JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Lipid Oxidation in Herring Fillets (*Clupea harengus*) during Ice Storage Measured by a Commercial Hybrid Gas-Sensor Array System

JOHN-ERIK HAUGEN*,† AND INGRID UNDELAND‡

MATFORSK, Norwegian Food Research Institute, Osloveien 1, N-1430 Ås, Norway and Department of Food Science, SIK−The Swedish Institute for Food and Biotechnology and Chalmers University of Technology, Box 54 01, S-402 29 Göteborg, Sweden

Volatile compounds released from herring fillets (*Clupea harengus*) during 15 days of storage on ice have been measured with a commercial hybrid gas-sensor array system. Using partial least-squares regression modeling, the sensor responses were correlated with data from chemical analyses (lipid oxidation products and antioxidants) and sensory analyses (odor). Eight of the 16 sensors proved significant in the correlation studies: 6 metal oxide semiconductor field effect transistor (MOSFET) sensors and 2 Taguchi type sensors. Correlation coefficients for chemical and sensory data ranged from 0.9 to 0.98 and from 0.49 to 0.92, respectively, with 0.92 referring to both "sharp/acrid" and "rancid" odors. Prediction errors ranged from 8 to 14% and from 11 to 25% for the chemical and sensory measures, respectively. That the prediction errors for oxidation product formation (5−9%) were close to the analytical errors of the chemical reference methods indicated close to "optimum" performance of the gas-sensor system. The sensor system predicted the storage time of the herring with a 1-day error. Results illustrate high potential of the gas-sensor technology in rapid nondestructive quality determination of ice-stored herring.

KEYWORDS: ***Clupea harengus*; herring; electronic nose; ice storage; lipid oxidation**

INTRODUCTION

Herring (*Clupea harengus*) is a fish with many advantages as a raw material for food production: abundance, low price, and high content of omega-3 fatty acids. Unfortunately, the development of lipid oxidation often limits the possibilities for storage and processing of this species. This is due to close contact between the highly unsaturated herring lipids and strong catalytic systems. A certain control of the lipid−catalyst interactions is provided for by the presence of natural antioxidants in the tissue, for example, vitamin E and C. However, *post mortem*, an array of changes takes place in the tissue that disturbs the delicate balance that initially exists between catalysts and antioxidants. Among these changes are decrease in reducing capacity (*1*), reduced muscle pH (*2*), increase in free iron (*3*), activation of hemoproteins (*4*), and membrane disintegration (*5*).

Freezing and refining of herring is most often preceded by a storage period on ice. Under these conditions, lipid oxidation occurs in parallel with bacterial growth. Small variations, for example, in storage temperature and ice quality, will determine whether rancidity or spoilage will be limiting for the shelf life. Some studies have pointed at microbial growth as the main process lowering the quality of fish during ice storage (*6*−*7*). However, several other studies have reported large losses of antioxidants (*8*−*10*) and substantial increases in both primary (*11*, *12*), secondary (*13*−*16*), and tertiary (*6*−*7*) lipid oxidation products.

A large fraction of the products from lipid oxidation (*17*) and bacterial growth (*18*) are volatile. Volatile lipid oxidation products have traditionally been analyzed by headspace gas chromatography mass spectrometry (HS-GCMS). A rapidly emerging new measurement technique for measuring volatiles is gas-sensor array technology (electronic nose) that has shown to have a great potential as a rapid method for quality analysis in foods (*19*−*21*).

Recently, several gas-sensor investigations to determine chemical and microbial degradation of fish during storage have been published using different gas-sensor technologies (*22*−*27*). Olafsdottir et al. (*22*) investigated spoilage in capelin during storage at 0 and 5 °C over 8 days using electrochemical gas sensors selective to SO_2, NH_3, and CO. They found a good correlation with sensor responses and total volatile bases. Schweizer-Berberich et al. (*23*) stored trout samples over 26 days at 3 °C and used eight commercial amperometric gas sensors optimized for CO, H_2S, SO_2, and NO. A significant correlation between sensor responses and ammonia released from the fish during storage was found. Di Natale et al. (*24*)

* To whom correspondence should be addressed. Phone: +47 64 97 01 00. Fax: +47 64 97 03 33. E-mail: john-erik.haugen@matforsk.no.
† Norwegian Food Research Institute.
‡ The Swedish Institute for Food and Biotechnology and Chalmers University of Technology.

10.1021/jf0255533 CCC: $25.00
Published on Web 12/20/2002

used four metalloporphyrin-coated quartz microbalance sensors to monitor spoilage of cod fillet at 5 °C for 1 and 7 days. By neural network modeling, they achieved a relative prediction error of 5% over 24 h of storage and 20% over 8 days of storage. Newman et al. (*26*) used an instrument with 12 conducting polymer sensors to measure odor and microbial changes in yellowfin tuna during 10 days of storage at 2, 7, and 13 °C. They obtained high classification rates (82−96) in prediction of sensory scores and microbial load on the basis of multiple discriminant analysis. Similar predictions of sensory scores were found during 10 days of storage of Atlantic salmon at 2, 7, and 13 °C (*25*). A sensor array system consisting of 32 conducting organic polymers showed a good agreement with microbial and sensory changes in yellowfin tuna during 9 days of storage at 0, 4,10, and 22 °C (*27*).

No studies exist so far on the use of gas sensors for the determination of lipid oxidation in fish, but a few papers have been published on oxidation in edible fats and fish oils (*28*−*30*). These studies point at the potential gas-sensor array technology could have in determining the rancidity of pure lipids. In particular, the so-called MOSFET sensors (a metal oxide semiconductor field effect transistor with a thin catalytic metal layer on top) proved high sensitivity to volatile lipid oxidation products (aldehydes and ketones). These sensors also have sensitivity to typical volatiles emerging from fish spoilage (amines and sulfides) and thus are thought to be very useful in measuring loss of freshness because of chemical/microbial changes.

The aim of the present study was to investigate the potential of a commercial hybrid gas-sensor array for indirect determination of lipid oxidation in herring fillets during 15 days of ice storage. Volatiles released from herring fillets were sampled using CO_2, MOSFET, and Taguchi sensors. The sensor responses were then correlated to the results from different chemical and sensory oxidation analyses that have been published earlier (*31*).

MATERIALS & METHODS

Samples. Herring ***(Clupea harengus)*** caught off the west coast of Sweden in October 1997 was stored in refrigerated seawater (RSW) tanks for 24 h before it was mechanically headed, gutted, and deboned with commercial equipments. The double fillets obtained, which had a length of 10.2 ± 1.3 cm and a weight of 30.8 ± 7.4 g, were packed in paper boxes (5 kg herring/box) and stored, between plastic bags filled with ice, in a refrigerated room (2 °C) for up to 15 days. The mean temperature of the fish during this period was −0.4 °C. After 0, 3, 6, 9, 12, and 15 days, fillets were removed from the boxes, packed individually in polyethylene film, and frozen at −40 °C in a tunnel freezer. After freezing, they were stored at −70 °C. At the day of analysis, the polyethylene film was removed from the fillets from the same storage point and these were placed in a polyethylene bag and thawed for 11 min in cold-running tap water. Following thawing, the skin was removed manually, and the 10 fillets were homogenized together for 1 min in a food processor. From this pooled herring mince, samples in replicates were removed for the different analyses.

Gas-Sensor Array. A commercial hybrid gas-sensor array instrument manufactured by Nordic Sensor Technologies A.B., Linköping (NST 3220) was used for the measurement experiment. The sensor configuration consisted of one IR-based CO_2-sensor, two blocks of five MOSFET sensors in each, set to respectively 140 °C and 170 °C, and one block with five Taguchi semiconductors set to 400 °C coupled in series. The MOSFET sensors consist of a thin catalytic metal layer on top of a metal oxide semiconductor field effect transistor and the MOS sensors were SnO_2 Taguchi type gas sensors. The catalytic metal gates of the MOSFET sensors were respectively palladium, iridium, and platinum, with a thickness of 5−35 nm. The output signal is based on a change of potential in the sensor because of electrical polarization when gas molecules react on the catalytic surface (*32*). The Taguchi sensors are metal oxide semiconductors (MOS) consisting of a metal oxide layer on top of a semiconductor (*33*). The gas-sensing principle is based on the reaction between adsorbed oxygen on the oxide surface with incoming molecules. The output signal is derived by a change in conductivity of the oxide caused by the reaction with the incoming molecule.

Gas-Sensor Measurements. Nine individual 15-g portions of deskinned, ground fillets from days 0, 3, 6, 9, 12, and 15 of storage were transferred to 250-mL glass vessels (Schott, Germany). The bottles were sealed with preheated (105 °C 15 h) silicon septa (AB Gummiteknik Bålsta, Sweden) and open screw caps. Samples were allowed to equilibrate at room temperature for 10 min before sample headspace gas was pumped into the sensor array.

During the measurements, a gas flow of 40 mL/min was used. The total measurement cycle 340 s consisted of 10 s air (baseline), 30 s sampling, and 300 s air recovery. During the recovery, the inlet system was flushed with air for 10 s. Ambient air filtered with activated silica and charcoal was used as reference gas during the recovery phase of the measurement cycle.

Chemical and Sensory Lipid Oxidation Analysis. Lipid oxidation was determined chemically and sensorially on the same sample material as was used in the gas-sensor analyses. Lipids were extracted according to the method described (*34*) from three individual samples of the ground fillets from days 0, 3, 6, 9, 12, and 15 and the lipids were subjected to duplicate analysis of peroxide value (PV), absorbance at 268 nm (A268), fluorescent lipid oxidation products (FP, ex. 367 nm and em. 420 nm), and α-tocopherol. Ascorbic acid was measured on an aqueous acid extract from each of two ground herring samples.

Sensory analyses were performed by a trained sensory panel. The odor of the pooled samples of whole herring fillets was assessed by descriptive sensory analysis. Prior to serving, the samples were equilibrated for 2 h at ambient temperature. Seven panel members were used, and four training sessions were performed prior to the sensory evaluation. Eight individual samples of ground fillets from each storage point were assessed on the basis of the intensity of five odor attributes: shellfish, fresh fish, old, sharp/acrid, and rancid. Details of the chemical and sensory methods, including results from these methods, have been published earlier (*31*).

Data Analysis. The sensor response defined as the average signal height relative to baseline during the last 30% of the transient signal was used as raw data from the sensor array. The multivariate statistical software package, The Unscrambler (version 6.11, CAMO A/S Trondheim, Norway), was used for the multivariate regression analysis between untransformed gas-sensor array response data and the chemical and sensory data. Partial least-squares regression (PLSR) and principal component regression (PCR) were performed to make prediction models of chemical oxidation parameters and sensory odor descriptors. PLS models both the X- and Y-matrixes simultaneously to find the latent variables in X that will best predict the latent variables in Y. Both PLS1 and PLS2 prediction models were calculated for comparison. PLS1 deals with only one response variable at a time, and PLS2 handles several responses simultaneously. PCR is a two-step procedure which first decomposes the X-matrix by principal component analysis (PCA), then fits a multiple linear regression (MLR) model, using the PCs instead of the raw data as predictors. Both untransformed raw data and autoscaled data were used in the modeling. An equal weighing of the gas-sensor responses by autoscaling (1/sd) was used. By autoscaling, each variable is standardized with the inverse of its standard deviation (1/sd) and has the effect that it gives all the variables the same variance. Both full cross validation (leaving one sample out at a time) and segmented cross validation (leaving one individual out at a time) have been applied in the regression models. The approximate uncertainty variance of the regression coefficients was estimated by modified jackknifing and univariate t-test was employed from regression coefficients and standard deviation (*35*).

RESULTS AND DISCUSSION

Gas-Sensor Responses. Most sensor responses increased with storage time, reflecting the production of volatile compounds

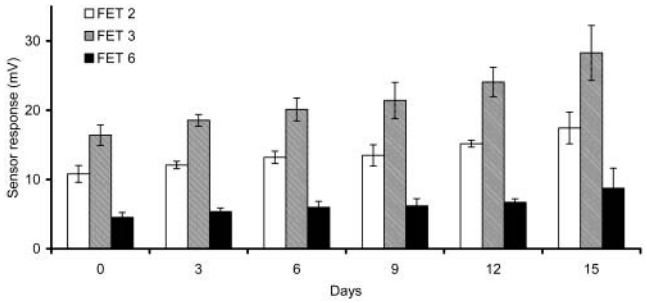

Figure 1. Untransformed responses from the MOSFET 2, 3, and 6 sensors to volatiles produced in herring fillets during 15 days of storage on ice. The bars show mean values from nine analyses and error bars indicate standard deviations.

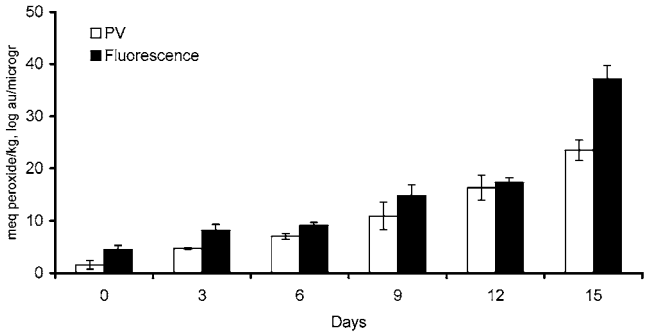

Figure 2. Changes in peroxide value (PV) and fluorescence in herring fillets during 15 days of storage on ice. Fluorescence values have been divided by 100 to make them comparable to the peroxide value scale. The bars show mean values from three analyses and error bars indicate standard deviations. Data from Undeland et al. (*31*).

during storage of herring fillets. **Figure 1** displays changes in the average response signals from MOSFET sensors 2, 3, and 6 between 0 and 15 days. There was a significant increase in these sensor responses over the 15 days of storage. For the MOSFET 3 sensor, a significant increase was found already after 3 days, suggesting that the measurements could have been sampled with a higher temporal resolution to detect changes at an earlier stage of storage. Previous studies have shown that release of volatiles from capelin (*22*) and cod (*24*) can be detected with gas sensors already within the first day of storage at 0 °C and 5 °C. The increase in standard deviation with increasing storage time (**Figure 1**) reflects that the biological variation between the individual fish samples is amplified with increasing storage time, particularly after day 9. **Figure 1** also illustrates how the sensor responses increased in a linear way between day 0 and 12. After 12 days, there was an increase in the rate of change. The development of oxidation products as measured by PV, FP (**Figure 2**), and A268 (not shown) also increased in linear manner up to day 12 (*31*). The bacterial lag phase lasted for about 7−8 days, although the bacterial number had not increased significantly until day 12. This indicates that the linear increase in sensor response observed with storage time over the first 12 days could reflect the release of volatile components generated by oxidation processes. The change in sensor responses seen after day 12 could reflect production of volatile compounds both from lipid oxidation and bacterial growth. The findings are in agreement with other studies on chilled stored herring fillets in air. Molin et al. (*36*) and Molin and Stenström (*37*) demonstrated that during 20 days at 2 °C, spoiled off-odors, corresponding to a cell count of about 10^8 cells/g, occurred after 8 days. In a study on Capelin stored at 0 °C, the fish became spoiled after 8 days (*22*). In similar studies carried out on cod (*38*−40) and haddock (*40*), bacterial production of volatiles became dominant after about 10 and 6 days, respectively, of chilled storage. In capelin (*22*) and haddock (*40*), production of bacterial volatiles was confirmed with gas-sensor measurements. In the present study, it is likely that the 5-day difference between significant changes in lipid oxidation parameters and bacterial growth would have been smaller if the fish had been in direct contact with the ice. Ice/melting water is a known source of bacterial contamination.

Table 1. Results from the PLS Regression Models Describing How Untransformed Responses from Eight of the Sensors (MOSFET 1, 2, 3, 5, 6, 10, and TGS 3 and 4) Were Correlated[a] to Storage Time/Lipid Oxidation Parameters[b]

measure	*r* (PLS2/1)	RMSEP	units	RMSEP %
storage time	0.98/0.98	0.79/0.70	days	5.3/4.6
peroxide value	0.95/0.96	2.29/2.07	meq peroxide/kg	8.8/8.1
fluorescence products	0.95/0.94	314/380	log area units/μg	7.9/9.5
absorbance at 268 nm	0.90/0.91	1137/1112	log area units/μg	8.3/8.2
α-tocopherol	0.91/0.94	0.022/0.015	g/kg	13.6/9.3
ascorbate	0.91/0.92	0.73/0.67	mg/kg	10.1/9.5

[a] The correlation coefficients (*r*) are obtained from PLS regression with full cross validation. Root-mean-square errors of prediction (RMSEP) are given in absolute values and as percentage of measurement range (RMSEP %). The two numbers listed correspond to PLS2 and PLS1 results, respectively. [b] Data on lipid oxidation products and α-tocopherol are expressed on a lipid weight basis while ascorbate data are expressed on a muscle weight basis. The results have previously been reported by Undeland et al. (*31*).

Multivariate Analysis of Responses from Chemical and Gas-Sensor Analyses. Table 1 shows data for the PLS regression models that describe the relation between untransformed gas-sensor response data and chemical oxidation parameters. By applying segmented cross validation in the prediction modeling, that is, leaving out the sample sets from each storage day at a time, similar predictions as by full cross validation was obtained. This confirmed the validity of the relationship of the gas-sensor measurements with the chemical lipid oxidation parameters. Eight statistically significant sensors were identified by means of their regression coefficients applying the jackknifing procedure in the PLS regression modeling. Two of them were Taguchi type sensors (TGS 3 and 4) and the other six were MOSFET sensors (MOSFET 1, 2, 3, 5, 6, and 10). These sensors have previously been demonstrated to have sensitivity to volatile secondary lipid oxidation products such as aldehydes and ketones (*28*). Homologous aliphatic aldehydes usually dominate the vapor phase during lipid oxidation (*17*, *41*−*42*). No headspace GC/MS analyses were performed in this study to verify the relationship between sensor responses and aldehyde/ketone production. However, a recent study of oxidation in herring fillets over 6 weeks of frozen storage showed that there was a significant increase in oxidation-derived volatile compounds such as 2,4-octadiene, butanal, hexanal, and octanal, already within the first two weeks (*43*).

An equal weighing of the gas-sensor responses by autoscaling (1/sd) gave slightly improved correlation to the chemical data than by using the untransformed sensor responses. PCR models were also evaluated but gave in general poorer correlations ($r < 0.85$) than the PLS models. The cross-validated correlations between sensor responses and chemical data were high, ranging from $r = 0.90$ to 0.98. Since only three samples were measured for the chemical oxidation parameters at each storage time, only a total of 18 samples (3×6) could be used in the PLS regression models describing the relation between the gas-sensor measure-

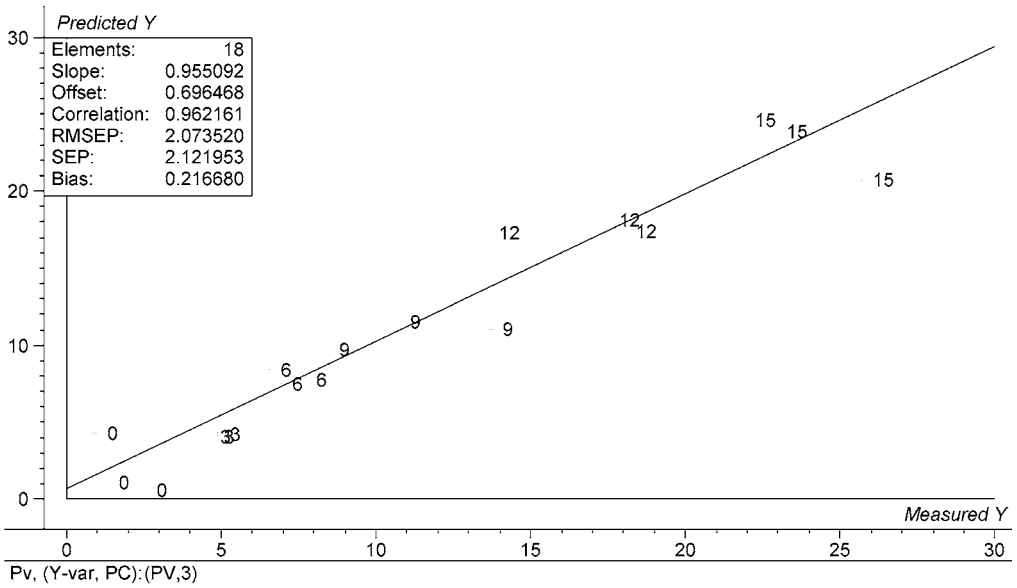

Figure 3. PLS1 prediction model for peroxide value (PV). Sample names correspond to storage times in days. Measured Y (*x*-axis) are the measured PVs and predicted Y (*y*-axis) represent PVs predicted by the gas-sensor response data.

ments and oxidation parameters. However, despite the limited number of measurements ($n = 18$) used in the models, the coefficients of correlation were high enough to be statistically significant.

Since there was high-time-dependent correlation and high covariance both among chemical oxidation measures and among gas-sensor array measures, high correlations were found between lipid oxidation and sensor data (**Table 1**). The high covariance in the chemical measures contributes to a stabilization of the PLS 2 modeling and explains why the PLS2 models came out with the same performance as the PLS1 models.

A notorious problems with solid-state sensors is their stability. During this study, sensor drift was insignificant in comparison to the day-to-day signal variation between the measured fish samples. In long-term sensor drift, however, the prediction models obtained may be valid for only a few weeks, but if the season in which the fish are caught is short, it may not be so much a problem. If the same models are to be applied for a longer period of time, this would require suitable reference standards and drift compenastion algorithms to recalibrate the gas-sensor responses for maintaining reliable predictions. The same will be required in sensor replacement. Both drift compensation and standardization algorithms have been applied to gas-sensor array data with success (*44*−*47*) and are becoming more commonly implemented as routine tools in commercial gas-sensor array system software.

The validation method used in the prediction models allowed for the biological variation expressed in the samples to be included in the prediction models. This made the gas-sensor method very robust. However, lipid oxidation in fish is species specific. The types and levels of oxidation products formed depend on the composition of pro-oxidants and of lipid substrates. In addition, the total quantity of lipids will affect the partitioning of formed oxidation products between the lipid and aqueous phase, the latter which will affect their release into the gas phase. Other fish species would therefore require new calibrations.

Changes and Predictions of Individual Chemical Measures. The correlation between PV-data and time was $r = 0.97$ (*31*) (**Table 1**). A high correlation was also found between the peroxide value and gas-sensor response data, $r = 0.96$ (PLS 1), with an average prediction error of 2.2 meq peroxide/kg, that is, 8.1 RMSEP% (**Table 1**). The prediction model for PV is shown in **Figure 3**. In a lipid oxidation study carried out on crude marine fish oils, a relative prediction error of 5% PV measured over a similar measurement range was obtained (*28*).

The A268 is a measure of both primary (conjugated triene hydroperoxides) and secondary (ethylenic diketones and oxodienes) lipid oxidation products (*48*, *49*). Also for this parameter, a high correlation ($r = 0.93$) was obtained between untransformed data and storage time (*31*). The correlation with the gas-sensor responses was $r = 0.91$ (PLS1) with a prediction error of 8.2% over the measurement range.

Autofluorescence is recognized as a sensitive method for determining the extent of lipid oxidation in muscle foods (*50*). Fluorescent tertiary oxidation products increased almost linearly up to day 12, with an increase in the rate between day 12 and 15. The correlation between fluorescence and time was $r = 0.90$ (*31*) and between fluorescence and gas-sensor responses $r = 0.95$, (PLS 2, **Table 1**). The prediction error was 8%. **Figure 4** shows the PLS1 prediction model.

Undeland et al. (*31*) demonstrated a high linearity regarding storage-induced loss of the antioxidants α-tocopherol and ascorbate from the herring fillets, $r = 0.94$ and $r = 0.93$, respectively. Rapid loss of these compounds was also found during ice storage of mackerel fillets (*9*). Although ascorbate loss was highly correlated with the development of rancid odor in whole herring fillets ($r = -0.97$), ascorbate loss did not reflect the large differences in oxidation product formation that was found between different parts of the fillets (*31*). The role of ascorbate as an indicator of lipid oxidation was therefore questioned. The gas-sensor based prediction model for ascorbate in the present study gave a correlation of $r = 0.92$ (PLS1) with a prediction error of 9.5% (**Table 1**). For α-tocopherol, the PLS2 correlation was $r = 0.91$ with a prediction error of 13.6%. These results suggest that measuring the volatile phase with gas sensors, the antioxidants ascorbate and α-tocopherol content in the whole fillets may be indirectly determined.

Although it is mainly the volatile secondary oxidation products that are detected with the gas-sensor array system (*28*−

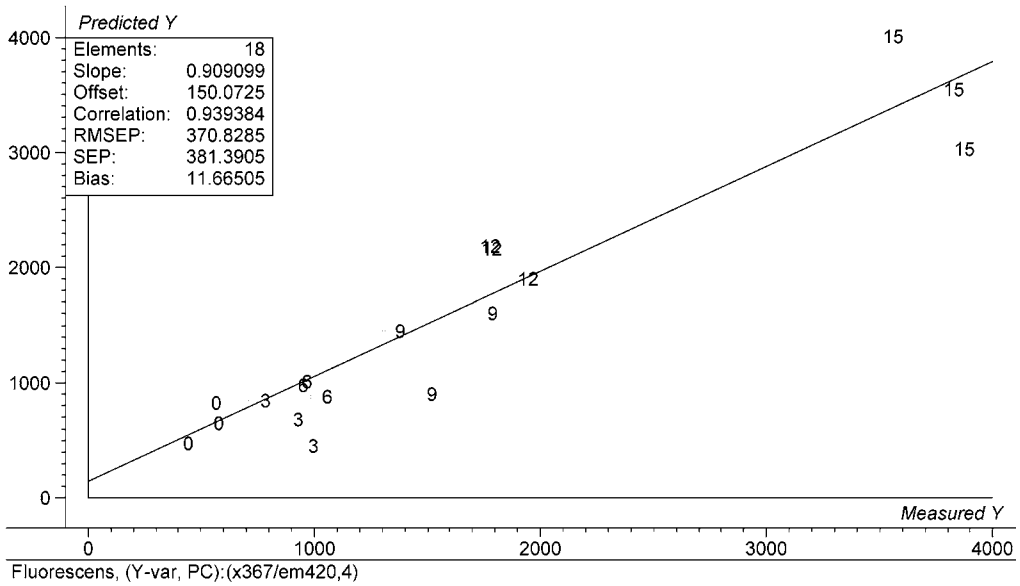

Figure 4. PLS1 prediction model for fluorescence. Sample names correspond to storage times in days. Measured Y (*x*-axis) are the measured absorbance values and predicted Y (*y*-axis) represent predicted values by the gas-sensor response data.

30, *47*), the results above indicate that this technique also predicted storage-induced changes in antioxidants and in nonvolatile oxidation products (e.g., lipid hydroperoxides and Schiff's bases) with high accuracy. This was thought to arise in the strong correlation seen between antioxidant loss and oxidation product formation, as well as between formation of different groups of nonvolatile and volatile oxidation products. This correlation contradicts descriptions of lipid oxidation as a process with its various steps well separated in time (*51*) but is in accordance with several previous freeze-storage studies involving both herring fillets (*52*) and herring mince (*53*). Most likely, the presence of multiple pro-oxidants in the herring muscle, acting at different stages of oxidation reactions, contributed to the "parallel kinetics" observed during ice storage of herring mince. The use of the gas sensors for measuring, for example, antioxidant changes, PV, and fluorescent products can therefore be regarded as an indirect methodology.

One reason for the high ability of the gas sensors to predict antioxidant loss and formation of nonvolatile oxidation products (e.g., lipid hydroperoxides and Schiff's bases) was the strong correlation seen between storage-induced changes in these and other oxidation products. Most likely, the presence of multiple pro-oxidants in the herring muscle, acting at different stages of oxidation reactions, contributed to the "parallel kinetics" observed during ice storage of herring mince. The fact that the gas sensors can predict, for example, PV so well is probably because of a high correlation between the formation of hydroperoxides and volatiles.

As a result of the high correlation obtained between sensor responses and most of the chemical oxidation parameters (**Table 1**), the prediction errors were within the range of the oxidation parameter methods themselves. A correlation method in the best case may not be better than the error within the reference method against which it has been calibrated.

Multivariate Analysis of Responses from Sensory and Gas-Sensor Analyses. Except for "shellfish" odor, the intensities of all the six descriptors used to assess odor changed almost linearly throughout the storage period, either increasing or decreasing (**Figure 5**) (*31*). "Sharp/acrid" and "rancid" were the most strongly related, $r = 0.99$ (*31*). On the basis of regression analysis of the data, sharp/acrid increased at the highest rate, but changes in rancid odor were the first to be significant, after 2.5 days, compared to 3 days for "sharp/acrid". "Fresh fish" and "shellfish" were also strongly correlated ($r = 0.98$) and had both decreased significantly after 3.5 days. The results from the PLS regression models between gas-sensor responses and sensory scores for the assessed attributes are listed

Table 2. Results from PLS Regression Models Describing How Untransformed Responses from Five of the MOSFET Sensors (1, 2, 5, 6, and 10) Were Correlated[a] to the Sensory Data[b]

attribute	*r* (PLS2/1)	RMSEP	RMSEP %
shellfish	0.49/0.40	9.0/9.4	23.6/24.7
fresh fish	0.66/0.68	7.4/7.2	16.8/16.4
old	0.84/0.83	9.4/9.5	13.8/14,0
sharp/acrid	0.91/0.92	8.6/8.8	12.5/12.7
rancid	0.92/0.92	8.5/8.5	12.5/12.5
total intensity	0.58/0.53	8.6/8.9	12.2/12.7

[a] Correlation coefficients (*r*) are obtained from PLS regression with full cross validation. Root-mean-square errorrs of prediction (RMSEP) are given as absolute values and as percentage of measurement range (RMSEP %). The first and second numbers listed correspond to PLS2 and PLS1 results, respectively. [b] Sensory data have previously been reported by Undeland et al. *(31)*.

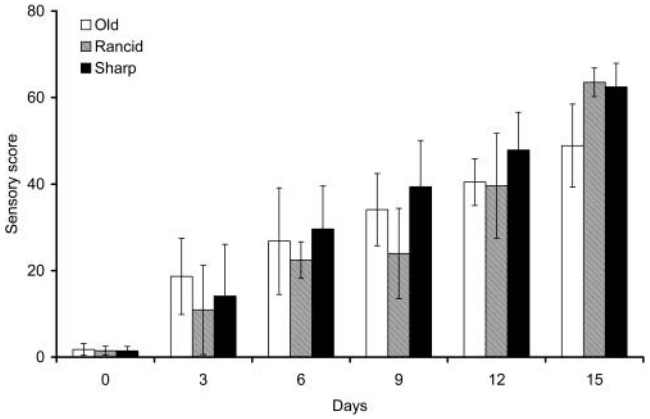

Figure 5. Untransformed intensity scores from sensory analysis of "old", "rancid", and "sharp/acrid" odors in herring fillets stored for 0–15 days on ice. The bars show mean values from eight analyses and error bars indicate standard deviations. Data from Undeland et al. (*31*).

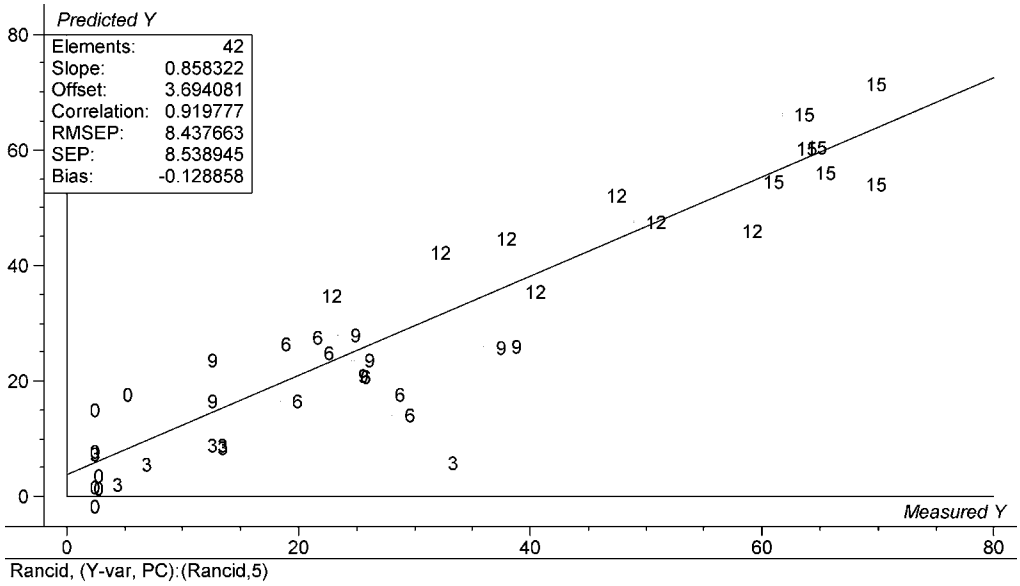

Figure 6. PLS1 regression model for the sensory attribute rancid odor. Sample names correspond to storage times in days. Measured Y (*x*-axis) are the measured sensory odor intensities and predicted Y (*y*-axis) represent the odor intensities predicted by the gas-sensor response data.

in **Table 2**. The MOSFET 1, 2, 5, 6, and 10 gas sensors were significantly correlated with the sensory attributes. The attributes sharp/acrid and rancid showed the highest correlation with sensor responses; $r = 0.92$ (PLS1) for both attributes. The prediction errors were 12.7% and 12.5% of the measurement range, respectively. Similar sensory prediction errors have also been obtained in two other studies using gas-sensor arrays. One of the investigations looked at yellowfish tuna and the other Atlantic salmon (*25*, *26*). In **Figure 6**, the PLS1 model for rancid is shown as an example. It is seen that one 3-day-old sample obtained a high-assessed odor (32) but a low-predicted odor intensity (6). An intensity of 6 was in agreement with the other predicted odor intensities of the 3-day-old samples. The high correlation between sensor responses and rancid odor indicates that the sensors are sensitive to volatile homologue aldehydes which usually make up a major proportion of the odor active compounds in the vapor phase released from oxidation of fish lipids. This has also been documented by previous headspace GC/MS studies on fatty fish and fish lipids (*41*, *43*, *54*).

Prediction of Storage Time. During the 15 days on ice, a high correlation was found between sensor responses and storage time ($r = 0.98$, **Table 1**). The prediction error was less than 1 day. By using only the MOSFET 2 sensor, which was the sensor that showed the highest correlation with storage time ($r = 0.86$), a prediction error of 2.6 days was obtained. This prediction error is in agreement with prediction errors that have been reported from similar fish storage studies using sensor array systems. During 8 days of storage of cod fillets at 5 °C, the use of QMB-sensors gave a prediction error of 1.6 days (*24*). During 10 days of storage of Atlantic salmon at 1.8 °C, a conducting polymer-based sensor array gave prediction errors of ∼1 day (25). Over 10 days of storage of North Atlantic salmon at 4 °C, a sensor system with the same sensor configuration as in the present study (*55*) demonstrated a prediction error of 1.5 day. These results show the potential of the gas-sensor array technology in fulfilling demands among fish mongers for rapid nondestructive tools to asses the storage history and to predict shelf life for fish.

ACKNOWLEDGMENT

The authors wish to thank the following people at SIK-The Swedish Institute for Food and Biotechnology: Hans Lingnert and Gunnar Hall for valuable input during the design of the study, Sheller Ariai and Mats Eskilsson for help with the gas-sensor analyses, and Berit Albinsson, Maud Berg, Ingela Gangby, and Ingela Lindbom for their help with the chemical and sensory analyses.

LITERATURE CITED

(1) Hultin, H. O. Oxidation of lipids in seafoods. In *Seafoods Chemistry, Processing Technology and Quality*; Shahidi, F., Botta, J. R., Eds.; Blackie Academic and Proffesional: London, 1994.

(2) Hultin, H. O.; Kelleher, S. D. Surimi processing from dark muscle fish. In *Surimi and Surimi Seafood*; Park, J., Ed.; Marcel Dekker: New York, 2000; pp 59−77.

(3) Decker, E. A.; Hultin, H. O. Factors influencing catalysis of lipid oxidation by the soluble fraction of mackerel muscle. *J. Food. Sci*. **1990**, *55*, 947−950 & 953.

(4) Kanner, J.; German, B.; Kinsella, J. E. Initiation of lipid peroxidation in biological systems. *CRC Crit. Rev. Food Sci. Nutr*. **1987**, *25*, 317−364.

(5) Huang, C.-H.; Hultin, H. O.; Jafar, S. S. Some aspects of Fe^{2+}-catalyzed oxidation in fish sarcoplasmatic reticular lipid. *J. Agric. Food Chem*. **1993**, *41*, 1886−1892.

(6) Aubourg, S.; Gallardo, J. M.; Medina, I.; Pérez-Martin, R. Fluorescent compound formation in sardine muscle during refrigeration and frozen storage. In *Proceedings of Euro Food Chemistry VIII*; Sonntag, W., Pfannhauser, W., Eds.; Austrian Chemical Society: Vienna, 1995; Vol. 3, pp 579−583.

(7) Harris, P.; Tall, J. Rancidity in fish. In *Rancidity in foods*; Allen, J. C., Hamilton, R. J., Eds.; Blackie A&P: London, 1989.

(8) Bandarra, N. M.; Undeland, I.; Nunes, M. L.; Batista, I.; Empis, J. M. Lipid oxidation indices to evaluate sardine freshness. In *Methods to determine the freshness of fish in research and industry*; International Institute of Refrigeration (IIR): Paris, France, 1998.

(9) Petillo, D.; Hultin, H. O.; Krzynowek, J.; Autio, W. R. Kinetics of antioxidant loss in mackerel light and dark muscle. *J. Agric. Food Chem.* **1998**, *46* (10), 4128−4137.

(10) Watanabe, F.; Goto, M.; Abe, K.; Nakano, Y. Glutathione peroxidase activity during storage of fish muscle. *J. Food Sci*. **1996**, *61*(4), 734−735 & 782.

(11) Botta, J. R.; Shaw, D. H. Chemical and sensory analysis of rundnose grenadier (*Coryphaenoides rupestris*) stored in ice. *J. Food Sci*. **1976**, *41*, 1285−1288.

(12) Sen, D. P.; Bhandary, C. S. Lipid oxidation in raw and cooked oil sardine (*Sardinella longiceps*) fish during refrigerated storage. *Lebensm.-Wiss. Technol.* **1978**, *2*, 124−127.

(13) Aubourg, S.; Sotelo, C. G.; Gallardo, J. M. Quality assessment of sardines during storage by measurement of fluorescent compounds. *J. Food Sci*. **1997**, *62*(2), 295−298.

(14) Kolakowska, A.; Czerniejewska-Surma, B.; Gajowwiecki, L.; Lachowicz, K.; Zienkowicz, L. Effect of fishing season on the shelf life of ice Baltic herring. In *Quality assessment in the fish industry*; Huss, H. H., Ed.; Elsevier Science Publishers B. V.: Amsterdam, 1992.

(15) Ramanathan, L.; Das, N. P. Studies on the control of lipid oxidation in Ground fish by some polyphenolic natural products. *J. Agric. Food Chem*. **1992**, *40*, 17−21.

(16) Wood, G.; Hintz, L. Decomposition in foods -Lipid changes associated with the degradation of fish tissue. *J. AOAC Int.* **1971**, *54*(5), 1019−1023.

(17) Frankel, E. N. *Lipid oxidation*; The oily Press Limited: Dundee, Scotland, 1998; ISBN 0 95141 719 3.

(18) Dainty, R. H. Chemical/biochemical detection of spoilage. *Int. J. Food Microbiol.* **1996**, *33*, 19−33.

(19) Schaller, E.; Bosset, J.; Escher, E. Electronic noses and their application to food. *Lebensm.-Wiss. Technol*. **1998**, *31*, 305−316.

(20) Haugen, J. E.; Kvaal, K. Electronic nose and artificial neural network. *J. Meat Sci.* **1998**, *49* (1), S273−S286.

(21) Haugen, J. E. Electronic nose in food analysis. In *Headspace analysis of foods and flavours*; Rouseff, R., Cadwaller, K. R., Eds.; Kluwer Academic/ Plenum Publishers: New York, 2001; pp 43−57; ISBN 0-306-46561-2.

(22) Ólafsdóttir G.; Martinsdóttir, E.; Jónson, E. H. Rapid gas sensor measurements to determine spoilage of capelin (*Mallotus villosus*). *J. Agric. Food Chem.* **1997**, *45*, 2654−2659.

(23) Schweizer-Berberich, P. M.; Vaihinger, S.; Göpel, W. Characterisation of foodfreshness with sensor arrays. *Sens. Actuators* **1994**, *B18*−*19*, 282−290.

(24) Di Natale, C.; Brunink, J. A. J.; Bungaro, F.; Davide, F.; D'Amico, A.; Paolese, R.; Boschi, T.; Faccio, M.; Ferri, G. Recognition of fish storage time by a metalloporphyrins-coated QMB sensor array. *Meas. Sci. Technol*. **1996**, *7*, 1103−114.

(25) Luzuriaga, D. A.; Balaban, M. O. Electronic nose odor evaluation of salmon fillets stored at different temperatures. In *Electronic Noses & Sensor Arrays based Systems, Design and Applications*; Hurst, J., Ed.; 1999; pp 163−169; ISBN 1 56676 780 6.

(26) Newman, D. J.; Luzuriaga, D. A.; Balaban, M. O. In *Electronic Noses & Sensor Arrays based Systems, Design and Applications*; Hurst, J., Ed.; 1999; pp 170−176; ISBN 1 56676 780 6.

(27) Du, W. X.; Kim, J.; Cornell, J. A.; Huang, T. S.; Marshall, M. R.; Wei, C. I. Microbial, sensory and electronic nose evaluation of yellowfin tuna under various storage conditions. *J. Food Prot.* **2001**, *64* (12), 2027−2036.

(28) Haugen, J. E.; Lundby, F.; Vogt, G.; Obach, A. Measurement of oxidation in marine fish oils using a hybrid gas-sensor array. *The Pittsburgh Conference,* Orlando, FL, 1999.

(29) Aparicio, R.; Rocha, S. M.; Delgadillo, I.; Morales, M. T. Detection of rancid defect in virgin olive oil by the electronic nose. *J. Agric. Food Chem.* **2000**, *48*, 853−860.

(30) Hahn, S. H.; Frank, M.; Weimar, U. Rancidity investigation on olive oil: a comparison of multiple headspace analysis using an gas sensor array system and GC/MS. In *Electronic noses and olfaction 2000*; Gardner, J. W.; Persaud, K. C., Eds.; Institute of physics series in sensors; Institute of physics publishing: London, 2000; pp 217−222; ISBN 0 7503 0764 1.

(31) Undeland, I.; Hall, G.; Lignert, H. Lipid oxidation in fillets of herring (*Clupea harengus*) during ice storage. *J. Agric. Food Chem.* **1999**, *47* (2), 524−532.

(32) Lundström, I. Approaches and mechanisms to solid state based sensing. *Sens. Actuators* **1996**, *B35*−*36*, 11−19.

(33) Azad, A. M.; Akbar, S. A.; Mhaisalkar, S. G.; Birkefeld, L. D.; Goto, K. S. Solid state gas-sensors: a review. *J. Electroch. Soc.* **1992**, *139*, 3690−3704.

(34) Undeland, I.; Härröd, M.; Lingnert, H. Comparison between methods using low-toxicity solvents for the extraction of lipids from herring (*Clupea harengus*). *Food Chem*. **1998**, *61* (1), 355−365.

(35) Westad, F.; Martens, H. Variable selection in NIR based on significance testing in Partial Least Squares Regression (PLSR). *J. Near Infr. Spectrosc*. **2000**, *8*, 117−124.

(36) Molin, G.; Stenström, I. M.; Ternström, A. The microbial flora of herring fillets after storage in carbon dioxide, nitrogen or air at 2 °C. *J. Appl. Bacteriol.* **1983**, *55*, 49−56.

(37) Molin, G.; Stenström, I. M. Effect of temperature on the microbial flora of herring fillets stores in air or carbon dioxide. *J. Appl. Bacteriol.* **1984**, *56*, 275−282.

(38) Perez-Villarreal, B.; Howgate, P. Spoilage of european hake (Merluccius merluccius) in ice. *J. Sci. Food Agric.* **1987**, *41*, 355−350.

(39) Oehlenschläger, J. Evaluation of some well established and some underrated indices for the determination of fresh and/or spoilage of ice stored wet fish. In *Quality Assurance in the Fish Industry*; Huss, H. H., Jakobsn, M., Liston, J., Eds.; Elsevier Science Publishers: Amsterdam, 1992; pp 339−350.

(40) Olafsson, R.; Martinsdottir, E.; Ólafsdóttir, G.; Sigfusson, P. I.; Gardner, J. W. Monitoring of fish freshness using tin oxide sensors. In *Sensors and Sensory Systems for an electronic nose*; Gardner, J. W., Bartlette, P. N., Eds.; Kluwer: Dordrect, The Netherlands, 1992; pp 257−272.

(41) Frankel, E. N. Formation of headspace volatiles by thermal decomposition of oxidized fish oils vs. oxidized vegetable oils. *J. Am. Oil Chem. Soc.* **1993**, *70*, 767−772.

(42) Shahidi, F. Headspace volatile aldehydes as indicators of lipid oxidation infoods. In *Headspace analysis of foods and flavours*; Rouseff, R. L., Cadwaller, K. R., Eds.; Kluwer Academic/Plenum Publishers: New York, 2001; pp 113−123; ISBN 0-306-46561-2.

(43) Andersen, T. Autofluorescence as a rapid nondestructive method to quantify lipid oxidation in single frozen fillets of Herring (*Clupea harengus*). Masters Thesis, Norwegian University of Agriculture, 2001; p 52.

(44) Haugen, J. E.; Tomic, O.; Kvaal, K. A calibration method for handling the temporal drift of solid-state gas-sensors. *Anal. Chim. Acta* **2000**, *407*, 23−39.

(45) Artursson, T.; Eklöv, T.; Lundström, I.; Mårtensson, P.; Sjöström, M.; Holmberg, M. Drift correction for gas sensors using multivariate methods. *J. Chemom.* **2000**, *14*, 711−723.

(46) Balaban, M. O.; Korel, F.; Odabasi, A. Z.; Folkes, G. Transportability of data between electronic noses: mathematical methods. *Sens. Actuators* **2000**, *B71*, 203−211.

(47) Tomic, O.; Ulmer, H.; Haugen, J. E. Standardization methods for handling instrument related signal shift in gas-sensor array measurement data. *Anal. Chim. Acta* **2002**, 99−111.

(48) IUPAC. Evidence of purity and determination from ultraviolet spectrophotometry. IUPAC Standard method II. D.23. In *Standard methods for oils, fats and derivatives*, 6th edition, Blackwell, Cambridge, MA, 1979.

(49) Brown, H. G.; Snyder, H. E. Conjugated dienes of crude soy oil: detection by UV spectrophotometry and separation by HPLC. *J. Am. Oil Chem. Soc.* **1982**, *59* (7), 280−28.

(50) Nakhost, Z.; Karel, M. Fluorescence due to interactions of oxidizing lipids and proteins in meat. In *Fluorescence in Food analysis*; Munk, L., Ed.; Longman Scientific and Technical, John & Wiley Sons: New York, 1989; pp 193−207; ISBN 0582494729.

(51) Gardner, H. W. In *Xenobiotics in Foods and Feeds*; Finley, J. W., Schwass, D. E., Eds.; American Chemical Society: Washington, DC, 1983; pp 63−84.
(52) Undeland, I.; Lingnert, H. Lipid oxidation in fillets of herring (Clupea harengus) during frozen storage. Influence of prefreezing storage. *J. Agric. Food Chem*. **1999**, *47*, 2075−2081.
(53) Undeland, I.; Ekstrand, B.; Lingnert, H. Lipid oxidation in minced herring (Clupea harengus) during frozen storage: Influence of washing and pre-cooking. *J. Agric. Food Chem*. **1998**, *46*, 2319−2328.
(54) Sérot, T.; Regost, C.; Prost, C.; Robin, J.; Arzel, J. Effect of dietary lipid sources on odour-active compounds in muscle of turbot (*Psetta maxima*). *J. Sci. Food Agric.* **2001**, *81*, 1339−1346.
(55) Haugen, J. E.; Spone, J.; Measurement of fish freshness with an electronic nose. Sensory and Instrumental Methods for quality evaluation of farmed fish. Reykjavik, Iceland, 1998.

Received for review March 22, 2002. Revised manuscript received September 27, 2002. Accepted November 7, 2002. This study was financed by Abba Seafood AB and the Swedish Council for Forestry and Agricultural Research as well as the EU collaboration project AIR3 CT94-2283.

JF0255533