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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.  $© 2005 Elsevier Ltd. All rights reserved.$ 

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

## 1. Introduction

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](#page-9-0)). The increase in smoked fish consumption began in the 1990s 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 45,000 tons of salmon are used in France to produce 18,000 tons of smoked salmon, 15% of which is exported to Italy, Belgium and, to a lesser extent, Germany [\(OFIMER, 2004\)](#page-9-0).

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A recent European study on smoked salmon quality ([Cardinal et al., 2001\)](#page-9-0) showed that the European market offers a large range of products with different salt levels and different phenol contents (the criteria used until now as indicators 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 from various European countries, indicated that customers do not all like the same kinds of products. Five classes of consumer, with different preferences, were identified ([Anonymous, 2004](#page-9-0)). These preferences are related to specific sensory properties. For example, it appears that, for the groups of consumers whose preferences are mainly explained by smoke odour or flavour, not only is the intensity of smoking important but also the kind of smoke note. While some people require a strong smoke odour and flavour, others want a specific ''wood fire smoke'' note. The control of this smoke characteristic can be of real interest to processors who want to adapt 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, 1988; Girard, Talon, & Sirami,](#page-9-0) [1982\)](#page-9-0). The number of volatile compounds identified in a smoke, more than 400, explains the difficulty of relating sensory perception to specific molecules ([Cardinal,](#page-9-0) Berdagué, Dinel, Knockaert, & Vallet, 1997; Maga, [1987\)](#page-9-0). Recent studies performed on phenolic compounds (Guillard & Grondin, 2003; Sérot, Baron, [Knockaert, & Vallet, 2004](#page-9-0)) have shown that their deposition depends on the smoking conditions and research conducted so far has suggested that phenolic compounds play a key role in smoke perception. However, the relationship between these compounds and sensory perception is not well detailed in the literature, especially for fish products, although some authors, cited by [Maga \(1987\)](#page-9-0), such as [Toth and Potthast \(1984\)](#page-9-0), have evaluated the effects of some pure molecules in solution on sensory properties. More recently, the study of Ojeda, Barcenas, Pérez-Elortondo, Albisu, and Guillen [\(2002\)](#page-9-0) has shown the difficulty of associating molecules with 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 relationship between phenolic compound content and sensory perception. It forms part of the same investigation as that carried out by Sérot [et al. \(2004\).](#page-9-0) This previous work clearly indicated that the process applied affects the content of phenolic compounds, so knowledge about the effects of these compounds on sensory properties would allow the process to be adapted according to the target product.

For practical and cost reasons, herring fillets were used. Two smoke generation techniques were tested, one based on the pyrolysis of sawdust sustained by air circulation (autocombustion) and the second producing smoke by friction of wood log. For each type of smoke generation, two different ways of smoke deposition were compared: exposure of fillets in a closed air-conditioned smokehouse (the traditional process) and the electrostatic method where smoke is accelerated towards fillets ([Bardin, Desportes, Knockaert, & Vallet, 1997; Collig](#page-9-0)[nan, Knockaert, Raoult-Wack, & Vallet, 1992\)](#page-9-0). The effects of these four techniques were compared to a fifth, the atomisation of liquid smoke.

# 2. Material and methods

#### 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 6 h, hand-salted with refined salt for 20 min at 12  $\rm{°C}$  before being rinsed on grids with water  $(15 \degree C)$  and stored in a cold room at  $2^{\circ}$ C for 14 h until smoking.

#### 2.2. Fish processing

Forty fillets were processed for each treatment. Production of smoke was performed by pyrolysis at  $450$  °C of beech wood sawdust (Thirode, France) or by friction of beech wood log at  $350^{\circ}$ C (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 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 m s<sup>-1</sup> above the products and with the exhaust valve position one-third open (1/ 3) or totally open (3/3). The second way consisted of an electrostatic method where smoke was led through an experimental tunnel  $(4000 \times 100 \times 150 \text{ mm})$ . This allowed continuous smoking with a production capacity of 125 kg/h. The voltage, applied between the positive pole (smoke ionisation) and the cathode (conveyor belt), was set by an HT14B high voltage supply (Sefelec, France). The distance between electrodes was 12 cm. Two positive voltages were tested, 37 and 42 kV, and the air speed above the fillet was around  $0.5 \text{ ms}^{-1}$ . The anode electrode, in stainless steel 316 L, was a rectangular grid with 4.5 by 2 cm spacing of bars 0.2 cm in diameter. The time of smoking was 3 h for the traditional method at 16, 24 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  $^{\circ}$ 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 h. 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 prior to analysis of phenolic compounds and sensory evaluation.

# 2.3. Sensory evaluation

A descriptive test with conventional profiling [\(Stone](#page-9-0) [& Sidel, 1985\)](#page-9-0) was performed on the odour characteristics of smoked herring with 12 trained panellists belonging to the IFREMER staff. 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 odour and to check the panellists' understanding of the descriptors. At this session, a selection of smoked herring samples was described by the panel. These products represented the main smoking parameters applied in the study. Each member of the group was asked to smell each product and to describe the main odour characteristics. A discussion with the panel elucidated a final consensus on the most adapted criteria and led to adopt common definitions. Table 2 gives the list of odours and their description. An experimental design was constructed in order to balance the characteristics and odour intensities of the products presented within a session. Five sessions were organised to test all the products, four with a presentation of four products and one with five products.

Sessions were performed in individual partitioned booths, as described in procedure NF V-09-105



Process and experimental conditions of smoking

Table 2 Odour characteristics and description

Descriptors of	Label	Description
Odour		
Global intensity	iglo	Overall odour whatever the characteristic
Wood fire smoke	wood	Odour of 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 a burnt sugar
Fat fish	fat	Odour of oil associated with fat fish
<b>Butter</b>	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

([AFNOR, 1995](#page-9-0)) and equipped with a computerised system (Fizz, Biosystémes, Couternon,France). Panellists rated the sensory attributes on a continuous scale displayed on a computer screen, from low intensity (0) to high intensity (10).

On the day of evaluation, 10 herring fillets from each process were thawed, cut into pieces, mixed together to reduce individual variability in fillets and put into closed flasks. Products were assigned 3-digit numbers, randomised and were served simultaneously after 30 min at ambient temperature.

## 2.4. Phenolic compound analysis

A simultaneous steam-distillation solvent extraction (SDE) of smoke compounds was performed in a [Likens](#page-9-0) [and Nickerson \(1964\)](#page-9-0) apparatus according to [Tanc](#page-9-0)[hotikul and Hsieh \(1989\).](#page-9-0) The SDE extracts were stored at  $-20$  °C before gas chromatography analysis. A derivatisation step (silylation) was performed before



<span id="page-3-0"></span>analysis. Conditions of gas chromatography are detailed in Sérot et al. (2004). Ten phenolic compounds were analysed: phenol, p-cresol, o-cresol, guaiacol, 4-methyl guaiacol, 4-ethyl guaiacol, syringol, eugenol, 4-propyl guaiacol and isoeugenol. These compounds have previously been identified by Sérot and Lafficher (2003) as major phenolic components of smoked fish.

# 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.

# 3. Results and discussion

#### 3.1. Sensory characteristics

#### 3.1.1. General

An analysis of variance was carried out with the effects of assessors and products on scores of each odour attribute given by the 12 panellists. The main results are presented in Table 3 according to a modified Flash table ([Schlich, 1998\)](#page-9-0) where descriptors are sorted in to columns by decreasing  $F$  value and products are sorted into rows by increasing means for the first attribute of the Table. The grand mean and the standard deviation calculated for the 21 products are also included in the Table and allow a rapid analysis of attributes as main contributors for discriminating samples. A  $(+)$  sign is added when the means score is higher than the grand mean plus one standard deviation,  $a(-)$  sign when the means score is lower than the grand mean minus one standard deviation. For easier reading, only the means

Table 3

Main odour characteristics of 21 smoked herring samples according to the procedure of the Flash table (mean scores and results of analysis of variance)

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

Global intensity (iglo), wood fire smoke (wood), cold ash (ash), phenol/medicinal (phen), rubber (rubb), caramel (cara), fat fish (fat), butter (butt), rancid (ranc), brine (brine), dried fish (drie), vegetable (vege), earthy (eart).

(The smoke generation procedure is indicated by: A, autocombustion, F, friction, L, liquid smoke atomisation; the smoke deposit method is either Ttraditional or E-electrostatic; smokehouse temperature was set at 16, 24 or 32 °C; +37 and +42 indicate the voltage (kV) for electrostatic process).

<sup>a</sup> F value of Fisher test.<br><sup>b</sup> Probability of Fisher test for product effect, significant differences between samples \*p < 0.05, \*\*p < 0.01, \*\*\*p < 0.001.

<sup>c</sup> Grand mean of the products.

<sup>d</sup> Standard deviation of the 21 mean scores.

<sup>e</sup> Initial product temperature ( $\degree$ C) for the electrostatic method, 10  $\degree$ C for all the other products.

 $f$  Exhaust valve position,  $1 = 1/3$  open,  $3 = 3/3$  open.

corresponding to these criteria are given; means close to the general mean are not presented in the Table. The descriptors ''cold ash'', ''global intensity'' and ''fat fish'' odours have the highest  $F$  values for product effect with a highly significant p-value. This means that great differences exist between samples for these odours.

Two extreme groups of products are identified. The first one presents a very high global odour intensity with a specific ''cold ash'' note. Samples smoked by the traditional process, using an autocombustion generator (AT), constitute this group. The second group, with extreme and opposite characteristics, gathers samples processed with a friction generator, associated with an electrostatic method of smoke deposition (FE). They have a low odour, mainly ''fat fish'' and ''brine'' odours, even ''rancid'' for one of them. We can suppose that the low level of smoke notes contributes to the perception of odours more related to fish characteristics. Fish samples that have been smoked at an initial product temperature of 20 C present the lowest ''wood smoke'' characteristics in this group. Samples smoked with an electrostatic process, but with an autocombustion generator (AE), have similar characteristics to other samples smoked by an electrostatic method (FE), a rather low odour but a lower "fat fish" score. Other odours, such as "caramel", "butter'' and ''wood fire smoke'' notes are detected when a voltage of 42 kV is used. A principal component analysis (PCA) with standardisation performed on the panel mean scores, obtained for each descriptor of the 21 products, allows the results from [Table 3](#page-3-0) to be completed and shows a general view of the main characteristics of the samples. Fig. 1 illustrates that the 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 ''brine''. Projection of samples in the first 1–2 plane ([Fig. 2\)](#page-5-0) gives the respective location of the products and shows the intermediate characteristics of liquid smoke (L) and friction/traditional processed samples (FT) with regard to their global odour intensity. Indeed, samples are ranked along the first component (46.7%) according to their odour intensity, from strong note on the lefthand side to low odour on the right-hand side of the figure. The second axis (15.7%) consists mainly of the ''vegetable'' odour on the positive axis and ''caramel'' and ''wood fire'' on the negative axis. The position of (L) products at the top of the Figure is due to their ''vegetable'' note detected in the three samples, whatever the smoking temperature. Regarding samples processed 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 below  $32^{\circ}$ C. If the smoking is performed at 32  $\mathrm{C}$  with a one-third open valve, products smell a little of ''rubber''.

These results show that all the studied parameters (smoke generation, deposition method, smoking temperature, exhaust valve opening in the smokehouse or



Fig. 1. Projection of variables in the plane 1–2 of the principal component analysis on sensory descriptors for odour *Odour*: global intensity (iglo), wood fire smoke (wood), cold ash (ash), phenol/medicinal (phen), rubber (rubb), caramel (cara), fat fish (fat), butter (butt), rancid (ranc), brine (brin), dried fish (drie), vegetable (vege), earthy (eart).

<span id="page-5-0"></span>

Fig. 2. Projection of samples in the plane 1–2 of the principal component analysis on sensory descriptors (the smoke generation procedure is indicated by: A, autocombustion; F, friction; L, liquid smoke atomisation; the smoke deposit method is either T-traditional or E-electrostatic; 16, 24, 32 are the smokehouse temperature applied ( $\degree$ C); 1 or 3 is the exhaust valve position, 1 = one-third open, 3 = totally open; 10 or 20 indicate the initial temperature of fish  $({\degree}C)$ ; +37 and +42 indicate the voltage (kV) for electrostatic process.)

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.

# 3.1.2. 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 than 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,  $350^{\circ}$ C for friction and around 450 °C for pyrolysis of sawdust, leads to a less advanced degradation of wood with friction than with the autocombustion method [\(Knockaert,](#page-9-0) [1990\)](#page-9-0) 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.

#### 3.1.3. 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  $16^{\circ}$ C have lower scores for odour global intensity and ''ash'' note than have those of samples smoked at 24 or 32 °C. When the valve is one-third open, odours of samples become ''phenolic'' and ''rubber'', mainly for smoking temperatures of 16 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, e.g.,  $32^{\circ}$ C, during the smoking step allows potential compounds with a higher molecular weight, involved in the smoking effect, to remain in the vapour phase ([Girard, 1988; Potthast,](#page-9-0) [1977, 1978\)](#page-9-0) 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 also does 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  $16^{\circ}$ C does not allow the deposition of great quantity of phenolic compounds, probably because of the low vaporisation of the liquid smoke, and this phenomenon could explain the sensory differences.

#### 3.1.4. Exhaust valve position effect

The effect of the exhaust valve position is mainly observed for the autocombustion process. If the exhaust valve in 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, under 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.

# 3.1.5. Smoking method effect

As previously described, samples smoked using our current electrostatic method have low smoke odours. However, smell characteristics could be modulate when smoke is produced by sawdust pyrolysis (AE). Indeed, under 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.

# 3.2. Relationships between odour characteristics and phenolic compound deposition

In order to find possible explanations for the sensory characteristics described in relation to the 10 major phenolic compounds analysed, a projection of the contents of these compounds was made on the first plane of PCA, performed on sensory descriptors. These chemical data were added as supplementary variables. The first plane shows a correlation between the first 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'' and ''phenolic'', which confirms the likely contribution of the phenol classes to smoke aroma, as reported by many researchers [\(Girard, 1988; Lustre &](#page-9-0) [Issenberg, 1970; Maga, 1987](#page-9-0)). The odour intensity of the smoked samples, scored by the trained panel, seems at first to accord with the content of phenolic compounds. However, the study of the relationship between the global 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 significant, is rather weak  $(R^2)$ adjusted =  $30.8\%$ ). The same weaker relationship is obtained between the ''cold ash'' note and the sum of phenolic compounds. The  $R^2$ , adjusted, of this model is  $31\%$ . The lack of fit is due partly to the characteristics of the



Fig. 3. Relationship between global odour and the total phenolic compounds  $R^2$  adjusted = 30.8% (the smoke generation procedure is indicated by: A, autocombustion, F, friction, L, liquid smoke atomisation; the smoke deposit method is either T-traditional or Eelectrostatic; smokehouse temperature was set at 16, 24 or 32 °C; Exhaust valve position, 1, 1/3 open, 3, 3/3 open).

samples smoked by a traditional smokehouse and pyrolysis of sawdust and especially the references AT-16 and AT-24. These products were among the highest sensoryscored samples for odour intensity but rank in the middle of the range of phenolic contents observed. In contrast, when the smoking temperature was set at  $32^{\circ}$ C, samples prepared by liquid smoke (L), or a traditional process with a friction generator (FT), had high contents of total phenolic compounds but intermediate sensory scores. Thus, it could be suggested that, not only the total content, but also the type of phenolic compounds deposited on the flesh is important. Perception thresholds are different from one compound to another ([Leffingwell &](#page-9-0) [Leffingwell, 1991\)](#page-9-0) and it is therefore obvious that odour characteristics cannot be related only to the quantity of phenolic molecules.

Backward stepwise multiple linear regression was performed between odour characteristics and 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 lesser extent, 4-ethyl guaiacol and 4-propyl guaiacol. The  $R^2$ , adjusted, of the model is 67.3%, which means that a fair part of the odour variability is not explained by this model. Nevertheless, it does allow identification of molecules that could have the most important impact on ''cold ash'' odour. In the case of ''wood smoke'' odour, it was impossible to find a relationship with specific compounds. It is likely that the sensory differences observed were not great enough to identify relationships with phenolic compounds.

Sérot et al. (2004) have shown that the total content of phenolic compounds increases with the time of processing and the temperature applied but that the relative percentage of these compounds is constant for a given smoking procedure and is independent of the process parameters used. In order to test the hypothesis of a <span id="page-7-0"></span>specific effect of the relative composition of phenolic compounds on sensory properties, percentages of phenolic compounds were added as supplementary variables to the PCA carried out with sensory descriptors (Fig. 4). This figure shows correlations between odours scored by the sensory panel and the percentage of each 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 observed with the compounds o-cresol, phenol and 4-ethyl guaiacol. In contrast, the sensory descriptors ''fat fish'', ''brine'' and ''butter'', and chemical compounds syringol, isoeugenol and eugenol, are positively correlated with the first principal component. As for guaiacol, the work of Sérot et al. [\(2004\)](#page-9-0) showed that this compound, as well as 4-methyl guaiacol, was identified as the main phenolic compound, whatever the process, and contributed to the discrimination of processes. However, this molecule does not seem to be related to a specific odour (Fig. 4) and does not allow the samples map to be explained [\(Fig. 2\)](#page-5-0).

Now, with the knowledge of the phenolic compound distribution and the correlation with sensory descriptors, is it possible to propose a hypothesis about the sensory differences observed between samples in [Fig. 2](#page-5-0) and not predicted by the total phenolic compounds? The case of sample L32, for example is interesting. This product received a lower score for ''global intensity'' and ''cold ash'' odour than did AT products and a high score for ''phenolic'' odour. We can suppose that its higher phenol percentage ([Figs. 2 and 4](#page-5-0)) is one of the possible explanations. Indeed, phenol is a compound with a high perception threshold, which could therefore make a lower contribution to smoke odour. Moreover, samples smoked with condensate vaporisation (L) have been described by the specific characteristics ''earthy'' and ''vegetable'', which suggests that other volatile compounds are involved in the perception, not only phenolic compounds. These molecules may contribute by adding more aromatic and complex odours but have less effect on smoke odour.

In the case of FT samples, and especially FT 32-3, a rather low global intensity is found, in spite of its quantity of phenolic compounds. Guaiacol, 4-methyl guaiacol and propyl guaiacol do not discriminate this sample from AT samples but these latter products have



Fig. 4. Correlation between phenolic compound percentage and components 1 and 2 of the principal component analysis from sensory descriptors Odour: global intensity (iglo), wood fire smoke (wood), cold ash (ash), phenol/medicinal (phen), rubber (rubb), caramel (cara), fat fish (fat), butter (butt), rancid (ranc), brine (brin), dried fish (drie), vegetable (vege), earthy (eart). Phenolic compounds are identified with • phenol (phenol), p-cresol (pcresol), o-cresol (ocresol), guaiacol (meguaiacol), 4-methyl guaiacol (guiacol), 4-ethyl guaiacol (etguaiacol), syringol (syringol), eugenol (eugenol), 4-propyl guaiacol (proguaiacol) and isoeugenol (isoeugenol).

higher percentages of phenol and *o*-cresol. However, if the hypothesis of a small effect of phenol in smoke odour is suggested for samples smoked with vaporisation of condensates, it is difficult to find a contrary effect with AT samples. On the other hand,  $o$ -cresol has previously been identified as a compound with a significant effect on the relationship between ''cold ash'' odour and phenolic compounds. This molecule could play an important role in explaining the observed differences. 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 ([Reiners, Nicklaus, &](#page-9-0) [Guichard, 2000\)](#page-9-0) has shown that the addition of protein decreases the odour 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 for understanding 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](#page-9-0)) 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 alkanes and aromatic compounds, such as m-xylene, styrene and alkyl benzene could be involved in sensory characteristics.

Regarding samples smoked under our current conditions, using the electrostatic method, the very low level of phenolic compounds deposited is probably the main reason for the low perception of smoked odour. [Ruiter](#page-9-0) [\(1979\)](#page-9-0) and Sirami (1981) indicated that the electrostatic field modifies the smoke compound ratio in the vapour phase, mainly by increasing the level of carbonyl compounds to the detriment of phenolic compounds. [Figs.](#page-7-0) [4 and 2](#page-7-0) show that syringol, isoeugenol and eugenol have the strongest correlation with "fat fish", "brine", and ''butter'' and constitute the main fraction of phenolic compounds in electrostatic samples. Thus, we can suppose that these compounds do not have a great impact on sample odour, for the quantity deposited. The comparison of the phenolic compound profile of the two AE samples treated with two different voltages does not lead to a possible explanation of the characteristics, lightly ''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 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.

# 4. 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.

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 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 smoke characteristics. The efficiency of the generator with sawdust pyrolysis is notable, especially for the traditional process of smoke deposition, since the temperature is high. A general trend is observed about the effect of smoking temperature. The global odour intensity generally increases with the temperature applied in the smokehouse. This is true for both the friction generator and the autocombustion generator. In the latter case, the interaction effects between temperature and other parameters, such as the exhaust valve position, can modulate these results. In particular, when the valve position is one-third open, the sensory characteristics of the samples smoked at 16, 24 or 32 °C are very similar. The higher residence time of the smoke could indicate that a saturation point is reached. If the valve is more open, the temperature effect on sensory characteristics is more significant. A temperature of  $16^{\circ}$ C is adequate to give smoked product characteristics without a strong ''cold ash'' note. This smoking procedure, with an 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.

The effects of phenolic compounds on sensory properties, are not clear enough to allow detailed conclusions. If we consider the results of odour characteristics, from both electrostatic and traditional smoked products, the content of phenolic compounds seems well related to smoked odour. Although the content of phenolic compounds can be an indicator of smoking intensity, this analysis does not always reflect the odour

<span id="page-9-0"></span>intensity perceived by a group of 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 extent, 4-ethyl guaiacol and 4-propyl guaiacol are the main components involved in ''cold ash'' odour. Study of the relationship between sensory descriptors and percentages of each phenolic compound leads to the hypothesis that syringol, isoeugenol and eugenol have no detectable effect on smoke odours, under the tested conditions.

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

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