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Analysis of Early Lipid Oxidation in Smoked, Comminuted Pork or Poultry Sausages with Spices

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Dynamic headspace/gas chromatography−mass spectrometry (GC-MS), front-face fluorescence spectroscopy, and a gas-sensor array technique (electronic nose) have previously detected lipid oxidation in pork back fat or mechanically recovered poultry meat earlier than or at the same time as a sensory panel. The present study was focused on measurement of early lipid oxidation in a more complicated product (freeze-stored, smoked sausages with spices). During the storage time, formation of components contributing to rancid odor and flavor (e.g., hexanal and 1-penten-3-ol) could be monitored with dynamic headspace/GC-MS. The GC-MS data also showed a decrease in 2-furancarboxaldehyde, which could indicate loss of Maillard type components often associated with acidic or meat odor and flavor. The fluorescence spectra were difficult to interpret, probably due to the simultaneous influence from increasing levels of lipid oxidation products and loss of fluorescent Maillard or spice components. The gas-sensor array responses were dominated by signals from, e.g., spice and smoke compounds.

KEYWORDS: Dynamic headspace/GC-MS; fluorescence; gas-sensor array; electronic nose; sensory analysis; lipid oxidation; rancidity; sausages; pork; poultry

INTRODUCTION

Lipid oxidation is one of the main causes of quality deterioration in processed meat products. In frozen products where microbiological spoilage is not an issue, the shelf life is limited by the development of rancid odor and flavor. Such undesirable sensory notes are formed due to autoxidation of unsaturated fatty acids. Primary oxidation products (hydroperoxides) have little or no direct impact on the sensory attributes of the food, but they are easily decomposed to secondary oxidation products with low sensory thresholds (*1*). The oxidizability of fatty acids is highly dependent on the number of doubly allylic hydrogen atoms present, i.e., how unsaturated they are. When the number of double bonds in a fatty acid increases from one to two, the oxidizability increases about 40 times. For each additional double bond, the increase is approximately 2-fold and docosahexaenoic acid (DHA, C22:6*n*-3) is about five times as oxidizable as linoleic acid (C18:2*n*-6) (*1*). The fatty acid composition is therefore an important factor with regard to the storage stability of a frozen food product. The total fat content as well as the presence of pro- and antioxidants can also influence the oxidation rates. Lipid oxidation can be inhibited by addition of antioxidants, low storage temperatures, and use of packaging that protects the food from exposure to oxygen and light.

Many studies of the effects of different raw materials, antioxidants, processing, and packaging on the quality of processed meat products have been published (*2*−*4*). Storage studies concerning lipid oxidation in frozen products take a long time, and analytical methods that can detect oxidative changes at an early stage are therefore valuable tools in research as well as product development or quality control. Dynamic headspace/gas chromatography−mass spectrometry (GC-MS), front-face fluorescence spectroscopy, and analysis of volatiles with a gas-sensor array technique (electronic nose) have previously been shown to be able to detect lipid oxidation earlier than or at the same time as a sensory panel (*5*). Dynamic headspace/GC-MS is highly sensitive and specific with regard to analysis of volatile oxidation products, and the data generally correlate well with sensory analysis of rancidity (*1*). Volatiles can also be analyzed with a gas-sensor array system. This is a very rapid method as compared to dynamic headspace/GC-MS but far less specific. The sensors in the electronic nose respond to lipid oxidation products as well as other volatiles present in the headspace over the sample (*6*). They may have varying sensitivity toward different types of components but must be regarded as relatively nonspecific. Front-face fluorescence spectroscopy is also a very rapid technique, which measures the fluorescence that arises when lipid oxidation products are combined with proteins, peptides, amino acids, etc. to fluorescent

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Table 1. Sausage Ingredients

	sausages % (w/w)	
	pork	poultry
rind-free pork back fat	22.0	
pork meat	20.2	
beef	17.4	
chicken meat (white)		60.0
salt	0.9	0.4
nitrite	0.9	1.4
color	0.3	0.4
potato flour	6.0	4.7
spices	0.4	0.6
milk powder	2.5	
milk		32.5
water	29.4	

Table 2. Fatty Acid Composition in Sausage Emulsion[a]

	pork		poultry	
fatty acid	mg/g	SD	mg/g	SD
C12:0	0.4	0.0	0.4	0.0
C14:0	3.0	0.2	1.7	0.1
C16:0	34.5	2.0	14.4	0.6
C18:0	29.3	6.9	5.2	0.3
C20:0	0.3	0.0	0.1	0.0
C16:1*n*-7	4.7	0.3	2.6	0.1
C18:1*n*-9	57.6	6.0	22.3	1.0
C18:1*n*-7	0.4	0.0	1.2	0.1
C20:1*n*-9	2.1	0.1	0.4	0.0
C18:2*n*-6	22.4	1.2	10.1	0.4
C20:2*n*-6	0.9	0.0	0.1	0.0
C20:4*n*-6	0.4	0.0	0.4	0.0
C18:3*n*-3	2.2	0.1	0.7	0.0
C20:3*n*-3	0.3	0.0		
C20:4*n*-3	0.3	0.0		
C20:5*n*-3	0.4	0.1	0.1	0.0
C22:5*n*-3	1.0	0.6		
C22:6*n*-3	1.0	0.1	0.3	0.0
total	167	19	63	3

[a] Averaged values of three replicates.

compounds. The samples are directly illuminated, and the emitted fluorescent light can, for example, be detected with a camera type detector (*7*). For a potentially wider use of these methods, their robustness needs to be explored with more complex matrixes.

The aim of the present study was to see if the methods listed above could detect early lipid oxidation in a complex matrix closely resembling a commercially available product. Smoked, comminuted pork and poultry sausages with spices were chosen as model systems.

MATERIALS AND METHODS

Preparation of Sausages. Sausages for the experiment were prepared from either pork and beef (= pork sausages) or from white chicken meat (= poultry sausages). They were produced by professional sausage makers with long experience in the trade and with R&D. The production took place in the product development facilities at Gilde Norsk Kjøtt BA (Oslo, Norway). The sausages (diameter 23 mm) were made from meat emulsion batches of 20 kg with the ingredients listed in **Table 1**. The fatty acid composition, analyzed as described elsewhere (*8*), is shown in **Table 2**. The sausages were processed with smoke from beech wood chippings for 30 min (60 °C, 60% RH) and subsequently heated to a core temperature of 74 °C in a Multimat 2000 smokehouse (Deutch, Darmstadt, Germany). After immediate cooling, the sausages were stored at 4 °C overnight before they were packaged in plastic bags and frozen at −20 °C the next day. Each package contained six sausages.

Sampling Procedure. Samples were taken prior to freezing and after storage for 1, 3, 6, and 11 months at −20 °C. For each type of sausage, three random packages were chosen as samples and split open. Two sausages from each package were assigned to sensory analysis, and the others were reserved for the instrumental analyses. The sausages for each type of analysis were then wrapped in aluminum foil, vacuum packed in plastic bags, and transferred to −80 °C without thawing. All samples were analyzed at once at the end of the experiment. Prior to the instrumental analyses, the samples were thawed for about 2 h at 4 °C and then ground for 30 s in a miniature food processor (Moulinex, Ecully Cedex, France). Portions for the individual analyses were immediately vacuum packed in aluminum foil and plastic bags and refrozen at −80 °C. The sausages for sensory evaluation were kept intact until analysis.

Sensory Analysis. A professional sensory panel with 10−12 assessors evaluated the samples in a descriptive test according to an accredited method (*9*). Prior to analysis, the panelists developed a vocabulary and were trained on use of the scale. Extra samples that had been stored in air for 11 months were used as the "extremes", and extra samples that had been stored at −80 °C from the start of the experiment were the "good" references. The panel was also calibrated with these references before they started on real samples at the days of analysis. Pork and poultry sausages were analyzed at different days. The vocabularies were slightly different but included odor, flavor, color, and textural attributes for both types of samples. The samples were prepared by vacuum packing six sausages in plastic bags and immersing them in a water bath at 80 °C for 30 min. Then, about 1 cm of each end of the sausages was cut off and discarded. The remaining part was cut in two, and the pieces were immediately distributed to the panelists, one to each assessor. The samples were marked with random three digit numbers and presented to the panelists in randomized order. Scores were recorded on a continuous, linear scale from 1 (no intensity) to 9 (distinct intensity) with Compusense Five software (v. 4.2, Compusense Inc., Guelph, ON, Canada).

Dynamic Headspace/GC-MS. Five gram aliquots of the homogenized samples were distributed at the bottom of 250 mL Erlenmeyer flasks, and a solution of ethyl heptanoate (>99%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) in methanol (p.a., Merck GmbH, Darmstadt, Germany) was injected in the flasks as an internal standard. The samples were heated to 50 °C in a water bath and purged with 100 mL/min nitrogen through a Drechsel-head for 30 min. Volatiles were adsorbed on Tenax GR (mesh size 60/80, Alltech Associates Inc., Deerfield, IL). Water was removed from the adsorber by nitrogen flushing (50 mL/min) for 10 min in the opposite direction of sampling. Desorption and chromatography were performed as described by Olsen et al. (*5*) with a slightly modified temperature program that started at 30 °C for 10 min, increased 1 °C/min to 40 °C, 3 °C/min to 70 °C, and 4 °C/min to 230 °C with a final hold time of 3 min. The concentration of the individual volatiles was calculated as ng per gram sample based on the internal standard. The analysis was performed in duplicate for all samples.

All of the sausage ingredients were analyzed to confirm the origin of the various volatiles. Many of the components found in the sausages originated from the added spice mix. The various meats that were used as ingredients yielded only small amounts of volatiles. Several components must have come from the smoking process. The spice and smoke compounds were dominating, although lipid oxidation products and products originating from degradation of amino acids were identified as well.

The peaks of lipid oxidation products were generally very small as compared to other components, and many of them were overlapped by more abundant components, resulting in poor resolution or even total overlap and confounded data. Peaks with components previously found to increase during frozen storage of pork back fat and mechanically recovered poultry meat (*5*) were specially examined with regard to peak purity and to see whether specific ions could be extracted and integrated. Compounds with peak areas influenced by other compounds were in general excluded from further data analysis.

Volatiles Analyzed with an Electronic Nose. The samples were analyzed with a hybrid gas-sensor array system (NST 3220, Applied

Table 3. Sensory Attributes in Pork Sausages during Storage in Vacuum or Air at −20 °C for 11 Months[a]

	vacuum					air				
storage time (months)	0	1	3	6	11	0	1	3	6	11
odor intensity[b]	6.2 a	6.3 a	6.5 ab	6.3 a	6.3 a	6.1 a	7.3 b	7.0 ab	7.0 ab	7.2 b
meat odor (pork)	4.8 a	4.0 abc	4.7 a	4.3 ab	3.9 abc	5.2 a	2.7 cd	2.7 cd	3.0 bcd	2.3 d
smoke odor	5.3	4.8	4.7	5.1	4.1	5.2	4.7	4.5	4.8	4.1
acidic odor[c]	4.6 a	3.2 abc	4.1 ab	3.8 ab	3.2 abcd	4.8 a	1.7 cd	1.8 cd	2.5 bcd	1.5 d
sour odor[d]	1.0 a	2.1 abc	2.1 abc	1.2 a	2.0 ab	1.9 ab	3.5 bc	3.5 bc	3.1 bc	3.8 c
spice odor	3.9	3.8	3.7	3.5	3.6	3.7	3.4	3.3	3.6	3.2
metallic odor	3.2	3.6	3.6	3.7	3.6	3.3	4.5	3.9	3.8	4.3
sickeningly sweet odor	1.0 a	2.2 abc	1.5 ab	1.7 abc	1.8 abc	1.1 a	3.0 bc	3.0 bc	2.5 abc	3.4 c
freezer odor	1.9 a	3.1 abcd	2.3 ab	2.7 abc	2.9 abc	1.5 a	4.7 cd	4.7 cd	4.4 bcd	5.1 cd
barn odor[e]	1.3 ab	1.8 abc	1.7 abc	1.4 ab	1.3 ab	1.0 a	1.9 abc	2.2 bc	2.0 bc	2.6 c
rancid odor	1.1 a	3.2 abc	2.5 ab	2.2 ab	2.0 ab	1.0 a	5.5 c	5.5 c	4.3 bc	5.7 c
diverging odor[f]	1.0	1.0	1.1	1.1	1.3	1.1	1.7	1.1	1.4	1.7
whiteness	5.8	5.8	5.8	5.7	5.5	5.5	5.8	5.5	5.6	5.5
color hue[g]	5.9	5.7	5.5	5.8	5.8	6.1	5.9	6.1	5.6	5.7
color strength	4.2	4.3	4.2	4.1	4.0	4.5	4.2	4.3	4.4	4.4
flavor intensity[b]	6.4 a	6.9 abc	6.7 a	6.9 abc	6.8 ab	6.4 a	7.6 bcd	7.6 bcd	7.6 cd	7.8 d
meat flavor (pork)	5.0 a	3.2 bc	4.1 ab	4.0 ab	4.0 ab	5.2 a	2.2 c	2.4 c	2.4 c	2.1 c
smoke flavor	5.0	4.2	4.6	4.7	3.9	5.2	4.1	4.2	4.3	3.9
acidic flavor[c]	4.5 ab	1.9 cd	3.0 c	3.0 bc	2.4 cd	4.6 a	1.4 d	1.4 d	1.6 cd	1.3 d
sour flavor[d]	1.1 a	3.2 bcd	3.0 bcd	2.1 abc	3.1 bcd	1.9 ab	4.0 d	4.2 d	4.0 d	4.0 cd
sweet flavor	3.2	3.2	3.1	3.2	3.2	3.0	3.3	3.3	3.1	3.0
salt flavor	5.3	5.0	5.2	4.9	4.6	5.4	5.2	5.3	5.5	5.0
spice flavor	4.5	3.8	3.9	4.0	3.9	4.6	3.8	3.8	4.0	3.8
sickeningly sweet flavor	1.4 a	3.4 bcde	2.7 bcd	2.2 abc	2.6 abcd	1.1 a	3.9 e	4.5 e	3.2 cd	3.7 cde
metallic flavor	1.6a	5.0 bc	3.6 abc	3.4 ab	4.3 bc	2.1 a	5.3 bc	5.7 c	5.3 bc	5.7 c
freezer flavor	3.1 a	4.3 ab	3.8 ab	3.6 ab	3.5 ab	3.2 a	4.6 b	4.2 ab	4.1 ab	4.7 b
barn flavor[e]	1.3 a	1.8 ab	2.0 ab	1.7 ab	1.6 ab	1.0 a	2.5 b	2.1 ab	1.9 ab	2.7 b
bitter flavor	3.7	4.3	4.3	4.0	3.9	3.6	4.7	4.5	4.2	4.6
rancid flavor	1.2 a	4.6 bcd	3.2 ab	3.4 ab	3.8 bc	1.0 a	6.1 cde	6.6 de	6.4 cde	7.2 e
diverging flavor[f]	1.0	2.1	1.2	1.2	1.3	1.1	1.9	1.1	1.4	1.7
hardness	4.9 ab	4.3 a	4.3 a	4.5 ab	4.5 ab	4.9 ab	4.7 ab	5.1 b	5.1 b	4.9 ab
fattiness	4.6	4.9	4.8	4.7	4.7	4.6	4.9	5.0	5.2	5.0
juiciness	5.2	4.9	5.0	5.0	5.0	4.8	4.9	4.6	4.9	5.1
graininess	5.0 ab	4.6 a	5.0 ab	4.8 a	4.8 a	4.7 a	5.1 ab	5.6 b	5.1 ab	5.2 ab

[a] Averaged scores from 10 panelists. Samples (all data for each line) that showed significant differences with Tukey's test ($p < 0.05$) are marked with different letters. [b] Intensity: total impression of odor or flavor intensity. [c] Acidic: fresh, fruity, acidic (positive attribute). [d] Sour: sour, fermented (negative attribute). [e] Barn: notes associated with pig, barn, urine. [f] Diverging: odor or flavor notes not characterized by the defined attributes. [g] Color hue: 1 = yellow, 9 = red/blue.

Sensor, Linköping, Sweden) as described elsewhere (*5*). For each sample two replicates were measured.

Front-Face Fluorescence Spectroscopy. Measurements were performed with an optical bench system described in detail by Wold et al. (*7*). Fluorescence emission spectra were measured directly on the illuminated samples of sausages and ingredients, all tempered at room temperature. Round, flat, black, plastic cuvettes (diameter = 5 cm) were filled with sample, and the top was flattened to a smooth surface. The samples were exposed to 382 nm excitation light, and emitted fluorescent light was measured from 410 to 750 nm. The spectra were collected by an imaging spectrograph (Acton SP-150, Acton Research Corp., Acton, MA) connected to a sensitive charge coupled device (CCD camera) (Roper Scientific NTE/CCD-1340/400-EMB, Roper Scientific, Trenton, NJ). The samples were illuminated for 3 s, rotated approximately 90°, and illuminated again, giving two readings for each sample. The readings were averaged prior to data handling. All samples were analyzed in duplicate.

Statistical Analysis. Analysis of variance of the sensory results was performed with the SAS system (v 8.2, SAS Institute Inc., Cary, NC). The statistical model included the individual samples and assessors as main effects. The assessor effect was taken to be random. The interaction between samples and panelists could not be calculated because there were not enough degrees of freedom available. For the sensory attributes where the sample effect was significant at the 0.05 level, mean values were compared with Tukey's test to determine which of the samples were significantly different. For the GC-MS data, corresponding tests were performed with Minitab (v. 14, Minitab Inc., State College, PA) with the two-factor interactions included. Multivariate analysis [principal component analysis (PCA) and partial least-squares (PLS) regression] was carried out with the Unscrambler (v. 9.1, Camo AS, Oslo, Norway). All data were weighted to equal variance before analysis, and the models were cross-validated.

RESULTS

Pork Sausages. In the pork sausages that were stored with free access to air, the intensity of many sensory attributes changed significantly ($p < 0.05$) during the storage time (**Table 3**). Meat odor and flavor scores showed a substantial decrease after only 1 month at −20 °C, and the same was observed for acidic odor and flavor. Rancid odor and flavor increased significantly ($p < 0.05$) during the first month, as did sour, sickeningly sweet, freezer, and barn odor and flavor. Metallic flavor, odor intensity, and flavor intensity also increased. Longer storage had little additional impact on the sensory attributes. In the vacuum-packed pork sausages, the observed increases or decreases were smaller and fewer significant ($p < 0.05$) changes were found (**Table 3**). Meat flavor and acidic flavor scores were significantly ($p < 0.05$) lower after 1 month than in the initial samples, whereas the intensity of sickeningly sweet, metallic, and rancid flavor was higher.

About 260 volatile compounds were detected in the pork sausage samples, and most of them were not lipid oxidation products. After elimination of compounds from spices, smoke, or wrapping compounds that showed no significant ($p < 0.05$) differences throughout the storage time, as well as impure peaks of oxidation products, the components listed in **Table 4** remained. Hexanal (**Table 4**) showed an almost 6-fold increase

Table 4. Selected Volatile Compounds in Pork Sausages during Storage in Vacuum or Air at –20 °C for 11 Months[a]

	vacuum					air				
storage time (months)	0	1	3	6	11	0	1	3	6	11
heptane	2.4 a	2.4 a	2.6 a	2.5 a	3.2 ab	2.4 a	2.9 ab	3.0 ab	4.4 bc	4.8 c
propanal + octane	3.7 a	3.8 a	4.4 a	3.9 a	4.6 ab	4.6 ab	4.2 a	4.4 a	7.2 ab	8.2 b
butanal	1.7 a	1.9 a	2.2 a	1.9 a	2.2 a		2.5 a	3.8 ab	7.1 bc	8.3 c
pentanal	8.0 a	9.5 a	9.9 a	11.3 a	12.8 a	10.5 a	10.0 a	14.0 a	32.0 b	36.8 b
hexanal	16.0 a	17.0 ab	19.8 ab	18.3 ab	20.1 ab	16.9 ab	22.4 ab	35.8 b	68.6 c	99.0 d
2-octenal (*E*)								2.5 a	4.9 ab	5.9 b
2-methylbutanal	3.8 ab	3.3 a	4.1 ab	3.7 a	5.0 ab	6.4 abc	5.9 abc	5.3 ab	8.3 cd	9.8 d
3-methylbutanal	9.4 ab	8.0 a	10.4 ab	9.3 ab	12.6 ab	15.7 bc	14.5 ab	13.6 ab	21.6 cd	25.3 d
2-butanone	21.5 a	22.7 a	31.6 a	24.3 a	30.7 a	30.9 a	37.8 ab	38.3 ab	59.9 c	55.0 bc
1-penten-3-one		2.0 a	2.2 a			2.6 a	3.3 a	4.0 ab	6.0 c	5.7 bc
2,3-pentanedione/3-hexanone	7.2 a	7.0 a	9.7 ab	10.2 ab	10.4 ab	9.3 ab	11.0 ab	16.5 b	34.4 c	45.6 d
2,3-octanedione	2.0 ab	1.7 a	2.0 ab	1.9 a	2.3 ab	2.1 a	1.4 a	2.4 a	5.3 bc	7.1 c
cyclohexanone	2.5 a	2.2 a	2.2 a	2.4 a	2.6 a	3.1 a	9.8 b	9.3 bc	17.3 c	14.1 bc
3-methyl-2-butanone	3.5 a	3.2 a	3.8 ab	3.6 ab	4.0 ab	4.3 ab	4.4 ab	4.8 abc	5.5 bc	6.2 c
4-methyl-2-pentanone			2.0 a	3.6 a		6.6 a	17.9 ab	17.7 ab	26.8 b	63.3 c
1-butanol							10.7 a	14.4 ab	22.9 c	20.5 bc
1-pentanol	6.8 a	6.1a	6.6 a	7.1 a	7.4 a	8.6 a	8.2 a	9.8 a	15.2 b	15.4 b
1-penten-3-ol	2.2 a	5.3 a	6.4 a	5.1 a	5.1 a	2.7 a	7.5 ab	14.2 b	28.6 c	39.2 d
2-penten-1-ol (*E*)		1.8 a					1.2 a	1.5 a	3.1 b	3.0 b
2-penten-1-ol (*Z*)	3.0 a	3.7 ab	4.3 ab	3.9 ab	4.4 ab	4.2 ab	4.5 ab	7.8 b	13.9 c	15.4 c
1-octen-3-ol							3.7 a	5.2 ab	9.8 bc	13.4 c
2-methyl-1-propanol	4.7 ab	4.2 a	4.9 ab	4.8 ab	5.4 ab	4.9 ab	6.9 bc	7.2 bcd	10.0 d	9.0 cd
1-propoxy-2-propanol		2.5 a			3.6 a	2.1 a	4.8 ab	5.6 ab	8.1 bc	10.9 c
3-methylpyridine	1.7 a					2.5 a	4.6 ab	4.6 ab	6.3 b	6.1 b
2-furancarboxaldehyde	50.7 ab	42.3 a	44.5 ab	44.7 ab	45.0 ab	65.5 b	44.5 ab	44.7 ab	45.4 ab	40.0 a
2-furancarboxaldehyde	563.8 ab	486.7 a	506.2 ab	498.8 ab	468.1 a	692.5 b	557.9 ab	529.2 ab	518.6 ab	418.2 a

[a] Averaged values of two replicates. Samples (all data for each line) that showed significant differences with Tukey's test ($p < 0.05$) are marked with different letters.

during the storage time and was the lipid oxidation product found in highest concentration in the pork sausages stored in air for 11 months. However, at this point, hexanal constituted less than 2% of the total volatiles, indicating that lipid oxidation products were minor compounds as compared to other types of low molecular components in the sausages. During the experiment, 1-penten-3-ol (**Table 4**) increased 14-fold in the sausages stored in air. The level of 1-penten-3-ol was significantly ($p < 0.05$) higher in samples stored for 3 months than in the initial samples. For hexanal, significant differences ($p < 0.05$) were found after 6 months as compared to earlier storage times. Many other volatile compounds increased in the samples stored in air (**Table 4**). Additionally, two isomers of 2-furancarboxaldehyde significantly ($p < 0.05$) decreased during the storage time (**Table 4**). The vacuum-packed pork sausages remained stable with regard to content of volatile compounds throughout the storage time (**Table 4**).

Volatile compounds were also analyzed with an electronic nose. PCA did not reveal any pattern in the sensor responses that could be attributed to volatile lipid oxidation products (data not shown).

For the pork samples stored in air, one could see indications of slightly increasing fluorescence intensity with longer storage times (**Figure 1**). The vacuum-packed pork sausages did not show any variation in fluorescence that could be directly associated with lipid oxidation, and the sample stored for 11 months showed lower fluorescence intensity than the initial samples.

Poultry Sausages. The data from the sensory analysis of the poultry sausages are shown in **Table 5**. The changes in these samples were less pronounced than in the pork sausages. Acidic flavor decreased and was significantly ($p < 0.05$) lowered after storage for 3 months in air or 6 months in a vacuum. Rancid flavor was higher after 11 months of storage in air than initially. Small changes were also seen for sour, salt, sickeningly sweet, bitter, and diverging flavor and for hardness and juiciness. Both

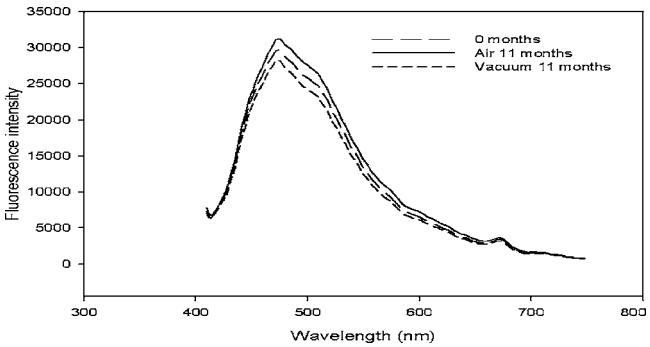

Figure 1. Fluorescence emission spectra of pork sausages initially and after storage in a vacuum or air at –20 °C for 11 months.

the vacuum-packed samples and those stored in air seemed to keep quite well.

As for the pork sausages, about 260 volatile compounds were detected in the samples made of poultry meat, and after the same elimination procedure, the components listed in **Table 6** remained. Hexanal and 1-penten-3-ol (**Table 6**) were among the compounds showing significant increases ($p < 0.05$) during the storage time even in the vacuum-packed samples. The hexanal concentration was significantly higher ($p < 0.05$) after 1 month of storage as compared to the initial sample in both packaging types. 1-Penten-3-ol was higher after 3 and 11 months than initially when the sausages were vacuum-packed and higher already after 1 month when stored in air. As for the pork sausages, many other compounds increased whereas 2-furancarboxaldehyde decreased (**Table 6**). 2-Furancarboxaldehyde was actually the most abundant volatile found in the initial poultry samples.

The electronic nose did not show any systematic differences in the sensor responses from the poultry sausages that could be attributed to lipid oxidation (data not shown).

Table 5. Sensory Attributes in Poultry Sausages during Storage in Vacuum or Air at –20 °C for 11 Months[a]

		vacuum				air			
storage time (months)	0	1	3	6	11	1	3	6	11
odor intensity[b]	6.4	6.0	6.5	6.4	6.4	6.2	5.9	6.1	5.8
chicken odor	4.1	4.1	4.5	4.0	3.6	4.3	4.1	3.8	3.9
smoked odor	5.4	4.7	5.6	5.3	4.8	4.9	4.6	5.0	4.6
acidic odor[c]	5.3 a	4.4 ab	5.3 a	4.6 ab	4.2 ab	4.7 ab	4.5 ab	4.6 ab	4.0 b
sour odor[d]	1.0	1.0	1.0	1.3	1.2	1.1	1.3	1.6	1.4
spice odor	4.1	3.7	4.2	4.0	4.0	3.9	4.0	4.0	3.8
metallic odor	2.9	3.1	2.8	2.8	3.3	2.8	3.1	2.7	3.2
sickeningly sweet odor	1.1	1.0	1.0	1.2	1.8	1.4	1.5	1.7	1.3
rancid odor	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.1
diverging odor[e]	1.0	1.1	1.0	1.1	1.4	1.3	1.2	1.5	1.0
whiteness	6.6	6.5	6.6	6.4	6.4	6.4	6.6	6.6	6.4
color hue[f]	3.9	3.5	3.7	3.5	3.4	3.3	3.4	3.5	3.5
color strength	2.6	2.7	2.7	2.7	3.1	2.7	2.6	2.9	2.8
flavor intensity[b]	6.4	6.4	6.5	6.4	6.9	6.7	6.6	6.6	6.6
chicken flavor	4.5	4.1	4.2	4.0	3.5	4.2	3.9	3.7	4.2
smoked flavor	5.0	4.7	5.0	4.5	4.5	4.4	4.3	4.6	4.2
acidic flavor[c]	5.4 a	4.4 abc	4.7 ab	4.1 bc	3.1 c	4.4 abc	3.6 bc	3.1 c	3.4 bc
sour flavor[d]	1.2 a	1.6 ab	1.4 ab	2.1 ab	2.4 ab	1.4 ab	2.1 ab	2.7 b	2.2 ab
sweet flavor	4.0	4.0	4.3	4.6	4.2	4.1	4.1	4.4	4.0
salt flavor	4.8 a	5.1 ab	5.2 ab	5.5 ab	5.7 ab	5.5 ab	5.9 b	6.1 b	5.5 ab
spice flavor	4.4	4.6	4.6	4.7	4.9	4.7	5.2	4.9	5.0
sickeningly sweet flavor	1.4 a	1.5 a	1.5 a	1.9 ab	2.9	2.0 ab	2.2 ab	3.0 b	2.3 ab
metallic flavor	2.7	2.6	2.8	3.1	3.4	2.9	2.9	3.1	2.9
bitter flavor	3.2 a	3.7 ab	3.7 ab	3.9 abc	4.4 bc	3.8 ab	3.9 abc	4.7 c	4.4 bc
rancid flavor	1.0 a	1.2 ab	1.0 a	1.1 a	1.3 ab	1.0 a	1.2 ab	1.7 ab	1.9 b
diverging flavor[e]	1.2 a	1.3 a	1.3 a	2.2 ab	2.9 b	2.2 ab	1.6 ab	2.4 ab	2.1 ab
hardness	3.9 a	4.1 ab	4.2 abc	4.9 abc	5.0 c	4.5 abc	4.4 abc	4.9 bc	4.5 abc
fattiness	3.5	3.5	3.2	3.4	3.5	3.4	3.5	3.7	3.7
juiciness	5.4 a	5.0 ab	4.8 ab	4.5 ab	4.3 ab	5.1 ab	4.6 ab	4.1 b	4.6 ab

[a] Averaged scores from 12 panelists. Samples (all data for each line) that showed significant differences with Tukey's test ($p < 0.05$) are marked with different letters. The sausage batch was split in two for storage in either vacuum or air, so the initial sample was the same for both storage methods. [b] Intensity: total impression of odor or flavor intensity. [c] Acidic: fresh, fruity, acidic (positive attribute). [d] Sour: sour, fermented (negative attribute). [e] Diverging: odor or flavor notes not characterized by the defined attributes. [f] Color hue: 1 = yellow, 9 = red.

Table 6. Selected Volatile Compounds in Poultry Sausages during Storage in Vacuum or Air at –20 °C for 11 Months[a]

		vacuum				air			
storage time (months)	0	1	3	6	11	1	3	6	11
propanal + octane	2.4 ab	2.3 a	2.3 a	2.3 ab	2.8 ab	2.5 ab	2.8 ab	3.0 ab	3.9 b
butanal	1.2 a	1.4 a	1.3 a	1.4 a	1.8 a	3.9 b	4.0 b	4.0 b	3.6 b
pentanal	5.6 a	8.2 bd	6.4 ac	6.4 ac	7.4 bc	9.4 d	9.7 d	9.9 d	13.9 e
hexanal	10.5 a	14.8 b	14.6 b	15.4 bc	17.3 c	15.8 bc	19.8 d	21.6 d	26.7 e
heptanal	3.6 a	5.4 b	5.4 b	5.8 b	6.0 b	5.0 b	7.4 c	8.1 c	10.5 d
octanal							9.2 a	10.5 a	12.8 b
nonanal	7.7 a	10.7 ab	9.9 ab	11.3 ab	10.0 ab	6.9 a	9.3 ab	9.3 ab	12.0 b
2-butenal (*E*)	2.3 a	3.0 abc	2.8 ab	3.0 abc	3.1 bc	4.0 d	3.6 cd	3.3 bc	3.6 cd
2-methylbutanal	8.5 a	9.9 ab	9.9 ab	10.3 ab	11.4 bc	8.8 a	10.6 ab	9.2 a	11.8 bc
3-methylbutanal	24.5 a	28.4 ab	28.5 ab	29.4 ab	32.6 bc	23.9 a	28.0 ab	24.8 a	33.2 bc
2-pentanone/2,3-butanedione	32.3 ab	38.0 bc	35.1 b	35.9 b	36.4 b	35.6 b	40.1 bc	38.5 bc	44.8 cd
2,3-pentanedione/3-hexanone	7.0 a	8.7 b	8.3 ab	8.3 ab	9.3 bc	8.9 b	9.8 bc	9.4 bc	12.4 d
2-heptanone	3.4 a	3.9 a	3.9 a	4.0 a	4.4 ab	3.8 a	4.0 a	4.0 a	4.7 b
2,3-octanedione	1.6 a	2.3 b	2.2 b	2.5 b	2.5 b	1.5 a	2.8 b	3.1 bc	4.2 c
cyclohexanone	2.4 a	2.4 a	2.4 a	2.4 a	2.6 a	4.3 b	4.4 b	4.7 b	4.4 b
3-methylcyclopentanone	2.7 a	2.9 ab	2.9 ab	3.0 ab	3.2 b	3.1 b	3.4 bc	3.2 b	3.8 c
3-methyl-2-cyclohexenone	12.3 a	14.3 a	14.5 ab	15.1 ab	14.8 ab	14.0 a	14.9 ab	15.2 ab	18.1 b
6-methyl-5-hepten-2-one	5.0 a	6.0 b	5.8 b	6.0 b	6.3 bc	5.7 abc	6.5 bc	6.6 cd	7.6 d
2-butanol	2.4 a	2.9 abc	2.7 ab	2.8 abc	3.1 abc	3.4 abc	3.6 bc	3.4 bc	3.8 c
1-pentanol	8.6 a	12.1 ab	9.0 a	14.1 a	9.6 a	15.3 b	15.5 b	15.7 b	18.1 b
1-hexanol	11.7 a	13.1 ab	13.2 ab	13.4 ab	13.9 ab	13.3 ab	14.6 bc	15.1 bc	16.6 c
1-penten-3-ol	1.8 a	2.2 ab	2.3 b	2.2 ab	2.3 b	3.4 c	3.8 cd	4.2 de	4.4 e
2-penten-1-ol (*Z*)	1.7 a	1.8 a	1.9 a	1.9 a	2.2 ab	2.3 b	2.4 b	2.6 bc	2.9 c
1-methylthio-1-propene	7.9 a	8.2 ab	8.6 ab	8.5 ab	10.2 bc	11.5 cd	11.7 cd	11.2 d	13.0 cd
1-nitropentane	2.1 a	3.6 b	3.7 b	4.6 c	4.1 bc	3.5 b	5.4 d	6.0 d	7.3 e
2-furancarboxaldehyde	461.9 a	430.2 a	387.0 a	333.6 b	301.2 b	429.9 a	390.9 a	335.0 b	305.4 b

[a] Averaged values of two replicates. Samples (all data for each line) that showed significant differences with Tukey's test ($p < 0.05$) are marked with different letters. The sausage batch was split in two for storage in either vacuum or air, so the initial sample was the same for both storage methods.

The sausages made of poultry meat showed higher fluorescence intensity in the initial samples than after storage (**Figure 2**). PCA of the spectra did not reveal any pattern typically recognizable as lipid oxidation during the storage time either for vacuum-packed samples or for samples stored in air.

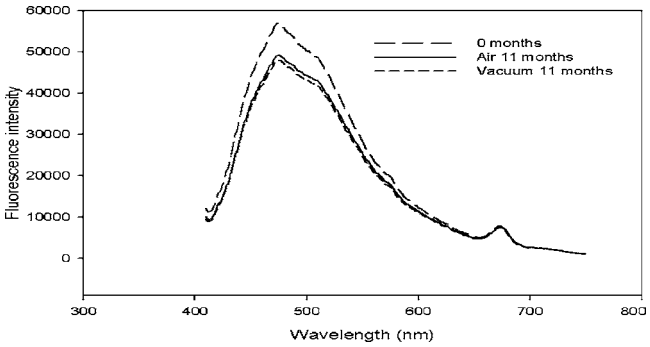

Figure 2. Fluorescence emission spectra of poultry sausages initially and after storage in a vacuum or air at −20 °C for 11 months.

DISCUSSION

Sensory Analysis. The sensory data for the sausages in the present study showed an increase in rancid odor and flavor as well as other sensory attributes associated with quality deterioration. Lipid oxidation leads to formation of volatile aldehydes and other low molecular compounds with low sensory thresholds. Such components can give odors and flavors typically associated with rancidity (*1*). Lipid oxidation products and compounds from other degradation reactions might also contribute to increased scores of other nondesirable sensory attributes (for example, metallic or sickeningly sweet flavors). Increasing rancid or oxidation-related warmed-over odor and flavor are often accompanied by decreasing acidic and meat flavor (*5*, *10*−*12*), and this was observed in the present study as well. The decrease might be caused by a loss of components contributing to these desirable attributes or by masking due to increasing amounts of lipid oxidation products.

The changes in the sensory attributes were more pronounced in the pork samples stored in air than in the vacuum-packed samples. This was as expected since the oxidation reactions could proceed further with unlimited access to oxygen than with restricted oxygen availability. For the vacuum-packed pork samples, it seemed reasonable that the largest changes in the sensory attributes associated with rancidity appeared during the first month of the storage time when a small residue of oxygen might have been present in the packages or in the product itself. However, when the available oxygen might have been consumed, the product seemed to be quite stable.

The lack of changes in the sensory attributes in the pork sausages stored in air for more than 1 month was more surprising and hard to explain. The sausages had a light brown surface after the heat treatment and smoking, and with the exposure to air, it might be possible that this outer layer could have dried to a protective surface. However, no change in juiciness was observed during the storage time and although some small significant ($p < 0.05$) differences in hardness were found, they could hardly be called conclusive.

Another explanation of the lack of further development of the sensory attributes in the pork sausages stored in air after the first month could be that the sensory panel somehow reached a plateau of what they were able to quantify in the samples. Smoked sausages with spices have fairly high total odor and flavor intensity. When the sausages were fresh, the sausage makers commented that the sausages in their opinion had mild flavors of smoke and spices, but such notes might still have masked the perception of rancid odor and flavor. Lawless (*13*) has discussed whether it really is possible to separate the perception of single sensory attributes (particularly odors) from a complex whole and says that judges usually do not perceive very distinctive notes in a complex mixture. The results from the present study might be interpreted as an expression of this difficulty. The sensory panel had a brainstorming session to determine relevant attributes prior to analysis and came up with a total of 34 variables, of which some might be intercorrelated. The panel had long experience with many types of samples and the training on relevant sausages prior to analysis ought to be the best preparation possible (*14*), but it might still have been a difficult challenge to differentiate between the attributes.

The poultry sausages appeared to have somewhat different odor and flavor from the pork sausages, and they were more stable during the storage time. No statistical analysis was performed on poultry vs pork data (**Tables 3** and **5**), but it looked like the poultry sausages got a bit higher scores for whiteness and lower scores for color hue and color strength than the pork sausages. The poultry sausages also appeared as slightly less acidic and more sweet, spicy, and metallic and with lower scores for fattiness. It is possible that these differences would influence the perception of, e.g., acidity or rancidity.

That the poultry sausages appeared less fatty than the pork sausages was not surprising due to their lower fat content (approximately 6% as compared to about 16% in the pork sausages, **Table 2**). Sausages can be looked at as an emulsion. In the pork sausages, pork back fat was added as a separate, solid ingredient that might be distributed in the emulsion as fat globules. In the poultry sausages, all of the fat was intrinsic in the ingredients and would therefore probably be differently distributed. It seems likely that this would lead to different distribution of flavor compounds in the two types of sausages so that for instance the lipid oxidation products in the pork sausages to a large extent would be located in the fat globules or at their interface. Flavor release and perception of various types of compounds are dependent on their location and interaction with other components (*15*). The different partition of oxidation products would also influence the yield and composition of volatiles that could be analyzed with the dynamic headspace technique.

Another factor that undoubtedly contributed to the different development of rancid odor and flavor in the two types of sausages was the different content of polyunsaturated fatty acids. The pork samples contained more than twice as much linoleic acid (C18:2*n*-6) and linolenic acid (C18:3*n*-3) as the poultry samples (**Table 2**). However, the susceptibility of various fatty acids toward oxidation is highly dependent on the number of doubly allylic hydrogen atoms present (*1*). Long-chained fatty acids with more double bonds must therefore be expected to be major contributors of lipid oxidation products in matrixes where they are present. Although the content of such fatty acids was low in both types of sausages, the pork samples contained more of, e.g., eicosapentaenoic acid (C20:5*n*-3), docosapentaenoic acid (C22:5*n*-3), and DHA (C22:6*n*-3) than the poultry samples (2.4 and 0.4 mg/g, respectively). It is likely that this difference would lead to more pronounced development of rancid odor and flavor in the pork than in the poultry sausages. The contents of pro- or antioxidants in the different types of sausages are not known but could obviously also influence the oxidation rates.

It is also likely that the composition of proteins and carbohydrates in the two types of sausages was different. Continuous phase proteins can affect the oxidative stability of emulsions through a combination of free radical scavenging and metal chelation (*16*). The presence of cysteine and ribose can affect the perception of, e.g., fishy notes in emulsions with linolenic acid (*17*). Fat nature and aroma compound hydropho-

bicity affect the flavor release from complex food emulsions (*18*). Lipid oxidation products might thus be differently formed and perceived in the two sausage types because of the influence of other components that lipids.

GC-MS. The volatile compounds listed in **Tables 4** and **6** were mostly in good accordance with components previously found in pork back fat, mechanically recovered poultry meat and other types of meat products (*5*, *19*−*21*). The volatiles included the components previously identified as good marker compounds for early lipid oxidation and other deterioration (*5*), for example, hexanal and 1-penten-3-ol. The concentration of these components increased as expected more in the samples stored in air than in the vacuum-packed samples during the storage time.

Hexanal can be a product of decomposition of hydroperoxides formed during autoxidation of *n*-6 fatty acids. Linoleic acid was the most abundant PUFA in the sausages (**Table 2**) so the high level of hexanal in the samples stored in air was reasonable. Hexanal and other oxidation products would be expected to contribute to development of rancid odor and flavor in the sausages.

1-Penten-3-ol originates from autoxidizing *n*-3 fatty acids (*22*). Vinyl alcohols have relatively high sensory thresholds (*1*), so 1-penten-3-ol might thus not by itself be a major cause of the rancid odor and flavor in the sausages. Although the contents of *n*-3 fatty acids in the sausages were low as compared to *n*-6 fatty acids (**Table 2**), the large increase in 1-penten-3-ol could indicate that oxidation of *n*-3 fatty acid strongly contributed to the oxidative deterioration of the samples. It is quite likely that these fatty acids could be the origin of flavor potent volatile oxidation products that might have been formed in too small amounts to be detected among the dominating spice and smoke compounds in the dynamic headspace analysis. One could for instance find traces of 2,4-heptadienal and many other well-known contributors to rancid odor and flavor (*1*), but these components could not be separated from the confounding effect of overlapping peaks. 1-Penten-3-ol was formed in somewhat larger concentrations and was easier to analyze, so this might be a good marker compound for early oxidation of *n*-3 fatty acids. Shahidi (*23*) has formerly suggested propanal and hexanal as markers for oxidation of *n*-3 and *n*-6 fatty acids, respectively. In the present study, the combined assessment of formation of 1-penten-3-ol and hexanal could give a simple but probably quite representative overview of main oxidation trends in the samples. The results illustrate the well-known fact that oxidative deterioration starts very quickly in materials where PUFAs (especially long-chained *n*-3 fatty acids) are present even if the content is low and the access to oxygen restricted.

The content of hexanal and 1-penten-3-ol seemed to be lower in poultry than in pork sausages during the storage time. This could match the low scores of rancid odor and flavor in the poultry sausages. However, the formation of the two marker compounds (and the other volatiles listed in **Tables 4** and **6**) only partly matched the development of rancid odor and flavor in the pork sausages, especially when the time scale was considered. The sensory perception of the pork sausages changed little after the first month of storage, whereas the concentration of volatile oxidation products increased throughout the storage time. The steady formation of volatiles would ordinarily be expected to correlate with increased sensory rancidity. These results might indicate that the previous suggestion about an upper "saturation threshold" for the sensory panel in the analysis of the pork samples could be likely.

2-Furancarboxaldehyde decreased during the storage time in both types of sausages. 2-Furancarboxaldehyde is a Maillard type component, formed in reactions between amino acids, peptides, or proteins and reducing sugars. Maillard reaction products are important aroma components in cooked meat (*24*). Some Maillard products might have antioxidative effects due to, e.g., metal chelation, reduction of hydroperoxides to non-radical products, or hydrogen donation to radicals (*25*). The reason for the decrease in 2-furancarboxaldehyde in the sausages in this study is not known, but one suggestion could be that 2-furancarboxaldehyde might have reacted with other components present in the samples and formed products that would not be recovered in the headspace analysis. 2-Furancarboxaldehyde can, for example, react with cystein and form 2-(2-furanyl)thiazolidine in microemulsions (*26*). Because 2-furancarboxaldehyde was so abundant, it might perhaps be used as an easily detectable marker compound for general deterioration or aging of samples where Maillard type components are present. 2-Furancarboxaldehyde has a high odor threshold and a not easily recognized odor (*27*). A decrease in this component could perhaps be associated with reactions causing loss of acidic or meat flavor.

Rapid, Nonspecific Methods: Electronic Nose and Front-Face Fluorescence Spectroscopy. The sensors in the electronic nose are relatively nonspecific, although they can give different responses for various classes of volatile components. Samples that contain high levels of volatiles of many types will give high sensor responses for many of the sensors. In this study, the sensor responses did not show any systematic pattern that could be attributed to volatile lipid oxidation products. The data from the dynamic headspace/GC-MS showed that the concentrations of such components were low even in the samples stored in air. The volatile components from the spice mix, the smoking process, etc. had a dominating impact on the sensor responses as compared to the lipid oxidation products, and the signals from the latter were masked by other variation in the data.

Fluorescence has previously been shown as a highly sensitive technique for detection of lipid oxidation in pork back fat (*5*) and poultry meat (*7*, *28*). The fluorescence spectra for the sausages in the present study were not easily interpreted, and they were probably influenced by many compounds and reactions in the samples during storage.

The apparent increase in fluorescence intensity over time in the pork sausages stored in air could be caused by formation of fluorescent Schiffs bases due to interactions between amino compounds and lipid oxidation products. It has previously been shown that the fluorescence intensity increases after amino acids have been exposed to oxidizing lipids or pure lipid oxidation products (e.g., *29*). Genot et al. (*30*) have recently compiled an overview of the current knowledge about degradation of proteins due to lipid oxidation in multiphase systems. Proteins can undergo radical reactions such as protein−protein or protein−lipid cross-linking, protein scission, or protein oxidation when exposed to, e.g., lipid hydroperoxides. The most labile amino acids are histidine, cysteine, methionine, lysine, tyrosine, and tryptophan. Lipid oxidation products can also contribute to Strecker degradation of amino acids (*31*). Tryptophan is sensitive to oxidative degradation and yields decreasing fluorescence when it is exposed to oxidized lipids (*30*). Tryptophan yields maximum fluorescence intensity around 330 nm, and in the present study, fluorescence was recorded upward from 410 nm so it was not possible to say anything about the disappearance of fluorescence from tryptophan or other amino acids or connect

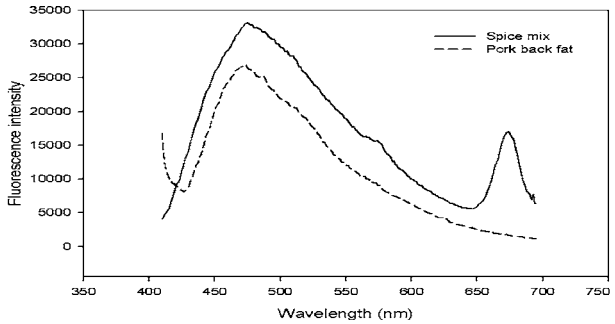

Figure 3. Fluorescence emission spectra of spice mix and pork back fat used as ingredients in pork sausages.

it directly to formation of new fluorophores with emission maxima at higher wavelengths. However, it seems likely that such interactions could occur in the sausage samples.

Not only lipid oxidation products but also aromatic components from the spice mix, compounds formed during the heat treatment (in, e.g., browning reactions) or absorbed from the smoke would be expected to contribute to the observed fluorescence of the samples. Rosemary extract has previously led to unsatisfactory results for measurement of fluorescence shift in wiener sausages (*3*). Fluorescence spectra of the spice mix and pork back fat used as ingredients in the pork sausages in the present study are shown in **Figure 3**. A comparison between the spectra in **Figures 1** and **3** showed that the spice mix and pork back fat both yielded high fluorescence in the same wavelength range as the sausages. Although the spice mix was not a major ingredient in the sausages by weight, the high content of fluorescent compounds might still contribute to the observed fluorescence of the sausages. This would make it more difficult to differentiate between small changes in fluorescence due to early lipid oxidation and other variations that might occur. Fluorescent components from the smoking process and browning reactions would make the picture even more complicated. This means that it generally would be more difficult to use the fluorescence technique for detection of early lipid oxidation in complex products such as the model sausages in the present study than in simpler matrixes such as pork back fat. However, fluorescence seemed still to be able to detect oxidative changes when the level of oxidation was somewhat higher, as in the pork samples stored in air. No pattern due to lipid oxidation was found for the vacuum-packed pork sausages, which corresponded well to the dynamic headspace/GC-MS data for these samples.

In contrast to the pork sausages stored in air, the vacuum-packed sausages stored for 11 months appeared to yield lower fluorescence than the initial samples (**Figure 1**). This was difficult to explain, but one might try by looking at the fluorescence intensity as the sum of many phenomena. The fluorescence intensity due to lipid oxidation (usually observed at approximately 450−550 nm) would be expected to increase with increasing storage time. However, if a relatively large part of the observed fluorescence originated from spice, smoke, and nonvolatile Maillard type components, and some of these reacted to nonfluorescing compounds during storage, one might see a decline in samples with low levels of lipid oxidation products. In samples with high levels of oxidation products, as in the samples stored in air, this decline would be masked, leading to a smaller than expected increase in fluorescence. The decrease in 2-furancarboxaldehyde that was observed in the dynamic headspace analysis might be an indication of such reactions as suggested here. 2-Furancarboxaldehyde might not by itself contribute very much to the observed fluorescence, but one might think that similar reactions could take place with other more strongly fluorescing nonvolatile components. The results for the poultry sausages could also support this. According to the GC-MS data for these samples, they were less oxidized than the pork sausages so no large increase in fluorescence intensity would be expected. The observed decrease from the initial samples to later storage times could then be interpreted as the same phenomenon that caused the low fluorescence intensity in vacuum-packed pork sausages.

It was not surprising that many types of compounds from ingredients as well as processing influenced the fluorescence readings. This led to lower sensitivity with regard to detection of fluorescence caused by lipid oxidation products. The possible disappearance of fluorescent components complicated the interpretation of the data. The present data set showed that it is more difficult to use a nonspecific technique like fluorescence spectroscopy to detect early lipid oxidation in a complex processed meat product than in less complex matrixes.

Correlations between Sensory Analysis and Other Analytical Methods. Correlations between various sensory attributes, GC-MS, and fluorescence are shown in **Table 7**. The GC-MS data were highly correlated with rancid flavor and some other sensory attributes in the pork sausages. The fluorescence spectra were negatively correlated with several of the sensory variables.

Table 7. Correlation Factors (*r*) from PLS Regression Models with Sensory Attributes[a] vs Volatile Compounds Analyzed with GC-MS[b] or Fluorescence Spectra[c]

	r GC-MS	*r* fluorescence
	pork sausages	
odor intensity	0.63	0.68
meat odor	0.75	0.67
acidic odor	0.63	
sour odor		0.66
freezer odor	0.78	0.66
barn odor	0.66	
color hue		−0.70
flavor intensity	0.84	0.70
meat flavor	0.82	
smoked flavor	0.62	
acidic flavor	0.84	
sour flavor	0.75	
sweet flavor		−0.65
spice flavor	0.77	−0.65
sickeningly sweet flavor	0.67	
metallic flavor	0.77	
rancid flavor	0.86	
hardness	0.75	0.64
fattiness	0.66	
	poultry sausages	
odor intensity		−0.92
chicken odor		−0.73
acidic odor	0.65	
sour odor		−0.81
spice odor		−0.62
metallic odor		−0.62
smoked flavor	0.79	
sour flavor		−0.69
sweet flavor	−0.73	−0.84
spice flavor	0.71	−0.70
bitter flavor	0.60	
rancid flavor	0.74	
fattiness		−0.85
juicyness		−0.65

[a] Only sensory attributes with $|r| > 0.6$ are shown. (Because of this, the table does not contain any data for the electronic nose.) [b] The volatiles included are shown in **Tables 4** and **6**. However, volatiles with many missing values were excluded from the calculations. [c] Whole spectra.

Concluding Remarks. The data from the present study showed that although two products such as the two sausage types superficially might appear fairly similar, they may develop in different ways. Fat content, fatty acid composition, and probably the fat distribution influenced the level of oxidation in the sausages. Lean poultry sausages developed less rancid odor and flavor during frozen storage for 11 months than fattier pork sausages with more PUFA. Odor and flavor of spices and smoke probably masked the perception of rancid odor and flavor in both types of sausages. For the pork sausages stored in air, the sensory panel seemed to reach an upper limit for differentiation of rancid odor and flavor from other sensory attributes.

Early oxidative events could be detected with dynamic headspace/GC-MS. Hexanal and 1-penten-3-ol were good marker compounds for lipid oxidation, and together, they gave an impression of the oxidation of both *n*-6 and *n*-3 fatty acids. 2-Furancarboxaldehyde decreased in both types of sausages and could perhaps be used as a marked compound for loss of, e.g., acidic flavor. The gas-sensor array system (the electronic nose) could not differentiate between low levels of lipid oxidation products and random variation in the data set. The sensor responses were dominated by signals from spices, smoke etc. that masked any pattern of lipid oxidation. The fluorescence results were difficult to interpret, and they were probably influenced by several different reactions occurring during the storage time. Lipid oxidation contributed to increasing fluorescence intensity in pork sausages stored in air. It is possible that deterioration of, e.g., Maillard type components during storage could lead to decreasing fluorescence in the sausages during the storage time.

The results showed that it is much more difficult to detect early lipid oxidation in complex matrixes such as smoked, comminuted sausages with spices than in simpler model systems. Even sensory analysis turned out as not quite straightforward. It might be possible to use fluorescence spectroscopy on such products when the oxidation levels are relatively high, however, other phenomena than lipid oxidation must then be taken into consideration. For complicated matrixes containing a wide array of components, a highly specific method like dynamic headspace/GC-MS might be the safest option. The detection of early lipid oxidation is very product specific with regard to which analytical methods that can be used. Because of this, more than one method should be used in all experiments to avoid misinterpretation of the results.

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