Determination of the total sodium metabisulphide level of shrimps (*Parapenaeus longirostris*) sold in Tekirdag

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Abstract. Shrimps, despite their high nutritional value, are aqua product forms that can spoil fast. After the hunting, spoil reactions become visible with darkened color. To prevent the emergence of this situation, the most popular method is application of sodium metabisulphide. Nonetheless this chemical has critical threats for health; hence particular attention must be paid in the use of shrimps. Present study aims to determine the amount of sodium metabisulphide residuals in the shrimps on market sale and compare with the approved limit of use by the Ministry of Food, Agriculture and Livestock. In our study the amount of sodium metabisulphide residuals in the shrimps sold within 40 different companies in Tekirdag has been investigated and obtained data have been statistically evaluated. Analyzed data manifested that although the amounts of sodium metabisulphide residuals in some samples were high, almost all samples were within the approved limit of sodium metabisulphide amount.
Key Words: shrimp, sodium metabisulfite, melanosis, impact.

Aims and background. Belonging to Crustacea class Decapoda team shrimps are shelled aqua products with high economic value. Shrimps' body consists of two main parts namely head-chest and ventral. With a fan-like tail on its end, ventral is the edible part. Shrimps meat is a valuable food with high protein content (18-20%) and easy to digest thanks to its weak connective tissue. It is, on top of that, a perfect source of selenium and vitamins D and B_{12}. Lastly it is a low-calorie food thanks to its low fat level (Bascinar 2004).

Shrimps are ubiquitous with their thousands of species in freshwater, hard water and seas. Approximately 300 species possess commercial value. Turkish seas are rich in shrimps. Up to present day, 61 species have been identified in Turkish seas. Seven of these species are: *Penaeus japonicus*, *Penaeus semisulcatus*, *Penaeus kerathurus Metapenaeus monoceros*, *Metapenaeus stebbingi, Trachypenaeus curvirostris,* and *Parapenaeus longirostris,* categorized as commercially valuable. Among them the most profitable species are *P. japonicus, P. semisulcatus* and *P. longirostris* (Kumlu et al 1999). The records manifest that global shrimps production via hunting was 4 096 120 tones in 1999 and 4 271 812 tones in 2002 (Colakoglu et al 2006). In Turkey shrimps production corresponding to 890 tones in 1999 rose to 4614 tones in 2009 and climbed to 5038 tones in 2012. In Turkey 2013-dated total of shrimps exportation was 1209 tones and this condition granted an income exceeding 5 million dollars (Anonymous 2013).

Shrimps, despite their high nutritional value, are aqua product forms that can spoil fast. Soon after being caught shrimps are exposed to a remarkably fast process of spoil due to the activation of bacteria and original enzymes (autolysis). Color darkening that occurs in the very aftermath of hunting is the major problem of shrimp traders. Known as “Melanozis” or “Black Spot” and degrading the quality badly, this transformation takes place as a result of the enzymatic deterioration triggered by oxygen in the air and light. Melanozis is induced by a biochemical mechanism oxidizing the phenols to quinones by polyphenoloxidase. Next, to obtain high molecular weighted dark-colored pigments, there is non-enzymatic polymerization of quinones. Melanozis (black spot) has no danger for consumer health but has lowering effect on product's acceptability and its market value (Varlik et al 2007). Aside from darkening, during the process of storing, color odor and shape changes can occur instantly due to microorganism activities. Compared to the fish, shelled animals contain higher amounts of free amino acids which make these products more susceptible to spoil (Cakli & Kisla 2003). Alkali quality of shrimp meat and high content level of water activity are also drivers of microbial-growth (Varlik 1993). Despite having low level of fat, shrimps' lipids contain high levels of polyunsaturated fat acids thus during conservation (frozen products in particular) fat oxidization is more sensitive. Oxidization causes physico-chemical changes, rancidity and bad taste in shrimps (Bak et al 1999).

To prevent the darkening of shrimps, melanozis inhibitors are put into practice. Sulfides and its derivatives (sodium metabisulphide most frequently) are the most widely used polyphenoloxidase (PPO) inhibitors. It is also argued that these agencies are likely to fuel allergic reactions and a number of disorders among its users. On the other hand insensible use of approved amounts of these agents may result in the accumulation of high levels of residuals that might be threatening for human health (Erkan et al 2007). As alternative agents 4-hexylresorcinol, ascorbic acid, kojik acid, ficin, citric acid, dodecyl gallat, oxalite acid, grape seed extract, ferulic acid have been tested; overall results were good despite specific disadvantages for each agent (Selcuk & Ozden 2014; Gokoglu & Yerlikaya 2007; Montero et al 2004; Nirmal & Benjakul 2009). Melanozis is delayed when shrimps are frozen immediately but continues when the products are unfrozen (Lopez-Caballero et al 2007).

In Turkey sodium metabisulphide is the most common additive used to prevent darkening in shrimps and applied by solving in water. Shrimps are, while still in the boat after hunting, treated with this solution and driven to the market after treatment. Therefore it becomes hard to trace the procedures of treatment and particularly the level of sodium metabisulphide used in the treatment. Only in the final product can the level of residual level be measured. This level is not to exceed the approved limits. Applicable regulation enforces that in the edible part of uncooked shrimps, sodium metabisulphide level in SO_2 class is maximum 150 mg kg^{-1} level and in cooked products, this figure can reach to maximum 50 mg kg^{-1} level (Anonymous 2008). Rotllant et al (2002) claim that parallel to the rise in sulfite concentration the residual level in shrimps climbs up. In addition they have also reported that less than 10% of sulfides can penetrate into edible parts and when used within reasonable levels residual levels are also within the legal limits. Insensible use of these agents may bring about high residual levels in the products. In present study sodium metabisulphide levels of a variety of shrimp samples collected from the market have been detected and compared with the approved limits in the relevant legislation to check their fitness.

Experimental. Shrimp samples in fresh form (Marmara shrimps; *Parapenaeus longirostris*) used in the research were collected from 40 distinct fish companies in Tekirdag and when still cold, transported shortly to the laboratory where the analysis would be executed. In the edible parts of shrimps, sodium metabisulphide residual amount in SO_2 form was detected when the product was uncooked. To achieve that, TS 8131 method was utilized (Anonymous 1990). The main principle of this method is, sulphur dioxide which is formed after distillation by using nitrogen gas as carrier, accumulated in hydrogen peroxide solution and after transforming into sulfuric acid here it is tittered in an adjusted base. In shrimp samples, sodium metabisulphide levels measured as SO_2 class are expressed as mg kg^{-1} and analyses have been conducted as 3- parallel format.

Results and Discussion. Sodium metabisulphide levels measured in shrimp samples are as shown in Table 1 and Figure 1.

Findings of our research manifest that there is no sodium metabisulphide in 9 samples and the amount of this agent varies between 10.32 mg kg^{-1} to 130.59 mg kg^{-1} in other samples. In none of the samples sodium metabisulphide residual level exceeded the approved limit of 150 mg kg^{-1}. The differences in residual levels among the samples indicate that there is no standard in the use of sodium metabisulphide. It is still good news for the consumers that all samples are within the approved residual limits.

There is a wide range of studies on detecting sodium metabisulphide residual levels in shrimp samples. Erkan et al (2007) in their study collected shrimp samples from 36 distinct fish sellers in İstanbul to measure sodium metabisulphide residual levels. They have concluded that in the edible part of uncooked products, residual levels changed from 36 mg kg^{-1} to 350 mg kg^{-1}. They have also ascertained that 2 shrimp samples exhibited residual levels exceeding the approved range. In the very same research, they cooked shrimp samples and detected that after cooking these values changed between 8.8 and 281.23 mg kg^{-1} (Erkan et al 2007).

Table 1

Sodium metabisulphide levels in shrimps (Bascinar 2004)

Sample	*Sodium metabisulphide (as SO_2 class, mg kg^{-1})*	*Sample*	*Sodium metabisulphide (as SO_2 class, mg kg^{-1})*
1	71.21±3.48	21	*
2	*	22	14.57±0.21
3	44.81±2.01	23	25.87±1.31
4	130.59±8.65	24	31.05±1.44
5	123.91±7.32	25	33.10±2.10
6	*	26	13.41±1.01
7	110.01±5.95	27	*
8	14.93±0.12	28	14.51±0.96
9	21.35±0.97	29	27.01±1.09
10	32.98±1.01	30	66.40±2.41
11	*	31	19.47±1.11
12	*	32	32.91±2.03
13	10.32±0.10	33	27.08±1.85
14	*	34	*
15	*	35	31.06±1.55
16	19.83±0.66	36	62.71±2.47
17	26.64±0.84	37	29.83±1.20
18	30.61±1.23	38	45.90±2.11
19	24.29±1.19	39	72.11±3.95
20	24.08±1.46	40	41.53±2.83

Values (±) represent the standard deviation; *could not be identified.

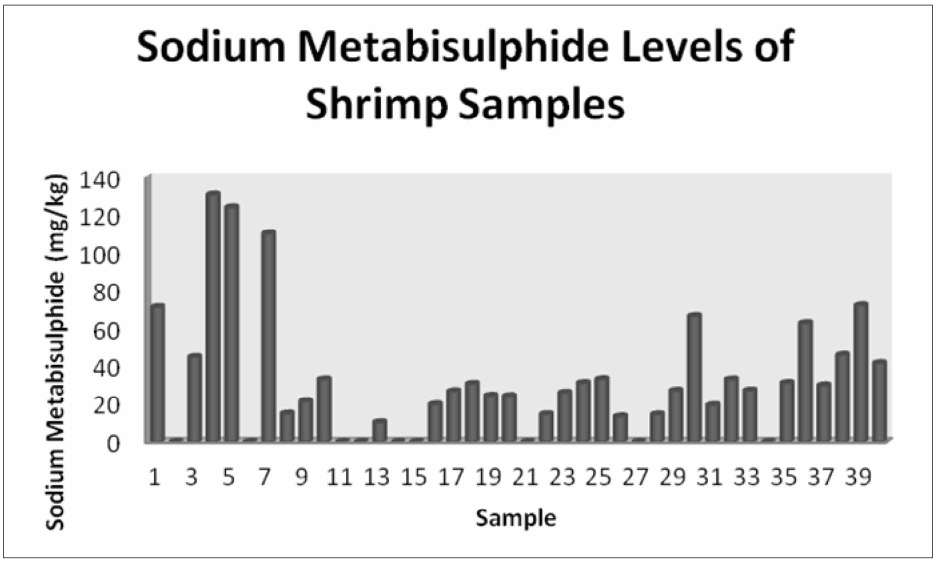

Figure 1. Sodium metabisulphide levels in shrimps.

In a study conducted in Spain it was found out that sulfide levels in the edible parts of 80 frozen shrimp samples varied between 10.7 mg kg^{-1} and 546 mg kg^{-1} and a great number of samples contained sulfide residual higher than 150 mg kg^{-1} (Hardisson et al 2002).

Weingartner et al (1977) investigated shrimps' storing at 2°C and the changes witnessed sodium metabisulphide residual levels during this process and determined that

5-minute of sinking into a 1.25% solution, 25 mg kg^{-1} sulfide residual emerged in the meat and at the end of a 15-day of storage this level decreased to 0 mg kg^{-1}. With the 5% solution application of sodium metabisulphide it was determined that residual level in shrimps indicated 110 mg kg^{-1} and the same figure fell to 45 mg kg^{-1} after 15-days of storage.

Conclusions. Shrimps, as the other aqua products, are highly nutritional and also financially valuable shelled sea products. Nonetheless spoil process starts immediately after being hunted from the sea and spreads in quite a short span of time. The foremost of these spoil reactions is darkening by enzymatic ways. A diverse number of studies have been put forth to delay the color darkening in shrimps and to achieve that objective hexylresorcinol, organic acid and plant extract solutions etc. have been used as alternative options for sodium metabisulphide. None of these agents proved to be as effective as sodium metabisulphide. As is the case for any other food additives, there is a certain limit in the application of sodium metabisulphide. Since the use of this chemical is outside the company, its control and track become really hard. In this case, in the ready-to-ear final product, there emerge sodium metabisulphide residuals in a variety of concentrations. In current study, residual levels in different shrimp samples have been investigated and it was concluded that none of the samples exceeded approved limit. Regardless of that compliance however, it would be beneficial to audit the use of this chemical and set control mechanisms to ensure that sodium metabisulphide residual levels of shrimps stay within the approved limits.

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Received: 21 July 2015. Accepted: 20 September 2015. Published online: 31 October 2015.
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How to cite this article:
Uran H., Yilmaz I., 2015 Determination of the total sodium metabisulphide level of shrimps (*Parapenaeus longirostris*) sold in Tekirdag. Ecoterra 12(3):79-83.