood log. For each type of smoke generation, two 98 different ways of smoke deposition were compared; exposure of fillets in a closed air-99 conditioned smokehouse (the traditional process) and the electrostatic method where smoke is 100 accelerated towards fillets (Collignan, Knockaert, Raoult-Wack, & Vallet, 1992; Bardin, 101 Desportes, Knockaert & Vallet, 1997). The effects of these four techniques were compared to a 102 fifth, the atomisation of liquid smoke.

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104 **2. Material and methods**

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106 **2.1. Fish samples**

Frozen fillets of herring (*Clupea harengus*) were purchased from the local fish market (Nantes,
France). On the day of processing, herring was thawed at +4°C for 6h, hand-salted with refined
salt for 20 min at 12°C before being rinsed on grids with water (15°C) and stored in a cold room
at 2°C for 14h until smoking.

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112 **2.2. Fish processing**

40 fillets were processed for each treatment. Production of smoke was performed by pyrolysis at 113 114 450°C of beech wood sawdust (Thirode, France) or by friction of beech wood log at 350°C 115 (Muvero, The Netherlands). For each kind of smoke production, two different methods of smoke deposition were tested. The first one was direct fillet exposure (traditional smoking) in a 116 117 smokehouse with a capacity of 380 kg mounted on a trolley with 28 grids (Thirode, PC 90 Model, France) and a relative hygrometry of $65\% \pm 3\%$, an air speed of 2 ms⁻¹ above the 118 119 products and with the exhaust valve position one-third open (1/3) or totally open (3/3). The 120 second way consisted of an electrostatic method where smoke was led through an experimental 121 tunnel (4000 X 100 X 150 mm). This allowed continuous smoking with a production capacity of 122 125 kg/h. The voltage applied between the positive pole (smoke ionisation) and the cathode 123 (conveyor belt) was set by an HT14B high voltage supply (Sefelec, France). The distance 124 between electrodes was 12 cm. Two positive voltages were tested, 37 and 42 kV, and the air speed above the fillet was around 0.5 ms⁻¹. The anode electrode, in stainless steel 316 L, was a 125 rectangular grid with 4.5 by 2 cm spacing of bars 0.2 cm in diameter. The time of smoking was 3 126 127 hours for the traditional method at 16°C, 24°C or 32°C, and 12 min for the electrostatic method at ambient temperature. The initial product temperature was considered to have a potential
impact on smoke compound deposit so two temperatures were tested, 10 and 20°C.

For the liquid smoke atomisation process, a purified condensate of beech smoke associated with aromatic additives (reference 1165) was purchased from Lutetia (France) and vaporised in the smokehouse (Thirode) for 3 hours. All the smoking parameters are presented in Table 1. Twenty-one different treatments were studied.

All the herring fillets were vacuum packed, frozen and stored for one month at -20° C until analysis of phenolic compounds and sensory evaluation.

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137 **2.3. Sensory evaluation**

138 A descriptive test with conventional profiling (Stone & Sidel, 1985) was performed on the odour 139 characteristics of smoked herring with twelve trained panellists belonging to the IFREMER staff. 140 This panel has many years of experience in the sensory evaluation of smoked fish. Before starting the study, a session was organised in order to select sensory descriptors for the product 141 142 odour and to check the panellists' understanding of the descriptors. Table 2 gives the list of 143 odours and their description. An experimental design was constructed in order to balance the 144 characteristics and odour intensity of the products presented within a session. Five sessions were 145 organised to test all the products, four with a presentation of four products and one with five 146 products.

Sessions were performed in individual partitioned booths, as described in procedure NF V-09105 (AFNOR, 1995) and equipped with a computerised system (Fizz, Biosystèmes, Couternon,
France). Panellists rated the sensory attributes on a continuous scale displayed on a computer
screen, from low intensity (0) to high intensity (10).

151 On the day of evaluation, 10 herring fillets from each process were thawed, cut into pieces, 152 mixed together to reduce individual variability in fillets and put into closed flasks. Products were

assigned 3-digit numbers, randomised and served simultaneously after 30 min at ambienttemperature.

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156 **2.4. Phenolic compound analysis**

157 A simultaneous steam distillation solvent extraction (SDE) of smoke compounds was performed 158 in a Likens-Nickerson (1964) apparatus according to Tanchotikul and Hsieh (1989). The SDE 159 extracts were stored at -20° C before gas chromatography analysis. A derivatisation step 160 (silvlation) was performed before analysis. Conditions of gas chromatography are detailed in 161 Sérot et al. (2004). 10 phenolic compounds were analysed: phenol, p-cresol, o-cresol, guaiacol, 162 4-methyl guaiacol, 4-ethyl guaiacol, syringol, eugenol, 4-propyl guaiacol and isoeugenol. These 163 compounds have previously been identified by Sérot and Lafficher (2003) as major phenolic 164 components of smoked fish.

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166 **2.5. Statistical analysis**

Analysis of variance (ANOVA) was performed on sensory data using Statgraphics Plus 5.1 software (Sigma Plus, Paris, France). The significant statistical level was set at p < 0.05. Multivariate data processing was performed with Uniwin Plus 5.0 software (Sigma Plus, Paris, France). Principal component analysis (PCA) with standardisation was performed on the means of the sensory scores and the means of each phenolic compound percentage were added as supplementary variables.

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174 **3. Results-Discussion**

175 **3.1. Sensory characteristics**

An analysis of variance was carried out with the effects of assessors and products on scores ofeach odour attribute given by the 12 panellists. The main results are presented in Table 3

178 according to a modified Flash table (Schlich, 1998) where descriptors are sorted in columns by 179 decreasing F value and products are sorted in rows by increasing mean for the first attribute of 180 the table. The grand mean and the standard deviation calculated for the 21 products are also 181 included in the table and allow a rapid analysis of attributes as main contributors to discriminate 182 samples. A (+) sign is added when the means score is higher than the grand mean plus one 183 standard deviation, a (-) sign when the means score is lower than the grand mean minus one 184 standard deviation. For easier reading, only the means corresponding to these criteria are given; 185 means close to the general mean are not presented in the table. The descriptors "cold ash", 186 "global intensity" and "fat fish" odours have the highest F values for product effect with a highly 187 significant p-value. This means that great differences exist between samples for these odours.

188 Two extreme groups of products are identified. The first one presents a very high global odour 189 intensity with a specific "cold ash" note. Samples smoked by the traditional process using an 190 autocombustion generator (AT) constitute this group. The second group, with extreme and 191 opposite characteristics, gathers samples processed with a friction generator, associated with an 192 electrostatic method of smoke deposition (FE). They have a low odour, mainly "fat fish" and 193 "brine" odours, even "rancid" for one of them. We can suppose that the low level of smoke notes 194 contributes to the perception of odours more related to fish characteristics. Fish samples that 195 have been smoked at an initial product temperature of 20°C present the lowest "wood smoke" 196 characteristics in this group. Samples smoked with an electrostatic process but with an 197 autocombustion generator (AE) have similar characteristics to other samples smoked by an 198 electrostatic method (FE), a rather low odour but a lower "fat fish" score. Other odours, such as 199 "caramel", "butter" and "wood fire smoke" notes are detected when a voltage of 42 kV is used. 200 A principal component analysis (PCA) with standardisation performed on the panel mean scores, 201 obtained for each descriptor of the 21 products, allows the results from Table 3 to be completed 202 and shows a general view of the main characteristics of the samples. Fig. 1 illustrates that the

203 first principal component is mainly defined by descriptors related to smoke, such as "global intensity", "cold ash", "rubber" and "phenol", and to fish characteristics, such as "fat fish" and 204 205 "brine". Projection of samples in the first 1-2 plane (Fig. 2) gives the respective location of the 206 products and shows the intermediate characteristics of liquid smoke (L) and friction/traditional-207 processed samples (FT) with regard to their global odour intensity. Indeed, samples are ranked 208 along the first component (46.7%) according to their odour intensity, from strong note on the left 209 -hand side to low odour on the right-hand side of the figure. The second axis (15.7%) consists 210 mainly of the "vegetable" odour on the positive axis and "caramel" and "wood fire" on the 211 negative axis. The position of (L) products at the top of the figure is due to their "vegetable" note 212 detected in the three samples, whatever the smoking temperature. Regarding samples processed 213 by a friction generator and traditional smoking (FT), they can have specific odours such as "wood fire smoke", "butter" and, to a lesser extent, "caramel", particularly when smoked under 214 215 32°C. If the smoking is performed at 32°C with a one-third open valve, products smell a little of "rubber". 216

These results show that all the studied parameters (smoke generation, deposition method, smoking temperature, exhaust valve opening in the smokehouse or voltage applied in the electrostatic tunnel) have an effect on the smell characteristics of smoked products, either on odour intensity and/or on the kind of smoke note.

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222 Smoke generator effect

The comparison of the level of smoking of the samples, evaluated by the odour intensity, shows that the friction generator has a lower efficiency for smoke production compared to the autocombustion generator. The difference is clearly observed for traditional smoking and, to a lesser extent, for the electrostatic smoking method. The difference in smoke production temperature, 350°C for friction and around 450°C for pyrolysis of sawdust, leads to a less advanced degradation of wood with friction compared to the autocombustion method
(Knockaert, 1990) and the oxidation of the volatile compounds occurs to a lesser extent. This
could be the reason for the differences in the sensory features observed.

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232 Temperature effect

For smoke production by sawdust pyrolysis, sensory perception is slightly affected by an increase in temperature when the exhaust valve is completely open since samples smoked at 16°C have lower scores for odour global intensity and "ash" note than those of samples smoked at 24°C or 32°C. When the valve is one-third open, odours of samples become "phenolic" and "rubber", mainly for smoking temperatures of 16°C and 24°C, while the samples smoked at 32°C have the strongest global odour.

The results show that our smoking conditions lead to products with high smoke notes for all the temperatures tested but a high temperature, like 32°C, during the smoking step allows potential compounds with a higher molecular weight involved in the smoking effect to remain in the vapour phase (Potthast 1977, 1978; Girard, 1988) and therefore to be deposited in higher proportions.

Conclusions about the temperature effect with a friction smoke generator are quite similar, even though the smoke perception is less intense than with autocombustion. There is an increase in global smell intensity with temperature, with the two valve positions tested (Fig. 2). The lower level of smoking allows the modification of sensory characteristics related to temperature to be followed with more accuracy without a saturation effect.

Smell characteristics of samples smoked by vaporisation of liquid smoke are also affected by temperature. The mean score of "cold ash", given by the trained panel, increases with temperature as well as the "earthy" note. At the same time, "vegetable" odour, a specific characteristic of this kind of product, and "brine" odour decrease. Differences are mainly observed between the 16°C smoked samples and those smoked at 32°C. As shown by Sérot et al.
(2004), a temperature of 16°C does not allow the deposition of a great quantity of phenolic
compounds, probably because of the low vaporisation of the liquid smoke, and this phenomenon
could explain the sensory differences.

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258 Exhaust valve position effect

The effect of the exhaust valve position is mainly observed for the autocombustion process. If the exhaust valve is one-third open, meaning a longer residence time for the smoke in the kiln, all the products have the same strong global intensity with a "cold ash" specificity. It is likely that, in these conditions, the level of smoke compound deposition is high enough at all the temperatures to reach a saturation point in odour evaluation. When the valve is completely open, the temperature effect is more noticeable. In the case of the friction generator, the position of the valve does not seem to affect odour characteristics.

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267 Smoking method effect

As previously described, samples smoked using our current electrostatic method have low smoke odours. However, smell characteristics could be modulated when smoke is produced by sawdust pyrolysis (AE). Indeed, in these conditions, a voltage of 42 kV instead of 37 kV gives products with more complex characteristics, lightly "butter", "caramel" and "wood fire". No voltage effect was observed when the electrostatic method and a friction generator (FE) were used. Smoke compounds produced during friction are probably different and therefore it is possible that they do not react equally in the electric field.

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276 **3.2.** Relationships between odour characteristics and phenolic compound deposition

277 In order to find possible explanations for the sensory characteristics described in relation to the 278 10 major phenolic compounds analysed, a projection of the contents of these compounds was 279 made on the first plane of PCA, performed on sensory descriptors. These chemical data were 280 added as supplementary variables. The first plane shows a correlation between the first 281 component and all the phenolic compounds, except eugenol (figure not presented). The content of these molecules increases with the characteristics of "global intensity", "cold ash", "rubber" 282 and "phenolic", which confirms the likely contribution of the phenol classes to smoke aroma as 283 284 mentioned by many researchers (Lustre & Issenberg, 1970; Maga, 1987; Girard 1988), The 285 odour intensity of the smoked samples, scored by the trained panel, seems at first to accord with 286 the content of phenolic compounds. However, the study of the relationship between the global 287 odour and the sum of the 10 phenolic compounds (Fig. 3) shows that, if a general trend is observed, the model of prediction of global intensity by total phenolic compounds, though 288 significant, is rather weak (R^2 adjusted = 30.8%). The same weaker relationship is obtained 289 between the "cold ash" note and the sum of phenolic compounds. The R² adjusted of this model 290 291 is 31%. The lack of fit is due partly to the characteristics of the samples smoked by a traditional 292 smokehouse and pyrolysis of sawdust and especially the references AT-16 and AT-24. These 293 products were among the highest sensory score samples for odour intensity but rank in the 294 middle of the range of phenolic contents observed. In contrast, when the smoking temperature 295 was set at 32°C, samples prepared with liquid smoke (L) or a traditional process with a friction 296 generator (FT) had high contents of total phenolic compounds but intermediate sensory scores. 297 Thus, it could be suggested that not only the total content but also the type of phenolic 298 compounds deposited on the flesh is important. Perception thresholds are different from one 299 compound to another (Leffingwell & Leffingwell, 1991) and it is therefore obvious that odour 300 characteristics cannot be related only to the quantity of phenolic molecules.

301 Backward stepwise multiple linear regression was performed between odour characteristics and 302 the analysed phenolic compounds. The results show statistically significant relationships between the "cold ash" note and some phenolic compounds such as o-cresol, p-cresol and, to a 303 lesser extent. 4-ethyl guaiacol and 4-propyl guaiacol. The R^2 adjusted of the model is 67.3%. 304 which means that a fair part of the odour variability is not explained by this model. Nevertheless, 305 it does allow identification of molecules that could have the most important impact on "cold ash" 306 307 odour. In the case of "wood smoke" odour, it was impossible to find a relationship with specific 308 compounds. It is likely that the sensory differences observed were not high enough to identify 309 relationships with phenolic compounds.

310 Sérot et al. (2004) have shown that the content of phenolic compounds increases with the time of 311 processing and the temperature applied but that the relative percentage of these compounds is 312 constant for a given smoking procedure and is independent of the process parameters used. In 313 order to test the hypothesis of a specific effect of the relative composition of phenolic 314 compounds on sensory properties, percentages of phenolic compounds were added as 315 supplementary variables to the PCA carried out with sensory descriptors (Fig. 4). This figure 316 shows correlations between odours scored by the sensory panel and the percentage of each 317 phenolic compound. On the first component, mainly defined by descriptors such as "global intensity", "cold ash", "rubber" and "phenolic" odours, the best correlation with these criteria is 318 319 observed with the compounds o-cresol, phenol and 4-ethyl guaiacol. In contrast, the sensory 320 descriptors "fat fish", "brine" and "butter", and chemical compounds syringol, isoeugenol and 321 eugenol are positively correlated with the first principal component. As for guaiacol, the work of Sérot et al. (2004) showed that this compound, as well as 4-methyl guaiacol, was identified as 322 323 the main phenolic compound whatever the process and contributed to the discrimination of 324 processes. However, this molecule does not seem related to a specific odour (Fig. 4) and does not 325 allow the samples map to be explained (Fig. 2).

326 Now, with the knowledge of the phenolic compound distribution and the correlation with 327 sensory descriptors, is it possible to propose a hypothesis about the sensory differences observed 328 between samples in Fig. 2 and not predicted by the total phenolic compounds? The case of 329 sample L32 for example is interesting. This product received a lower score for "global intensity" 330 and "cold ash" odour compared to AT products and a high score for "phenolic" odour. We can 331 suppose that its higher phenol percentage (Fig. 2 and Fig. 4) is one of the possible explanations. Indeed, phenol is a compound with a high perception threshold, which could therefore have a 332 333 lower contribution to smoke odour. Moreover, samples smoked with condensate vaporisation (L) 334 have been described by the specific characteristics "earthy" and "vegetable", which suggests that 335 other volatile compounds are involved in the perception, not only phenolic compounds. These 336 molecules may contribute by adding more aromatic and complex odours but have less effect on 337 smoke odour.

In the case of FT samples, and especially FT 32-3, a rather low global intensity is found in spite 338 of its quantity of phenolic compounds. Guaiacol, 4-methyl guaiacol and propyl guaiacol do not 339 340 discriminate this sample from AT samples but these latter products have higher percentages of 341 phenol and o-cresol. However, if the hypothesis of a small effect of phenol in smoke odour is 342 suggested for samples smoked with vaporisation of condensates, it is difficult to find a contrary 343 effect with AT samples. On the other hand, o-cresol has previously been identified as a 344 compound with a significant effect on the relation between "cold ash" odour and phenolic 345 compounds. This molecule could play an important role in explaining the observed differences. 346 Regarding FT samples, the low global intensity observed in spite of a high percentage of eugenol could also be explained by interaction of this compound with proteins. Indeed, a recent study 347 348 (Reiners, Nicklaus & Guichard, 2000) has shown that the addition of protein decreases the odour 349 perception of eugenol.

The results of this experiment and the difficulty of reaching clear conclusions suggest that the study of only 10 phenolic compounds is certainly too restrictive an analysis to understand all the sensory characteristics. Moreover, the simultaneous quantitative and qualitative variation of phenolic compounds leads to a more complex evaluation of their effects.

It is certain that molecules other than phenolic compounds are deposited during the traditional process with autocombustion (AT), and that these are also involved in the strong odour detected. Previous work on smoked salmon (Cardinal et al., 1997) has already shown the high global intensity of products processed with this technique and different classes of compound have been specifically identified. Among the molecules found, butenal, 3-methyl butanal, methyl alcanes and aromatic compounds such as m-xylene, styrene and alkyl benzene could be involved in sensory characteristics.

361 Regarding samples smoked in our current conditions using the electrostatic method, the very low 362 level of phenolic compounds deposited is probably the main reason for the low perception of 363 smoked odour. Ruiter (1979) and Sirami (1981) indicated that the electrostatic field modifies the 364 smoke compound ratio in the vapour phase, mainly by increasing the level of carbonyl 365 compounds to the detriment of phenolic compounds. Figures 4 and 2 show that syringol, 366 isoeugenol and eugenol have the strongest correlation with "fat fish", "brine", and "butter" and 367 constitute the main fraction of phenolic compounds in electrostatic samples. Thus, we can 368 suppose that these compounds do not have a great impact on sample odour, for the quantity 369 deposited. The comparison of the phenolic compound profile of the two AE samples treated with 370 two different voltages does not lead to a possible explanation of the characteristics, lightly 371 "butter", "caramel" and "wood fire", detected in the AE sample when a voltage of 42 kV is applied. This shows the difficulty of finding relations between sensory perception and chemical 372 373 compounds, especially when only one class of compounds has been followed.

However, the results of our study, through the comparison of extreme products, electrostatic samples and autocombustion/traditional samples, tend to confirm the importance of phenolic compounds in smoke perception. They show that some of the 10 compounds analysed determine, to a certain extent, the smoked characteristics of products, even if other molecules can also modulate their perception.

379

380 Conclusion

This study has confirmed, through the large range of smoked products investigated, the strong effect of smoking conditions on final odour characteristics. These results also indicate to processors the possibility of adapting smoked characteristics to consumer demand.

384 Products smoked with our current electrostatic process, regardless of the kind of generator, have low smoked characteristics and mainly "fat fish" and "brine" notes but recent results show that 385 386 some modifications of the equipment could improve smoke deposition. The kind of smoke generator used leads to products not only with different global odour intensities but also different 387 388 smoke characteristics. The efficiency of the generator with sawdust pyrolysis is observed, 389 especially for the traditional process of smoke deposition since the temperature is high. A 390 general trend is observed about the effect of smoking temperature. The global odour intensity 391 generally increases with the temperature applied in the smokehouse. This is true for both the 392 friction generator and the autocombustion generator. In the latter case, the interactions effect 393 between temperature and other parameters, such as the exhaust valve position, can modulate 394 these results. In particular, when the valve position is one-third open, the sensory characteristics 395 of the samples smoked at 16, 24 or 32°C are very close. The higher residence time of the smoke 396 could indicate that a saturation point is reached. If the valve is more open, the temperature effect 397 on sensory characteristics is more significant. A temperature of 16°C is enough to reach smoked 398 product characteristics without a strong "cold ash" note. This smoking procedure, with an Friday, October 22, 2004

autocombustion generator and traditional smoke deposition by direct exposure of fillets, is the
most frequent practice in industry. It is therefore of considerable interest for processors to know
the effects of these parameters and how to control them.

402 Regarding the role of phenolic compounds on sensory properties, it is not clear enough to give 403 detailed conclusions. If we consider the results of odour characteristics from both electrostatic 404 and traditional smoked products, the content of phenolic compounds seems well related to 405 smoked odour. Although the content of phenolic compounds can be an indicator of smoking 406 intensity, this analysis does not always reflect the odour intensity perceived by a group of 407 panellists. Indeed, phenolic compounds have different perception thresholds and do not have the same impact on sensory perception. Our study suggests that o-cresol, p-cresol and, to a lesser 408 409 extent, 4-ethyl guaiacol and 4-propyl guaiacol are the main components involved in "cold ash" 410 odour. The study of the relation between sensory descriptors and percentage of each phenolic 411 compound leads to the hypothesis that syringol, isoeugenol and eugenol have no detectable 412 effect on smoke odours, in the tested conditions.

413 However, these results show that it does not seem reasonable to explain the sensory properties of 414 smoked products with only the class of the 10 major phenolic compounds detected in the flesh. 415 Indeed, many other volatile compounds have been identified such as ketones, aldehydes, acids, 416 alcohols, esters, furans, lactones and many other molecules (Maga, 1987). It is suggested that, in 417 order to identify the main compounds involved in the sensory properties of smoked fish, the 418 study be extended to all volatile compounds, taking into account the relative percentage of each 419 component as well as its content in the flesh. Knowledge of the matrix effect on the threshold perception of each compound would be helpful to understand their role in odour characteristics 420 421 and identify the potent odorants in smoked fish.

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Friday, October 22, 2004

486	Figure captions
487	
488	Table 1. Process and experimental conditions of smoking
489	
490	Table 2. Odour characteristics and description
491	
492	Table 3. Main odour characteristics of 21 smoked herring samples (mean scores and results of
493	analysis of variance)
494	
495	^a F value of Fisher test
496	^b Probability of Fisher test for product effect, significant differences between samples * p<0.05,
497	** p<0.01, *** p<0.001,
498	^c Grand mean of the 21 products
499	^d Standard deviation of the 21 mean scores
500	^e Initial product temperature (°C) for the electrostatic method, 10°C for all the other products
501	^f Exhaust valve position, $1 = 1/3$ open, $3 = 3/3$ open
502	
503	
504	Figure 1. Projection of variables in the plane 1-2 of the principal component analysis on sensory
505	descriptors for odour
506	
507	Odour: global intensity (iglo), wood fire smoke (wood), cold ash (ash), phenol/medicinal (phen),
508	rubber (rubb), caramel (cara), fat fish (fat), butter (butt), rancid (ranc), brine (brin), dried fish
509	(drie), vegetable (vege), earthy (eart)
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512 Figure 2. Projection of samples in the plane 1-2 of the principal component analysis on sensory513 descriptors

514

- 515 AT: Autocombustion generator and traditional smoking, FT: Friction generator and traditional
- 516 smoking, AE: Autocombustion generator and electrostatic smoking, FE: Friction generator and
- 517 electrostatic smoking
- 518 16, 24, 32: smoking temperature (°C)

519 1 or 3: exhaust valve position

520 10 or 20: initial temperature of fish (°C)

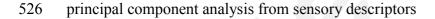
521

522 Figure 3. Relationship between global odour and the total phenolic compounds

523 R^2 adjusted = 30.8%

524

525 Figure 4. Correlation between phenolic compound percentage and components 1 and 2 of the



527

- 528 <u>Odour:</u> global intensity (iglo), wood fire smoke (wood), cold ash (ash), phenol/medicinal (phen),
- 529 rubber (rubb), caramel (cara), fat fish (fat), butter (butt), rancid (ranc), brine (brin), dried fish
- 530 (drie), vegetable (vege), earthy (eart)
- 531 <u>Phenolic compounds</u> are identified with •
- 532 phenol (phenol), p-cresol (pcresol), o-cresol (ocresol), guaiacol (guaiacol), 4-methyl guaiacol
- 533 (meguaiacol), 4-ethyl guaiacol (etguaiacol), syringol (syringol), eugenol (eugenol), 4-propyl
- 534 guaiacol (proguaiacol) and isoeugenol (isoeugenol)

536

Table 1.

Smoke deposit method Smoke Generation	Traditional method (T) direct exposure smoking time = 3h	Electrostatic method (E) voltage (kV) 37 or 42 smoking time = 12 min			
Autocombustion (A)	(AT)	(AE)			
Smokehouse temperature (°C)	16 - 24 - 32	ambient			
Initial product temperature (°C)	10	10			
Exhaust valve opening	1/3 -3/3				
Friction (F)	(FT)	(FE)			
Smokehouse temperature (°C) Initial product temperature (°C)	16 - 24 - 32 10	ambient 10-20			
Exhaust valve opening Liquid smoke atomisation (L)	<u>1/3 -3/3</u> (L)				
Smokehouse temperature (°C) Initial product temperature (°C) Exhaust valve opening	16 - 24 - 32 10 closed				

540 Table 2.

 Descriptors of odour	label	Description
 Global intensity	iglo	Overall odour whatever the note
Wood fire smoke	wood	Odour of a wood fire
Cold ash	ash	Odour of ashes once the fire is out
Phenol / Medicinal	phen	Odour of a solution of phenol
Rubber	rubb	Odour of a burnt tyre
Caramel	cara	Odour of burnt sugar
Fat fish	fat	Odour of oil associated with fat fish
Butter	butt	Odour developed by butter
Rancid	ranc	Odour of oxidised fish oil
Brine fish	brin	Odour of fish salted in brine
Dried fish	drie	Odour developed by fish meal
Vegetable	vege	Odour of freshly cut grass, plant
Earthy	eart	Odour of earth or mud

Table 3.

Odours	ash	iglo	fat	eart	ranc	vege	phen	rubb	brin	cara	drie	butt	wood
F ^a	12.0	7.9	7.0	2.7	2.6	2.4	2.4	2.2	2.2	2.0	2.0	1.8	1.7
P ^b	***	***	***	***	***	***	***	**	**	**	*	*	*
Gmean ^c	2.6	6.4	2.9	1.1	1.3	1.1	0.9	0.8	1.7	0.5	1.3	0.9	2.8
std ^d	2.0	1.0	1.3	0.8	0.7	0.8	0.6	0.5	0.7	0.4	0.6	0.6	0.8
FE+42	0.2-	5.3-	4.9+	0.3-			0.2-	0.1-	2.7+	0.1-	0.2-		
FE+37-20 ^e	0.3-		4.8+		3.0+				2.5+	0.1-	0.5-		1.9-
FE+42-20	0.5-	5.1-	4.4+	0.2-					2.5+				2.0-
FT16-3 ^f				0.3-			0.3-			0.1-		1.7+	
FT16-1							0.3-	0.3-	2.6+		0.4-	2.0+	3.7+
FE+37		5.1-	4.8+										
FT24-3			4.7+	0.3-	3.0+					0.9+	2.2+		
AE+37		5.2-					0.2-				0.6-		
L16						3.5+	2.0+				0.0		1.8-
AE+42									2.8+	1.4+	0.6-	1.6+	4.0+
FT32-3				0.2-			0.3-		1.0-				
FT24-1									2.8+	1.6+		1.9+	4.1+
FT32-1					2.0+	0.3-		1.4+			2.3+		
L24				2.5+		2.4+				0.9+			
AT16-3										0.9+		0.3-	
L32				2.6+		2.0+	1.7+		1.0-			0.3-	1.4-
AT32-3	4.6+	7.6+	1.1-	2.2+	0.6-	0.4			0.9-	0.1-	2.4+	0.1-	
AT24-1	5.3+	7.5+				0.3-	1.8+	1.7+				0.1-	
AT16-1	5.7+	7.7+	1.5-				2.1+	2.3+		0.9+			
AT32-1	6.1+	8.4+	1.3-		0.3-			1.3+	0.6-			0.3-	4.4+
AT24-3	6.4+	7.6+							0.6-			0.3-	1.7-

547

^aF value of Fisher test

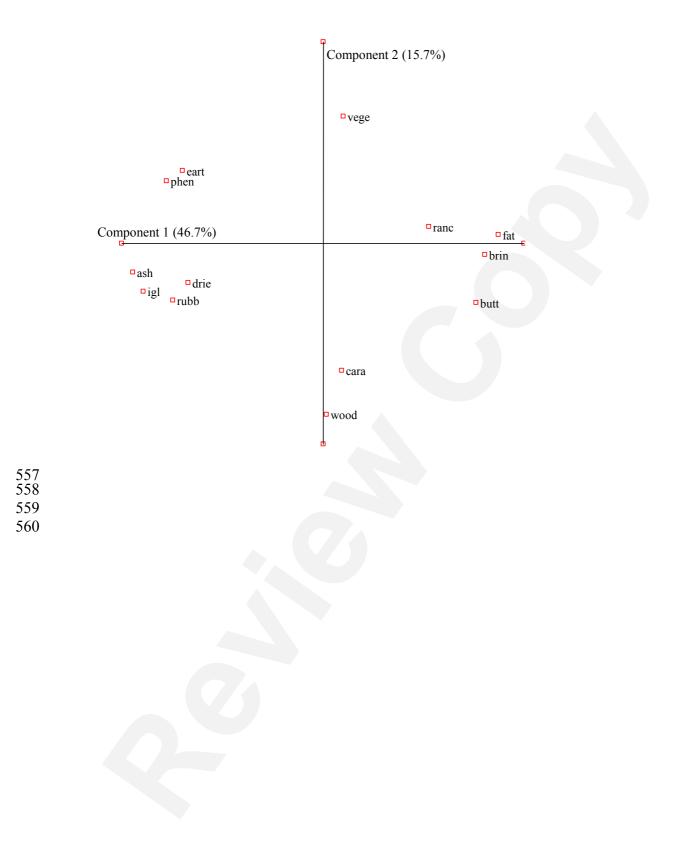
^bProbability of Fisher test for product effect, significant differences between samples * p<0.05,

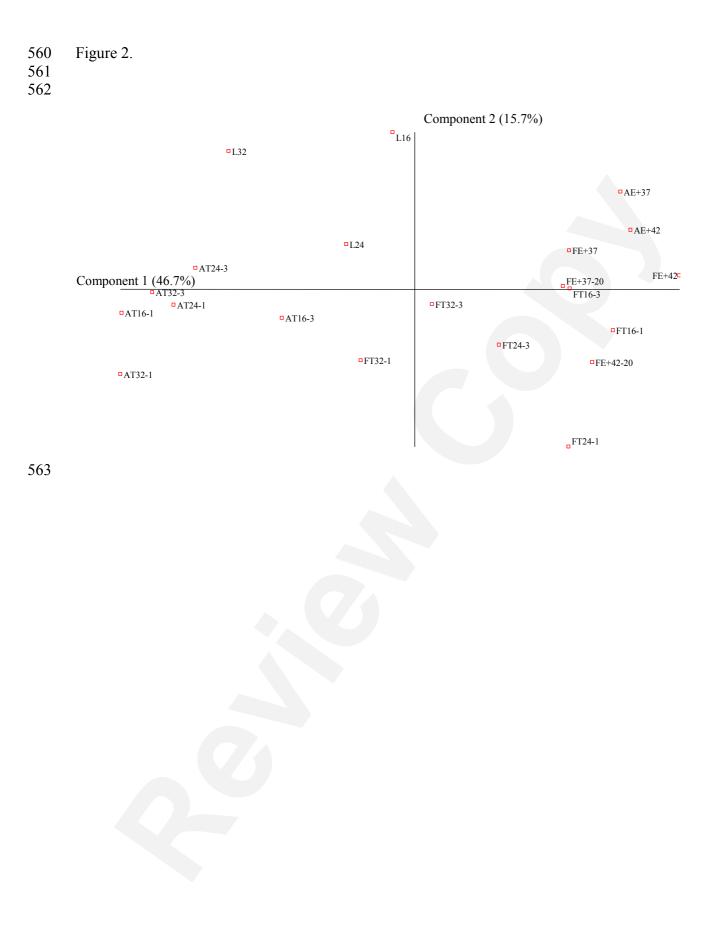
** p<0.01, *** p<0.001, Grand mean of the 21 products

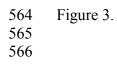
^dStandard deviation of the 21 mean scores

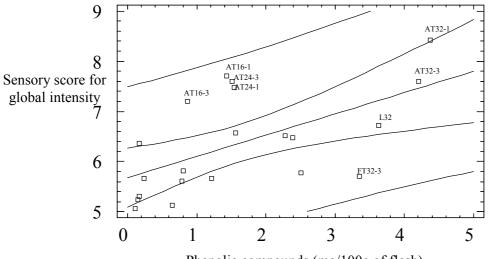
^eInitial product temperature (°C) for the electrostatic method, 10°C for all the other products ^fExhaust valve position, 1 = 1/3 open, 3 = 3/3 open

556 Figure 1.









Phenolic compounds (mg/100g of flesh)

