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Rapid analysis of VOCs with SIFT-MS as a decision-making support tool for caviar producers

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ABSTRACT

This work was an exploratory study on caviar products using selected ion flow tube - mass spectrometry (SIFT-MS) analysis of volatile organic compound profiles. The main objective was to look for the principal contributing factors that drove the volatile profile and the sensory perception of caviar. France is the fourth largest world producer of caviar and is currently trying to obtain a protected geographical indication (PGI) label “Caviar d'Aquitaine” that will characterize traditional know-how and ethical farming practices. Over a one-year period, we performed untargeted selected ion flow tube - mass spectrometry (SIFT-MS) measurements and sensory analysis of 51 samples of caviar from Prunier Manufacture. We conducted statistical analyses to look for correlations with aquaculture, processes, storage and sensory factors. Thus, we highlighted the great impact on SIFT-MS profiles of the sturgeon species, the production sites, the underlying water quality, the relation between seasonality of the production and “milky” sensory perception and finally the effect of the storage time on global product quality. This preliminary work demonstrated the potential of SIFT-MS to serve as a strategic decision-making support tool for sturgeon producers.

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1. Introduction

Originally imported from ancient Persia and Russia, caviar is a famous and luxurious food product made from the salted eggs of wild sturgeon fishes. Sturgeons are primitive fishes dating back to the late Cretaceous period and have an average lifespan of 50–60 years. However, due to pollution and overexploitation of wild fishes, 90% of caviars are currently produced from fisheries (Tavakoli et al., 2021) from several species, including Beluga (*Huso huso*), Ocietre (*Acipenser gueldenstaedtii*) and *Acipenser baeri* (Shen et al., 2020). Female sexual maturity does not occur before 6–10 years, so it is essential for farmers to understand and control all fish farming parameters to obtain healthy animals and high-quality products. Before collecting roes, echography was performed on the females to evaluate the roes' maturity. Then, the ovaries were harvested, and the roes were sifted and washed to remove impurities. To be transformed into caviar, the sturgeons' roes are salted and stored in a 1.8 kg “original box” with little or no oxygen or directly vacuum-packed in 30, 50, 125 and 250 g cans. All steps were performed

at cold temperature to prevent any evolution or bacterial development during the process. The caviar then begins to mature, during which the flavors sought by the consumers develop. After several weeks of maturation, the caviar was then stored in a smaller metallic box under vacuum. The delicacy of caviar is related to the physical and chemical properties of these fish roe (Vilgis, 2020). Similar to other fish species, the composition of sturgeon eggs is approximately 52–54% water, 24–27% protein, up to 3–5% minerals and 13–17% fats. However, the fatty composition of saturated and unsaturated acids and their distribution in the oocyte is particularly associated with quality. It is also during the maturation period that incidents and aromatic deviations can occur. It is currently accepted that the flavor of caviar is mainly impacted by three main factors. The first is considered an off-flavor due to environmental contamination with *Cyanobacteriaceae* and results in the presence of geosmin and/or 2-methyl-isoborneol (Ruan et al., 2013; Suurnäkki et al., 2015). This requires producers to add a ripening step with fresh water to clean fishes and to prevent these earthy and musty unpleasant flavors (Lindholm-Lehto et al., 2019). The second type of

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Table 1
Samples list of caviar.

sample	Ripening time	Saison	Species	Fish farm
A	1–2 months	autumn	BAE	Site 1
B	1–2 months	autumn	BAE	Site 1
C	1–2 months	autumn	BAE	Site 2
D	1–2 months	autumn	BAE	Site 2
E	1–2 months	autumn	BAE	Site 2
F	1–2 months	autumn	GUE	Site 2
G	1–2 months	autumn	BAE	Site 2
H	1–2 months	autumn	BAE	Site 1
I	1–2 months	autumn	BAE	Site 2
J	1–2 months	autumn	BAE	site 1
K	1–2 months	spring	GUE	site 2
L	1–2 months	spring	BAE	site 2
M	1–2 months	spring	BAE	site 2
N	5–7 months	autumn	BAE	site 1
O	5–7 months	autumn	BAE	site 2
P	5–7 months	autumn	BAE	site 1
Q	5–7 months	autumn	BAE	site 1
R	5–7 months	autumn	BAE	site 2
S	1–2 months	spring	BAE	site 2
T	1–2 months	spring	BAE	site 2
U	5–7 months	autumn	BAE	site 2
V	5–7 months	autumn	BAE	site 2
W	5–7 months	autumn	GUE	site 2
X	5–7 months	autumn	BAE	site 1
Y	5–7 months	autumn	BAE	site 2
Z	1–2 months	spring	BAE	site 1
AA	8–9 months	spring	BAE	site 2
AB	8–9 months	spring	BAE	site 2
AC	8–9 months	spring	GUE	site 2
AD	11–13 months	autumn	BAE	site 1
AE	8–9 months	spring	BAE	site 2
AF	8–9 months	spring	BAE	site 1
AG	8–9 months	spring	BAE	site 2
AH	8–9 months	spring	BAE	site 2
AI	8–9 months	spring	BAE	site 2
AJ	11–13 months	autumn	BAE	site 1
AK	11–13 months	autumn	BAE	site 2
AL	11–13 months	autumn	BAE	site 1
AM	11–13 months	autumn	BAE	site 2
AN	1–2 months	autumn	BAE	site 1
AO	1–2 months	autumn	BAE	site 1
AP	1–2 months	autumn	BAE	site 1
AQ	1–2 months	autumn	BAE	site 1
AR	1–2 months	autumn	GUE	site 2
AS	1–2 months	autumn	BAE	site 2
AT	1–2 months	autumn	BAE	site 1
AU	1–2 months	autumn	BAE	site 1
AV	1–2 months	autumn	BAE	site 1
AW	1–2 months	autumn	BAE	site 1
AX	1–2 months	autumn	BAE	site 1
AY	1–2 months	autumn	BAE	site 1
AZ	1–2 months	autumn	BAE	site 1

flavor comes from the enzymatic activity of proteases and phospholipases during ripening (Xu et al., 2022) and possible contamination with bacteria (Lopez et al., 2021). Only a few studies have been conducted on the volatile organic compounds of caviar (Caprino et al., 2008; Golovnya & Uralets, 1972; Lopez et al., 2020, 2021; Xu et al., 2022). Most studies on caviar have focused on lipid and protein composition (Czesny et al., 2000; Ma et al., 2020) and evaluated the evolution of caviar quality with metabolomic analysis (Heude et al., 2016). However, recent advances in analytical chemistry showed that the volatile part of the metabolism, also called volatilomics, gave interesting results with food products (Lytou et al., 2019; Villano et al., 2017). In this work, we used for the first time untargeted analysis of the head space of caviars with a selected ion flow tube mass spectrometer (SIFT-MS) using soft chemical ionization with 8 different precursor ions that increase its selectivity. The untargeted use of direct injection mass spectrometry (DIMS) instruments allowed the classification of samples according to their origin (Bajoub et al., 2018; Bergamaschi et al., 2016; Kharbach et al., 2018; Yener et al., 2016), transformation process (Deuscher et al., 2019; Ozcan-Sinir, 2020;

Reyrolle et al., 2023) or typicality of food products (Reyrolle et al., 2022). In this study, we determined the conditions for untargeted SIFT-MS analysis of caviar samples head space to identify the factors contributing most to the volatile compound profile. Thus, 51 cans containing 50 g of caviar from two sturgeon species from two different fish farms and collected in spring or autumn were analyzed over 1 year at different maturation ages (1–2 months, 5–7 months, 8–9 months and 12–13 months). We also compared the results to those obtained with a sensory jury.

2. Materials and methods

2.1. Sample collection

Fifty-one different samples of caviar were selected by Prunier Manufacture (Table 1). Two different species of sturgeon representative of the product classes of the partner were selected: Siberian sturgeon (*Acipenser baeri* BAE) and Russian sturgeon (*Acipenser Gueldenstaedtii* GUE). The fishes were grown in two different fish farms (site 1 and site 2) and were collected during autumn 2020 or spring 2021-. During this project and to prevent any artifact when opening the “original boxes” several times, the roes were directly placed in 50-g cans and stored for 1–12 months at 4 °C until sensory or SIFT-MS analysis.

2.2. Sensory analysis

A jury was created by Prunier Manufacture with 12 people working, trading or eating caviar. Indeed, this food product is not commonly consumed, and it was difficult to find expert people who are accustomed to eating caviar and who are able to identify its aromatic variations. To date, there is no consensus across the sector concerning the aroma wheel of caviar. During this project, a jury was trained to identify several sensory attributes, of which nuts, milky, fish, shellfish and vegetal tastes were highlighted. The homogeneity of the panel was evaluated and validated on the different texture, color, flavor and odor attributes on a scale from 0 to 10.

2.3. SIFT-MS analysis

Headspace analysis with SIFT-MS was performed as previously described by Reyrolle et al., 2022. All the 1-L glass vials (Schott, Colombes, France) and the caps (Duran Wheaton Kimble, Holzminden, Germany) were cleaned in a dishwasher before be warmed over night at 60 °C and flushed with dry air (ZeroAir Alliance ZA1500, F-DGSi, Evry France) during 1 day. For every sample, a blank analysis of the empty vial, tightly fitted with a polypropylene screw cap with two connection ports fitted with 0.6 cm PFA tubes (Swagelock, Lyon, France), was recorded. During measurements, the first PFA tube was connected to the SIFT-MS, the second to a 1 L Tedlar © (Supelco, Bellefonte, PA, USA) bag filled with zero air (ZeroAir Alliance ZA1500, F-DGSi, Evry France), to compensate for the volume taken during the analysis. The conditions of head space analysis were first established to have enough signal of VOCs with less than 80% of water clusters of precursor ions ($\text{H}_3\text{O}^+(\text{H}_2\text{O})$ m/z 37 + $\text{H}_3\text{O}^+0.2(\text{H}_2\text{O})$ m/z 55 + $\text{H}_3\text{O}^+0.3(\text{H}_2\text{O})$ m/z 73) than with the blank experiment. Thus, 5g of caviar were introduced in a 1 L vial and heated at 60 °C during 2 h. Then, the vial was plugged to the SIFT-MS Voice 200 Ultra (SYFT Technologies, Christchurch, New Zealand) equipped with the dual polarity ion source generating 8 different precursor ions (H_3O^+ , O_2^+ , NO^+ , O^+ , OH^- , O_2^- , NO_2^- and NO_3^-). The sample was introduced through a heated inlet line (373 K) into the flow tube at a checked flow rate of 20 ml min⁻¹. The carrier gas was nitrogen 6.0 (air liquid, Alphagaz 2). The flow tube temperature was maintained at 393 K at a pressure of 0.48 torr. The instrument was daily calibrated with a standard gas (ScottTM gas mixtures, Air Liquid USA) containing standards at 2.0 ppmV in nitrogen (Air Liquide, Alphagaz 2). Each sample was analyzed in triplicate. The full scan raw data files of each

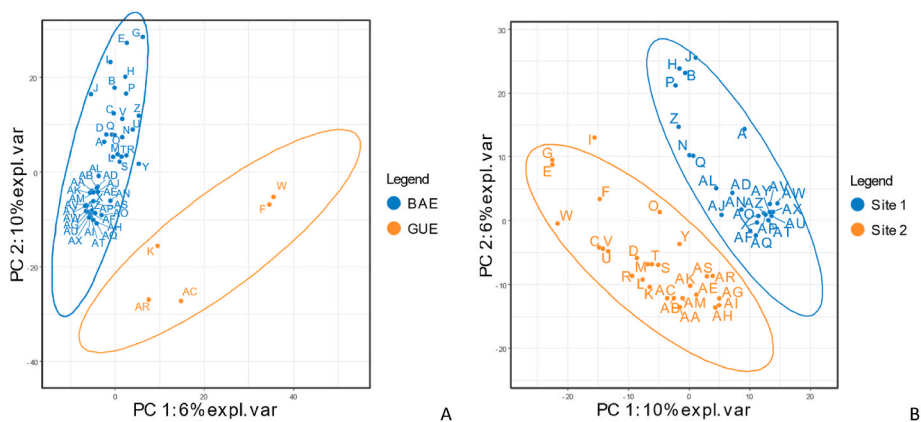


Fig. 1. A: sPLS-DA of SIFT-MS volatile profiles of caviar samples according to the descriptive factor “sturgeon species”. B: sPLS-DA of SIFT-MS volatile profiles of caviar samples according to the descriptive factor “Fish farming site”.

sample and the corresponding blank measure, containing product ion intensities with 15–250 m/z range were collected for a compilation and pre-processing step.

Compilation and pre-processing of the full scan raw data were performed as described in a previous study (Reyrolle et al., 2022) using Python language. The product ions were coded into numerical variables of the XAB type with X a constant letter, A ranging from 1 to 8 indicating the precursor ion used and B the value of m/z ranging from 15 to 250. Data was pre-processed by subtracting background noise (signal of bottle without samples) for each replicate. Triplicates of each sample were averaged to obtain a single value of signal intensity for each ion. This value was multiplied by the ICF factor corresponding to the instrument calibration correction. The dataset was cleaned by suppressing constant quantitative variables. Statistical analysis, including

non-supervised and supervised methods, was performed using the R language and MixOmics package (Rohart et al., 2017); sparse principal component analyses (Sparse PCA) and sparse partial least-squares discriminant analyses (sPLS-DA) were used to show the dispersion or discrimination of the sample based on descriptive variables. Labsyft® 1.6.2 software (SYFT Technologies, Christchurch, New Zealand) was used to identify the putative molecules with the known product ions registered in the database.

3. Results and discussion

A principal component analysis was conducted on this dataset but did not allow spontaneous classification of samples. We observed that the global ion intensities were weak except for the water cluster of

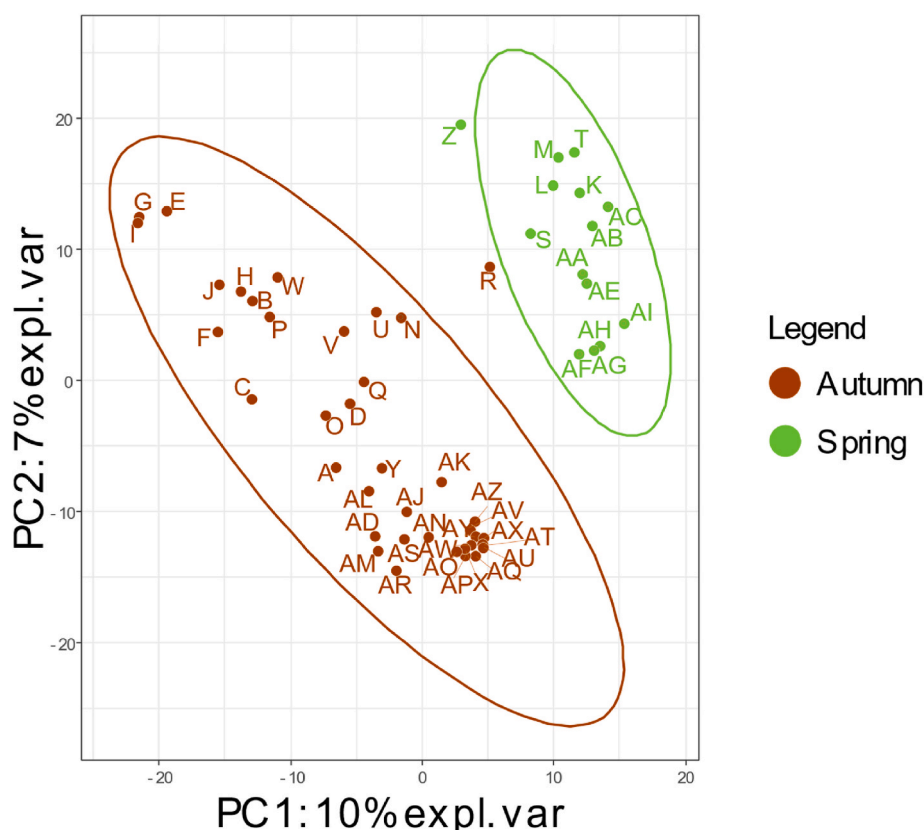


Fig. 2. sPLS-DA of SIFT-MS volatile profiles of caviar samples according to the descriptive parameter “seasonality”.

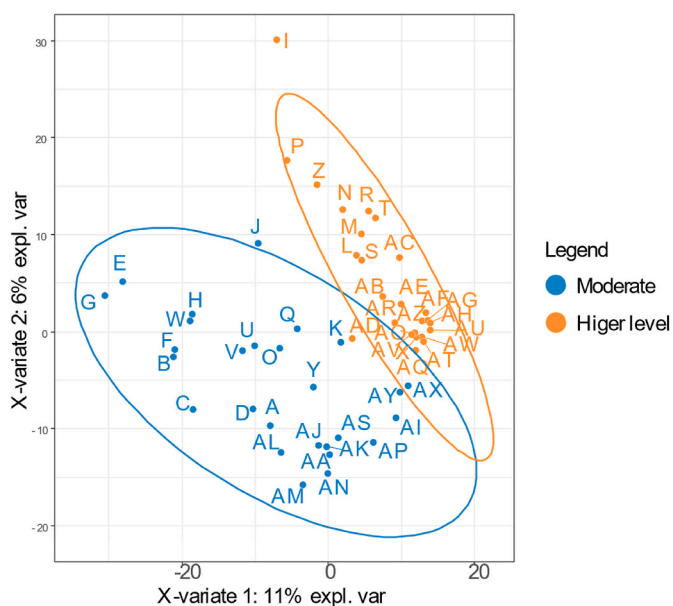


Fig. 3. sPLS-DA of SIFT-MS volatile profiles of caviar samples according to the descriptive parameter “Milky taste level”.

precursor ions. This means that the headspace of caviar samples mostly contained water vapor and low levels of VOCs. At the least, these analytical conditions were not optimal for SIFT-MS measurements. However, we successfully performed sPLS-DA on the dataset with different descriptive parameters: fish farming parameters, sensory attributes and storage parameters.

3.1. Fish farming parameters

The parameter most emphasized by producers and that has been well illustrated in the literature was the diversity of caviars from different species of sturgeons. In our sample list, two different species were present: *Acipenser baeri* (BAE) and *Acipenser Gueldenstaedtii* (GUE). The sPLS-DA analysis of the volatile species profiles of caviar samples according to the descriptive parameter “sturgeon species” clearly showed two separated populations (Fig. 1A). The sample distribution was not equal between the two groups and this observation should be accounted for. However, Heude et al., 2016 observed the same trend with H^1 NMR metabolic fingerprints with the same species in France. In addition, Gessner et al., 2008; Wirth et al., 2002 observed different levels of mono-unsaturated fatty acid (oleic acid) or triglycerides along the studied sturgeon species, whereas the polyunsaturated fatty acids (linoleic and arachidonic acids) seemed not to vary. The same studies also showed the impact of the origin (wild or farms) on the fatty acid

composition. Indeed, the composition of fish tissues and roes depends on environmental conditions (water quality and temperature) and food diet. In this study, all the fish were fed the same diet. Thus, we analyzed our dataset with supervised statistical analysis according to the parameter “fish farming site” (Fig. 1B). We observed that the 5 samples of caviar made from GUE were then grouped with 23 other samples produced with BAE in “Site 2”, supporting the idea that the site of production also impacted the volatile profile of caviars. Thus, these two fish farming parameters (species and farm site) have an impact on the SIFT-MS volatile profile in isolation from each other and confirmed the scientific literature and producers’ knowledge.

3.2. Sensory perception

As described in the PGI specification for “Caviar d’Aquitaine”, some sensory perceptions such as a “milky taste”, which includes both “butter” and “crème fraiche”, are desired, whereas others have to be avoided, such as for “earthy” or “metallic”. In this study, the sensory jury did not detect any earthy off-flavor in samples, and none of the SIFT-MS ions corresponding to geosmin and 2-methyl-isoborneol were significantly detected (Table S11). Caviar producers also know that the period of roe collection is important for flavor. Indeed, a person skilled in the art knows that caviar collected during the spring would be more intense in terms of odor (fresh, herbal ...) and flavor (milky, nuts ...) whereas the autumn caviars are less scented, with undergrowth smells. We performed supervised statistical analysis according to the parameter “Season of collection”, and we obtained two clearly separated populations, although one sample (R) was in an intermediate position (Fig. 2). Sample R was collected during autumn and stored 7 months before the sensory and SIFT analysis as well as the sample S. This intermediate position can be explained by a certain individual variability within the farmed sturgeons. In fact, despite the controlled rearing conditions, our partner’s caviar is not intended to be standardized but rather to be classified into different categories depending on how the quality of the product is assessed. During this study, the trained jury gave different sensory levels from 0 to 10, which we merged into low, moderate and high levels for “milky taste” (Figure S12). We performed a second sPLS-DA on the SIFT-MS dataset according to the parameter “milky taste level”, but we did not succeed in completely separating the two populations (Fig. 3A). To go further, we observed that 11/24 samples described as “high level” of milky taste were spring samples, whereas only 3/27 samples described as “moderate level” were collected during the autumn (Figure S13). Two hypotheses could explain this result: first, there was no correlation between the milky taste and the VOCs detected in caviar samples; second, the sensory perception by the jury was not absolute, and there should be a correlation between seasonality and milky taste. Thus, we tried to identify the molecules responsible for the classification of samples according to season. We extracted the 50 most relevant ions of the first component of sPLS-DA, and we tried to identify the corresponding molecules based on the Labsyft® software database

Table 2

putative molecules corresponding to the most discriminating ions according to the parameter season. ** correspond to 0.01 significance and *** to 0.001 significance according one-way ANOVA.

Molecule	Ion	Spring		Autumn		p value (Welch test)
		Mean	SD	Mean	SD	
Butanol	NO ⁺ 73	13 667.12	12 062.85	3 651.08	1 547.79	***
	OH ⁺ 73	1 703.22	1 533.47	421.89	266.39	***
	H ₃ O ⁺ 75	7 229.26	6 019.67	2 524.88	826.91	**
	O ₂ ⁺ 56	10 351.98	5 143.26	6 807.72	1 945.55	**
Oct-2-en-1-ol	NO ⁺ 109	613.21	425.61	1 960.00	1 767.77	***
	H ₃ O ⁺ 111	1 241.52	723.82	3 316.88	2 597.19	***
	NO ⁺ 111	462.45	155.37	759.46	411.03	***
2-acetyl-furan	NO ⁺ 110	188.65	134.33	719.07	647.89	***
	NO ⁺ 140	93.97	39.68	265.27	216.36	***
Thymol	NO ⁺ 150	261.62	147.03	464.88	234.02	***
Citral	NO ⁺ 151	115.02	62.16	183.77	83.41	***

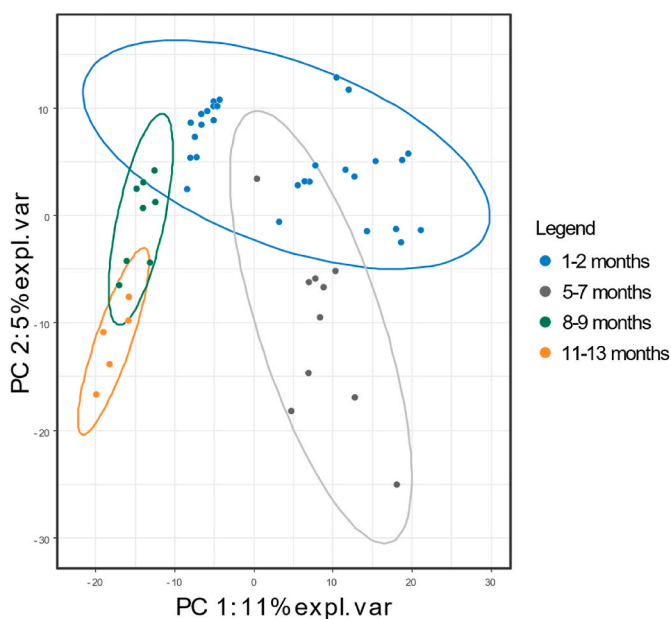


Fig. 4. sPLS-DA of SIFT-MS volatile profiles of caviar samples according to the descriptive parameter “time of maturation” 1–2 months in blue, 5–7 months in grey, 8–9 months in green and 11–13 months in orange).

(Figure S14). The distribution of discriminative ions according to precursor ions was the following: 6 with H_3O^+ , 6 with O_2^+ , 14 with NO^+ , 3 with O^+ , 11 with OH^- , 3 with O_2^+ , 4 with NO_2^- and 3 with NO_3^- . This distribution depends on the chemical function of VOCs but also on the instrument performance. In our case, the precursor ion levels in blanc samples are about 10^6 in positive mode and 10^5 in negative mode. Four product ions potentially corresponding to butanol (NO^+ m/z 73, OH^- m/z 73, H_3O^+ m/z 75 and O_2^+ m/z 56) were found in the 50 most discriminating ions and were significantly overexpressed in spring samples, whereas three ions corresponding to oct-2-en-1-ol (NO^+ m/z 109, H_3O^+ m/z 111 and NO^+ m/z 111) and 2 ions corresponding to 2 acetyl furan (NO^+ m/z 110 and NO^+ m/z 140) were also identified and significantly most concentrated in autumn samples (Table 2). Finally, 2 other product ions potentially corresponding to carvone or thymol (NO^+ m/z 150) and to citral or camphor (NO^+ m/z 151) were also highlighted in autumn samples. These signals were intense and may correspond to odorant molecules that were not linked to milk flavor. Butanol corresponded to aliphatic alcohol with a rancid sweet odor, oct-2-en-1-ol corresponded to green or vegetable odor and fatty, oily, sweet or fruity flavor, 2-acetyl-furan was correlated to sweet, balsamic, almond,

caramel or coffee odor, and finally, the terpene molecules were linked to minty and citrus odors. These results have led us to conclude that there is no correlation between the VOC profiles of caviars and milky taste in the mouth, which was probably due to nonvolatile molecules. Nevertheless, volatile profiles of caviars collected in spring or autumn were clearly different, and this observation, complementary to flavor results, provides marketing tools to the producer to recommend different types of caviar to consumers.

3.3. Maturation time

The production of caviar requires experience, delicacy and time. This fresh fish food product is not sterilized. Therefore, roe collection, washing, salting and packaging must be performed at cold temperatures and in good hygienic conditions to guarantee the final quality of the product and to prevent any microbial contamination. Twenty-nine cans of 50 g of caviar were analyzed after 1–2 months, 10 cans after 5–7 months, 8 cans after 8–9 months and finally 5 cans after 11–13 months. We performed sPLS-DA on the dataset according to the parameter “maturation time”, and we observed a partial separation of the four classes (Fig. 4). By grouping the samples into two classes (less than 6 months or more than 6 months of maturation), we obtained two separated groups (Fig. 5A) and even more separated groups with the two classes “less than 9 months” and “more than 9 months” (Fig. 5B). We extracted the 50 most discriminative ions on the first component of the sPLS-DA (less or more than 6 months of maturation) (Figure S15). The distribution of discriminative ions according to precursor ions was the following: 15 with H_3O^+ , 11 with O_2^+ , 19 with NO^+ , 4 with O^+ , 4 with OH^- , 0 with O_2^+ , 0 with NO_2^- and 0 with NO_3^- . Some potential molecules were identified thanks to the presence of several known product ions listed in the SIFT-MS software Labsyft® (Table 3). Thus, the second (O_2^+ m/z 17) and the sixth (H_3O^+ m/z 18) most discriminating ions of the plot loadings may correspond to ammonia, and these three ions increased significantly after 6 months (Figure S16). A second molecule (butanol) might correspond to four ions, NO^+ m/z 73, O_2^+ m/z 73, H_3O^+ m/z 75 and O_2^+ m/z 56. Interestingly, these four ions (classified 5th, 7th, 8th and 37th) present a significantly higher intensity for the class 6–9 months and a return to basal level for 11–13 months. Finally, the last two putative molecules we identified were octanol and pent-1-en-3-ol with the corresponding ions NO^+ m/z 129 and H_3O^+ m/z 45, whose intensities significantly increased during the maturation time. These results confirmed the evolution of volatile fingerprints of caviar samples during the time reported by Lopez et al., 2020; 2021 and identified a critical period between 6 and 9 months. Octanol and pent-1-en-3-ol were already identified in caviar and are related to lipid peroxidation of mono-unsaturated or poly-unsaturated lipids. Moreover, Dalsvåg et al.,

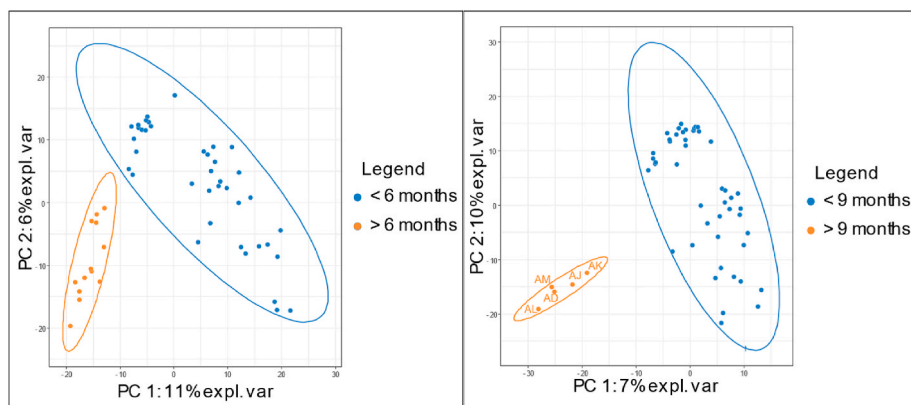


Fig. 5. A: sPLS-DA of SIFT-MS volatile profiles of caviar samples according to the descriptive parameter “time of maturation” (less than 6 months in blue and more than 6 months in orange). B: sPLS-DA of SIFT-MS volatile profiles of caviar samples according to the descriptive parameter “time of maturation” (less than 9 months in blue and more than 9 months in orange).

Table 3

putative molecules corresponding to the most discriminating ions according to the maturation time. * correspond to 0.1 significance, ** correspond to 0.01 significance and *** to 0.001 significance according one-way ANOVA.

Putative molecule	Product ion	Maturation time	mean	sd	n	Significance
Ammonia	O ₂ ⁺ 17	1–2 months	46	13	29	
			833.22	579.17		
		5–7 months	25	10	10	
			032.58	821.47		
		8–9 months	80	6	8	***
			381.51	434.85		
		11–13 months	61	10	5	
			784.55	142.58		
	H ₃ O ⁺ 18	1–2 months	61	15	29	
			589.89	999.56		
		5–7 months	42	19	10	
			772.67	680.11		
	8–9 months	121	22	8	***	
		589.81	568.83			
	11–13 months	73	20	5		
		069.44	091.91			
butanol	NO ⁺ 73	1–2 months	3	1	29	
			383.96	585.85		
		5–7 months	3	1	10	
			440.83	248.80		
		8–9 months	21	9	8	***
			989.48	229.27		
		11–13 months	4	1	5	
			324.39	494.19		
	O ₂ ⁻ 73	1–2 months	317.15	190.43	29	
			598.85	288.76	10	
		5–7 months	2	1	8	***
			614.41	449.42		
		11–13 months	755.19	127.59	5	
	H ₃ O ⁺ 75	1–2 months	2	876.65	29	
			325.74			
		5–7 months	2	664.95	10	
			461.20			
		8–9 months	11	4	8	***
			265.48	869.18		
			2	563.58	5	
			994.58			
	O ₂ ⁺ 56	1–2 months	6	1	29	
			432.25	922.82		
		5–7 months	7	1	10	
		755.16	686.24			
8–9 months		13	4	8	***	
		492.76	755.34			
	11–13 months	6	393.52	5		
		318.38				
octanol	NO ⁺ 129	1–2 months	333.89	159.51	29	
			340.95	141.18	10	
		5–7 months	562.33	132.12	8	**
			892.61	235.47	5	***
		11–13 months				
pent-1-en-3-ol	H ₃ O ⁺ 45	1–2 months	104	57	29	
			100.8	646.10		
		5–7 months	76	26	10	
			412.8	188.85		
		8–9 months	144	32	8	*
			477.8	172.94		
	11–13 months	241	37	5	***	
		349.6	057.39			

2022 highlighted the increase of ammonia and butanol during storage of fish products with SIFT-MS and related these molecules to enzymatic activities from the tissues or from bacteria. To go further in the analysis of the evolution during maturation, we looked for the most known volatile molecules, already identified in caviar, and we measured the evolution of the corresponding product ions. Interestingly, we observed that the signals of ethanol, dimethylamine, methyl-butanol and methyl-butanol increased over time (Figure S17). These molecules were also related to the enzymatic degradation of lipids. Finally, we did not

observe significant evolution of product ions corresponding to terpenes, nonanal, octanal or trimethylamine, as in Lopez et al. or Xu et al., 2022.

4. Conclusions

In this work, we determined the conditions to analyze the head space of caviar samples with a SIFT-MS instrument. This real-time analysis coupled with chemometric tools allowed us to discriminate samples according to fish farming parameters, such as species of sturgeons or production sites. We also observed a classification according to seasonality. The sensory jury, trained during this project, identified a typical flavor of spring caviar, including a higher level of “milky taste” than in autumn samples. Volatile fingerprints also succeeded in grouping samples with seasonality tanks into molecules that were not correlated with milk flavor but were complementary to typical flavors. Finally, we studied the effect of maturation on the volatile profile and identified a critical period between 6 and 9 months after which the global quality of caviar changed. These results were consistent with the jury’s perception and previous studies on VOCs or on lipid composition. Despite the high level of humidity and the low level of VOC concentrations, we demonstrated the usefulness of the SIFT-MS instrument to perform a simple and rapid characterization of caviar samples. This work was done with a commercial dual polarity SIFT-MS Voice 200 ultra with up to 8 different precursor ions (3 positives and 5 negatives). The efficiency of the plasma source and of the first mass filter varies with the polarity and we observed ten time more precursor ions in positive mode than in negative mode. Furthermore, most of the VOCs already identified in caviar head space were alcohol, aldehyde and carboxylic acids, which molecules show high reactivity towards protonation (H₃O⁺), deprotonation (O⁻, O₂⁻ and OH⁻) or electron transfer (O₂⁺, NO⁺, O[•], O₂[•], OH⁻) (Ghislain et al., 2019; Smith et al., 2023). This could explain the distribution of the most discriminating product ions according to the precursor ions. Finally, it should be mentioned that the Labsyft® software database contain only positive mode results. The database was completed with previous results of our team on negative ionization. The conflicting ions inherent to the technology and the unitary mass resolution of SIFT-MS also constituted limitations for the identification of key molecules. Despite this, we identified putative molecules, in which product ions evolved in the same way and were already highlighted in the literature. We did not detect signals of geosmin, 2-methyl-isoborneol or characteristic markers of microbial contamination such as trimethylamine and 3-methyl-2-butanone, which indicates the good control of the caviar packaging process by the partner company. We confirmed the “feeling” of differences observed by the sensory jury between the two different sites and the time limit of maturation. This preliminary work introduces the SIFT-MS instrument as a decision-making support tool for caviar producers. The next step will be to apply this technology to a greater number of samples to develop predictive algorithms based on volatile profiles and to test its robustness. Prunier Manufacture also called on wine experts to refine the descriptors. Flavors of cream, butter, porcini mushrooms, undergrowth, vegetal, fish, shellfish, umami, and soy were found. Other new parameters must be investigated, such as the stability over several years and the impact of the diet on the volatile compound fingerprint and the caviar’s quality.

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CRedit authorship contribution statement

Mickael Le Bechec: Project administration, Supervision,

Visualization, Validation, Writing – original draft. **Marine Reyrolle:** Investigation, Formal analysis, Data curation. **Valérie Chesneau:** Conceptualization, Validation, Writing – review & editing. **Marine Breuil:** Investigation, Data curation. **Valérie Desauziers:** Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodcont.2023.110094>.

References

- Bajoub, A., Medina-Rodriguez, S., Ajal, E. A., Cuadros-Rodriguez, L., Monasterio, R. P., Vercammen, J., Fernández-Gutiérrez, A., & Carrasco-Pancorbo, A. (2018). A metabolic fingerprinting approach based on selected ion flow tube mass spectrometry (SIFT-MS) and chemometrics: A reliable tool for Mediterranean origin-labeled olive oils authentication. *Food Research International*, *106*, 233–242. <https://doi.org/10.1016/j.foodres.2017.12.027>
- Bergamaschi, M., Cecchinato, A., Biasioli, F., Gasperi, F., Martin, B., & Bittante, G. (2016). From cow to cheese: Genetic parameters of the flavour fingerprint of cheese investigated by direct-injection mass spectrometry (PTR-ToF-MS). *Genetics Selection Evolution*, *48*(1), 89. <https://doi.org/10.1186/s12711-016-0263-4>
- Caprino, F., Moretti, V. M., Bellagamba, F., Turchini, G. M., Busetto, M. L., Gianì, I., Paleari, M. A., & Pazzaglia, M. (2008). Fatty acid composition and volatile compounds of caviar from farmed white sturgeon (*Acipenser transmontanus*). *Analytica Chimica Acta*, *617*, 139–147.
- Czesny, S., Dabrowski, K., Christensen, J. E., Van Eenennaam, J., & Doroshov, S. (2000). Discrimination of wild and domestic origin of sturgeon ova based on lipids and fatty acid analysis. *Aquaculture*, *189*(1–2), 145–153. [https://doi.org/10.1016/S0044-8486\(00\)00364-1](https://doi.org/10.1016/S0044-8486(00)00364-1)
- Dalsvåg, H., Cropotova, J., Jambrak, A. R., Janči, T., Španěl, P., Dryahina, K., Smith, D., & Rustad, T. (2022). Mass spectrometric quantification of volatile compounds released by fresh atlantic salmon stored at 4 °C under modified atmosphere packaging and vacuum packaging for up to 16 days. *ACS Food Science & Technology*, *2*(3), 400–414. <https://doi.org/10.1021/acscfoodscitech.1c00259>
- Deuscher, Z., Andriot, I., Sémon, E., Repoux, M., Preys, S., Roger, J.-M., Boulanger, R., Labouré, H., & Le Quéré, J.-L. (2019). Volatile compounds profiling by using proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS). The case study of dark chocolates organoleptic differences. *Journal of Mass Spectrometry*, *54*(1), 92–119. <https://doi.org/10.1002/jms.4317>
- Gessner, J., Würtz, S., Kirschbaum, F., & Wirth, M. (2008). Biochemical composition of caviar as a tool to discriminate between aquaculture and wild origin. *Journal of Applied Ichthyology*, *24*(s1), 52–56. <https://doi.org/10.1111/j.1439-0426.2008.01092.x>
- Ghislain, M., Costarramone, N., Sotiropoulos, J.-M., Pigot, T., Berg, R. V. D., Lacombe, S., & Le Behec, M. (2019). Direct analysis of aldehydes and carboxylic acids in the gas phase by negative ionization selected ion flow tube mass spectrometry: Quantification and modelling of ion–molecule reactions. *Rapid Communications in Mass Spectrometry*, *33*(21), 1623–1634. <https://doi.org/10.1002/rcm.8504>
- Golovnya, R. V., & Uralets, V. P. (1972). Monocarbonyl compounds in the volatile components of rossiiskii cheese, flesh salmon, sturgeon and salmon caviar. *Food*, *16*(5), 497–506. <https://doi.org/10.1002/food.19720160510>
- Heude, C., Elbayed, K., Jezequel, T., Fanuel, M., Lugan, R., Heintz, D., Benoit, P., & Piotto, M. (2016). Metabolic characterization of caviar specimens by 1H NMR spectroscopy: Towards caviar authenticity and integrity. *Food Analytical Methods*, *9*(12), 3428–3438. <https://doi.org/10.1007/s12161-016-0540-4>
- Kharbach, M., Kamal, R., Mansouri, M. A., Marmouzi, I., Viaene, J., Cherrah, Y., Alaoui, K., Vercammen, J., Bouklouze, A., & Vander Heyden, Y. (2018). Selected-ion flow-tube mass-spectrometry (SIFT-MS) fingerprinting versus chemical profiling for geographic traceability of Moroccan Argan oils. *Food Chemistry*, *263*, 8–17. <https://doi.org/10.1016/j.foodchem.2018.04.059>
- Lindholm-Lehto, P. C., Vielma, J., Pakkanen, H., & Alén, R. (2019). Depuration of geosmin- and 2-methylisoborneol-induced off-flavors in recirculating aquaculture system (RAS) farmed European whitefish *Coregonus lavaretus*. *Journal of Food Science and Technology*, *56*(10), 4585–4594. <https://doi.org/10.1007/s13197-019-03910-7>
- Lopez, A., Bellagamba, F., Tirloni, E., Vasconi, M., Stella, S., Bernardi, C., Pazzaglia, M., & Moretti, V. M. (2021). Evolution of food safety features and volatile profile in white sturgeon caviar treated with different formulations of salt and preservatives during a long-term storage time. *Foods*, *10*(850), 16.
- Lopez, A., Vasconi, M., Bellagamba, F., Mentasti, T., Pazzaglia, M., & Moretti, V. M. (2020). Volatile organic compounds profile of ripening by multiple headspace solid phase microextraction. *Molecules*, *25*(1074), 15.
- Lytou, A. E., Panagou, E. Z., & Nychas, G.-J. E. (2019). Volatilomics for food quality and authentication. *Current Opinion in Food Science*. <https://doi.org/10.1016/j.cofs.2019.10.003>. S2214799319300724.
- Ma, S., Li, L. H., Hao, S. X., Yang, X. Q., Huang, H., Cen, J. W., & Wang, Y. Q. (2020). Fatty-acid profiles and fingerprints of seven types of fish roes as determined by chemometric methods. *Journal of Oleo Science*, *69*(10), 1199–1208. <https://doi.org/10.5650/jos.ess20061>
- Ozcan-Sinir, G. (2020). Detection of adulteration in extra virgin olive oil by selected ion flow tube mass spectrometry (SIFT-MS) and chemometrics. *Food Control*, *118*, Article 107433. <https://doi.org/10.1016/j.foodcont.2020.107433>
- Reyrolle, M., Bareille, G., Epova, E. N., Barre, J., Bérail, S., Pigot, T., Desauziers, V., Gautier, L., & Le Behec, M. (2023). Authenticating teas using volatile element signatures, strontium isotope ratios, and volatile compound profiling. *Food Chemistry*, *136271*. <https://doi.org/10.1016/j.foodchem.2023.136271>
- Reyrolle, M., Ghislain, M., Bru, N., Vallverdu, G., Pigot, T., Desauziers, V., & Le Behec, M. (2022). Volatile fingerprint of food products with untargeted SIFT-MS data coupled with mixOmics methods for profile discrimination: Application case on cheese. *Food Chemistry*, *369*, Article 130801. <https://doi.org/10.1016/j.foodchem.2021.130801>
- Rohart, F., Gautier, B., Singh, A., & Lê Cao, K.-A. (2017). mixOmics: An R package for 'omics feature selection and multiple data integration. *PLoS Computational Biology*, *13*(11), Article e1005752. <https://doi.org/10.1371/journal.pcbi.1005752>
- Ruan, E. D., Aalhus, J. L., Summerfelt, S. T., Davidson, J., Swift, B., & Juárez, M. (2013). Determination of off-flavor compounds, 2-methylisoborneol and geosmin, in salmon filets using stir bar sorptive extraction–thermal desorption coupled with gas chromatography–mass spectrometry. *Journal of Chromatography A*, *1321*, 133–136. <https://doi.org/10.1016/j.chroma.2013.10.038>
- Shen, Y., Yang, N., Liu, Z., Chen, Q., & Li, Y. (2020). Phylogenetic perspective on the relationships and evolutionary history of the Acipenseriformes. *Genomics*, *112*(5), 3511–3517. <https://doi.org/10.1016/j.ygeno.2020.02.017>
- Smith, D., Španěl, P., Demarais, N., Langford, V. S., & McEwan, M. J. (2023). Recent developments and applications of selected ion flow tube mass spectrometry (SIFT-MS). *Mass Spectrometry Reviews*. , Article e21835. <https://doi.org/10.1002/mas.21835>
- Suurnäkki, S., Gomez-Saez, G. V., Rantala-Ylänen, A., Jokela, J., Fewer, D. P., & Sivonen, K. (2015). Identification of geosmin and 2-methylisoborneol in cyanobacteria and molecular detection methods for the producers of these compounds. *Water Research*, *68*, 56–66. <https://doi.org/10.1016/j.watres.2014.09.037>
- Tavakoli, S., Luo, Y., Regenstein, J. M., Daneshvar, E., Bhatnagar, A., Tan, Y., & Hong, H. (2021). Sturgeon, caviar, and caviar substitutes: From production, gastronomy, nutrition, and quality change to trade and commercial mimicry. *Reviews in Fisheries Science & Aquaculture*, *29*(4), 753–768. <https://doi.org/10.1080/23308249.2021.1873244>
- Vilgis, T. A. (2020). The physics of the mouthfeel of caviar and other fish roe. *International Journal of Gastronomy and Food Science*, *19*, Article 100192. <https://doi.org/10.1016/j.ijgfs.2019.100192>
- Villano, C., Lisanti, M. T., Gambuti, A., Vecchio, R., Moio, L., Frusciantè, L., Aversano, R., & Carputo, D. (2017). Wine varietal authentication based on phenolics, volatiles and DNA markers: State of the art, perspectives and drawbacks. *Food Control*, *80*, 1–10. <https://doi.org/10.1016/j.foodcont.2017.04.020>
- Wirth, M., Kirschbaum, F., Gessner, J., Williot, P., Patriche, N., & Billard, R. (2002). Fatty acid composition in sturgeon caviar from different species: Comparing wild and farmed origins. *International Review of Hydrobiology*, *87*(5–6), 629–636. [https://doi.org/10.1002/1522-2632\(200211\)87:5/6<629::AID-IRHO629>3.0.CO;2-C](https://doi.org/10.1002/1522-2632(200211)87:5/6<629::AID-IRHO629>3.0.CO;2-C)
- Xu, X., Lu, S., Li, X., Bai, F., Wang, J., Zhou, X., Gao, R., Zeng, M., & Zhao, Y. (2022). Effects of microbial diversity and phospholipids on flavor profile of caviar from hybrid sturgeon (*Huso dauricus* × *Acipenser schrenckii*). *Food Chemistry*, *377*, Article 131969. <https://doi.org/10.1016/j.foodchem.2021.131969>
- Yener, S., Sánchez-López, J. A., Granitto, P. M., Cappellin, L., Märk, T. D., Zimmermann, R., Bonn, G. K., Yeretizian, C., & Biasioli, F. (2016). Rapid and direct volatile compound profiling of black and green teas (*Camellia sinensis*) from different countries with PTR-ToF-MS. *Talanta*, *152*, 45–53. <https://doi.org/10.1016/j.talanta.2016.01.050>