Odors in the Food Industry

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Library of Congress Control Number: 2006926455

ISBN-10: 0-387-33510-2

ISBN-13: 978-0387-33510-0

e-ISBN-10: 0-387-34124-2

e-ISBN-13: 978-0387-34124-8

9 8 7 6 5 4 3 2 1

springer.com

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Electronic-Nose Technology: Application for Quality Evaluation in the Fish Industry

Guðrún Ólafsdóttir and Kristberg Kristbergsson

1. INTRODUCTION

The odor of fresh fish is one of the most important quality parameters used to determine whether fish is acceptable for consumption. The composition of volatile compounds in fish contributing to the characteristic odors can be determined and related to quality. Currently there is a need for rapid, automated, and objective tools for process monitoring and quality assurance of perishable food products. The possibility of using electronic nose for rapid quality control of fish therefore is of interest. Knowledge about the composition of the headspace of different fish products during storage is useful to guide the development of electronic noses for quality monitoring of fish products. Complicated postmortem processes in the fish are responsible for the loss of freshness and the onset of spoilage. The spoilage processes are a combination of physical, chemical, biochemical, and microbiological interactions that are species dependent and additionally various extrinsic factors such as handling and different storage conditions will further influence the spoilage pattern and the development of spoilage odors.

2. VOLATILE COMPOUNDS AS INDICATORS OF FISH QUALITY

The odor of fish can be classified as species-related fresh fish odor, microbial spoilage odor, oxidized odor, processing odor, and environmentally derived odor, based on the origin of the volatile compounds (Table 1).

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Because of the nonspecific selectivity and low sensitivity of gas sensors in electronic noses it is necessary to correlate their responses to the main classes of quality indicating volatile compounds of the products. Some compounds present in concentrations below the detection limit of the gas sensors in electronic noses may have an impact on the odor and can function as key odorants due to their low flavor threshold.

Compounds contributing to characteristic fresh fish odors like alcohols, carbonyls, and dienals causing oxidation odors are present in very low concentrations (ppb) but have an impact on the overall odor because of their low odor threshold (see Table 1). Microbially formed degradation compounds like alcohols are present in much higher concentrations (ppm) in the headspace of fish but their odor threshold is much higher so their impact on the odor is less (Olafsdottir and Fleurence, 1998). Therefore, it cannot be assumed that the gas sensors are measuring the overall odor, but rather detecting the components that are in the highest concentration in the headspace, which may be of both odorous and nonodorous nature. In some cases the compounds may have little or no effect on the human olfactory system, but they may be detected by the gas sensors.

Characteristic odor and the progression of odor in fish during storage have been associated with varying levels of different volatile compounds present in the headspace of fish (Lindsay *et al.*, 1986; Josephson *et al.*, 1986).

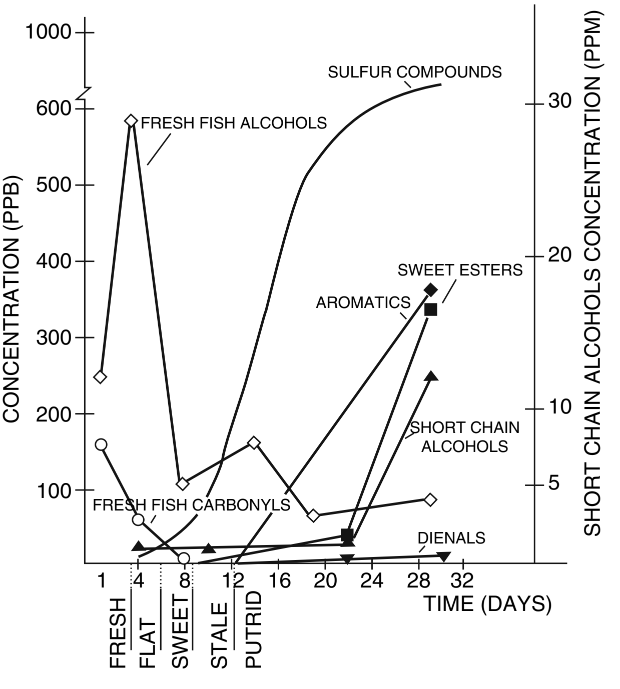

Figure 1. Generalized changes in concentration of groups of influential aroma compounds and sensory quality stages of refrigerated whitefish (from Josephson *et al.*, 1986)

Table 1. Classes of Odors in Fish and Examples of Compounds Contributing to the Odors (from Olafsdottir and Fleurence, 1998)

Fish odor	Class of chemical species	Examples of compounds	Aroma description	Odor threshold in water
Species-related fresh fish odor	C6-C9 alcohols and carbonyls	Hexanal / t-2-hexenal,	Green, aldehyde-like	4,5ppb / 17ppb [a]
		1-octen-3-ol, /1-octen-3-one	Mushroom	10ppb/ 0,009ppb[a]
		1,5-octadiene-3-ol	Heavy earthy, mushrooms	10ppb[a]
		1,5-octadiene-3-one	Geranium	0,001ppb[a]
		2,6-nonadienal	Cucumber	0,001ppb[a]
		3,6-nonadienol	Cucumber, melon-like	10ppb[a]
	Bromophenols	2,6-dibromophenol	Iodine- and shrimp-like	0,0005µg/kg[b]
		2,4,6-tribromophenol	Saltwater fish, brine-like.	0,6µg/kg[b]
		2-bromophenol	Sea, marine-like flavor	
	N-cyclic compounds	Pyrrolidine piperidine	Earthy	
	Short chain alcohols	ethanol, propanol, butanol, 3-methyl-1-butanol	Solvent like	1–100 ppm[c]
Microbial spoilage odor	Short chain carbonyls	acetone, butanone ethanal, propanal	Solvent like	
		3-methylbutanal	Malty	0,06ppm [d]
		2-methylbutanal	Malty	0,04ppm [d]
	Amines	ammonia,	Ammoniacal	110 ppm[c]
		TMA	fishy, ammoniacal	30 ppm[c]
		DMA		0,6 ppm[c]
		histamine, putrecine, cadeverine	Putrid, rotten	
	Sulfur compounds	hydrogen sulfide	Sulfury, boiled eggs	5–40 ppb [e]
		methyl mercaptan	Rotten, cabbage	0,05 ppb [e]
		methyl sulfide	Cabbage-like	0,9µg/kg[f]
		dimethyl disulfide	Putrid, onion-like	12 ppb [g]
		dimethyl trisulfide	Putrid, cabbage and onion-Garlic like	0.01ppb[g]
		bis-methylthio methane thioesters		0,3 µg/kg[f]
	Aromatics	phenethyl alcohol	Old roses	
		phenol,	Phenolic,	2 ppm
		p-cresol	Pigpen-odors ,horse manure	300 µg/kg[f]
	N-cyclic compounds	indole skatole	Moth ball or fecal like	
	Acids	acetic acid,		34,2ppm[c]
		butyric acid	Sour, rotten, old socks	32,8ppm[c]
		isobutyric acid		
Oxidized odor	Unsaturated aldehydes	hexanal	green, planty	4,5ppb[f]
		c4-heptenal	cardboard-like, potato-like	0,04ppb[h]
		2,4-heptadienal,	fishy oxidised flavor	
		2,4,7-decatrienal,	burnt, fishy, cod-liver oil-like	

(*Continued*)

Table 1. Classes of Odors in Fish and Examples of Compounds Contributing to the Odors (from Olafsdottir and Fleurence, 1998)—Cont'd

Processing odors	2,4-heptadienal and 3,5-octadien-2-one	ripened anchovies
	methional	boiled potato - like odor
	2-methyl-3-furanthiol	meaty odor in canned tuna
Environ-mental odors	methyl sulfide geosmin	petroleum odors
	2-methyl-iso-borneol	earthy, muddy odors

[a]Josephson (1991); [b] Whitfield *et al*. (1988); [c] Kawai T. (1996); [d] Sheldon *et al*. (1971); [e] Fazzalari (1978); [f] Whitfield and Tindale (1984); [g] Buttery *et al*. (1976); [h] McGill *et al*. (1974).

Species-related fresh fish odors have been attributed to long-chain alcohols and carbonyl compounds like 1,5-octadien-3-ol and 2,6-nonadienal, respectively, which are oxidatively derived from polyunsaturated fatty acids such as eicosapentaenoic acid 20:5ω3 (Josephson *et al*., 1984). Spoilage odors develop as a result of microbial activity and oxidative degradation of the fish components. Compounds such as trimethylamine (Oehlenschläger, 1992), short-chain alcohols (Kelleher and Zall, 1983; Ahmed and Matches, 1983), carbonyls, esters, and sulfur compounds like hydrogen sulfide, methylmercaptan, dimethyl disulfide, and dimethyl trisulfide are produced by microbial degradation of fish constituents (Herbert *et al*.,1975; Kamiya and Ose,1984). Oxidation of fatty acids contributes to the rancid odors of fish with the formation of aldehydes like hexanal, 2,7-heptadienal, and 2,4,7-decadienal (McGill *et al*., 1974). All these compounds are to some degree volatile and may be used to monitor freshness and spoilage of fish.

Both single compounds or a combination of compounds representing the different changes occurring during spoilage have been suggested as indicators for freshness and spoilage of fish (Lindsay *et al*., 1986). Ethanol, 3-methyl-1-butanol, 2-methyl-1-propanol, 3-hydroxy-2-butanone, ethyl acetate, and butanoic acid ethyl ester were the most abundant volatiles in the headspace of haddock stored in ice (Olafsdóttir, 2003). Similar volatile compounds were found in cold-smoked salmon during refrigerated storage (Joffraud *et al*., 2001; Jörgensen *et al*., 2001). This is expected since similar profiles of microflora emerge in different food products when subjected to the same conditions despite being heterogeneous initially (Gram *et al*., 2002). The volatile compounds detected in spoiled cold-smoked salmon were mainly alcohols produced by microbial activity. Some of the volatile compounds produced during spoilage of cold-smoked salmon contributed to the spoilage off-flavor of cold-smoked salmon as confirmed by gas chromatography-olfactometry. These were trimethylamine, 3-methyl butanal, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-penten-3-ol, and 1-propanol (Jörgensen *et al*., 2001).

It is likely that the same set of sensors can be used for monitoring spoilage changes in different fish products because similar volatile compounds emerge

Fish stored as fillets at 0–2°C (May 2000) spoiled faster than whole fish and had a shelf life of only 8–9 days.

The results of the electronic nose measurements and the microbial and chemical analysis were mostly in agreement with the sensory analysis (Figures 5 and 6). The traditional microbial analysis (TVC) and electronic nose measurements (CO sensor) showed a similar overall trend in the storage studies of whole fish (May 1999 and Sept 1999) and fillets (May 2000) (Figure 5) and likewise the results of TVN chemical measurements and the NH_3 electronic nose sensor showed similar overall trends (Figure 6).

The electronic nose measurements showed that the responses of the sensors were highest for the (May 2000) samples indicating the most rapid spoilage for fish stored as fillets. The results from the sensory analysis, the TVN (total volatile bases) measurements, and the NH_3 sensor showed that recently spawned fish from the spring season (May 1999), stored as whole fish, had higher spoilage rate than fish from the autumn season (Sep 1999). Contradictory to these results the TVC and CO measurements indicated that the spoilage rate appeared to be higher in the fall (Sep 1999) than in the spring (May 1999). However, based on the results of sensory analysis it appears that the spoilage potential of the microflora might have been greater in the spring. This suggests that the role of specific spoilage organisms producing offensive odors should be emphasized and the validity of TVC measurement may be questionable as has been suggested by other researchers (Gram *et al.*, 2002).

When the end of the shelf life was reached, as indicated by sensory analysis, the responses of the NH_3 and SO_2 sensors detecting microbially produced amines and sulfur compounds start to increase rapidly in all experiments. The conclusions drawn from these results indicate that spoilage patterns are different depending on season and fillets spoil faster than whole fish, as was to be expected.

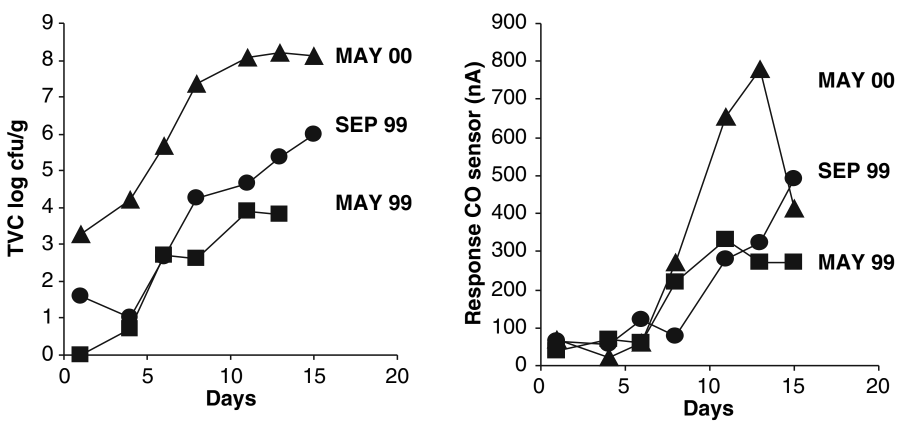

Figure 5. Microbial analysis (TVC) and electronic nose measurements (CO sensor) of haddock fillets from storage studies at 0–2 °C for up to 15 days of whole fish [May 99 (-■-); Sept 99 (-●-)] and fillets [May 00 (-▲-)].