

Effect of Citric Acid on the Quality and Shelf-Life of Dried Shrimp

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Abstract

Dried shrimp was processed by soaking fresh shrimp in citric acid solution of 0, 0.1, 0.3, 0.5% for 20 minutes, then boiling in 5% brine to select appropriate concentration of citric acid. Shelf-life storage of dried shrimp under vacuum and air packed at 30 ± 2°C and 10 ± 2°C was studied. Chemical (astaxanthin, ammonia, moisture, NaCl, pH), microbiological (TVC, anaerobe, yeast and mould, E. coli, S. aureus, Salmonella, Vibrio), physical (A_w, colour using L. a, b system) analysis, and sensory evaluation were conducted. It was found that astaxanthin content and overall acceptability of samples soaked in 0.1, 0.3, 0.5% citric acid solution were not significantly different (P>0.05) but they were significantly better than samples without citric acid dipping. Therefore the lowest concentration of citric acid solution, 0.1% was selected for studying the changes of quality during storage under vacuum and air packed. The results showed that dried shrimp under all conditions of packaging stored at 10 ± 2°C had shelf life longer than 14 weeks, and had better quality than samples stored at 30 ± 2°C. Samples stored under air packed and vacuum at 30 ± 2°C had shelf life of 6 and 8 weeks, respectively. Moreover dried shrimp dipped in citric acid solution had better colour, higher astaxanthin content and higher acceptability score as well as lower ammonia content than samples without citric acid dipping (P<0.01) both stored under vacuum and air packed at 30 ± 2°C and 10 ± 2°C.

Introduction

Dried shrimp is a Thai traditional fishery product processed not only for domestic consumption but also for export to foreign countries. The major markets for export are Hong Kong, the United States and Japan (Department of Commerce, 1990). It is an intermediate moisture product with A_w 0.72-0.76. Generally, dried shrimp is produced from fresh shrimp boiled in 3-4% of salt and then sun dried. The main qualities of dried shrimp are colour and aroma which are normally unstable. That is the reason the producers prefer to add some colouring agents

even though the Thai Food and Drug Administration Act forbids the addition of any colouring agent to exporting dried and salted fishery products. However, some countries still use them. Therefore, the problem is the misuse of colouring agents in this product, such as dyes etc.

Since colour of dried shrimp is a major characteristic, the method or other additives have been taken into account. Citric acid is the one widely used in processed foods. Its major advantages as an acidulant are its high solubility in water, the appealing effects on food flavour, and its potent metal-chelating action including water holding capacity. Citric acid has been used in foods in the United States for over 100 years (Lopez, 1981). It chelates trace metals which may cause haze or deterioration of colour or flavour. It is also employed to adjust the acidity of relishes, sauces, and other food products requiring flavour enhancement. In canned crab meat, lobster meat, scallops, and oysters, citric acid is used to prevent discoloration and development of off-flavours and odours (Lopez, 1981).

Therefore, the development of dried shrimp processing by using citric acid to stabilize the colour as well as modified packaging to extend the shelf life have been conducted.

The objectives of this study are to : 1) determine the suitable concentration of citric acid, and 2) study quality changes during storage of dried shrimp with and without citric acid in vacuum and atmospheric packaging.

Materials and Methods

1. Raw material : Fresh shrimp (*Metapeneaus* spp.).
2. Methods :
 - a. Determine the suitable concentration of citric acid (Fig. 1).

Fresh shrimp was washed and divided into 4 lots. Each lot was soaked in different concentration of citric acid at 0, 0.1, 0.3 and 0.5%, respectively for 20 minutes. The shrimp was then boiled in 5% brine at the ratio of brine to shrimp 1:1 for about 8-10 minutes, dried at 55°C for about 6-7 hours in a hot air oven (Torry kiln), and

shelled. Then 100-gram lots were packed in low density polyethylene (LDPE) bags and stored at $30 \pm 2^\circ\text{C}$. The packed dried shrimp was sampled for quality assessment by physical and chemical analysis (A_w , sensory evaluation, moisture contents, astaxanthin, ammonia and pH) once a week until unacceptable. The appropriate treatment was selected for further experiments.

b. Shelf-life study on the quality changes of dried shrimp in packages (Fig. 2).

Dried shrimp was produced by using the suitable concentration of citric acid from the previous step. Each 75 grams was vacuumed and atmospheric packed (air packed) in polyamide/low density polyethylene (PA/LDPE) bags. The samples were kept at $30 \pm 2^\circ\text{C}$ and $10 \pm 2^\circ\text{C}$.

3. Physical analysis :

Sensory evaluation was conducted using hedonic rating scale (Larmond, 1970) 9 points with 10-20 trained panelists, comprising 25% men and 75% women. A_w using A_w meter (Novasina Thermoconstanter TH/RTD 733).

4. Chemical analysis :

- a. Astaxanthin (Biede, 1982);
- b. Ammonia (AOAC, 1990);
- c. Moisture (AOAC, 1990);
- d. Salt (FAO, 1981); and
- e. pH (Miwa and Low, 1992).

5. Microbial analysis :

- a. Total viable count (Miwa and Low, 1992);
- b. Yeast and mould (AOAC, 1984);
- c. *Staphylococcus aureus* (AOAC, 1984);
- d. *Escherichia coli* (AOAC, 1984);
- e. *Salmonella* (AOAC, 1984);
- f. *Vibrio cholera* (AOAC, 1990); and
- g. *Clostridium* spp. (AOAC, 1984).

6. Statistical analysis :

Split plot in randomized block design was used, and the SAS computer program version 6.03 was used to analyse the data from this experiment.

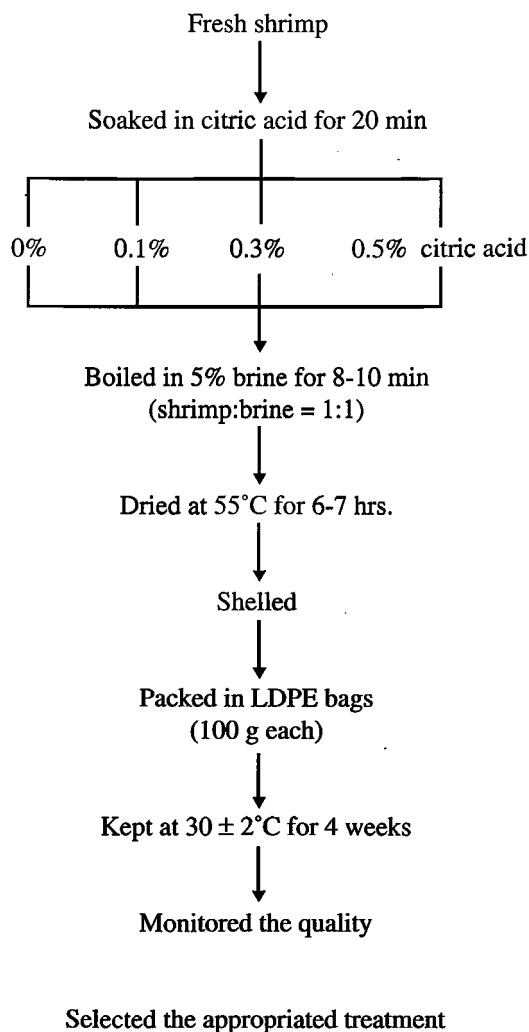


Fig.1. The suitable concentration of citric acid for dried shrimp.

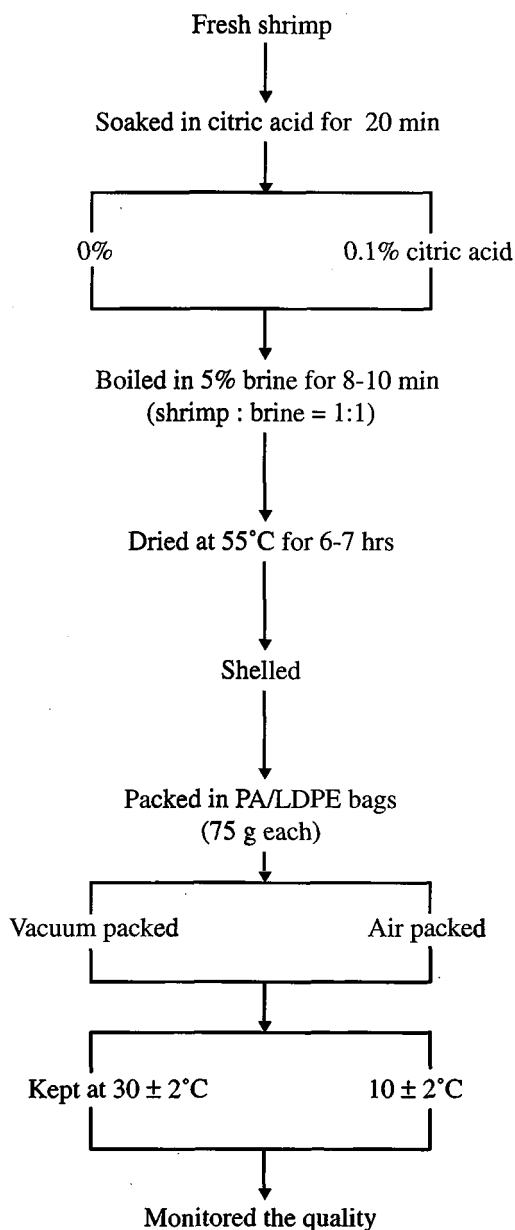


Fig.2. Dried shrimp in package during storage.

Results And Discussion

1. The suitable concentration of citric acid for dried shrimp.

Dried shrimp samples produced by citric acid soaking treatments at various concentrations of 0, 0.1, 0.3 and 0.5% were packed and stored at $30 \pm 2^\circ\text{C}$. Quality assessment was carried out once a week until unacceptable. It was found that the sample of all treatments had moisture content in the range of 19-24% and A_w less than 0.95 which is able to inhibit the bacterial growth (Lesiture and Podel, 1976). The sample with 0.1% citric acid

was the lowest in moisture content of about 19-20% (Table 1) and varied significantly ($P < 0.05$) among treatments throughout the storage (Tables 2&3). The initial pH of sample at week 0 was about 8.15-8.18. However, it could not be decided whether the variation of pH during storage was due to storage time or concentration of citric acid.

In addition, astaxanthin which is a good index for colour was higher in every sample of dried shrimp with citric acid than the untreated samples ($P < 0.05$) (Table 4). Ammonia content of all treatments increased during storage but the lowest reading was also found in dried shrimp with 0.1% citric acid (Table 5). By sensory evaluation, no significant difference ($P < 0.05$) was found in aroma, colour, flavour and texture of all treatments throughout the storage, although the dried shrimp with citric acid had higher acceptable scores than those without citric acid (Table 6).

According to the Thai Industrial Standard (TIS 1003-1990), the requirements of good quality of dried shrimp are moisture content $\leq 20\%$, NaCl $\leq 10\%$ (dried weight), pH < 8.0 , no colouring agents, TVC $\leq 10^5/\text{g}$, *Escherichia coli* < 10 (MPN/g), *Staphylococcus aureus* $< 100/\text{g}$, no Salmonella in 25 g sample, no *Clostridium perfringen* in 0.1 g sample, mould $\leq 2 \times 10^2/\text{g}$, no trace of decomposed-odour and no adulterant. It could be concluded that the quality of dried shrimp of all treatments met the requirements of TIS throughout the period of storage. However, the results of physical and chemical analysis showed that dried shrimp with citric acid had better quality than the samples without citric acid. In terms of astaxanthin, the colour index of good quality dried shrimp, those with 0.1% citric acid gave a higher reading throughout the period of storage. Therefore, this treatment was selected for the further experiments.

2. The quality changes of dried shrimp during storage. a. At $30 \pm 2^\circ\text{C}$

As an integral part of this experiment, dried shrimp was produced and packed by the method shown in Fig. 2. At this temperature, astaxanthin of both dried shrimp with and without citric acid in vacuum packed were higher than in air packed ($P \leq 0.01$) and decreased as storage time increased (Fig. 3). It means that oxygen in air packed causes oxidation of astaxanthin while vacuum packed slows down this reaction. (Biede *et al.*, 1982; Wibulset *et al.*, 1986; Braekkan, 1971).

Ammonia content, which is another good quality index of dried shrimp was recorded as in Fig. 4. The ammonia of all samples increased as the time increased but was still lower than 800 ppm which was the criteria for good quality dried

shrimp (Chukpiwong, 1983; Worapong, 1988). However, there was no interaction of ammonia content between treatments, packaging conditions and storage time ($P \leq 0.01$); the readings in air packed were higher than in vacuum packed throughout the storage.

In addition, there was not much difference in moisture content, A_w , pH and NaCl in all treatments during storage (Fig. 5). Dried shrimp with citric acid had a slightly higher moisture content than without citric acid due to the water holding capacity of citric acid (Sharma and Seltzer, 1979) and corresponded to A_w . It was found that both packaging conditions and storage time did not affect moisture content and A_w . The observed A_w of all samples were less than 0.76, indicating a safe condition from microorganisms.

Besides astaxanthin, colour measurement has been conducted by using Chroma meter (Minolta SR-300). Colour was read by L, a, b system (Fig. 6). The results corresponded to both the content of astaxanthin and sensory scores.

By sensory evaluation, the panelists accepted all treatments during 8 weeks of storage (Fig. 7). The colour and texture scores of dried shrimp with 0.1% citric acid were higher than without citric acid due to the higher moisture content. It was found that colour scores had a linear regression with astaxanthin of $R^2 = 0.63$.

According to microbial inhibitory effect of citric acid (Brannen *et al.*, 1990), no growth of microorganisms, and prolonged shelf-life in all treatments were found during 8 weeks of storage; but growth of mould was observed in dried shrimp without citric acid after 5 weeks of storage (Fig. 8). It could be concluded that microbial quality of dried shrimp in this experiment met the requirements of TIS 1003-1990.

Therefore, vacuum packed incorporated with citric acid gave better quality dried shrimp than air packed without citric acid.

b. At $10 \pm 2^\circ\text{C}$

The changes of astaxanthin and ammonia content of dried shrimp in air and vacuum packed stored at this temperature showed the similar trend to that of $30 \pm 2^\circ\text{C}$ (Figs. 9,10). However, the vacuum packing had the advantage of slowing down the oxidation of astaxanthin and ammonia formation. These results corresponded with sensory scores of flavour (Fig. 11) - the panelists detected less ammonium odour from the samples in vacuum packed than in air packed at corresponding periods of storage. Moreover, the decrease of astaxanthin and increase in ammonia at $10 \pm 2^\circ\text{C}$ were slower than at $30 \pm 2^\circ\text{C}$. Crook and Ritchie (1983) reported that the increase of ammonia content in fish flesh slowed down when

stored at $4-5^\circ\text{C}$ because decomposition of protein was slow. Not only astaxanthin and ammonia contents, but the other qualities (pH, moisture and A_w) were also more stable than those at $30 \pm 2^\circ\text{C}$ (Fig. 12).

The colour measurement using Chroma meter (Minolta SR-300) by L, a, b system (Fig. 13) gave results similar to the samples kept at $30 \pm 2^\circ\text{C}$, and also corresponded with the content of astaxanthin. At both storage temperatures, a linear correlation equation using SAS computer program version 6.03 was obtained as

$$Y = 1.5 + 0.51a - 0.14b$$

and $R^2 = 0.855$ when $Y =$ astaxanthin content, $a =$ a value or hue, $b =$ b value or chroma. In addition, bacterial analysis (Fig. 14) was lower than that of samples kept at $30 \pm 2^\circ\text{C}$ due to slower activity at lower temperature. The quality of dried shrimp stored at $10 \pm 2^\circ\text{C}$ was still acceptable during 14 weeks of storage.

Therefore, citric acid incorporated with vacuum package and low temperature storage at $10 \pm 2^\circ\text{C}$ gave the best quality, and prolonged the shelf-life of dried shrimp for more than 14 weeks.

Conclusions

1. Citric acid was appropriated to produce the good quality of dried shrimp.
2. Shelf life of dried shrimp with 0.1% citric acid, vacuum packed and stored at $10 \pm 2^\circ\text{C}$ was longer than 14 weeks. Whereas the shelf life of dried shrimp without citric acid, air packed and kept at $30 \pm 2^\circ\text{C}$ was only 8 weeks.
3. Colour measurement (L,a,b system) could be applied for astaxanthin content by using the linear regression equation: $Y = 1.54 + 0.51a - 0.14b$, when $Y =$ astaxanthin, $a =$ a(hue), $b =$ b (chroma).

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Table 1. Moisture content (%) of dried shrimp at various citric acid concentrations during 4 weeks.

Storage time (weeks)	Moisture content (%)			
	Concentrations of citric acid (%)			
	0	0.1	0.3	0.5
0	22.62 ^{de} ± 0.12	19.13 ⁱ ± 0.12	23.47 ^{bc} ± 0.10	24.47 ^a ± 0.03
1	21.94 ^f ± 0.21	19.01 ^j ± 0.15	23.54 ^{bc} ± 0.09	23.13 ^{ad} ± 0.11
2	21.06 ^g ± 0.16	20.15 ⁱ ± 0.29	24.68 ^a ± 0.18	23.25 ^{bc} ± 0.31
3	20.94 ^{gh} ± 0.29	19.18 ^j ± 0.16	23.31 ^{bc} ± 0.07	23.29 ^{bc} ± 0.24
4	20.43 ^{bi} ± 0.12	19.06 ⁱ ± 0.27	22.45 ^{ef} ± 0.21	23.73 ^b ± 0.19

a.....i are significantly different ($P \leq 0.05$).

Table 2. Water activity (A_w) of dried shrimp at various citric acid concentrations during 4 weeks.

Storage time (weeks)	Water activity (A_w)			
	Concentrations of citric acid (%)			
	0	0.1	0.3	0.5
0	0.78 ^d ± 0.02	0.76 ^{ef} ± 0.01	0.80 ^{ab} ± 0.01	0.08 ^{bcd} ± 0.01
1	0.77 ^e ± 0.02	0.75 ^{fg} ± 0.02	0.80 ^{ab} ± 0.01	0.78 ^{cd} ± 0.01
2	0.75 ^{fg} ± 0.01	0.76 ^{ef} ± 0.01	0.81 ^a ± 0.01	0.80 ^{ab} ± 0.01
3	0.75 ^{ef} ± 0.01	0.76 ^{fg} ± 0.02	0.81 ^a ± 0.01	0.79 ^{bc} ± 0.01
4	0.73 ^h ± 0.01	0.74 ^{gh} ± 0.01	0.79 ^{cd} ± 0.01	0.78 ^{cd} ± 0.01

a.....h are significantly different ($P \leq 0.05$).

Table 3. Astaxanthin content (unit per gram dried weight) of dried shrimp at various citric acid concentration during 4 weeks.

Storage time (weeks)	Astaxanthin content (unit per gram dried weight)			
	Concentrations of citric acid (%)			
	0	0.1	0.3	0.5
0	4.14 ^b ± 0.05	4.23 ^a ± 0.03	4.28 ^a ± 0.01	4.28 ^a ± 0.05
1	3.35 ^c ± 0.04	3.34 ^c ± 0.01	3.35 ^c ± 0.04	3.36 ^c ± 0.01
2	3.03 ^f ± 0.03	3.11 ^e ± 0.01	3.21 ^d ± 0.01	3.14 ^e ± 0.04
3	2.57 ⁱ ± 0.05	2.65 ^h ± 0.01	2.74 ^g ± 0.03	2.63 ^h ± 0.02
4	2.05 ^l ± 0.01	2.30 ^j ± 0.07	2.27 ^j ± 0.02	2.16 ^k ± 0.06

a.....l are significantly different ($p \leq 0.05$)

Table 4. Ammonia content (ppm) of dried shrimp at various citric acid concentrations during 4 weeks.

Storage time (weeks)	Ammonia content (ppm)			
	Concentrations of citric acid (%)			
	0	0.1	0.3	0.5
0	32.59 ^g ± 3.77	14.54 ^{hi} ± 4.41	20.28 ^h ± 4.14	11.37 ⁱ ± 2.94
1	62.49 ^d ± 1.96	31.82 ^g ± 1.17	51.94 ^e ± 1.31	41.83 ^f ± 2.64
2	100.05 ^a ± 1.06	40.56 ^f ± 1.88	60.01 ^d ± 1.10	59.82 ^d ± 1.48
3	98.65 ^a ± 2.62	42.05 ^f ± 3.80	70.52 ^c ± 2.21	71.96 ^c ± 3.15
4	95.00 ^a ± 3.07	44.29 ^f ± 2.06	79.20 ^b ± 3.15	78.72 ^b ± 3.96

a.....i are significantly different ($P \leq 0.05$).

Table 5. pH of dried shrimp at various citric acid concentration during 4 weeks.

Storage time (weeks)	pH			
	Concentrations of dried shrimp(%)			
	0	0.1	0.3	0.5
0	8.18 ^d ± 0.01	8.16 ^d ± 0.03	8.18 ^d ± 0.03	8.15 ^d ± 0.01
1	8.32 ^b ± 0.02	8.38 ^{ab} ± 0.05	8.34 ^b ± 0.02	8.33 ^b ± 0.01
2	8.44 ^a ± 0.01	8.49 ^a ± 0.01	8.51 ^a ± 0.02	8.48 ^a ± 0.02
3	8.31 ^c ± 0.06	8.25 ^c ± 0.09	8.24 ^c ± 0.07	8.33 ^c ± 0.04
4	8.38 ^{bc} ± 0.01	8.29 ^{bc} ± 0.01	8.33 ^{bc} ± 0.02	8.27 ^{bc} ± 0.03

a.....d are significantly different ($P \leq 0.05$).

Table 6. Sensory evaluation scores of dried shrimp at various citric acid concentrations

Storage time (weeks)	Overall acceptability scores			
	Concentrations of dried shrimp(%)			
	0	0.1	0.3	0.5
0	4.23 ^a	4.47 ^a	4.48 ^a	4.60 ^a
1	3.79 ^a	4.18 ^a	4.10 ^a	4.42 ^a
2	3.45 ^b	3.76 ^b	3.69 ^b	3.84 ^b
3	2.47 ^c	2.75 ^c	2.54 ^c	2.83 ^c

a.....c are significantly different (p≤0.05)

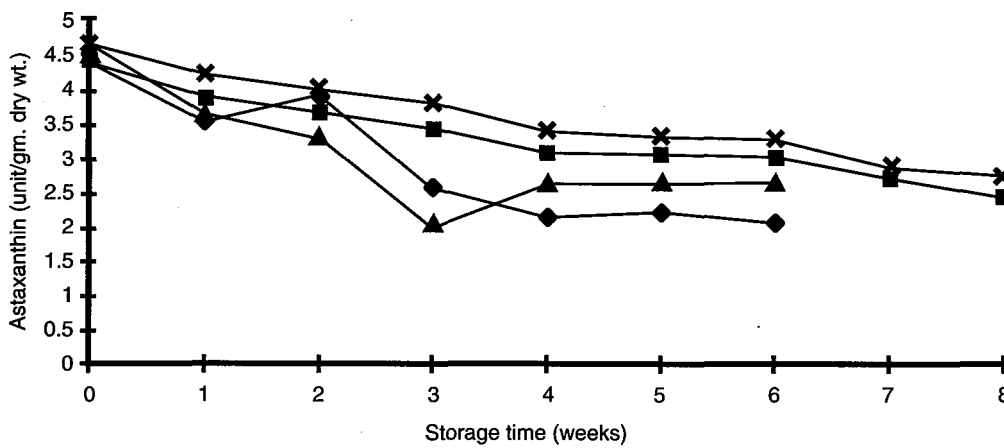


Fig. 3. Astaxanthin content of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at 30±2°C.

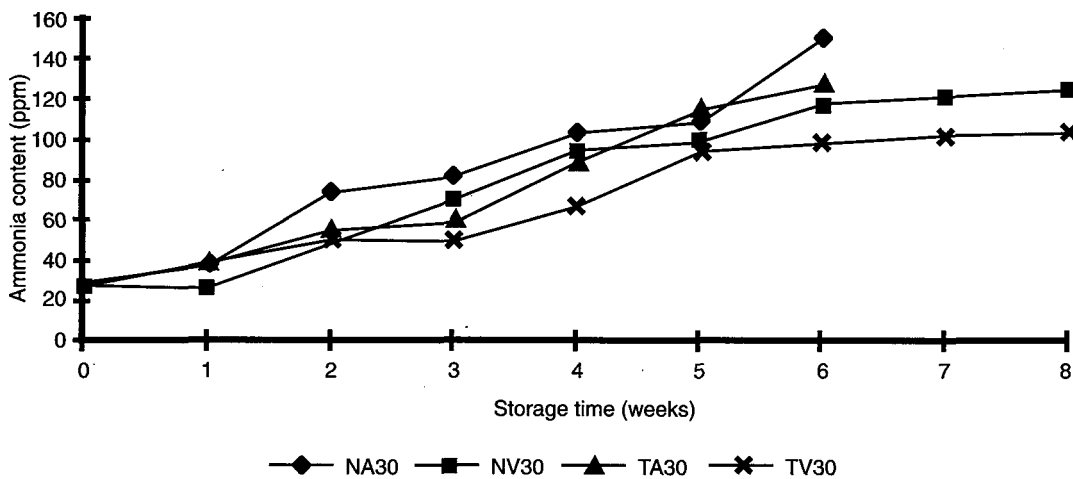


Fig. 4. Ammonia content of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at 30 ± 2°C.

NA30 = No treatment, atmospheric condition, 30°C; NV30 = No treatment, vacuum condition, 30°C; TA30 = Citric acid treatment, atmospheric condition, 30°C; TV30 = Citric acid treatment, vacuum condition, 30°C.

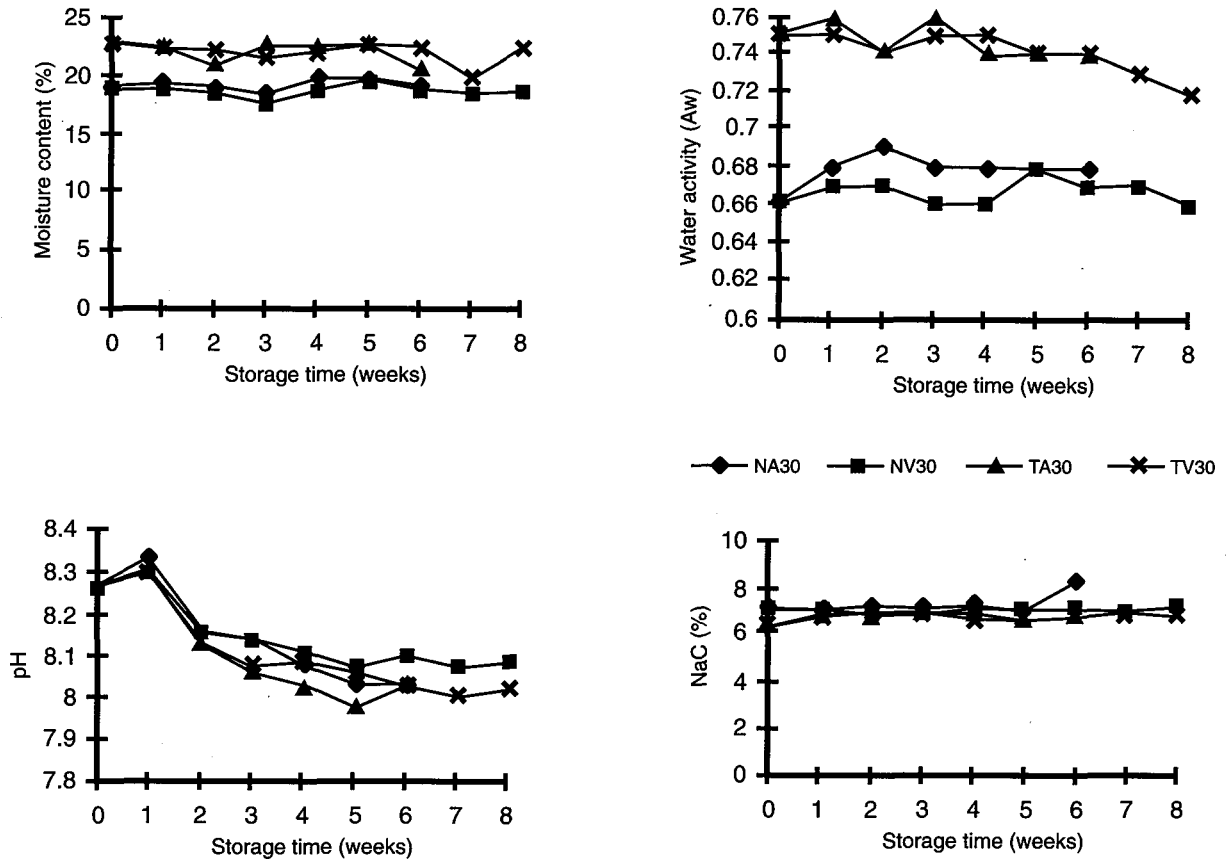


Fig. 5. Moisture, A_w , pH and sodium chloride content of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at $30 \pm 2^\circ\text{C}$. NA30 = No treatment, atmospheric condition, 30°C ; NV30 = No treatment, vacuum condition, 30°C ; TA30 = Citric acid treatment, atmospheric condition, 30°C ; TV30 = Citric acid treatment, vacuum condition, 30°C .

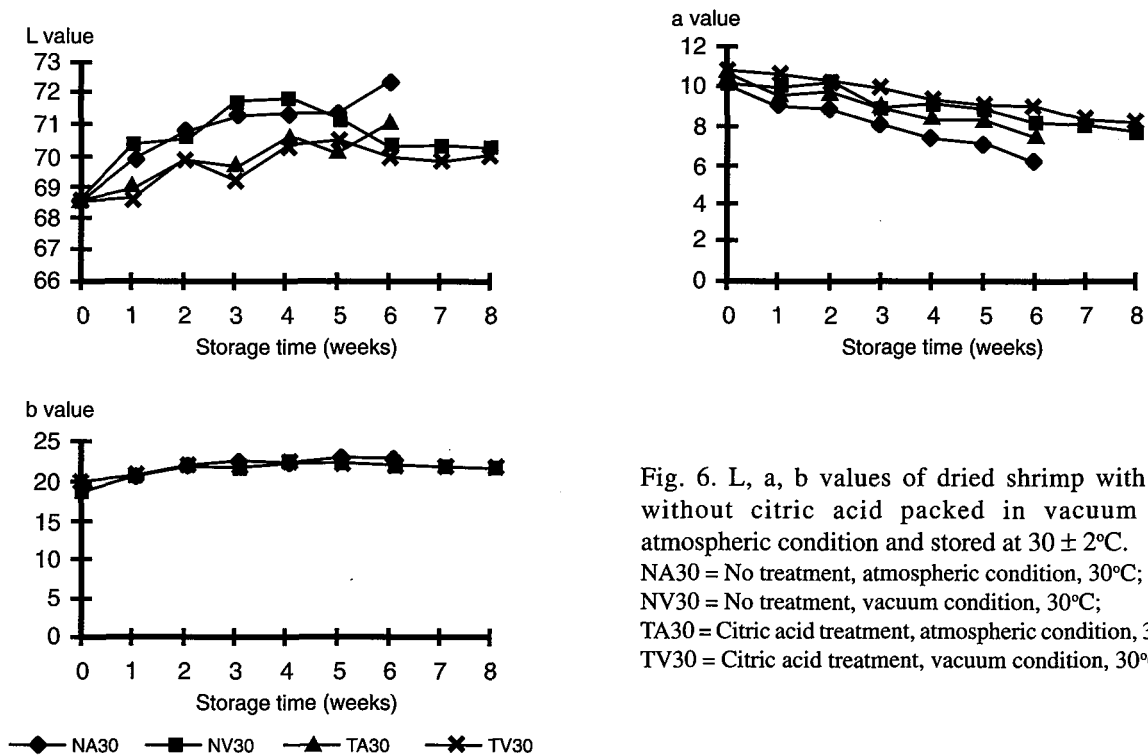


Fig. 6. L, a, b values of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at $30 \pm 2^\circ\text{C}$. NA30 = No treatment, atmospheric condition, 30°C ; NV30 = No treatment, vacuum condition, 30°C ; TA30 = Citric acid treatment, atmospheric condition, 30°C ; TV30 = Citric acid treatment, vacuum condition, 30°C .

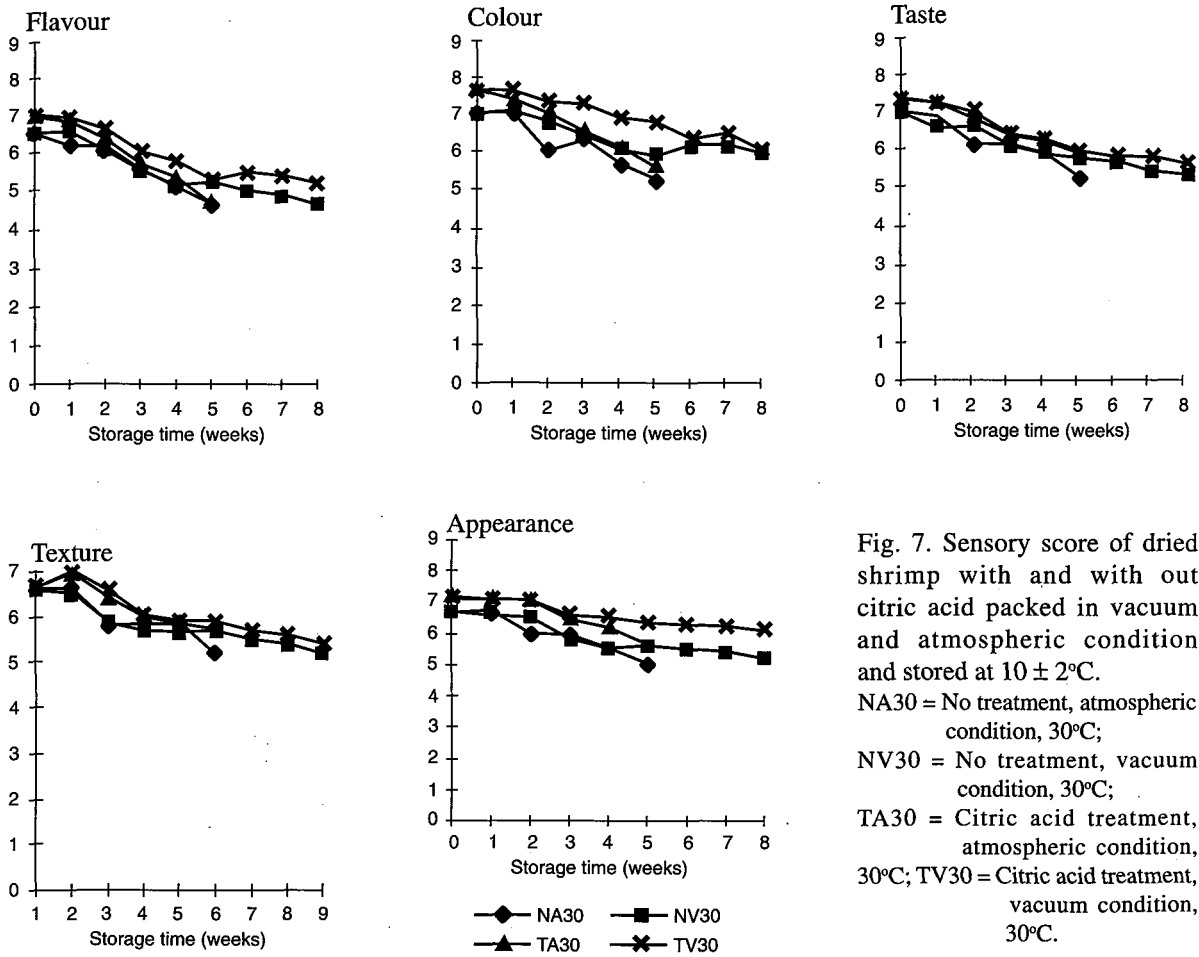


Fig. 7. Sensory score of dried shrimp with and with out citric acid packed in vacuum and atmospheric condition and stored at $10 \pm 2^\circ\text{C}$.
 NA30 = No treatment, atmospheric condition, 30°C ;
 NV30 = No treatment, vacuum condition, 30°C ;
 TA30 = Citric acid treatment, atmospheric condition, 30°C ;
 TV30 = Citric acid treatment, vacuum condition, 30°C .

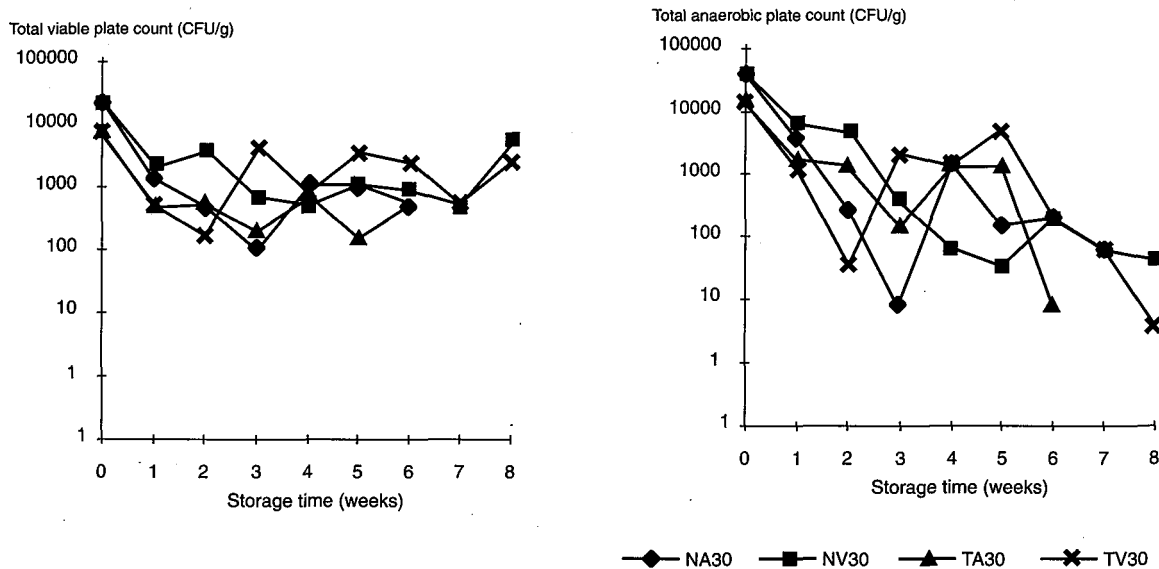


Fig. 8. Total viable plate count and anaerobic plate count of dried shrimp with and without citric acid packed in vacuum and atmospheric conditions and stored at $30 \pm 2^\circ\text{C}$.
 NA30=No treatment, atmospheric condition, 30°C ; NV30=No treatment, vacuum condition, 30°C ; TA30= Citric acid treatment, atmospheric condition, 30°C ; TV30= Citric acid treatment, vacuum condition, 30°C .

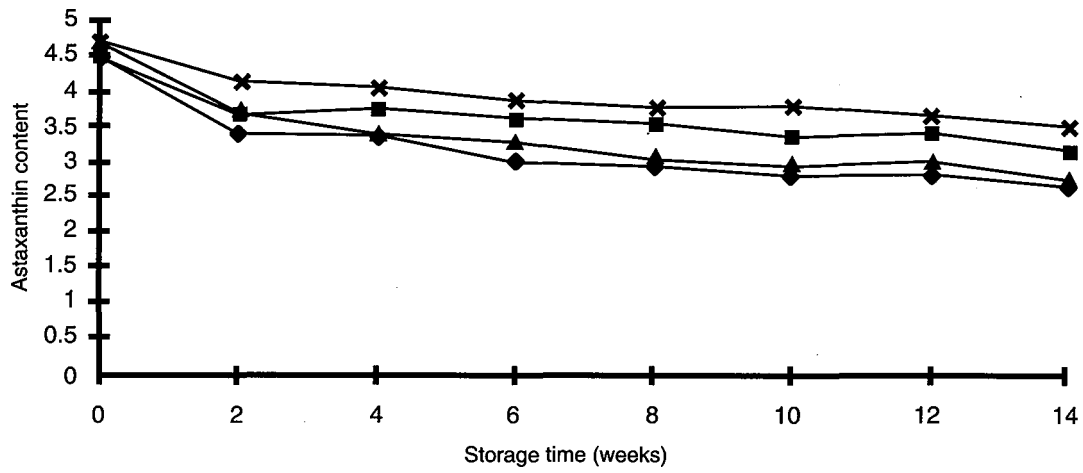


Fig. 9. Astaxanthin content of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at $10 \pm 2^\circ\text{C}$.

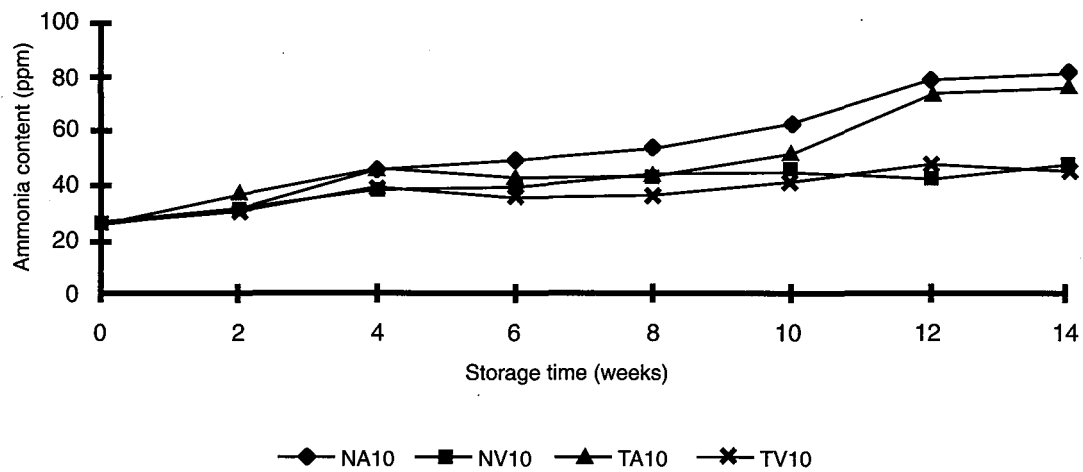


Fig. 10. Ammonia content of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at $10 \pm 2^\circ\text{C}$.

NA10 = No treatment, atmospheric condition, 10°C ; NV10 = No treatment, vacuum condition, 10°C ; TA10 = Citric acid treatment, atmospheric condition, 10°C ; TV10 = Citric acid treatment, vacuum condition, 10°C .

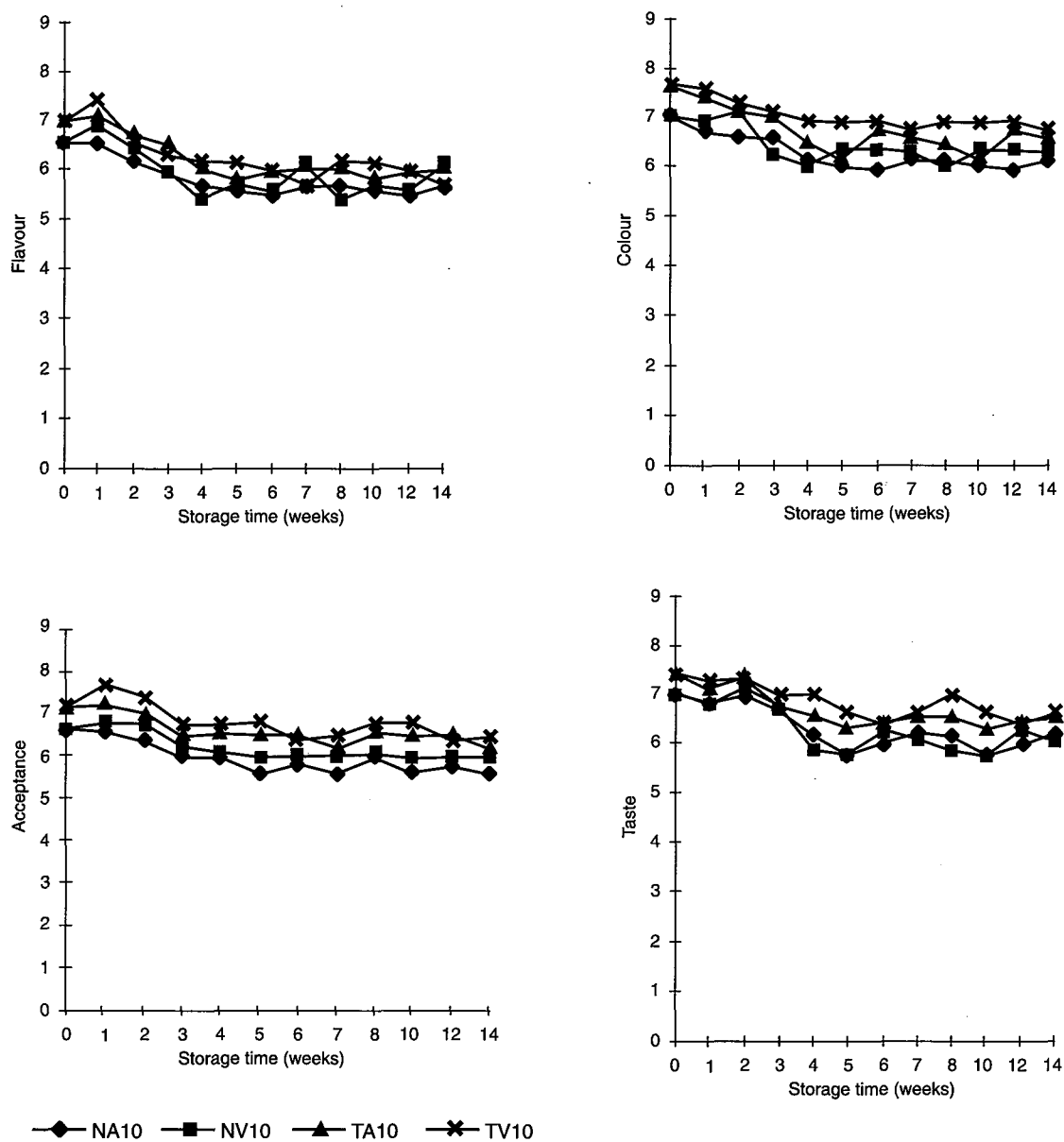


Fig. 11. Sensory score of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at $10 \pm 2^\circ\text{C}$.
 NA30 = No treatment, atmospheric condition, 30°C ;
 NV30 = No treatment, vacuum condition, 30°C ;
 TA30 = Citric acid treatment, atmospheric condition, 30°C ;
 TV30 = Citric acid treatment, vacuum condition, 30°C .

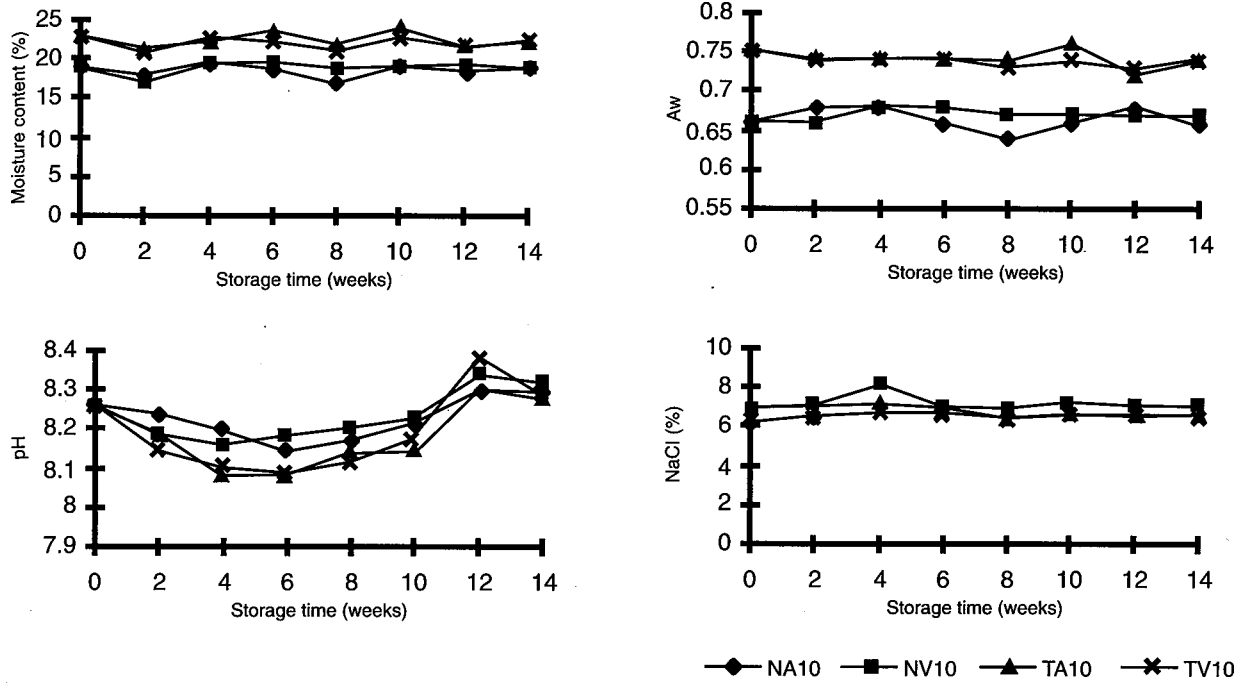


Fig. 12. Moisture, A_w , pH and sodium chloride content of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at $10 \pm 2^\circ\text{C}$.

NA10 = No treatment, atmospheric condition, 10°C ; NV10 = No treatment, vacuum condition, 10°C ; TA10 = Citric acid treatment, atmospheric condition, 10°C ; TV10 = Citric acid treatment, vacuum condition, 10°C .

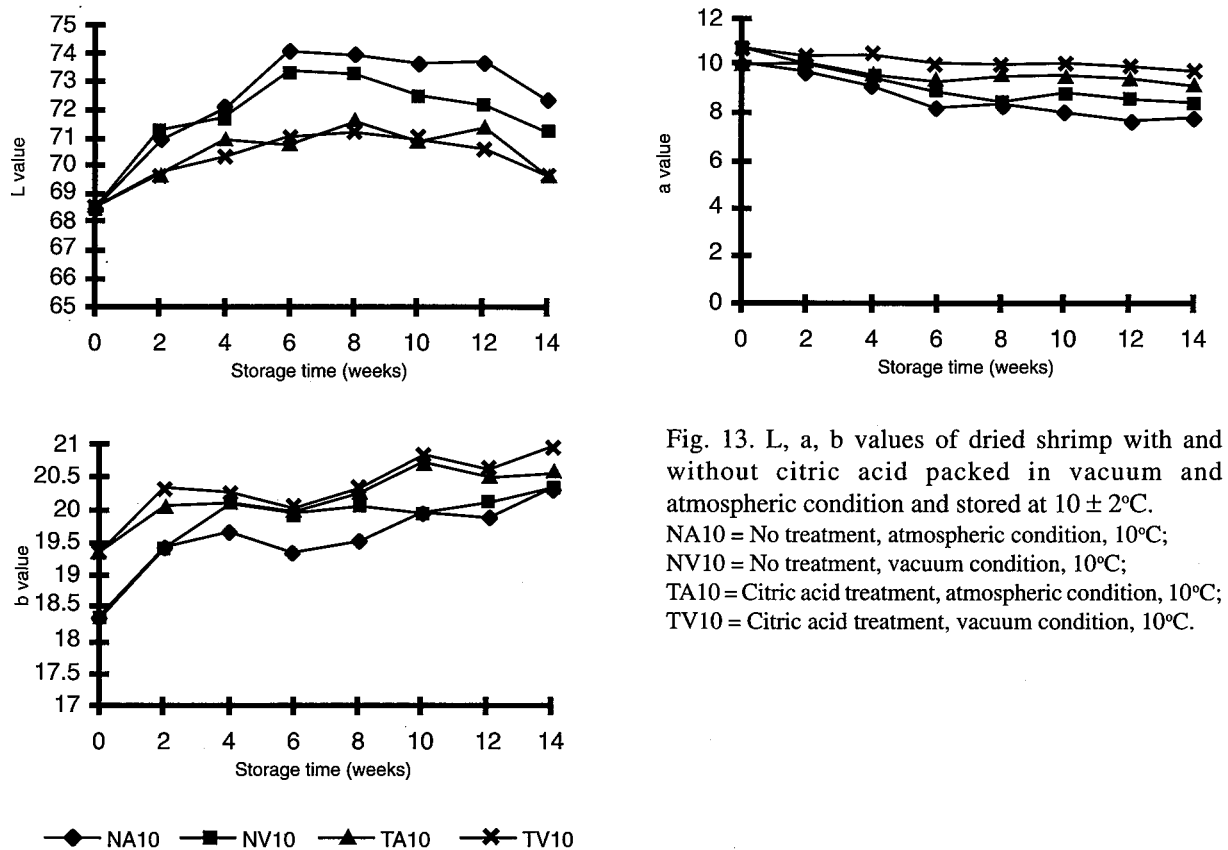


Fig. 13. L, a, b values of dried shrimp with and without citric acid packed in vacuum and atmospheric condition and stored at $10 \pm 2^\circ\text{C}$.

NA10 = No treatment, atmospheric condition, 10°C ; NV10 = No treatment, vacuum condition, 10°C ; TA10 = Citric acid treatment, atmospheric condition, 10°C ; TV10 = Citric acid treatment, vacuum condition, 10°C .

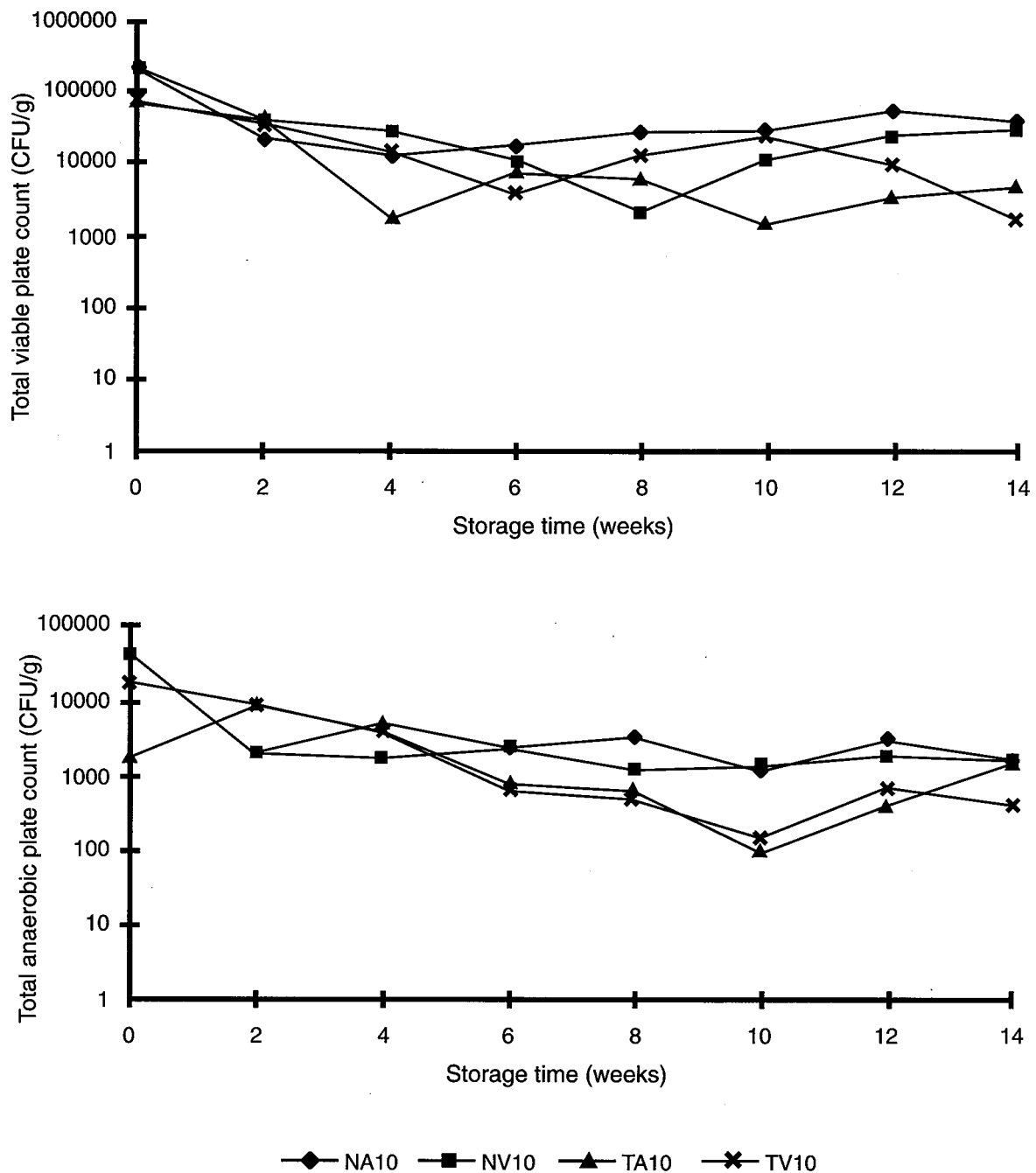


Fig. 14. Total viable plate count and anaerobic plate count of dried shrimp with and without citric acid packed in vacuum and atmospheric conditions and stored at $10 \pm 2^\circ\text{C}$.
 NA10 = No treatment, atmospheric condition, 10°C ; NV10 = No treatment, vacuum condition, 10°C ; TA10 = Citric acid treatment, atmospheric condition, 10°C ; TV10 = Citric acid treatment, vacuum condition, 10°C .