PAPER

QUALITY ASSESSMENT OF MEDITERRANEAN SHRIMPS DURING FROZEN STORAGE

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ABSTRACT

Aim of the research was to evaluate the effects of frozen storage on the quality of two Mediterranean wild shrimps, namely *Parapenaeus longirostris* (deepwater pink shrimp) and *Parapandalus narval* (narwal shrimp) in order to promote the marketing of these little-known shrimp species as frozen products, strengthening and enhancing their economic value. Quality changes were determined by sensory evaluation combined with chemical and chemical/physical analyses, including determination of volatile aroma constituents. In particular, raw and cooked shrimp samples were evaluated at various frozen storage intervals up to sixteen months. The variation observed for the chemical and chemical-physical indices did not diminish the sensory quality of both shrimp species. The results confirmed that freezing allows maintaining a good sensory quality of the considered shrimp species.

Keywords: Deepwater pink shrimp, frozen storage, narwal shrimp, sensory evaluation, volatile aroma compounds

1. INTRODUCTION

The Mediterranean shrimp species include, among others, the deepwater pink shrimp (*Parapenaeus longirostris*, Lucas 1846) and the narwal shrimp (*Parapandalus narval*, Fabricius 1787). Both species live in deep waters on muddy or muddy-sandy bottoms. *Parapenaeus longirostris* has a wide geographical distribution, being found both in the Eastern and Western Atlantic (OLASO, 1990), as well as in the Mediterranean and its adjacent seas (MASSUTTI, 1963); Italy is the country with the largest catches (HOLTHUIS, 1980) especially in the channel of Sicily and in the Ionian Sea. *Parapandalus narval* has an Eastern Atlantic-Mediterranean distribution (THESSALOU-LEGAKI, 1992) and is very common in the sea of Ustica Island.

Shrimps presumably represent the most important market for seafoods. In 2014 the global shrimp production was around 7×10^6 metric tons, of which almost 4×10^6 from aquaculture (LARKIN *et al.,* 2015). The international trade is dominated by USA, Japan and European countries as importers, whereas developing nations, especially South East Asian countries, act as the main shrimp suppliers of the world.

Italy imports most of its demand mainly as farmed shrimp whereas the two Mediterranean wild shrimps, namely *Parapenaeus longirostris* and *Parapandalus narval*, are of little commercial importance, sold only as fresh locally and close to the fishing grounds since their limited shelf life.

Although freezing is an effective method for preserving foods, some deterioration in frozen food quality can occur during storage, such as colour fading (CHANDRASEKARAN, 1994; OKPALA and BONO, 2016), lipid oxidation (RIAZ and QADRI, 1990), denaturation of protein (BHOBE and PAI, 1986), sublimation and recrystallization of ice (LONDAHL, 1997). These can result in off-flavours, rancidity, dehydration, loss of juiciness, textural changes (BHOBE and PAI 1986; YAMAGATA and LOW 1995; LONDAHL, 1997) and increase in volatile basic nitrogen (RIAZ and QADRI 1990; YAMAGATA and LOW, 1995).

Some papers are present in literature on the quality changes of frozen shrimps during storage (YAMAGATA and LOW 1995; BAK *et al.,* 1999; BOONSUMREJ *et al.,* 2007; TSIRONI *et al.,* 2009; BONO et al., 2016). Only few of these evaluated the sensory quality or related the sensory evaluation to the volatile aroma compounds (ROCHAT *et al.,* 2009; ALAM and SOLBERG, 2009), but according to our knowledge, no informations are reported on *Parapenaeus longirostris* and *Parapandalus narval*.

In view of the fact that frozen shrimp is a product of high commercial value and increasing demand due to its competitive price and extended shelf life (TSIRONI *et al.,* 2009), the aim of the research was to evaluate the effects of frozen storage time on the quality of the deepwater pink and narwal shrimps in order to promote the marketing of these little-known shrimp species as frozen products, strengthening and enhancing their economic value. Since the consumer is the ultimate judge of quality, chemical and instrumental methods were matched with the sensory evaluation: chemical and chemical-physical indices, volatile aroma constituents and sensory properties were determined at different times during frozen storage both on raw and cooked samples.

2. MATERIALS AND METHODS

2.1. Sampling

Shrimp specimens of *Parapenaeus longirostris*, Lucas 1846 (FAO name: deepwater pink shrimp) and *Parapandalus narval*, Fabricius 1787 (FAO name: narwal shrimp) were caught

off the southeast coast of Sicily (Porto Palo, Siracusa, Italy - FAO 37: Mediterranean, Black sea; Subarea 37.2: Central Mediterranean; Division 37.2.2: Ionian) in March 2013. Samples of frozen shrimps (size: *Parapenaeus longirostris*, 10-15 cm; *Parapandalus narval*, 7 cm) were provided by a Sicilian company that owns and operates both the fishing boats and the packing and storage facilities. After catch, shrimps were put into ice, then quick-frozen at -40°C, stored at - 18°C under vacuum (-0.8 bar) and transported frozen (at constant - 18°C) to the laboratory. All shrimp samples came from the same frozen batch; for each shrimp species eight packages in total were purchased and stored at constant - 18°C for sixteen months. The chemical and sensory analyses were carried out immediately after arriving at the lab and at specific intervals during storage. At fixed time, one package was thawed at room temperature and sufficient quantities were used for analyses. Unpeeled raw and cooked shrimp samples were analysed immediately after thawing. Cooked shrimps were obtained steaming unpeeled specimens for 15 min. All determinations were made in triplicate.

2.2. pH Measurement

The pH values of the raw samples were determined on homogenates of samples in distilled water (1:2 w/w) by using a pHmeter MP220 (Mettler Toledo, Milan, Italy) at 25°C.

2.3. Determination of the total volatile basic nitrogen (TVB-N)

For the determination of the total volatile basic nitrogen (TVB-N) of the raw samples, steam distillation of an extract deproteinised by trichloroacetic acid extraction was used according to official method (EU, 1995). Results were expressed as mg TVB-N/100 g of wet sample.

2.4. Colour measurement

Quantification of the colour change was based on measurement of CIELab values (L^*-value: lightness; a^*-value: redness and greenness; b^*-value: yellowness and blueness), using a NR-3000 Colourimeter (Nippon Denshoku Ind. Co. Ltd, Tokyo, Japan). The instrument was standardized under ''C'' illuminant condition according to the CIE (Commission International de l'Eclairage) using a standard white reference tile. At predetermined times of storage, according to the design, measurements were conducted for raw and cooked shrimp at five points. All measurements were carried out on three different shrimp samples.
The average values were reported and values of ΔE were determined:

$$\Delta E = \sqrt{(L^*-L_0^*)^2 + (a^*-a_0^*)^2 + (b^*-b_0^*)^2}$$

where L_0^*, a_0^*, and b_0^* are the values of L^*, a^* and b^* colour parameters at storage time zero.

2.5. HS-SPME sampling

The method of headspace solid phase microextraction (HS-SPME/GC-MS) was used for the isolation and concentration of volatiles. The analyses were conducted on peeled raw and cooked shrimp samples. To 5 g of each shrimp sample, placed in a 40 ml vial, 14 ml of a NaCl saturated aqueous solution were added. Extraction was performed in the headspace vial kept at 35°C using a DVB/CAR/PDMS fibre of 50/30 μm film thickness (Supelco, Bellefonte, PA, USA) housed in its manual holder (Supelco, Bellefonte, PA,

USA). The sample was equilibrated for 30 min and then extracted for 30 min. During the extraction, the sample was continuously stirred. After the sampling, the SPME fibre was introduced onto the splitless injector of the GC/MS maintained at 260°C for 3 min for the thermal desorption of the analytes. No artefacts were observed after a SPME analysis of the saturated saline solution performed as blank analysis.

2.6. GC-MS analysis

A Varian 3800 gas chromatograph directly interfaced with a Varian 2000 ion trap mass spectrometer (Varian Spa, Turin, Italy) was used. The conditions were as follows: injector temperature, 260 °C; injection mode, splitless; capillary column, CP-Wax 52 CB, 60 m, 0.25 mm i.d., 0.25 μm film thickness (Chrompack Italy s.r.l., Turin, Italy); oven temperature, 45°C held for 5 min, then increased to 200°C at a rate of 5°C/min and to 240°C at 3°C/min; 240°C held for 20 min; carrier gas, helium at a constant pressure of 10 psi; transfer line temperature, 250°C; acquisition range, 40–250 *m*/*z*; scan rate, 1 scan/s. Each volatile component was identified using mass spectral data, NIST 11 library (NIST/EPA/NIH Mass Spectra Library, version 2.0 g, USA), linear retention indices, literature data and injection of standards where available. The linear retention indices (LRI) were calculated according to VAN DEN DOOL and KRATZ (1963) equation.

2.7. Sensory analysis

The sensory profiles of the shrimp samples were evaluated following the UNI 10957, 2003 method. Twenty-five judges were submitted to preliminary tests to determine their sensory performance on basic tastes and the aromas associated with shrimps. The sensory profile (UNI 10957, 2003) was defined by using a selected panel of twelve judges trained over four sessions. Panelists were asked to score appearance and odour of raw peeled shrimp and appearance, odour, texture, and taste of cooked shrimp. A list of descriptors was selected based on the frequency (60 %) of the terms used by the judges in several sessions. Reference standards were available to define descriptors. The descriptors were quantified using a nine-point intensity scale, where 1 = "not perceptible" and 9 = "strongly perceptible". The shrimp samples were tested in triplicate. Each judge evaluated the shrimp samples in two sessions. All evaluations were conducted from 10.00 to 12.00 AM in individual booths (ISO 8589, 2007) illuminated with white light. The order of presentation was randomized among judges and sessions. Water was provided for rinsing between shrimp samples. All data were acquired by a direct computerized registration system (FIZZ Biosystemes. ver. 2.00 M, Couternon, France).

2.8. Statistical analysis

Chemical and sensory data were subjected to analysis of variance (ANOVA), using Statgraphics Plus software (ver. 5.1). Duncan's multiple range test was applied to the data to identify any significant differences between the analysed samples. The model was statistically significant with $P<0.05$.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the variation of the pH values during frozen storage in raw deepwater pink and narwal shrimps. For both shrimp species the pH values ranged between 7.3-7.8 in agreement with CADUN *et al.* (2005) who reported pH values of 7.64 for frozen

deepwater pink shrimp; no statistically significant (P>0.05) increase resulted till four month. The pH determination is one of the most frequently used physical methods for the quality control of seafood products since they are affected by the changes in the concentrations of free hydrogen and hydroxyl ions because of the shifts in the oxidation–reduction balance of the food by the activity of micro-organisms or enzymes (VARLIK *et al.*, 2000). Generally, the pH value of crustaceans is higher than that of fish and mammal species because of their higher content of nonprotein nitrogenous compounds (SHAHIDI, 1994). From our results, the pH values of analysed shrimp samples during storage resulted always below 8, the critical acceptability limit for most shellfish products (SCHORMULLER, 1968).

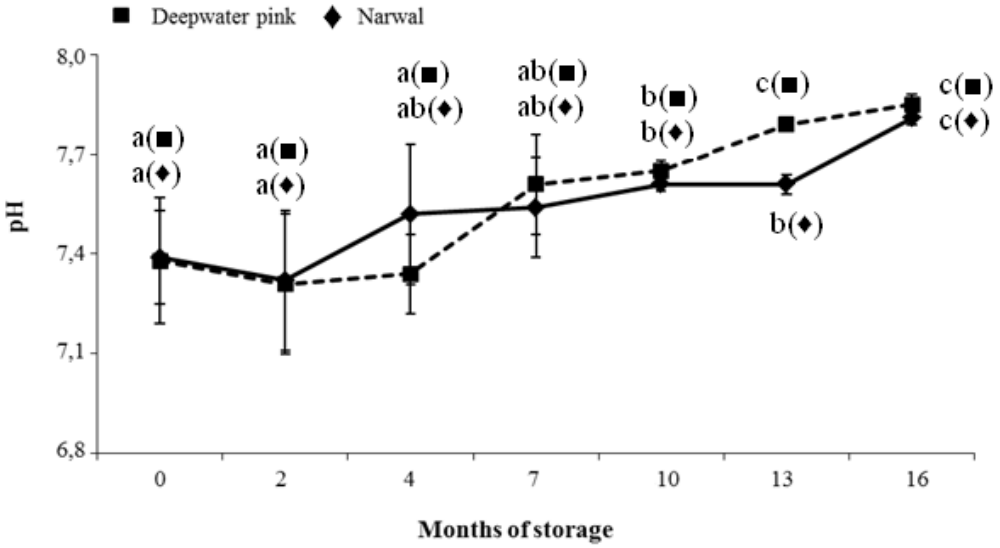

Figure 1: pH variations of raw shrimp samples during frozen storage (Error bars indicate standard error of measurements).
For each species different letters indicate statistically significant differences among mean values at $P \leq 0.05$ by Duncan's multiple range test.

Figure 2 shows the total volatile basic nitrogen (TVB-N) values in raw deepwater pink and narwal shrimps during storage. The TVB-N content resulted around 29 mg/100 g of wet weight in the shrimp samples of the two species at the beginning of storage, and increased reaching the values of 35.09 mg/100 g and 35.85 mg/100 g at the end of storage for deepwater pink and narwal shrimps, respectively. Statistically significant increases were observed after four month of storage for both shrimp species. The increase in TVB-N values is consistent with the results of the pH values: the TVB-N increase during the storage turns the medium alkaline and as a result pH increases. The level of TVB-N is considered a useful index of microbial spoilage in different fresh and lightly preserved seafood (OZOĞUL and OZOĞUL, 2000). The limit of TVB-N values for seafood products of good sensory quality has been reported to be 30 mg/100 g. However, this limit may be questionable for shrimp species since the average TVB-N values for fresh crustaceans are often higher (OEHLENSCHLÄGER, 1997); in a study by COBB *et al.* (1973) the initial TVB-N content of fresh shrimp tails from different batches of shrimp stored on ice, ranged from 13.5 to 38.2 mg N/100 g; however a high sensory quality of shrimp samples was

perceived. As a consequence, TVB-N content cannot be considered as an indicator of freshness by itself but it must be always enhanced by the sensory tests (CHEN *et al.*, 1995).
Table 1 illustrates the changes of L^*, a^* and b^* in raw and cooked deepwater pink and narwal shrimps during frozen storage. L^* values increased whereas a^* and b^* values decreased when storage time increased; the colour of shrimp changed from red and yellow to dull lighter colour. In Table 1 ΔE values for raw and cooked shrimps are also reported. ΔE values, indicating the total colour changes, increased with an increase in storage time. For raw deepwater pink shrimp statistically significant variations resulted at the beginning and at the end of storage, whereas for cooked samples a significant increase was observed only after thirteen months. Regarding the narwal shrimps, ΔE values significantly increased until ten months both in raw and cooked samples. The rate of increase was higher for narwal shrimp samples, both raw and cooked, than for deepwater pink shrimps probably due to the deeper colour of the former as indicated by the higher scores of the colour sensory descriptor (Table 3). Shrimp colour is linked to the content of astaxanthin and its esters, that are the major pigments in shrimps; drying and storage conditions affect shrimp colour due to the astaxanthin oxidation and isomerisation reactions that lead to colourless compounds and, thus, to the loss of the typical redness and yellowness (CHEN *et al.*, 1995; NIAMNUY *et al.*, 2008).
Table 2 shows the amount of the volatile compounds detected in raw and cooked deepwater and narwal shrimp samples at different storage time. A total of thirty compounds have been observed, such as aldehydes, ketones, alcohols, esters, acids, nitrogen- and sulfur- containing compounds.

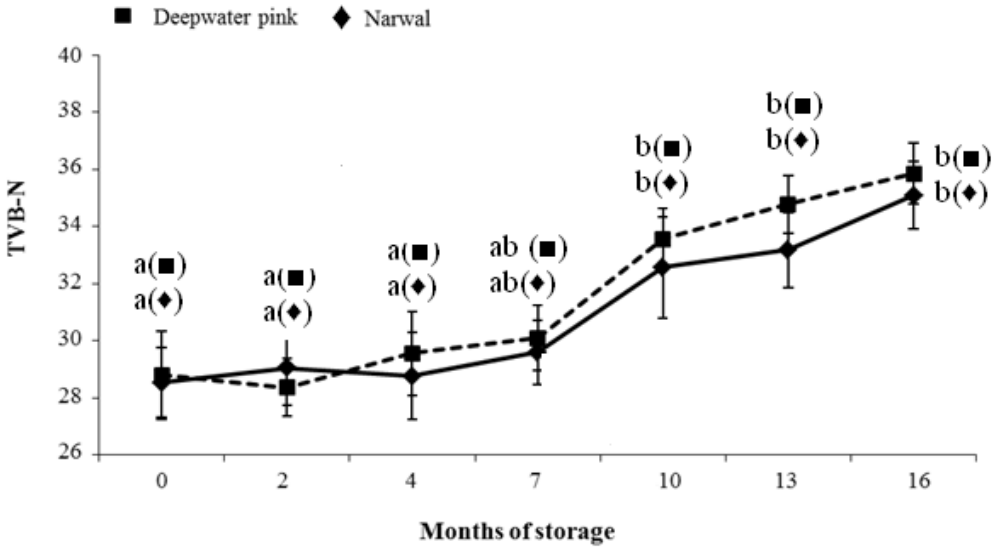

Figure 2: Total volatile basic nitrogen values (mg N/100 g shrimp flesh) of raw shrimp samples during frozen storage (Error bars indicate standard error of measurements).
Figure legend: For each species different letters indicate statistically significant differences among mean values at $P \leq 0.05$ by Duncan's multiple range test.

Slight differences in the qualitative and quantitative volatile composition of the two shrimp species and during the storage period, as well as between raw and cooked samples, resulted. In raw shrimps, hexanal, 2-ethyl-1-hexanol and dimethylsulphide were

the most abundant compounds, followed by 6-methyl-5-hepten-2-one and nonanal; 1-penten-3-ol, octanal (only in deepwater pink shrimp samples), 1-octen-3-one and γ-butyrolactone were also detected in a good amount. Some of these volatiles, namely dimethyl sulphide, 1-penten-3-ol, 1-octen-3-one, 2-ethyl-1-hexanol and γ-butyrolactone, decreased during the storage period but they remained among the most abundant components of volatile fraction up to sixteen months. Aldheydes, ketones and alcohols containing 6, 8 and 9 carbon atoms are derived from long-chain polyunsaturated fatty acid via 12- or 15-lipoxygenases and hydroperoxide lyase (BAEK and CADWALLADER, 1997) and are responsible of the pleasant planty, green and melony aromas and flavours of fresh seafoods. In particular hexanal contributes to the distinct green plant-like, grassy and apple-like aromas of fresh shrimp, whereas 2-ethyl-1-hexanol, together with short-chain alcohols, contributes to the typical sweet aroma of shrimps (ALASALVAR *et al.,* 1997). Also dimethyl sulphide provides a pleasant seashore-like smell in fresh seafoods (IIDA, 1988); in fact, although sulphur compounds are usually associated with deteriorated seafoods, there is evidence that they can be present even in fresh ones and are considered important volatile aroma components in marine crustaceans (ALASALVAR *et al.,* 1997). γ-Butyrolactone has faintly sweet odour reminiscent of rancid butter; lactones have been identified in roasted shrimp and boiled scallops; they derived from aliphatic saturated and unsaturated γ-hydroxycarboxylic and δ-hydroxycarboxylic acids (PAN and KUO, 1994).

Dimethylamine, trimethylamine, acetic acid, and phenol were detected in low amount in fresh samples and slightly increased during frozen storage, except for trimethylamine, whose variations during storage were not statistically significant both in narwal and in deepwater shrimp samples. The formation of trimethylamine in frozen seafoods is prevented by the inhibition of microbial growth, yet dimethylamine is produced enzymatically: CASTELL *et al.* (1970) reported the increase of dimethylamine content in frozen fish muscle due to enzymatic breakdown of trimethylamine oxide. Also acetic acid could be formed by enzymatic decomposition of either lipid autoxidation or secondary hydroperoxides of fatty acids (ALASALVAR *et al.,* 1997), whereas phenol formation occurs via decarboxylation of phenolic carboxylic acids (SPURVEY, 1998).

In all the samples, 6-methyl-5-hepten-3-one and geranylacetone (spicy and flowery notes) were present; these compounds, deriving from carotenoid degradation, showed a statistically significant increase during storage. Their amount and the rate of increase during storage are higher in narwal than in deepwater pink shrimps.

2,4-Decadienal, (*E*,*Z*)-2,4-heptadienal, (*E*,*Z*)-3,5-octadien-2one and (*Z*)-4-heptenal, deriving from lipid autoxidation during storage, were not detected. The absence of these compounds, responsible of stale and oxidized aromas and of fish cold-stored off-flavours (ALASALVAR *et al.,* 1997), was probably due to the very low fat content of deepwater pink and narwal shrimps.

As expected, the cooked shrimps showed some differences in volatile aroma profile compared to the raw ones. After cooking, hexanal and dimethylsulphide remained the main constituents of the volatile fraction but their amount decreased when freezing time increased. 2-Methylbutanal, 3-methylbutanal, 2,6-dimethylpyrazine, dimethylsulfoxide, 1-dodecanol were detected only in cooked shrimps samples and their amount did not vary among the cooked samples. Among these compounds, 1-dodecanol, with a flower-like odour, has been already recognized as an important volatile of cooked shrimps (MANDEVILLE *et al.,* 1992). 2-Methylbutanal and 3-methylbutanal are well known as amino acid degradation products and may be generated either thermally (Strecker degradation) or enzymatically from isoleucin and leucin.

Table 1: ΔE, *L**, *a** and *b** values of shrimp samples during frozen storage.

Months of storage	Deepwater pink shrimp								Narwal shrimp							
	Raw				Cooked				Raw				Cooked			
	ΔE	*L**	*a**	*b**	ΔE	*L**	*a**	*b**	ΔE	*L**	*a**	*b**	ΔE	*L**	*a**	*b**
0		31.31a	10.87d	-2.03d		45.47a	3.07d	-1.46d		43.99a	17.66c	10.84b		23.06a	12.73c	14.63c
2	0.54a[(a)]	33.86a	9.93c	-4.12c	1.13a	58.76b	1.46c	-2.59c	0.92a	44.86a	11.73c	9.92b	0.18a	28.88a	12.17c	13.52c
4	0.93b	38.22b	6.41b	-4.51c	1.15a	58.69b	-1.44b	-3.12b	1.18b	45.47a	11.56c	9.04b	0.59b	36.75b	11.38b	11.34b
7	0.99b	39.16b	6.29b	-5.41b	1.16a	58.31b	-3.22a	-3.78b	1.30c	48.72a	8.07b	2.53a	0.78c	38.33b	11.33b	11.13b
10	1.04b	39.79b	4.72a	-5.67b	1.17a	58.39b	-3.92a	-4.12b	1.40d	53.57b	6.82a	1.37a	1.16d	43.52c	10.89b	8.34a
13	1.13c	42.47c	4.41a	-6.32b	1.22b	60.13c	-4.07a	-4.88b	1.41d	58.84b	6.06a	1.11a	1.25d	43.53c	6.61a	6.73a
16	1.19c	48.43c	3.40a	-8.29a	1.28b	62.11c	-4.97a	-6.73a	1.45d	59.98b	5.12a	1.02a	1.29d	46.07c	4.83a	6.68a

[(a)] Different letters in the same column indicate statistically significant differences among mean values at $P \leq 0.05$ by Duncan's multiple range test.

Table 2: Volatile fraction composition[a] of shrimp samples during frozen storage.

Months of storage	Deepwater pink								Narwal							
	Raw				Cooked				Raw				Cooked			
	0	4	10	16	0	4	10	16	0	4	10	16	0	4	10	16
Volatiles[b]																
Dimethylamine	84b[d]	90b	114a	149a	60b	68b	88a	99a	50b	67b	107a	113a	90b	92b	109a	111a
Trimethylamine	48	46	40	43	52	56	57	54	56	51	51	54	64	67	62	65
Dimethyl sulphide	920a	875a	585b	332c	2246a	2352a	1391b	596b	704a	743a	304b	298b	2656a	2021a	1231b	698c
3-Hydroxy-2-butanone	25	28	38	43	-	-	-	-	-	-	-	-	-	-	-	-
2-Butanone	65	60	53	48	-	-	-	-	-	-	-	-	-	-	-	-
2-Methyl butanal	-[c]	-	-	-	68	71	75	69	-	-	-	-	82	79	86	89
3-Methyl butanal	-	-	-	-	52	63	58	57	-	-	-	-	60	71	68	75
Hexanal	1120	1155	1051	1197	1855a	1693a	1076b	1038b	1157	1136	1156	1098	1931a	1832a	1123b	1311b
1-Penten-3-ol	232a	160b	115c	48d	96a	41b	38b	16c	104a	88b	41c	48c	29a	17b	10b	9b
Heptanal	-	-	-	-	32	42	32	28	-	-	-	-	23	22	28	11
2-Methyl-1-butanol	33	24	35	29	-	-	-	-	78	59	60	65	29	25	11	12
1-Pentanol	-	-	-	-	39	31	25	17	-	-	-	-	31	28	14	21
Octanal	100	116	115	126	127	143	143	121	21	36	24	43	59	60	89	34
6-Methyl-5-hepten-2-one	321b	358b	397b	498a	119b	130b	168b	262a	413b	452b	479b	681a	121b	164b	279a	325a
2,6-Dimethylpyrazine	-	-	-	-	43	37	38	46	-	-	-	-	46	56	53	47
Nonanal	260	287	242	225	350	327	321	312	330	341	294	288	380	372	222	287
Ethyl octanoate	-	-	-	-	-	-	-	-	-	-	85	93	-	-	-	-
1-Octen-3-one	186a	148a	96b	82b	41a	49a	18b	11b	216a	228a	182a	106b	-	-	-	-
Acetic acid	99b	108b	120b	160a	236b	246b	254b	294a	89b	99b	111b	142a	47b	54b	116a	135a
2-Ethyl-1-hexanol	913a	605b	465c	428c	-	-	-	-	1589a	1295b	861c	973c	-	-	-	-
Dimethyl sulfoxide	-	-	-	-	59b	68b	125a	130a	-	-	-	-	19b	31b	49a	66a
1-Nonanol	43	39	53	32	36	42	59	48	45	40	28	32	7	7	5	3
γ-Butyrolactone	191a	70b	68b	74b	143a	89b	66b	64b	122a	56b	21c	25c	111a	53b	22c	20c
4-Butoxy-1-butanol	48	34	39	30	30	25	26	28	58	48	51	63	50	49	47	53
Dodecanal	-	-	-	-	58	63	83	64	-	-	-	-	91	86	93	89
Methyl dodecanoate	8	4	5	5	-	-	-	-	10	8	15	13	-	-	-	-
Hexanoic acid	23	28	32	35	31	28	36	38	8	7	10	6	31	28	34	36
1-Dodecanol	-	-	-	-	158	174	164	169	-	-	-	-	201	198	231	243
Geranylacetone	11b	15b	42a	50a	166b	164b	236a	242a	62b	45b	125a	175a	185a	179a	265b	271b
Phenol	54b	46b	71a	86a	-	-	-	-	26b	23b	42a	53a	-	-	-	-

[a] Expressed as peak areas, arbitrary scale. [b] Volatile compounds have been reported according to the order of elution on the column CP-WAX 52 CB column. [c] Not detected. [d] Different letters in the same row indicate statistically significant differences among mean values at $P < 0.05$ by Duncan's multiple range test.

Table 3: Sensory scores of shrimp samples during frozen storage.

	Deepwater pink								Narwal							
	Raw				Cooked				Raw				Cooked			
Months of storage	**0**	**4**	**10**	**16**	**0**	**4**	**10**	**16**	**0**	**4**	**10**	**16**	**0**	**4**	**10**	**16**
Volatiles																
Flesh colour	3.5b[(a)]	2.9a	2.8a	2.1a	3.5b	3.7b	2.3a	2.6a	7.5c	6.2b	2.7a	2.8a	7.4d	6.8c	6.0b	4.8a
Sheen	4.5b	4.4b	4.1a	3.9a	-	-	-	-	6.5c	5.8b	6.0b	4.0a	-	-	-	-
Compactness	6.5	6.2	6.0	6.2	-	-	-	-	6.5	5.9	6.3	6.4	-	-	-	-
Sea aroma	5.1	4.8	4.7	5.0	4.2	4.7	4.2	4.3	5.3	4.8	4.8	5.1	5.8	4.4	4.5	4.1
Algae aroma	4.3	4.9	4.5	4.7	-	-	-	-	4.9	4.9	4.7	4.3	-	-	-	-
Shrimp aroma	5.0	5.9	5.4	5.4	6.9	6.3	6.6	6.3	6.2	5.9	5.4	6.4	7.1	6.3	6.5	6.2
Off-odour	2.5	2.7	3.3	3.3	2.2	2.9	3.3	3.4	2.6	2.6	3.7	3.8	2.0	2.8	3.4	3.8
Flesh firmness	5.3	4.2	4.5	4.8	4.6	3.3	3.8	3.8	5.1	4.2	5.0	5.5	4.8	3.6	3.3	3.6
Bitter	-	-	-	-	2.5	3.3	2.6	3.0	-	-	-	-	3.0	3.1	2.8	2.8
Salty	-	-	-	-	3.4	3.0	3.1	2.8	-	-	-	-	3.8	3.7	4.5	3.7
Sour	-	-	-	-	2.3	2.1	2.0	1.9	-	-	-	-	2.3	2.1	2.5	1.7
Sweet	-	-	-	-	4.6	3.8	4.0	3.9	-	-	-	-	5.7	4.6	4.0	4.5
Juicy	-	-	-	-	5.1	4.8	4.1	4.2	-	-	-	-	5.5	4.4	4.5	4.7
Chewy	-	-	-	-	3.9	4.0	4.2	4.5	-	-	-	-	3.4	3.6	4.0	4.0
Sea flavour	-	-	-	-	4.8	3.8	3.7	4.6	-	-	-	-	4.4	4.0	3.9	4.0
Shrimp flavour	-	-	-	-	6.8	5.9	5.9	6.8	-	-	-	-	7.0	6.2	6.6	6.4
Off-flavour	-	-	-	-	2.2	2.8	3.0	3.0	-	-	-	-	2.3	3.3	3.5	3.0
Overall	7.4	7.1	7.4	7.2	7.6	7.6	7.4	7.5	8.0	8.1	7.8	7.9	8.3	8.2	8.2	8.1

[(a)] Different letters in the same row indicate statistically significant differences among mean values at $P < 0.05$ by Duncan's multiple range test.

Since these branched aldehydes were not present in uncooked samples, their thermal generation could be presumed. Also 2,6-dimethylpyrazine has a thermal origin: in fact alkylpyrazines may be formed by the involvement of lipid oxidation products in Maillard reaction (HUANG *et al.,* 1987) by heating of food at or above 100 °C. Alkylpyrazines, including methylpyrazine, 2,5- and 2,6-dimethylpyrazine have been detected in several cooked crustaceous, identified as having a roasted, nutty/meaty aromas in boiled crayfish and considered to contribute more to boiled rather than roasted odours in proteinaceous food (SPURVEY, 1998).
Other volatiles such as the 2-ethyl-1-hexanol were not identified in the cooked shrimps. Otherwise, as below reported 2-ethyl-1-hexanol, together with short-chain alcohols, contributes to the typical sweet aroma of raw shrimps (ALASALVAR *et al.,* 1997).
As happened for the raw shrimps, both deepwater pink and narwal, the volatile profile of the cooked shrimps considered as a whole, remained almost stable at least until ten months of freezing storage.
Table 3 reports the results of sensory evaluation of raw and cooked deepwater pink and narwal shrimps. In particular, for the raw samples the descriptors were three for the appearance (colour of flesh, sheen, compactness) four for the aroma (shrimp, sea, algae, off odour) and one for the rheological properties (flesh firmness). Regarding the cooked shrimps four descriptors for the aroma (shrimp, sea, algae odour, off odour), three for the flavour (shrimp, sea, off flavour), one for the rheological properties (flesh firmness), four for the taste (bitter, salty, sour, sweet), one for the oral perception (juicy) and finally, one for the texture (chewy) were selected.
The analysis of variance applied to the sensory data showed statistically significant differences only for sensory scores linked to colour and sheen descriptors both for raw and cooked deepwater pink and narwal shrimps. This was in accordance with the colour analysis that showed colour changes during storage and with the volatile analysis that evidenced an increase in the amount of carotenoid degradation products. No statistically significant variation was observed for the "overall" descriptor up to sixteen month of frozen storage. The differences observed in chemical indices and volatile aroma constituents little influenced the sensory attributes of raw shrimp samples during the freezing storage. The same occurred for the sensory attributes of the samples cooked after different periods of freezing.

4. CONCLUSIONS

The main goal of this research was to evaluate the effect of freezing storage on the quality of deepwater pink shrimps and narwal shrimps. To this end, pH, TVB-N, colour analysis, volatile fraction analysis and sensory evaluation were carried out. The assessment of shrimp quality mainly considered the impact of the preservation method on the sensorial characteristics since they are major concerns of consumers. The chemical and chemical-physical data and the volatile profile, considered the most important parameter for shellfish flavour quality, evidenced slight variations during the freezing storage but were unable to affect the sensory quality as confirmed by the maintenance of high scores for the "overall quality" descriptor throughout the entire storage period. Our results demonstrate the maintenance of a good sensory quality during the considered period, therefore these two shrimp species could be of great economic interest if marketing as frozen products.

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