ABSTRACT: Sockeye and pink salmon were canned according to constant and variable temperature retort processes. A total of 102 volatile constituents were detected by gas chromatography-mass spectrometry. Based on principal component analysis (PRIN) applied to the different classes of volatiles, PRIN1 explained 72.2% of variation and was significant (P < 0.0001) for species differentiation. PRIN2 and PRIN4 extracted smaller variations (14.5% and 3.1%, respectively) but were significant (P < 0.05 and P < 0.01, respectively) for differences in retort regimes. However, sensory panelists did not find flavor differences between retort modes. Olfactometry revealed that aldehydes, sulfurs, and ketones constituted the major volatile classes of aroma-impact constituents in canned sockeye salmon.

Key Words: retort process, salmon, volatiles, flavor, sensory evaluation

Introduction

The influence of volatile aroma components is often regarded as a critical factor of food flavor quality. Due to both economic importance and academic interest, research has been carried out on the identification of volatile flavor compounds in various foods, including fish. Static headspace analysis is one approach that has been applied to measure various classes of volatile constituents (e.g., sulfurs, amines, halocarbons, alcohols) in seafood (Sipos and Ackman 1964; Miller and others 1972; Entz and Hollifield 1982; Hollingworth and others 1986; Girard and Nakai 1991). Dynamic headspace analysis is another technique that has received substantial attention over the years. It is based on a ‘dynamic’ process in which the sample volatiles are swept by a stream of an inert gas, trapped, and then desorbed by various means into a gas chromatograph (GC). The purged headspace volatiles of tuna (Khayat 1979; Human and Khayat 1981) and herring (Hughes 1964) have been condensed by cryogenic trapping while adsorbent trapping was used for pickled smelt (Josephson and others 1987), north sea fish oil (Christensen and others 1982; Hollingworth and others 1986; Girard and Nakai 1991). Dynamic headspace analysis is another technique that has received substantial attention over the years. It is based on a ‘dynamic’ process in which the sample volatiles are swept by a stream of an inert gas, trapped, and then desorbed by various means into a gas chromatograph (GC). The purged headspace volatiles of tuna (Khayat 1979; Human and Khayat 1981) and herring (Hughes 1964) have been condensed by cryogenic trapping while adsorbent trapping was used for pickled smelt (Josephson and others 1987), north sea fish oil (Christensen and others 1982; Hollingworth and others 1986; Girard and Nakai 1991). Dynamic headspace analysis is another technique that has received substantial attention over the years. It is based on a ‘dynamic’ process in which the sample volatiles are swept by a stream of an inert gas, trapped, and then desorbed by various means into a gas chromatograph (GC). The purged headspace volatiles of tuna (Khayat 1979; Human and Khayat 1981) and herring (Hughes 1964) have been condensed by cryogenic trapping while adsorbent trapping was used for pickled smelt (Josephson and others 1987), north sea fish oil (Christensen and others 1982; Hollingworth and others 1986; Girard and Nakai 1991). Dynamic headspace analysis is another technique that has received substantial attention over the years. It is based on a ‘dynamic’ process in which the sample volatiles are swept by a stream of an inert gas, trapped, and then desorbed by various means into a gas chromatograph (GC). The purged headspace volatiles of tuna (Khayat 1979; Human and Khayat 1981) and herring (Hughes 1964) have been condensed by cryogenic trapping while adsorbent trapping was used for pickled smelt (Josephson and others 1987), north sea fish oil (Christensen and others 1982; Hollingworth and others 1986; Girard and Nakai 1991). Dynamic headspace analysis is another technique that has received substantial attention over the years. It is based on a ‘dynamic’ process in which the sample volatiles are swept by a stream of an inert gas, trapped, and then desorbed by various means into a gas chromatograph (GC). The purged headspace volatiles of tuna (Khayat 1979; Human and Khayat 1981) and herring (Hughes 1964) have been condensed by cryogenic trapping while adsorbent trapping was used for pickled smelt (Josephson and others 1987), north sea fish oil (Christensen and others 1982; Hollingworth and others 1986; Girard and Nakai 1991). Dynamic headspace analysis is another technique that has received substantial attention over the years. It is based on a ‘dynamic’ process in which the sample volatiles are swept by a stream of an inert gas, trapped, and then desorbed by various means into a gas chromatograph (GC). The purged headspace volatiles of tuna (Khayat 1979; Human and Khayat 1981) and herring (Hughes 1964) have been condensed by cryogenic trapping while adsorbent trapping was used for pickled smelt (Josephson and others 1987), north sea fish oil (Christensen and others 1982; Hollingworth and others 1986; Girard and Nakai 1991). Dynamic headspace analysis is another technique that has received substantial attention over the years. It is based on a ‘dynamic’ process in which the sample volatiles are swept by a stream of an inert gas, trapped, and then desorbed by various means into a gas chromatograph (GC). The purged headspace volatiles of tuna (Khayat 1979; Human and Khayat 1981) and herring (Hughes 1964) have been condensed by cryogenic trapping while adsorbent trapping was used for pickled smelt (Josephson and others 1987), north sea fish oil (Christensen and others 1982; Hollingworth and others 1986; Girard and Nakai 1991).
salmon, and 11 of them consisted of co-eluting compounds (Table 1). The volatile classes (and their relative total concentrations averaged over all treatments) included 26 hydrocarbons (2390 ± 1264 ng/g), 9 sulfurs (1784 ± 868 ng/g), 4 furans (1317 ± 483 ng/g), 18 aldehydes (1087 ± 653 ng/g), 15 ketones (818 ± 267 ng/g), and 18 alcohols (340 ± 173 ng/g). Although hydrocarbons, aldehydes, and ketones were dominant in qualitative terms, hydrocarbons followed by sulfurs and furans were quantitatively highest. Dimethylsulphide (1366 ± 873 ng/g), 2-ethylhexan (823 ± 356 ng/g), heptane (452 ± 329 ng/g), 2-methyl-furan (406 ± 141 ng/g), 2-butanol (330 ± 80 ng/g), and propanol (308 ± 230 ng/g) were the 6 most prominent volatiles that collectively provided nearly half of the total relative concentration in canned salmon.

To simplify the interpretation of relationships between treatments, principal component analysis was carried out on the volatile classes. The scores for the 6 principal components were computed and submitted to an analysis of variance (Table 2). PRIN1 was significant for species differences (P < 0.0001). The significant interaction (P < 0.01) indicated that the direction of the differences between salmon species was dependent on the retort processing regime. In addition, significant variations between constant and variable retort processes were observed in PRIN2 (P < 0.05) and PRIN4 (P < 0.01). PRIN1 accounted for 72.2% of the variation, and its principal component loadings (eigenvectors)
were all positive and relatively even across the volatile classes (Table 3). The majority of the variation captured by PRIN1 for all volatile classes served to differentiate canned pink and sockeye salmon (Fig. 2). Although notably smaller variations were assigned to PRIN2 (14.5%) and PRIN4 (3.1%), they were nevertheless important delineating factors for retort processing regimes (Table 3, Fig. 2). Because of the bipolarity in algebraic signs (positive and negative eigenvectors), PRIN2 contrasted sulfurs with aldehydes and alcohols, while PRIN4 contrasted hydrocarbons with sulfurs and alcohols. The differences in precursor composition that may exist between pink and sockeye salmon had a general impact on volatile classes. However, the milder heat treatment offered by VRT as compared to CRT primarily and selectively influenced some sulfur, aldehyde, alcohol, and hydrocarbon compounds.

Similar results were obtained when applying principal component analysis directly on volatile constituents (results not shown). The scores of PRIN1 were significant for the species effect, while differences in retort processing mode were found in principal components capturing smaller variances (eigenvalues) in the dataset (PRIN2 and PRIN5). Among the 6 prominent volatiles, heptane, propanal, and ethylfuran had high eigenvectors for PRIN1, 2-butanone for PRIN2, and dimethylsulfide and heptane for PRIN5.

Sensory evaluation

Experienced sensory panelists were not able to distinguish between salmon of the same species processed by constant retort temperature from that processed by variable retort temperature. Eleven of 24 responses to the triangle test were correct. Therefore, the variations captured by the higher principal components (PRIN2, PRIN4, and PRIN5) of the volatiles did not significantly translate into sensory differences. This may be due to a combination of factors related to threshold aroma values of the components, the magnitude of the variation in component concentrations, and the relative impact of the components on the overall integrated sensory effect.

Odor-active constituents

Thirty-two aromas were detected in canned sockeye salmon

![Fig. 1](image1.png)

![Fig. 2](image2.png)
by GC-olfactometry (Table 4). Volatile classes with most odorous constituents were aldehydes, sulfurs, and ketones. Sulfur compounds with highest APVF values were dimethylsulfide, dimethylsulfoxide, and dimethyltrisulfide. Methylated sulfides were assigned seafood- and cruciferous-related descriptive terms. Heterocyclic sulfur compounds had meaty odors. Due to their low sensory threshold values, volatile organic sulfur compounds are an important fraction of aroma in numerous foods. These sulfur compounds have previously been reported in raw and thermally processed fish and crustaceans (Sipos and Ackman 1964; Josephson and others 1985; Hughes 1964; Vejaphan and others 1988; Girard and Nakai 1993, 1994a, 1994b, 1994c; Milo and Grosch 1995). They can be formed principally during heat treatments from the free, peptide, and proteinic sulfur-amino acids as well as the glutathione pool in fish tissue (Herbert and Shewan 1975, 1976; Maruyama 1970; Christensen and others 1981). Thiophenes are important volatiles in the flavor of cooked muscle foods; Fors (1983) reported several heterocyclic compounds possessed a braised, roasted, and meaty flavor. The sulfur in thiophenes and thiazoles may be derived from amino acids (cysteine, cystine, methionine) or from thiamine (vitamin B1). It has been suggested that thiophenes are formed by the action of hydrogen sulfide on sugar degradation products such as dehydroreductones and furans (Vernin and Parkanyi 1982), furfural (Shibamoto 1977), and furanones (van der Ouweelen and Peer 1975), during the course of the Maillard reaction. Phospholipid oxidation products such as 1,4-ketoaldehydes or unsaturated aldehydes have also been suggested to interact with ammonia and hydrogen sulfide, derived from the Strecker degradation of cysteine, to give 2-alkylthiophenes (Mottram and Whitfield 1987).

Although found in traces, (E)-1-octen-3-one had the second highest APVF value. This unsaturated C8 ketone and its corresponding alcohol were responsible for mushroom and earthy characters (Table 4). Diones such as 2,3-pentanedione are constituents of many food aromas and provide a buttery flavor (Arctander 1969). Autoxidation of fatty acids, particularly unsaturates (via hydroperoxides), has been proposed as a mechanism for the formation of methyl ketones (Thomas and others 1971). Selke and others (1975) reported the formation of a homologous series of methyl ketones from heated tristearin and concluded that they could be the result of β-oxidation (from the carbonyl end) of the carbon chain followed by decarboxylation. 1-(2-Furaldehyde) has been previously identified in baked salmon (Josephson and others 1991a) and may be derived from the Maillard reaction. Similarly, various other ketones could possibly be produced from distinct secondary degradation reactions involving diverse substances from the lipid fraction during heating.

Aldehyde was the class with the highest number of odor-active constituents (Table 4). Straight- and branched-chain aldehydes provided herbaceous, grassy, and pungent aromas, while unsaturated aldehydes were linked with vegetal and fishy notes. The formation of alkanals can be attributed to thermal decomposition of hydroperoxides and peroxy radicals proposed to be initial products of thermally-oxidized fats (Sink 1973). In some cases, they can originate from the Strecker degradation of amino acids; for example, 2-methyl-butanal may be derived from isoleucine (Dwivedi 1975). Due to their low threshold values, aldehydes are important aroma compounds in foodstuffs. They can contribute to desirable aroma as well as rancid odor and flavor during spoilage of fats and fatty foods (Fors 1972).

Although hydrocarbons were found in high concentration (Table 1), their contribution was minimal toward the make-up of canned salmon aroma (Table 4). Hydrocarbons identified in this study included a homologous series of n-hydrocarbons ranging from C5 to C12 (Table 1). Watanabe and Sato (1971) suggested that saturated alkanes could result from decarboxylation and splitting of carbon-carbon chains of higher fatty acids. When heating tristearin in air, the presence of n-hydrocarbons among the volatiles was interpreted by Selke et al. (1975) to arise from the reaction of alkyl-free radicals, which were the product of thermally decomposed hydroperoxides with free hydrogen radicals. In the past, alkanes have been reported to possess sensory characteristics that resembled aliphatic alcohols (Ohloff and others 1985). Several unsaturated and cyclic hydrocarbons were identified in canned salmon (Table 1). Unsaturated and aromatic hydrocarbons have been reported to contribute to marine flavors of shellfish and seaweed; some of the branched and cyclic hydrocarbons may be secondary reaction products from the thermal oxidation of carotenoids and other unsaturated lipids (Ohloff and others 1985; Pippen and others 1969; Min and others 1977; Nonaka and others 1967). Even if none of these compounds have a meat or fish odor, they may play a role in the overall flavor (Min and others 1977).

Nearly half of the volatile alcohol class was composed of (E)-1-penten-3-ol (Table 1). This volatile compound has been found in canned tuna (Kim and Lindsay 1992) and canned salmon (Girard and Nakai 1993). Alcohols may be formed by decomposition of secondary hydroperoxides of fatty acids. In a pathway similar to that involved in the generation of 1,5-octadien-3-ol (Wurzenburger and Grosch 1986), a rearrangement and cleavage of hy-
droperoxides from linoleic or arachidonic acids could yield (E)-1-penten-3-ol.

2-Ethylfuran was the only furan reported to provide an odor-impact. Furans can be found in dehydrated and thermally degraded condensates of carbohydrate or formed by Amadori rearrangement pathways (Whistler and Daniel 1985). They can also be produced by oxidation of fatty acids as 2-pentyl furan has been reported to impart reversion, beany, grassy, and licorice-like flavors in soybean oil (Taylor and Mottram 1990; Krishna-murthy and others 1967).

No individual odor-impact compound was associated with the characteristic flavor of canned salmon by sniffing at the exit port of the GC. A variety of compounds instead appeared to have contributed towards the total flavor. The typical aroma of canned salmon likely resulted from the sum of the sensory effects of sulfurs, aldehydes, and ketones thermally generated from the degradation of fatty acids, carotenoids, and amino acids. The differences in volatiles noted between retort processing regimes did not significantly alter the sensory perception of canned salmon flavor. More work is needed to complement the data accumulated thus far and delineate the relative variations in volatile concentrations responsible for species differences and to investigate the interactions of the important aroma components in order to further elucidate the canned salmon flavor system.

### Materials and Methods

#### Origin of fish and retort processing

Sockeye (Oncorhynchus nerka) and pink (O. Gorbuscha) salmon were purchased frozen from B.C. Packers Ltd. (Vancouver, B.C., Canada) and processed within one mo of capture. Fish were filleted, skinned, cut into 2.5 cm cubes, pooled, and mixed to form a single lot per species. Lots of each species were packed in 307 × 115 cans and assigned to one of 2 steam retort processes as previously described (Durance and others 1997). One treatment consisted of a conventional constant retort temperature (CRT) process with a 6 min vent followed by 64 min in saturated steam at 118.4 °C, then water cooled. The other treatment consisted of a variable retort temperature process (VRT) (Fig. 1). All processes provided an equal batchet spore lethality (F0) of 8 min at the center of the containers, but the VRT processes resulted in about 15% reduction in the cook (Fsurface, z = 23 °C, reference temperature = 121.1 °C) received at the outer surface of the food (Durance and others 1997).

#### Analysis of volatile constituents

Each can of salmon to be examined for headspace volatiles was opened, and the liquid drained by tilting the can and its lid for 2 min. Salmon muscle (60 g), deionized distilled water (60 mL), and internal standard (0.1 mL of 431 ppm cyclohexanone) were transferred to a jacketed 150 mL 3-neck jar (Wheaton, Millville, N.J., U.S.A.) thermostated with a circulating waterbath. The jar was modified to accept a blade assembly, which fit the base of a Waring blender. Teflon lines were used to connect the jar to a Tekmar LSC 2000 purge and trap unit (Tekmar Corp., Cincinnati, Ohio, U.S.A.) through an off-line circuit. This off-line circuit made of 2 stainless steel three-way valves, a mass flow controller, and heating tape was incorporated to bypass the existing purging line which caused problems of pressure control due to bore restriction. The sample was homogenized at low speed and the headspace volatiles were collected on a preconditioned glass trap (4 mm i.d. × 180 mm length) packed with Tenax (60/80 mesh, 100 mg), according to the following conditions: purging temperature 50 °C, purge gas helium, purge rate 50 mL/min, prepurge time 1.5 min, purge time 20 min, drypurge time 2 min, bake temperature 225 °C, bake time 15 min, transfer line temperature 220 °C. Volatiles were then desorbed at 200 °C for 5 min and cryofocussed in the GC oven onto a 1 m length of deactivated fused silica capillary precolumn immersed in a Dewar flask of liquid nitrogen. The oven temperature program was initiated upon removal of the Dewar flask. Separation was performed on a Supelcowax 10 fused silica capillary column (60 m length × 0.25 mm i.d. × 0.25 μm film thickness) housed in a Hewlett Packard 5890 GC. Oven temperature was held initially at 35 °C for 10 min and then increased by 4 °C/min to 200 °C. The column head pressure of prepurified helium supplied through the Tekmar transfer line was maintained at 30 psi. Mass spectral data were recorded with a HP 5970 GC-MSD system under the following conditions: MS transfer line temperature 220 °C, scan mode 33 to 200 amu, threshold 400, sampling rate 2 scan/s, ionizing energy 70eV, and electron multiplier 1800 V. Identification of compounds was obtained with an HP G1034C MS Chem Station, containing an HP G1035A Wiley (138.1) PBM library, and confirmed with retention data of available authentic compounds. Volatiles in 4 to 6 samples per treatment were quantified relative to the concentration of the internal standard cyclohexanone and the mass of salmon muscle used.

#### Odor analysis by decreasing serial purge volumes

Odor assessment of canned sockeye salmon was carried out using an olfacto detector system (SGE International Pty Ltd, Ringwood, Australia). The end of the GC column was connected to a variable effluent outlet splitter set to deliver equal flow (1:1, v/v) to the MSD and the olfactory detector port. This aroma port was fitted to a vacant detector housing, and the tubing passing through the oven wall was heated with oven temperature air by means of an air venturi. A stream of humidified air swept the effluent from the capillary column to alleviate dryness of the nasal passages during assessment and maintain adequate linear velocity. After preliminary familiarization with the samples and the technique, a three-member panel used to record retention times and sensory descriptions of the odors chromatographed from a series of decreasing purge volumes (1000 mL, 500 mL, 250 mL, 125 mL, 62.5 mL, 31.2 mL, 15.6 mL, 7.8 mL). Odor attributes were reported when detected by at least 2 out of the 3 panelists. The aroma purge volume factor (APVF) was the smallest volume at which an aroma-active constituent was detected and corresponded to log2 (1000/v), where v is the serial volume.

#### Sensory evaluation

Panelists were selected from staff and students at the University of British Columbia Food Science department who had volunteered for other sensory tests. Individuals who expressed dislike of canned salmon, or who rarely or never ate canned salmon, were screened out. The panel consisted of 5 males and 7 females. Three were between the ages of 40 and 50, 3 were 30 to 40, and 6 were 20 to 30 years of age. Duplicate triangle tests (Poste and others 1991) were employed to compare flavor and aroma of 15 g samples of pooled, flaked,
canned salmon flesh at room temperature. The tests took place in temperature controlled sensory booths at 20 °C and 65% relative humidity under daylight spectrum fluorescent lights. Samples were presented in 57 g (2 oz) disposable plastic cups randomly coded with 3 digit numbers. Unsalted soda crackers and water were provided for cleansing the palette between samples. A maximum of 3 triangles were tested by each judge per session. Panelists attempted to distinguish CRI and VRT salmon of like species, sockeye and pink. Identity of odd and even samples in individual triangles was balanced but randomly assigned to panelists. Significance of results was tested with a Student t-test, P > 0.05. Differences in texture, flavor, and appearance between species were obvious and, therefore, were not tested formally.

References


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