

# Flavor Characterization of Ripened Cod Roe by Gas Chromatography, Sensory Analysis, and Electronic Nose

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Characterization of the flavors of ripened roe products is of importance to establish a basis for a standardized product. Flavor profiles of commercially processed ripened roe from Iceland and Norway were studied by sensory analysis, gas chromatography—olfactometry (GC-O), gas chromatography—mass spectrometry (GC-MS), and an electronic nose to characterize the headspace of ripened roe. Sensory analysis showed that ripened roe odor and flavor in combination with caviar flavor and whey/caramel-like odor give the overall positive effect of the complex characteristic roe flavor. Analysis of volatiles by GC-MS and electronic nose confirmed the presence of aroma compounds contributing to the typical ripening and spoilage flavors detected by the sensory analysis. Methional, 1-octen-3-ol, and 2,6-nonadienal were the most important compounds contributing to ripened roe odor. Spoilage flavors were partly contributed by 3-methyl-1-butanol and 3-methylbutanal, which can be measured by the electronic nose and are suggested as quality indicators for objectively assessing the ripening of roe. Principal component analysis of the overall data showed that GC-O correlated well with sensory evaluation and the electronic nose measurements.

KEYWORDS: Cod roe; ripening; flavor; odorants; electronic nose; gas chromatography—olfactometry; gas chromatography—mass spectrometry

#### INTRODUCTION

Roe is a seasonal product obtained during a short period each year. The processing of cod roe is a traditional industry in northern Europe, based on craftsmanship and rules and regulations of former years. The process involves sugar-salting of roe sacks in both plastic and wooden barrels in which they are ripened over a long period (1–2 years). The ripened roe sacks are finally smoked, deskinned, and used in products such as cod roe paste.

Fresh cod roe contains about 70-75% water and 15-26% protein, depending on the maturation stage. The lipid content is  $\sim 1\%$  (13-15% of dry weight) (1). The main lipid class is polar lipids, which can constitute  $\sim 76\%$  of total lipids. Other lipid classes are triglycerides, free fatty acids, and sterols (2). Polar lipids contain high levels of polyunsaturated fatty acids that are potential precursors for flavor development in ripened products (3).

Processing odors have been studied in various seafood products such as pickled fish (4), ripened anchovies (5), ripened herring (6), boiled salmon and cod (7), and canned tuna (8). Josephson et al. (4) have shown that reductions in intensity of the fresh fish flavor in pickled fish correlate with lower levels

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of fresh fish alcohols and carbonyls. The remaining fresh fish alcohols and carbonyls contribute to the mild but distinct flavor of pickled fish. Triqui and Guth (5) showed that methional and (Z)-1,5-octadien-3-one were potent odorants in ripened anchovy. Aldehydes such as acetaldehyde, 2-methylpropanal, and 3-methylbutanal were the key, highly volatile components of ripened anchovy. During ripening of anchovy it has been noted by some manufacturers that some degree of proteolysis is necessary before flavor can develop during ripening. Gudmundsdottir and Stefansson (6) found that muscle enzymes appeared to be of great importance for the development of characteristic ripened taste of salted herring and that the rate of salt uptake was an important regulator of ripening. (Z)-1,5-Octadien-3-one, (E,Z)-2,6-nonadieanal, propionaldehyde, acetaldehyde, methional, and (E,E)-2,4-decadienal have been identified as the character impact odorants of boiled salmon (7). 2-Methyl-3-furanthiol has been identified as being responsible for the characteristic meaty flavor in canned tuna (8).

It is well-known that the desired flavor and texture develop during many months of processing as the consequence of protein and fat degradation, that is, proteolysis and lipolysis, in ripened meat products (3, 9). Similar characteristic changes occur during ripening of muscle food, and the formation of the flavor is due to complex combinations of enzymatic or chemical reactions, such as lipid oxidation, Maillard reactions, and Strecker degradations. For example, >260 volatiles have been detected in dry-cured ham, most of them generated from chemical or

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enzymatic oxidation of unsaturated fatty acids and further interactions with proteins, peptides, and free amino acids (10).

Knowledge about the identity of the volatile compounds contributing to the characteristic flavor of ripened roe is lacking. Information about the compounds influencing the flavor of roe during ripening will add to the understanding of the chemical basis of the ripening processes. Because of their low level, it is difficult to detect volatile compounds using traditional gas chromatography—mass spectrometry (GC-MS); however, by using a GC—olfactometry (GC-O) technique it is possible to detect compounds that have very low odor thresholds.

Sensory evaluation is used in the roe-processing industry to determine if fresh roe is fit or mature enough for sugar salting. Characteristic appearance and flavor of the roe determine the ripening stage. Fully ripened roe typically have a balanced mixture of sweet, salt, bitter, and whey-like flavors.

The increasing demand for rapid methods for industrial application has brought attention to the possibility of using electronic noses that can detect changes in the headspace composition to monitor the ripening stage. Earlier work using an electronic nose based on electrochemical gas sensors (Fresh-Sense) has been suggested as a rapid technique to monitor volatile compounds during ripening of sugar-salted roe (11) and to monitor spoilage of capelin (12, 13).

The aim of this study was to characterize the flavor of ripened sugar-salted cod roe by sensory analysis and analysis of volatile compounds to gain an understanding of the chemical basis for the ripened flavor. Well-characterized products facilitate product development and process management in the roe industry. The properties of the ripened roe products were characterized using sensory analysis, gas chromatography techniques, and electronic nose.

# **MATERIALS AND METHODS**

Eleven samples of traditionally ripened roe that were considered fit for further processing of cod roe paste were obtained from major roe-processing companies. All of the samples had been ripened for at least 1 year before analysis. Four samples were from Iceland (I-1, I-2, I-3, and I-4) and two from Norway (N-1 and N-2). These samples were analyzed at the same time. One year later, five samples of ripened roe were obtained from Lofoten in Norway and analyzed (N-3, N-4, N-5, N-6, and N-7). All samples were analyzed by sensory analysis, GC-MS, GC-O, and electronic nose, except samples from the second year, N-3 to N-7, were not analyzed by GC.

Sensory Analysis. The Icelandic Fisheries Laboratories (IFL) sensory panel was trained in quantitative descriptive analysis (QDA), introduced by Stone and Sidel (14), to assess ripened roe. Sensory assessments were carried out by 8-12 assessors (age range = 30-55 years). They were all trained according to international standards (15), including the detection and recognition of tastes and odors, and trained in the use of scales and in the development and use of descriptors. The assessors evaluated the samples each time by using 13 descriptors of appearance, odor, and flavor for ripened roe: whey/caramel odor, seaweed odor (salty, marine-, stockfish-, amine-like), ripening odor (characteristic for ripened roe), spoilage odor (sour, sickeningly sweet, amine), sweet taste, salty taste, sour taste, bitter taste, caviar flavor (cod roe paste), ripening flavor, egg flavor, metallic flavor, and spoilage flavor. A visual analogue scale (0-100%) was used. The samples,  $\sim 30$ g in a small plastic container, were allowed to equilibrate at room temperature for 30 min before evaluation. Each sample was evaluated in triplicate.

**Electronic nose measurements** were performed using a gas sensor instrument called FreshSense, developed by the IFL and Bodvaki-Maritech (Kópavogur, Iceland). The instrument is based on electrochemical gas sensors (Dräger, Germany, CO, H<sub>2</sub>S, and SO<sub>2</sub>; City Technology, U.K., NH<sub>3</sub>) and static headspace sampling at room temperature. The measurements were performed as described earlier

(13). Approximately 300 g of roe was placed in the glass container (2.3 L,  $\varnothing$  17 cm). The temperature of the roe mass was recorded before measurement was begun, and the temperature was varied from 12 to 14 °C. Measurements were taken every 10 s over a period of 10 min. The reported value (current) is the average of the last three measurements of the 10 min measurement cycle minus the average of six signals before measurement began (1 min). All measurements were done in triplicate.

**Purge-and-Trap Sampling.** Prior to GC-MS and GC-O analysis, samples were collected by a purge-and-trap sampling (16). The samples were kept at room temperature for  $\sim 1$  h before analysis. Samples were prepared by weighing  $100\pm2$  g of roe and  $100\pm5$  g of saturated aqueous solution of NaCl into a 250 mL round-bottom flask. Saturated NaCl solution (200  $\pm$  5 g) was prepared as a blank sample. Heptanoic acid ethyl ester was added as an internal standard to all samples by adding 1 mL of a 10 ppm aqueous solution of the standard to the 200 g of roe/NaClsat solution. The sample was purged at room temperature with nitrogen at  $\sim 100$  mL/min for 2.5 h (15 L). Volatiles were collected on 250 mg of Tenax 60/80 (Alltech, Deerfield, IL) in stainless steel tubes (Perkin-Elmer, Buckinghamshire, U.K.) for the combined ATD 400 and GC-MS measurements or 150 mg of Tenax in a Pasteur pipet for GC-O measurements. Each sample was prepared in duplicate.

**GC-MS Measurements.** Volatile compounds were thermally desorbed (ATD 400, Perkin-Elmer) from the Tenax tubes and separated on a DB-5ms column (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m, J&W Scientific, Folsom, CA) using a GC-MS (HP G1800C GCD, Hewlett-Packard, Palo Alto, CA). Helium was used as a carrier gas, and the following temperature program was used: 50 °C for 7 min, raised from 50 to 120 °C at 5 °C/min and from 120 to 220 °C at 10 °C/min. The injector temperature was 250 °C, and the detector temperature was 280 °C. The mass detector ion range was m/z 35–300. Semiquantitative evaluation of the concentration of volatiles was based on comparison of peak area to the peak area of the internal standard.

GC-O Measurements. Volatiles were extracted from the Tenax traps with 1 mL of diethyl ether. The sample was then concentrated by passing nitrogen over the solution, leaving a small amount of sample,  $20-30 \mu L$ . The sample (1  $\mu L$ ) was then injected splitless onto the column. Measurements were performed on a GC (HP 5890, Hewlett-Packard) with the same type of column and the same conditions as for the GC-MS measurements. The end of the column was split 1:1 between a flame ionization detector (FID) and an ODO-1 olfactory detector outlet (SGE International Pty. Ltd., Australia). Nitrogen, bubbled through water to add moisture, was used to drive the sample to the sniffer. Two persons describing the odor sniffed the effluent. Intensity (quality and duration/retention times) of each odor was determined using an intensity from 0 to 5: 0, not present; 5, very strong. The FID responses were not useful for quantification mainly because some of the odor active compounds were present in very low concentrations and were hardly noticed as peaks in the chromatogram. In addition, because diethyl ether was used for extracting the volatiles from the Tenax traps for the GC-O analysis, some of the early eluting low molecular compounds were lost in the solvent peak in the chromatogram. Quantification of low molecular weight polar compounds on the Tenax is also difficult because of their large breakthrough volume on the Tenax.

**Identification of the volatiles** was done by matching retention indices (RI), calculated according to the method of Van den Dool and Kratz (17) and based on ethyl esters (i.e., RI of ethyl pentanoate is 500) and verified by the database Flavornet (18) and mass spectra of samples with authentic standards (Sigma-Aldrich Chemical Co., St. Louis, MO). Tentative identifications were based on standard MS library data (Hewlett-Packard Co., 1997).

**Data Handling.** Sensory analysis of roe was performed using the software Hypersense (IFL, Iceland). Statistical analysis was done on the sensory and electronic nose data using one-way ANOVA on Number Cruncher Statistical Software (NCSS 2000 and Pass Trial, Kaysville, UT). Multivariate analysis was performed by the Unscrambler 7.5 software package (Camo AS, Trondheim, Norway). The main variance in the data set was studied using principal component analysis (PCA). The PCA was performed on sensory, GC-O, and electronic nose data. Average scores of assessors were used for the sensory data and average

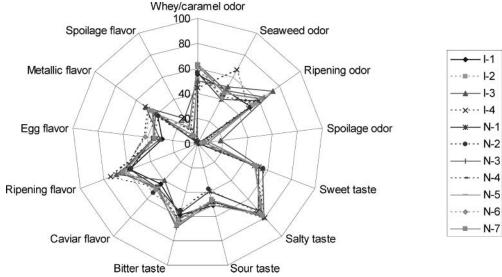


Figure 1. Comparison of sensory profiles of 11 samples of traditional ripened cod roe from Iceland (I) and Norway (N).

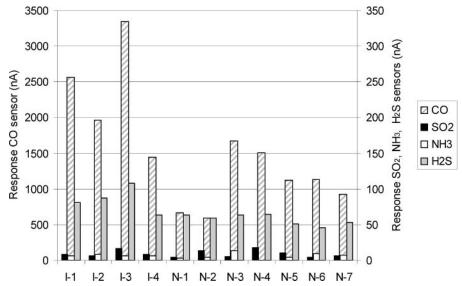


Figure 2. Responses of the electronic nose sensors for traditional ripened cod roe from Iceland (I) and Norway (N).

of sample replicates for each sample. All of the data were mean centered and scaled to equal variance prior to PCA. Cross-validation was used in the validation method.

# **RESULTS AND DISCUSSION**

Roe sacks were sugar-salted in wooden barrels and stored over a period of 1-2 years. During storage, changes in appearance and flavor occurred as a result of ripening. Fully ripened roe samples from different seasons and countries were selected by the roe-processing industry according to their criteria for production of cod roe paste. The flavor of the fully ripened roe was characterized by sensory analysis, gas chromatography, and electronic nose.

**Sensory Analysis.** Traditional ripened roe is known to have a balanced mixture of sweet, salt, bitter, and whey-like flavors. The results of this study are in agreement with this description (**Figure 1**), showing that all 11 samples of ripened roe have similar sensory characteristics. The intensities of attributes such as ripening flavor, ripening odor, whey/caramel odor, and salty and bitter tastes were always high and characterized all of the products. Spoilage odor and flavor was detected in some of the samples, but the scores were in general low. One sample (I-3) had significantly (p < 0.001) higher spoilage odor and flavor

compared to other samples and was considered to be overripened. The ripening odor was also significantly higher for this sample. Sample I-4, which had an overall stockfish-, amine-like character, sometimes noticed in fully ripened roe, had significantly higher seaweed odor (p < 0.001) than all of the other samples. The presence of amines in seafood products is known to contribute to the characteristic stockfish-like odor (19).

Electronic Nose Analysis. The FreshSense sensors (CO, H<sub>2</sub>S, SO<sub>2</sub>, and NH<sub>3</sub>) are selective for the detection of different classes of compounds that are present in fish during storage or processing. The CO sensor detects alcohols, carbonyls, and esters, the H<sub>2</sub>S and SO<sub>2</sub> sensors are sensitive to sulfur compounds, and the NH<sub>3</sub> sensor is selective toward amines (11). **Figure 2** shows the responses of the electronic nose sensors for all of the samples analyzed. The main electronic nose response was in the CO sensor for all of the samples, giving > 10 times higher responses compared to the other sensors. The significantly (p < 0.001) highest value for the CO sensor was seen in the Icelandic samples described as over-ripened I-3, confirming the presence of volatile degradation compounds indicating spoilage. A similar trend was seen for the H<sub>2</sub>S sensor as for the CO sensor, and the small response of the SO<sub>2</sub> sensor suggested the presence of volatile sulfur compounds. No

Table 1. Characteristic Odor and Volatile Compounds Identified by GC-O and GC-MS in Ripened Cod Roe from Iceland (I) and Norway (N)

				odor intensity							
compound		odor description		I-1	I-2	I-3	I-4	N-1	N-2	RI DB-5ms <sup>b</sup>	ID means <sup>c</sup>
dimethyl sulfide 2-methylpropanal 2-butanone ethyl acetate 3-methylbutanal 1-penten-3-ol pentanal 3-hydroxy-2-butanone 3-methyl-1-butanol dimethyl disulfide unknown hexanal unknown unknown nonane (Z)-4-heptenal heptanal methional benzaldehyde 1-octen-3-ol (E,E)-2,4-heptadienal unknown	}	nd <sup>d</sup> caramel, malt-like, sweet, flowery, fruit  nd sweet, flowery		0.4	1.0	4.0	4.5	2.2	2.6	191 200 209 218 245 255 264 282 291 314 324 344	MS MS MS MS, 1, 2 MS MS MS MS MS MS MS, 1 2
		nd cheesy (Roquefort) flowery, sweet, solvent, geranium  rancid, potato fatty boiled potato nd mushroom, earthy sweet, flowery oriental, spicy, heavy, burnt, rubbery	}	3.6	5.0	3.4	4.6	3.6	2.3	381 440 451 494 497	MS 2 2 MS MS, 1, 2
				5.0	3.7	<ul><li>5.0</li><li>3.8</li><li>3.3</li></ul>	<ul><li>5.0</li><li>4.2</li><li>2.4</li></ul>	5.0 4.7 3.9	5.0 4.6 3.8	500 502 560 579 611 688	MS, 1, 2 MS, 1, 2 MS MS, 1, 2 MS, 1, 2 2
heptanoic acid ethyl ester ( <i>E,Z</i> )-2-6-nonadienal		internal standard cucumber-like			1.9	4.4	3.4	3.4	2.5	700 758	2

<sup>&</sup>lt;sup>a</sup> Odor intensity from 0 to 5: 0, not present; 5, very strong. Average scores of two assessors. <sup>b</sup> Calculated ethyl ester retention index on DB-5ms capillary column (17). <sup>c</sup> MS, mass spectra; 1, authentic standards; 2, odor identification. <sup>d</sup> nd, not detected at sniffing port.

significant differences between the samples were seen in the responses of  $SO_2$  and  $NH_3$  sensors.

GC-O and GC-MS measurements were done to study the influence of individual flavor compounds, characteristic for ripened roe. The GC-MS analysis was mainly done to identify and verify the presence of the key odor components detected by GC-O. Quantifications of the GC-MS data based on comparison to the internal standard are only semiquantitative. Table 1 shows the key odors identified by GC-O in the ripened roe and verified by GC-MS. The highest odor scores were given for boiled potato, rancid, mushroom, caramel, malty, sweet, cheesy, cucumber, and oriental spice-like odors, which were noticed in most of the samples. Combinations of these odors give the ripening odor and flavor characteristics of the ripend roe.

Compounds contributing to characteristic roe-, caviar-like odor were identified as a combination of cis-4-heptenal, heptanal, and methional (Table 1). These compounds were detected in low concentrations by GC-MS, but because of their low odor thresholds, they had high sensory impact as seen by high GC-O scores in all samples. These compounds elute close to each other on the GC column, making the separation of their individual odor difficult by GC-O. Therefore, only one score is given for their combined odor intensity. Methional, a compound formed via Strecker degradation of methionine, was identified as one of the most important odorants in all of the samples, giving a boiled potato-like odor. Methional has been detected in various boiled seafood (7, 20), processed seafood (21), and ripened anchovy samples (5). cis-4-Heptenal is derived from lipid oxidation of n-3 unsaturated fatty acids (PUFA) (22). The odor of cis-4-heptenal has been described as boiled potato-like (23), similar to that of methional. Cardboard or paint-like odor and, furthermore, the "cold storage flavor" of cod have also been associated with cis-4-heptenal (22, 24). The odor thresholds in water for cis-4-heptenal and methional are 0.04 ppb (22) and 0.2 ppb (25), respectively.

A combination of compounds eluting early in the chromatogram (RI < 320) gave mild sweet, flowery, caramel, maltylike odors and influenced the flavor of ripened roe. These compounds were identified by GC-MS as, for example, 2-methylpropanal, 3-methylbutanal, 3-hydroxy-2-butanone, and 3-methyl-1-butanol (Table 1). These compounds, which are derived from amino acids, can act as substrates for Maillard reactions with sugars in ripened products (3). 3-Methyl-1-butanol, with a solvent-like, sweet odor, and 3-methylbutanal, with a characteristic malty odor, were detected in highest concentration by GC-MS in the fully ripened roe. The highest concentration of 3-methyl-1-butanol was detected in sample I-3, which was considered to be over-ripened, and in sample I-4, which had an overall stockfish-like character. Even though detected in high concentrations, their flavor impact is moderate because the odor threshold of, for example, 3-methylbutanal is 0.06 ppm (26), which is much higher than those for *cis*-4-heptenal (0.04 ppb) and methional (0.2 ppb). Triqui and Zouine (27) suggested using 3-methylbutanal as an indicator for the ripening process of anchovy. Similarly, 3-methyl-1-butanol and 3-methylbutanal could be used to objectively assess the ripening of roe. Shortchain alcohol and carbonyl compounds that are produced by microbial degradation have been analyzed in fish at various stages of storage and have been suggested as indicators of spoilage (28, 29). Similar compounds were detected in a preliminary study on spoilage of fresh cod roe on ice in our laboratory, and 3-methylbutanal and 3-methyl-1-butanol were identified as potential indicators of spoilage.

It is very likely that the Roquefort cheesy odor is contributed by butyric acid. According to Flavornet the ethyl ester RI for butyric acid is close to that of the unknown compound. This was not verified by GC-MS because the nonpolar DB-5 column does not allow for accurate analyses of acids because of large fronting peaks.

Polyunsaturated fatty acids originating from polar lipid, which is the main lipid class in cod roe, are potential precursors for

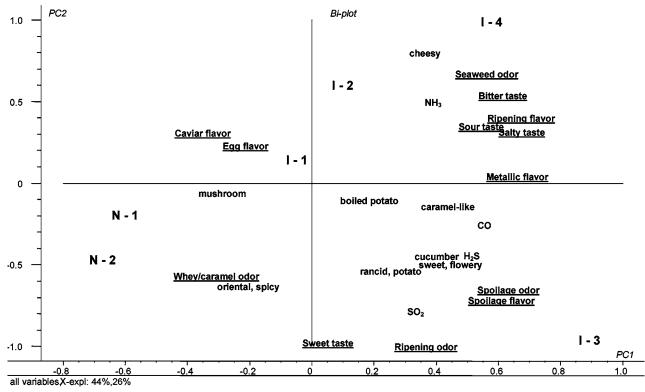


Figure 3. PCA biplot of sensory attributes (underlined), electronic nose sensors (NH<sub>3</sub>, CO, SO<sub>2</sub>), and GC-O attributes for selected samples from Iceland (I) and Norway (N).

flavor development in ripened products (3). GC-O results showed, for example, that two odorants in the ripened roe giving characteristic mushroom and cucumber-type odors were identified by GC-MS as 1-octen-3-ol and 2,6-nonadienal, respectively. Both of these compounds are known to be derived by oxidation in fish (30). Similarly, Triqui and Guth (5) found that 2,6nonadienal was associated with the green, marine algae-like notes of anchovy odor. The results confirmed that lipid-derived compounds are present and contribute to ripening odor. Higher concentrations of lipid-derived compounds such as 1-pentanol, 2-hexanone, hexanal, 1-hexanol, 2-heptanone, and 1-octen-3ol were found in I-3, which had a high ripening odor. During the processing of dry-cured ham (a ripened product) an intensive lipolysis has been observed. Free fatty acids are generated as a result of phospholipid hydrolysis, indicating a major role of phospholipases, whereas the triglycerides remain almost intact. The free fatty acids accumulate during the process, and because of oxidative processes various volatile compounds such as hydrocarbons, aldehydes, alcohols, and ketones are formed (3). Further research on ripened roe odor should include studies on phospholipase activity.

Comparison of Sensory, Electronic Nose, and GC-O. PCA was done for selected samples (Figure 3) to compare the different data from sensory evaluation, electronic nose measurements, and GC-O. Only samples that had been analyzed by GC-O were selected. The GC-O quantifications were used to compare to the sensory data in the PCA to study the correlation of individual odor active components to the sensory descriptors and their contribution to the characterization of the samples. Samples N-3 to N-7 were therefore not included; their overall sensory characteristics (Figure 1) and electronic nose responses (Figure 2) were similar to those of the N-1 and N-2 samples, but their CO responses were higher. The PCA yielded three interpretable factors explaining 87% of the variance of the data set, 44% by PC1, 26% by PC2, and 17% by PC3. The boiled

potato-like odor (methional), which was identified as one of the most important odorants in all of the samples, lies in the middle of the PCA plot and therefore does not contribute to the variation in the data set but was, however, very characteristic for all of the samples. The typical sensory attributes for ripened roe are caviar flavor and whey/caramel odor and attributes such as oriental/spicy-like (unknown compound) and mushroom-like, 1-octen-3-ol odors identified by GC-O. Samples N 1, N 2, I-1, and I-2 were characterized by these attributes as seen in **Figure** 

The Icelandic samples were described by overall higher electronic nose responses as seen by the positions of their scores and loadings of the sensors on the right side of the PCA plot (**Figure 3**). It should be pointed out that the dominant influences of the H<sub>2</sub>S, SO<sub>2</sub>, and NH<sub>3</sub> sensors in the PCA plot may be partly due to the scaling of the data. The sample (I-3) that was considered to be over-ripened had higher values of spoilage attributes and ripening odor. Higher responses of CO, H<sub>2</sub>S, and SO<sub>2</sub> sensors were also observed, as expected, because these sensors are sensitive to volatile degradation compounds associated with spoilage odors. These attributes correlated also with odors described as sweet/flowery, rancid/potato, and cucumber as seen on the PCA plot (**Figure 3**). Rancid/potato-like odor was identified as *cis*-4-heptenal and cucumber odor as 2,6-nonadienal.

Response of the NH<sub>3</sub> sensor correlated with seaweed odor and bitter taste identified by sensory evaluation and with cheesy-like odor (unknown compound) identified by GC-O. Sample I-4, which had an overall stockfish-like character, was described by these variables. The NH<sub>3</sub> sensor is sensitive to TMA and other amines such as ammonia and DMA that are known to contribute to saltwater fish odor during storage, which is also reminiscent of dried fish and stockfish odor. TMA and ammonia are the main constituents of total volatile bases (TVB), which are commonly used as a quality indicator for chilled fish (*31*).

Olafsdottir et al. (13) showed that the NH<sub>3</sub> sensor can be used to predict TVB value as an indicator of capelin quality. The bitter taste may be explained by the presence of peptides formed during ripening. The activity of proteases during the processing of raw ham leads to the formation of small peptides and free amino acids that can contribute to the taste (10). Further studies of the ripening process of roe should focus on the role of proteases and the formation of taste active amino acids and peptides.

Conclusion. The samples supplied by the industry and described as fully ripened roe had overall similar sensory characteristics but slight variations in spoilage odor and flavor. The basis for a standardized product has been established by characterizing the odor profile. The GC-O and GC-MS results indicate that oxidatively derived compounds (e.g., 1-octen-3-ol and 2,6-nonadienal) and Strecker aldehydes (e.g., methional) are the key aroma compounds detected in ripened roe. Proteolytic and lipolytic reactions appear to occur during ripening of salted roe and contribute to the development of ripening flavors. One sample was considered to be over-ripened by sensory analysis and was described by higher spoilage odor. This sample had also higher odor scores for short-chain volatile compounds detected by GC-O and by higher responses of the electronic nose. High concentrations of 3-methyl-1-butanol and 3-methylbutanal present in over-ripened samples are suggested to account for the high responses of the CO sensor of the electronic nose. Thus, the electronic nose has a potential to be used as a rapid technique to detect over-ripened or spoiled samples. The higher ripened odor of this sample correlates with higher odor scores of lipid-derived carbonyl compounds such as hexanal and 1-octen-3-ol. The detection of spoilage odor in the ripened roe products is of importance to ensure consistent quality of ripened roe for further processing and will help manufacturers to select cod roe products of optimal quality.

# **ABBREVIATIONS USED**

GC-MS, gas chromatography—mass spectrometry; GC-O, gas chromatography-olfactometry; IFL, Icelandic Fisheries Laboratories; QDA, quantitative descriptive analysis; ATD, automated thermal desorber; RI, retention indices; PCA, principal component analysis; TMA, trimethylamine; TVB, total volatile bases.

#### **ACKNOWLEDGMENT**

We thank all of the partners in the Fish Roe Processing project: Ivar Storrø, A. Osvik, K. Thyholt, B. Kirkhus, and M. Fonstad, Mills DA, Norway; H. Thorarinsson, Bakkavör Group, Iceland; K. D. Josefsen and M. Aursand, SINTEF, Norway; and T. Rustad, Norwegian University of Science and Technology (NTNU), Norway.

#### LITERATURE CITED

- (1) Martinsdottir, E.; Magnusson, H. Sensory, Chemical and Microbiological Changes in Cod Roe during Ripening; Icelandic Fisheries Laboratories: Reykjavik, Iceland, 1997; p 8.
- (2) Kaitaranta, J. K.; Ackman, R. G. Total lipids and lipid classes of fish roe. Comp. Biochem. Physiol. 1981, 69B, 725-729.
- (3) Toldrá, F. Proteolysis and lipolysis in flavour development of dry-cured meat products. Meat Sci. 1998, 49, 101-110.
- (4) Josephson, D. B.; Lindsay, R. C.; Stuiber, D. A. Influence of processing on the volatile compounds characterizing the flavor of pickled fish. J. Food Sci. 1987, 52, 10-14.

- (5) Triqui, R.; Guth, H. Determination of potent odorants in ripened anchovy (Engraulis encrasicholus L.) by aroma extract dilution analysis and by gas chromatography-olfactometry of headspace samples. In Flavour and Lipid Chemisty of Seafoods; Shahidi, F., Cadwallader, K. R., Eds.; ACS Symposium Series 674; American Chemical Society: Washington, DC, 1997; pp 31-
- (6) Gudmundsdottir, G.; Stefansson, G. Sensory and chemical changes in spice-salted herring as affected by handling. J. Food Sci. **1997**, 62, 894–897.
- (7) Milo, C.; Grosch, W. Changes in the odorants of boiled salmon and cod as affected by the storage of the raw material. J. Agric. Food Chem. 1996, 44, 2366-2371.
- (8) Withycombe, D. A.; Mussinan, C. J. Identification of 2-methyl-3-furanthiol in steam distillates from canned tuna. J. Food Sci. 1988, 53, 658.
- (9) Toldrá, F.; Aristov, M. C.; Flores, M. Contribution of muscle aminopeptidases to flavor development in dry-cured ham. Food Res. Int. 2000, 33, 181-185.
- (10) Toldrá, F.; Flores, M. The role of muscle proteases and lipases in flavor development during the processing of dry-cured ham. Crit. Rev. Food Sci. 1999, 38, 331-352.
- (11) Olafsdottir, G.; Högnadottir, A.; Martinsdottir, E. Application of gas sensors to evaluate freshness and spoilage of various seafoods. In Methods To Determine the Freshness of Fish in Research and Industry; International Institute of Refrigeration: Paris, France, 1998; pp 100-109.
- (12) Olafsdottir, G.; Martinsdottir, E.; Jonsson, E. H. Rapid gas sensor measurements to predict the freshness of capelin (Mallotus villosus). J. Agric. Food Chem. 1997, 45, 2654-2659.
- (13) Olafsdottir, G.; Högnadottir, A.; Martinsdottir, E.; Jonsdottir, H. Application of an electronic nose to predict total volatile bases in capelin (Mallotus villosus) for fishmeal production. J. Agric. Food Chem. 2000, 48, 2353-2359.
- (14) Stone, H.; Sidel, J. L. Sensory Evaluation Practices; Academic Press: Orlando, FL, 1985; p 311.
- (15) ISO. Sensory Analysis—General Guidance for the Selection, Training and Monitoring of Assessors. Part 1: Selected Assessors, 8586-1; The International Organization for Standardization: Geneva, Switzerland, 1993; pp 1–10.
- (16) Olafsdottir, G.; Steinke, J. A.; Lindsay, R. C. Quantitative performance of a simple Tenax-GC adsorpiton method for use in the analysis of aroma volatiles. J. Food Sci. 1985, 50, 1431-
- (17) Van den Dool, H.; Kratz, P. D. A generalization of the retention index systerm including linear temperature programmed gasliquid partition chromatography. J. Chromatogr. 1963, 11, 463-
- (18) Acree, T.; Arn, H. http://www.nysaes.cornell.edu/fst/faculty/ acree/flavornet/index.html; Flavornet, Cornell University, 1997.
- (19) Lindsay, R. C. Fish flavors. Food Rev. Int. 1990, 6, 437–455.
- (20) Schlüter, S.; Steinhart, H. Changes in the odorants of boiled carp fillet (Cyprinus carpio L.) as affected by increasing methionine levels in feed. J. Agric. Food Chem. 1999, 47, 5146-5150.
- Cha, Y. J.; Cadwallader, K. R. Aroma-active compounds in skipjack tuna sauce. J. Agric. Food Chem. 1998, 46, 1123-1128.
- McGill, A. S.; Hardy, R.; Burt, J. R. Hept-cis-4-enal and its contribution to the off-flavour in cold stored cod. J. Sci. Food Agric. 1974, 25, 1477-1489.
- (23) Josephson, D. B.; Lindsay, R. C. c4-heptenal: An influential volatile compound in boiled potato flavor. J. Food Sci. 1987, 52, 328-331.
- (24) Hardy, R.; McGill, A. S.; Gunstone, F. D. Lipid and autoxidative changes in cold stored cod (Gadus morhua). J. Sci. Food Agric. **1979**, 30, 999-1006.
- (25) Guadagni, D. G.; Buttery, R. G.; Turnbaugh, J. G. Odour thresholds and similarity ratings of some potato chip components. J. Sci. Food Agric. 1972, 23, 1435–1444.
- (26) Sheldon, R. M.; Lindsay, R. C.; Libbey, L. M.; Morgan, M. E. Chemical nature of malty flavour and aroma produced by streptococcus lactis. Applied Microbiol. 1971. 22, 263-266.

- (27) Triqui, R.; Zouine, K. Sensory and instrumental assessments of the ripening process of anchovy (*Engraulis encrasicholus*.). Food Sci. Technol-Leb. 1999, 32, 203–207.
- (28) Dainty, R. H. Biochemistry of undesirable effects attributed to microbial growth on proteinaceous foods stored at chill temperatures. *Food Chem.* **1982**, *9*, 103–113.
- (29) Lindsay, R. C.; Josephson, D. B.; Olafsdottir, G. Chemical and biochemical indices for assessing the quality of fish packaged in controlled atmospheres. In *Proceedings of an International Symposium*, University of Alaska Sea Grant Program, Anchorage, AK; Kramer, D. E., Liston, J., Eds.; Elsevier Science Publishers: Amsterdam, The Netherlands, 1986; pp 221–234.
- (30) Josephson, D. B.; Lindsay, R. C.; Stuiber, D. A. Variations in the occurrences of enzymically derived volatile aroma com-

- pounds in salt- and freshwater fish. J. Agric. Food Chem. 1984, 32, 1344–1347.
- (31) Oehlenschläger, J. Evaluation of some well established and some underrated indices for the determination of freshness and/or spoilage of ice stored wet fish. In *Quality Assurance in the Fish Industry*; Huss, H. H., Jakobsen, M., Liston, J., Eds.; Elsevier Science Publisher: Amsterdam, The Netherlands, 1992; pp 339—350.

Received for review April 2, 2004. Revised manuscript received June 23, 2004. Accepted June 27, 2004. We thank the Nordic Industrial Fund for their support.

JF049456G