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STUDIES ON THE USE OF SULFITES TO CONTROL SHRIMP MELANOSIS (BLACKSPOT)

FLORIDA SEA GRANT COLLEGE

STUDIES ON THE USE OF SULFITES TO CONTROL SHRIMP MELANOSIS (BLACKSPOT)

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SCREENING ALTERNATIVES TO SULFITING AGENTS TO CONTROL SHRIMP MELANOSIS

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INTRODUCTION

Shrimp melanosis, commonly known as 'blackspot' is a harmless but objectionable surface dicoloration caused by polyphenoloxidase enzyme systems which remain active during refrigeration or ice storage. In the early 1950's sulfiting agents, particularily sodium bisulfite was first introduced to prevent or inhibit melanosis, thus yielding a more valuable harvest (1). Such use of sulfites was 'prior sanctioned' by the U.S. Food and Drug Administration (FDA) in 1956 (2). More recent FDA decisions reaffirmed this practice (3), but continuing regulatory scrutiny could restrict or eliminate the application of sulfite on shrimp. The regulatory action is prompted by an increasing concern for adverse 'allergic' reactions most common amongst hyper-(sulfite) sensitive asthmatics. Thus work was initiated to find alternatives to replace or reduce the amount of sulfites required to inhibit shrimp melanosis. This work would screen for possible alternatives which would require subsequent verification with field tests and statistical evaluations.

MATERIAL AND METHODS

Preliminary investigations were necessary to describe the rate and extent of shrimp melanosis. Samples of fresh, untreated white shrimp (Penaeus setiferus) and pink shrimp (P. duorarum) were observed in refrigeration. The occurrence of melanosis was recorded in photographs to establish a subjective scale for comparisons. The white shrimp (harvested off Jacksonville and Apalachicola, FL) did not develop melanosis in a consistent or predictable fashion. Attempts to induce melanosis in white shrimp exposed to elevated oxygen levels in sealed containers or ultraviolet lighting were unsuccessful. The pink shrimp (harveted near Key West, FL) developed melanosis in a predictable fashion usually first evident within 2 days on ice and becoming progressively more prominent during subsequent storage for 14 days. Thus pink shrimp was the choice species for further tests relative to the scale developed to describe melanosis (Table 1). This choice was consistent with the original work by Camber et. al (4) which introduced the use of sulfites through field tests with Key West, pink shrimp.

TABLE 1. Scale used to describe and rate the occurrence of melanosis (black-spot) on pink shrimp.

Melanosis Scale	
0	Absent
2	Slight, noticeable on some shrimp
4	Slight, noticeable on most shrimp
6	Moderate, noticeable on most shrimp
8	Heavy, noticeable on most shrimp
10	Heavy, totally unacceptable

TABLE 2. Compounds used individually and in mixtures to prepare dips for treating fresh pink shrimp to control melanosis.

Compound	Comments
Sodium Bisulfite	Reducing agent
Sodium Bicarbonate	Baking soda
Potassium Bromate	Oxidizing agent; interact sulphydial transport bonds
Calcium Chloride	Geling agent; interfer oxygen
Erythrobate	Acidulant, chelator, reducing agent
Ascorbic Acid	Acidulant; antioxidant
Boric Acid	Acidulant
Citric Acid	Acidulant, antioxidant, chelator
Phosphoric Acid	Acidulant
Sodium Tripolyphosphate	Water control, sequestrant
Disodium phosphate	Water control, buffer
Sodium Hexametaphosphate	Water control, sequestrant
Ehtylene Diamine Tetra Acetate	Chelator
Glycine	Complex with quinones
Taurine	Bond sulfonic acid
Formaldehyde	Complex with proteins
Hydrogen Peroxide	Oxidizing and bleaching
BL7*	Sulfite (67%) + phosphate + erythrobate + phosphates + citrate + tartrate + glutamate + tryptophan (descending order)

*Composition of BL7 provided by letter (1978) from Food Chemistry Division, Environmental Sanitation Bureau, Ministry of Health and Welfare, Japanese Government.

SO/ts/3.22

The melanosis scale can be related to existing recommendations developed by the National Marine Fisheries Service for grading raw shrimp (5). A scale rating of 4 or greater represents a measurable defect in product quality. A rating of 8 or greater would represent a severe defect, approaching unacceptable product.

Harvests were arranged such that the investigators obtained fresh, heads-on pink shrimp while working on the vessel or within less than 12 hours post-harvest at the dock. All shrimp were routinely washed on-board and temporarily stored in ice. The basic experimental procedure was to rinse 400-600 grams of shrimp in 2.5 liters of variable dip compositions and concentrations for 1 minute, then drain and package in plastic bags to be stored in ice. The bags were considered necessary to eliminate the variable influence of melting ice. Iced containers with packaged shrimp were stored in 35°F (1.7°C) refrigeration, and reicing every other day.

Development of melanosis was scored and photographed routinely during 2 weeks storage. The bags of shrimp had been numbered such that the investigator could not distinquish amongst the various treatments. One experienced investigator did all scoring relative to the aforementined scale (Table 1). The scale was accompanied by pre-developed color prints depicting common examples of the advancing stages for melanosis. The intent was to screen for obvious differences between treatments, thus selecting the best treatments for subsequent tests with statistical evaluations.

The various dips or chemical treatments included controls (no treatment), customary sodium bisulfite used in varying concentrations, and a variety of single compounds and/or mixtures prepared in varying concentrations (Table 2). The dip solution was fresh tap water.

Two field trials (I and II) were necessary to accomodate all the variable treatments. Trial I was for shrimp harvested 6/26/85 and Trial II commenced 12/13/85. Water temperatures and atmospheric conditions were clear and similar in Key West during both harvests. The common practice for pink shrimp is night harvest, thus avoiding influence of sunlight. One set of controls (no treatment) and bisulfite treatments were included for each trial to account for any variations amongst shrimp per harvest. Trial II included an additional series of treatments using 3.5% saltwater as the dip solution. The saltwater was made from the same source of fresh tapwater plus 3.5% commerical marine (aquarium) salts.

RESULTS AND DISCUSSION

Preliminary experience in developing a rating scale with accompanying photographs depicting the degrees for melanosis

proved successful. Rating for controls and bisulfite treatments were similar for both trials (compare Table 3 and 4). Melanosis on pink shrimp seem to progress in a linear manner. In controls, melanosis was obvious within 3 days, becoming a defect within 5 days, and approaching a severe defect (unacceptable) on day 7. Thus pink shrimp was a practical test species as opposed to white shrimp which in some instances did not display melanosis.

All bisulfite treatments (0.25 to 2.50% dips) inhibited the onset of melanosis (Talbe 3 and 4). The most effective concentration was 2.50%, thus demonstrating the encouragement for employing treatments in excess of the legally recognized 1.25% dip for 1 minute. The 1.25% bisulfite dip inhibited melanosis until blackening was only slightly noticable on some shrimp after 12 days storage. Melanosis increased to a measureable defect on day 12 after treating with 0.25 and 0.50% dip concentrations.

No treatments in Trial I were as effective as 1.25% sodium bisulfite. The next effective treatment was the commercial preparation, BL7. The inhibitor influence of BL7 at a dip strength of 1.0% was similar to sodium bisulfite at 0.50%. This is expected relative to the formulation for BL7 which is 67.2% sodium hydrogen sulfite. Thus a 1.0% BL7 dip contains the equivalent of 0.67% sodium bisulfite.

A variety of chemical combinations (treatments no. 4-8) provided initial inhibition still evident on the 7th day of storage (Table 3). All of these mixtures contained some level of bisulfite (0.25 or 0.50%). After 12 days storage, shrimp from all these treatments exceeded a score of 6 and some were judged unacceptable. Thus the influence of the other constituents (Asc, DSP, EDTA, SHP, or STP) did not enhance the influence of bisulfite over that recorded for similar, individual bisulfite treatments (0.25 and 0.50%). This suggests the bisulfite provided the dominant influence in these mixtures. The mixture which included ascorbate (treatment no. 4) appeared to have an objectionable yellow tint obvious on day 3.

All remaining dips in Trial I (treatment nos. 9-17) resulted in melanotic shrimp scored within the 3rd day of storage (Table 3). Despite the early onset of melanosis after dips with STP (4.0 and 8.0%) and Ery/EDTA (1.0/0.1%), the final melanosis rating on day 12 did not exceed 6, suggesting some partial control. The adverse results after sodium bicarbonate dips dispell some fishermen's common belief that baking soda can prevent melanosis. Treatments with calcium chloride, hydrogen peroxide and potassium bromate promoted melanosis.

Results from Trial II reaffirm the distinct influence of bisulfite dips (Table 4). Again, the mixtures which were less effective, but approximating the influence of bisulfite dips,

TABLE 3. Trial I. Ratings for the occurrence of melanosis on pink shrimp in refrigerated storage (per day) after treatment in a variety of dips for 1 minute. The dip solution was fresh tapwater. After controls the treatments are numbered and placed in a general order for decreasing effectiveness.

Trt. No.	Dips %	Day Storage 3	7	12
1.	Control (No dip)	2-3	7-9	10
2.	Sodium Bisulfite			
	0.25	2	3	6
	0.50	0	0	3
	1.25	0	0	2
	2.50	0	0	0
3.	BL 7 (Commercial)			
	0.25	0	3	6
	0.50	0	3	6
	1.00	0	0	5
4.	Bis/EDTA/Asc			
	0.5/0.1/1.0	2	3	6
	0.25/0.1/1.0(y)	0	4	6
5.	Bis/STP			
	0.5/2.0	0	2	8
	0.5/5.0	0	3	6
	0.25/2.0	2	4	7
	0.25/5.0	0	3	9
6.	Bis/EDTA/DSP			
	0.5/0.1/1.0	0	4	7
	0.5/0.1/2.0	0	4	6
	0.5/0.1/4.0	0	5	8
7.	Bis/EDTA/STP			
	0.25/0.1/2.0	0	5	8
	0.25/0.2/2.0	2	5	9
	0.25/0.2/5.0	0	4	8
	0.25/0.1/5.0	0	4	7
	0.50/0.1/2.0	0	4	7
	0.50/0.2/5.0	0	4	9
8.	Bis/EDTA/SHP			
	0.5/0.1/1.0	0	4	9
	0.5/0.1/4.0	2	6	10
9.	Ery/EDTA			
	1.0/0.1	2	4	6
10.	STP			
	2.0	3	6	10
	4.0	2	4	6
	8.0	2	4	6
11.	Phosphoric Acid			
	0.5	3	5	7
	1.0	3	6	10
12.	STP/EDTA			
	2.0/0.1	0	3	10
	2.0/0.2	5	8	10
	4.0/0.1	3	6	10
	4.0/0.2	3	6	10
13.	Sodium Bicarbonate			
	2.0	3	8	8
	4.0	3	8	8
14.	Asc/EDTA			
	1.0/0.1(y)	3	8	10
15.	Calcium Chloride			
	1.0	8	8	10
	2.0	4	6	7
	5.0	6	8	10
16.	Hydrogen Peroxide			
	0.1	6	7	10
	0.5	8	10	10
	1.0	8	10	10
17.	Potassium Bromate			
	0.1	10	10	10
	0.5	10	10	10
	1.0	10	10	10

KEY
Asc = Ascorbic Acid
Bis = Sodium Bisulfite
Cit = Citric Acid
DSP = Disodium Phosphate
EDTA = Ethylene Diamine Tetra Acetate
Ery = Erythrobate
SHP = Sodium Hexameta phosphate
STP = Sodium Tripolyphosphate
BL7 = Commercial melanosis inhibitor
(y) = yellowing

TS/3.22

TABLE 4. Trial II. Ratings for the occurrence of melanosis on pink shrimp in refrigerated storage (per day) after treatment in a variety of dips for 1 minute. The dip solution was fresh tapwater. Ratings within parenthesis are for shrimp treated when the dip solution was 3.5% saltwater (commercial marine salts). After controls, the treatments are numbered and placed in a general order for decreasing effectiveness.

	DIP %'s	Days Storage 3	5	7	12
1.	**Control (no dip)**				
	freshwater rinse	2-4	5-6	7-9	10
	saltwater rinse	(4-5)	(5-7)	(9-10)	(10)
2.	**Sodium Bisulfite**				
	0.25	0(0)	0(0)	6(2)	6(5)
	0.50	0(0)	1(0)	2(4)	6(5)
	1.25	0(0)	0(0)	0(2)	2(4)
	2.50	0(0)	0(0)	0(0)	0(2)
3.	**Bis/EDTA/Cit.**				
	0.5/0.1/0.5	0(0)	0(1)	2(4)	5(3)
	0.5/0.2/0.5	0(0)	0(0)	2(3)	3(5)
	0.25/0.1/0.5	0(0)	0(1)	3(5)	3(5)
	0.25/0.2/1.0	0(0)	2(2)	3(5)	4(6)
4.	**Boric Acid**				
	0.5	0(0)	0(0)	5(5)	6(7)
	1.0	0(0)	0(0)	1(3)	4(2)
5.	**Bis/Cit**				
	0.5/0.5	0(0)	1(0)	4(5)	4(4)
	0.25/1.0	0(0)	3(2)	5(6)	7(5)
	0.25/0.5	0(0)	2(1)	4(5)	8(4)
6.	**Bis/Ery**				
	0.5/0.5	0(0)	0(0)	1(2)	2(4)
	0.5/0.1	0(0)	1(2)	4(7)	4(6)
	0.25/0.5	0(0)	2(5)	3(10)	6(10)
	0.25/0.1	0(0)	2(3)	7(4)	6(10)
7.	**Bis/EDTA**				
	0.5/0.5	0(0)	2(3)	5(7)	5(4)
	0.5/0.2	0(0)	1(3)	5(6)	5(5)
	0.25/0.1	0(0)	1(2)	4(7)	5(5)
	0.25/0.2	0(0)	3(5)	6(6)	5(7)

TABLE 4 continued

8.	**Asc/Cit**				
	1.0/1.0(Y)	0(0)	1(1)	5(4)	9(2)
	1.0/0.5(Y)	1(1)	5(4)	5(5)	7(5)
	0.5/1.0(Y)	0(0)	1(1)	5(7)	1(1)
	3.0/1.0(Y)	1(0)	1(1)	1(3)	1(1)
9.	**Formaldehyde**				
	0.5	0(0)	2(4)	3(7)	10(7)
	1.0	0(0)	2(1)	4(1)	7(7)
10.	**BIS/EDTA/ERY**				
	0.5/0.1/0.5	0(0)	2(2)	6(5)	7(7)
	0.25/0.1/0.5	0(0)	2(2)	6(7)	7(7)
	0.25/0.2/1.0	0(0)	1(2)	7(7)	8(7)
11.	**EDTA**				
	0.1	2(2)	3(2)	5(5)	5(4)
	0.2	2(2)	5(3)	6(5)	5(5)
	0.4	2(2)	3(2)	5(5)	5(5)
12.	**ERY/EDTA/CIT**				
	0.5/0.1/0.5	0(0)	3(5)	9(7)	10(10)
	0.1/0.2/0.5	0(0)	5(5)	8(8)	10(9)
13.	**CITRIC ACID**				
	0.5	1(1)	4(4)	9(8)	10(10)
	1.0	1(2)	4(4)	7(6)	10(10)
14.	**GLYCINE**				
	0.5	1(1)	4(4)	8(7)	10(10)
	1.0	1(1)	4(7)	9(9)	10(10)
15.	**ERYTHROBATE**				
	0.1	3(3)	5(5)	10(9)	10(10)
	0.5	4(3)	6(5)	8(7)	10(10)
	1.0	3(3)	5(5)	5(9)	10(10)
16.	**TAURINE**				
	0.5	3(3)	7(6)	9(10)	10(10)
	1.0	3(3)	7(7)	9(10)	10(10)

ASC = Ascorbic Acid
Bis = Sodium Bisulfite
Cit = Citric Acid
Ery = Erythrobate
EDTA = Ethyl Diamine Tetra Acetate
(Y) = Noticeable yellowing

SO/ts/3.22

all included a portion of bisulfite (treatments nos. 3 and 5-7). The most effective mixtures amongst these treatments were essentially equivalent to a 0.50% bisulfite dip and not better than a 1.25% bisulfite dip (Figure 1). The most effective mixture was Bis/Ery (0.5/0.5%), but this effect was not substantiated by similar dips including EDTA (treatments no. 10). All of these moderately effective mixtures contained a portion of bisulfite (0.25 or 0.50%). The mixtures with 0.50% bisulfite appeared superior to similar mixtures with less bisulfite (0.25%). For example, the Bis/Cit dip at 0.5/0.5% provided more prolonged control of melanosis than did the mixtures of 0.25/0.5% or 0.25/1.0%. These results again suggest the dominant influence of bisulfite.

Although boric acid and formaldehyde are not included on the U.S. Food and Drug Administration's 'GRAS' list (generally recoginized as safe), these dips provided some inhibition, thus demonstrating the influence of acidulants and protein binding (Table 4). The Asc/Cit dip retarded melanosis, yet produced a distinct yellowish tint obvious from day 3 through 7. Additional dips (treatments no. 11-16) were least effective, some yielding unacceptable shrimp within 7 days storage.

In Trial II the melanosis rating in parenthesis per treatment and day of storage are results for shrimp rinsed in dips made with 3.5% saltwater (Table 4). General comparisons with the complementary tapwater dips indicate a more favorable response, or less melanosis after freshwater dips. This observation is preliminary and restricted to interpretation relative to the use of a marine (aquarium) grade salt mixture. Further field work with statistical designs and actual seawater (as may be used by the fishermen) would be required before concluding recommendations.

SUMMARY

1. The choice of shrimp species can influence the occurrence of melanosis and the interpretation of tests to develop alternatives to sulfites. The results from this study are relative to the use of pink shrimp (Penaeus duorarum).

2. Raw, untreated pink shrimp develop melanosis in a linear manner, initially obvious on some shrimp within 3 days refrigerated storage and progressing as a severe product defect after 7 days. Thus pink shrimp require some measures to prevent melanosis to assure marketability.

3. A 2.50% bisulfite dip (1 minute) was more effective in preventing melanosis than was the legally recognized 1.25% bisulfite dip.

4. The 1.25% bisulfite dip (1 minute) was superior in preventing melanosis than was any treatment, single

Figure 1. Ratings for the degree of melanosis on pink shrimp following treatment in a variety of alternative dips (% composition) and sodium bisulfite dips (0.50 and 1.25%).

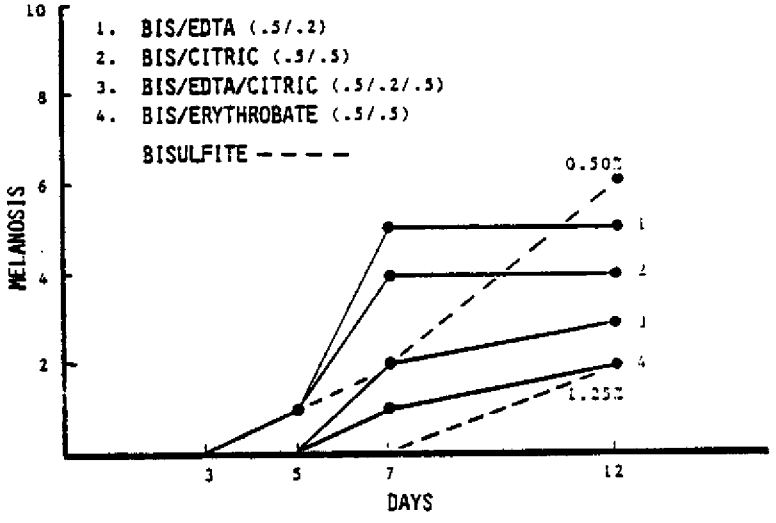
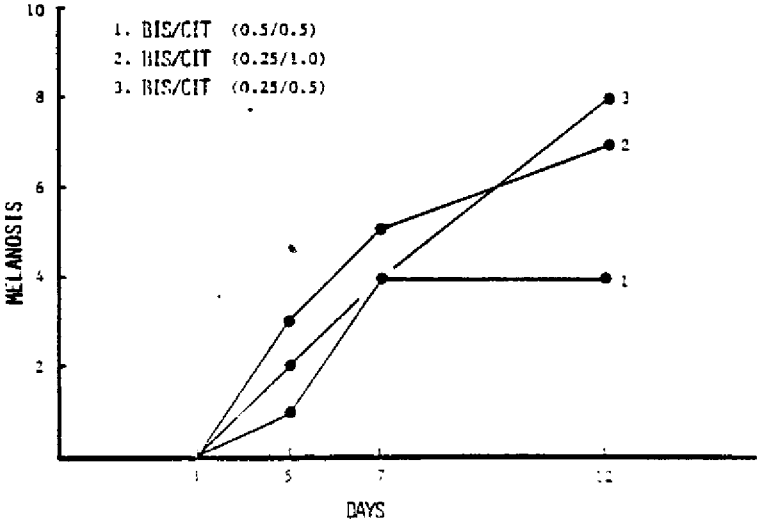


Figure 2. Ratings for the degree of melanosis on pink shrimp following treatment in dips with varying mixtures (% composition) of sodium bisulfite (Bis) and citric acid (Cit).



compounds or mixtures, used in this study.

5. Comparative results suggest dips containing mixtures of bisulfite plus citric acid, erythrobate, and/or EDTA could offer moderate prevention of melanosis. These mixtures are more effective at higher bisulfite concentrations. The bisulfite appears to impart a dominant influence.

6. Further field trials approximating actual fishing practices and employing statistical evaluations are necessary to verify the effectiveness of mixtures including bisulfites, citric acid, erythrobate and/or EDTA This work could also evaluate the influence of freshwater vs. seawater as the dip solution.

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INFLUENCE OF WASHING AND COOKING ON SULFITE RESIDUALS ON TREATED SHRIMP

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INTRODUCTION

Sulfiting agents as food additives have come under close scrutiny due to possible adverse health problems, most common amongst certain asmatics, such as nausea, diarrhea, anaphylactic shock, loss of consciousness, and possible death (Hecht and Willis, 1983). This has caused various federal, state and local food regulatory agencies to propose limiting the residual sulfite on food products. The FDA has placed an acceptable residual sulfite level on shrimp at 100 ppm as SO_2. Thus, shrimp containing residual sulfite greater than the 100 ppm level would be considered adulterated (CFR. 1985).

Processor's concerns that shrimp (either domestically produced and/or imported) meet FDA guidelines, have prompted interest in the possibility of reclaiming adulterated product. Processors, consumers, scientists, and regulatory agencies have inquired about the effect of various cooking methods on the residual sulfite of shrimp. The Codex Alimentarius Commission Standards are 100 ppm (SO_2) residual on raw edible product and 30 ppm on cooked product (FAO/WHO, 1984; CFR. 1984). This international recommendation lacks analytical verification. Therefore, the objective of this work was to examine the effect of cooking on residual sulfite levels and to compare the effectiveness of various reclamation (washing) treatments on lowering excessive sulfite residuals.

MATERIALS AND METHODS

COOKING STUDY

Headless, shell-on white shrimp (Penaeus setiferus), medium size were obtained immediately post-harvest, transported to the Food Science and Human Nutrition Dept. and stored on ice for 1 day. The fresh shrimp were treated with various bisulfite dips (0.5, 1.25, and 2.0% $Na_2S_2O_5$, for 1 min), drained (30 sec), and all samples were stored frozen

(-30°C). A portion of the shrimp was commercially breaded with "Golden Dip + DCA" batter. Cooking treatments included: boiling, shell-on and -off; broiling, shell-on; sauté, shell-off; and frying, shell-off/breaded.

Shrimp (400-500 g) were thawed overnight at room temperature, mixed and drained for 1 min and then divided into two groups of approximate equal weights. Group 1 (control) were raw shrimp, shell-off, which were then chopped, combined and four samples (40-50 g) were weighed, to determine residual sulfite levels. Group 2 (cooking treatments) were shrimp which would be cooked to an internal temperature in excess of 170°C using the following cooking protocol:

Boiling - Shell-on or -off: Place 200-250 g shrimp in 2 l of vigorously boiling tap water for 1.5 min. After cooking, drain and cool to room temperature.

Broiling - Shell-on: Preheat oven 10 min on broiler setting, place 200-250 g shrimp on flat pan and place on rack set at second division, 6 inches from the heating coil (approximately 213°C). Cook for 2.5 min and then turn shrimp over and cook another 2.0 min. Drain and cool to room temperature.

Sauté - Shell-off: Place 15 g of vegetable oil in a teflon pan, heat on a setting of 7 (approximately 199-204°C), and spread shrimp (200-250 g) in pan making sure shrimp are always in contact with the surface. Cook for 2.5-3.0 min with constant stirring and making sure shrimp are turned at least once. Drain and cool to room temperature.

Frying - Breaded, Shell-off: Preheat oil in deep-fat fryer until temperature reaches 149°C (use fresh vegetable oil each time). Place shrimp (200-250 g) in fryer and cook for 2-3 min. Remove shrimp and place on paper towel to drain and cool to room temperature.

Shrimp cooked with shell-on had the shell removed prior to analysis. The edible portion of shrimp for each cooking treatment was chopped, combined, and four samples (40-50 g) analyzed for residual sulfite according to standard AOAC Monier-Williams (M-W) method (AOAC, 1980). The breaded shrimp (frying) were analyzed with breading included as part of the edible portion. An additional experiment was performed as above, however, for the frying treatment, the breading was removed before M-W analysis.

RECLAMATION STUDIES

Two sizes of frozen shrimp (26/30 and 51/60 individual count/lb) having adulterated levels (>100 ppm) of sulfite were obtained from a commercial processor. Three boxes or 15 lb from each size remained frozen as a control. The remaining shrimp were subjected to various reclamation treatments (trt.) using 2 boxes (10 lb) per size per treatment. The frozen shrimp were thawed in flowing water with in-line chlorine (less than 10 ppm) and re-frozen (Thawed trt.), while more shrimp were thawed as above and then commercially peeled and re-frozen (Thawed/Peeled trt.). The final treatment was thawing more of the same shrimp as above, commercially peeling and then washing in flowing cold water (less than 4.4°C) with in-line chlorine (less than 10 ppm) for 30 min and re-freezing (Thawed/Peeled/Washed trt.). Samples from the controls and three treatments were brought to the Food Science and Human Nutrition Dept., Gainesville, FL for sulfite analysis (M-W method).

Pink headed shrimp (Penaeus duorarum), medium size were obtained immediately post-harvest and transported on ice to the Food Science and Human Nutrition Dept., Gainesville, FL. Fresh shrimp were dipped in 1.25% and 2.5% $Na_2S_2O_5$ for 1 min, and a portion of the shrimp from each sulfite dip were frozen for a control. A portion of the remaining shrimp were dipped in ozonated water (1 mg ozone/l water) for 5 min at a ratio of 1 lb per gallon and frozen (-30°C) until analyzed. Ozone was generated using a portable ozone generator, model 25 HF-1000 (OPT Systems, Inc., Arlington, VA). The remaining portion of fresh shrimp was divided into thirds and treated either by dipping in 3% hydrogen peroxide (H_2O_2), soda or seltzer water for 5 min, then drained and frozen (-30°C) until analyzed. Sulfite analysis on edible tail was performed for all reclamation samples using M-W method.

RESULTS AND DISCUSSION

COOKING EFFECTS

Two cooking methods (broil and fry) did not significantly (α=0.05) reduce residual bisulfite on shrimp (Table 1). A significant (α=0.05) reduction in bisulfite levels occurred at the higher dip (2.0%) concentration for boiled shell-on and shell-off when ANOV and multiple comparison (Duncan) analysis were performed. However, this reduction only averaged approximately 23%. High intensity cooking, sauté, caused a significant (α=0.05) reduction in residual bisulfite levels at all dip concentrations (Table 1). Reductions of 52, 51 and 28% resulted during sauté cooking for 0.5, 1.25, and 2.0% dip concentrations, respectively.

The Codex Alimentarius Commission (CAC) standard for raw edible shrimp is 100 ppm as SO_2 and 30 ppm on cooked shrimp (FAO/WHO, 1984; CFR. 1984). This recommendation implies cooking causes a 70% reduction in residual bisulfite. Our results are contradictory to the CAC standard, indicating the residual bisulfite from the raw product is not reduced by most common cooking methods. Because of the potential significance of this finding, a second experiment was performed.

Table 1. Residual bisulfite levels (ppm as SO_2) on shrimp after various cooking methods: Experiment 1.

Cooking trt.	Dip Concentration 0.5% Raw	0.5% Cook	1.25% Raw	1.25% Cook	2.0% Raw	2.0% Cook
Boiled (shell)						
-on	72 ±30	65 ±32	133 ±17	124 ±23	301 ±100	258 ±75*
-off	42 ±2	66 ±30	141 ±16	115 ±21	270 ±18	197 ±21*
Broiled	41 ±8	52 ±5	188 ±9	184 ±6	215 ±13	230 ±10
Fry	44 ±25	46 ±28	72 ±15	63 ±30	112 ±30	89 ±16
Sauté	46 ±6	22 ±3*	150 ±10	73 ±13*	230 ±29	169 ±22*

[1]Mean ± s.d., n=7 replications.
Numbers followed by an (*) are significantly different (α=0.05) from the raw sample (Duncan's Multiple Comparison).

The second ANOV demonstrated that four of the five cooking methods: boiling, shell-on, -off; broiled; fry; again did not cause significant (α=0.05) reductions in residual bisulfite levels at lower dip concentrations (Table 2). A reduction in residual bisulfite on shrimp may result at the 2.0% dip treatment for these four cooking methods, but the reduction again only averaged 21% (Tables 1 and 2). The second experiment confirmed the results of the first and also, contradicts the CAC standard for cooked shrimp. High intense cooking again caused significant reductions in residual bisulfite levels from uncooked product (Table 2).

Table 2. Residual bisulfite levels (ppm SO_2) on shrimp after various cooking methods: Experiment 2.

Cooking trt.	Dip Concentration 0.5% Raw	0.5% Cook	1.25% Raw	1.25% Cook	2.0% Raw	2.0% Cook
Boiled (shell)						
-on	28 ±2	25 ±2	78 ±18	58 ±4	131 ±10	99 ±11*
-off	22 ±2	16 ±2	56 ±10	58 ±6	115 ±13	130 ±25
Broiled	27 ±2	28 ±2	64 ±10	66 ±6	120 ±7	97 ±7*
Sauté	21 ±7	5 ±0*	55 ±6	19 ±2*	110 ±11	63 ±2*

[1]Mean ± s.d., n=4 replications.
Numbers followed by an (*) are significantly different (α=0.05) from the raw sample (Duncan's Multiple Comparison).

Analyzing fried shrimp with (+) and without (-) breading indicates sulfites do not seem to migrate into the breading upon frying and the breading actually "dilutes" the amount of residual bisulfite on the edible portion of shrimp (Table 3).

Reclamation Effects

Thawing, and thawing and peeling resulted in an approximate 14-20% reduction in residual sulfite on this commercial product (Table 4). Thawing, peeling and then washing for 30 min reduced the residual sulfite levels by 40%. The percent reduction per treatment was similar for either size shrimp. Thus reclamation by common procedures (thawing, peeling, and washing) used in commercial shrimp processing can reduce the concentration of residual sulfites, but the percent reduction is limited.

Table 3. The influence of breading on residual bisulfite levels (ppm as SO_2) in fried shrimp.

	1.25% Dipped Treated Shrimp			
	+ Breading[1]		- Breading[1]	
Trials	Raw	Cooked	Raw	Cooked
1	41	46	63	60
2	33	41	64	59
3	36	36	56	79
4	41	50	71	59
$\bar{X}$ ±sd =	38 ±4	43 ±6	54 ±6	64 ±10

[1](±)Breading implies M-W analysis with (+) or without (-) breading present on fried shrimp.

Ozonated water did not reduce the residual bisulfite levels on shrimp at the 1.25% dip but did reduce (16%) the level on the 2.5% dipped shrimp (Table 5). Again a wash treatment was more effective at a higher residual level, but the ozone treatment enhanced subsequent melanosis. Hydrogen peroxide did reduce substantially the levels of sulfite on shrimp at all dip treatments and the reduction was within FDA guidelines (Table 5). However, the shrimp turned severely melanotic after this treatment and were considered an inferior product. Soda and seltzer water reduced sulfite levels on shrimp approximately 60% and resulted in FDA borderline levels on shrimp. The product appeared to remain free of blackspot after this reduction. Since the chemical washes were applied fairly soon (10-15 min) after bisulfite dipping, a water control must be performed to fully evaluate these treatments. However, soda and seltzer water, unlike ozone and H_2O_2, appear to protect the shrimp from further melanosis after washing.

Table 4. Reclamation of a commercially abused shrimp product after thawing, peeling, and washing treatments.

Treatment	M-W Sulfite[1] (ppm as SO_2) LG[2]	SM[2]	% Reduction LG	SM
Frozen (control)	250	188	-	-
Thawed	216	150	14	20
Thawed and Peeled	216	168	14	11
Thawed and Peeled and Washed	154	111	38	40

[1]Values are averages of two boxes with two reps. per box.
[2]Large (LG) size, 26-30 count/lb; Small (SM) size, 51-60/lb.

Table 5. Reclamation of shrimp dipped in 1.25 and 2.5% $Na_2S_2O_5$ for 1 min and then dipped in ozonated water, H_2O_2, and soda and seltzer water.

	Average M-W Value[1] (ppm as SO_2) 1.25% control	1.25% wash[2]	2.5% control	2.5% wash
Ozone water	127 ±18	180 ±7	309 ±20	260 ±20 (16)[3]
3% H_2O_2	127 ±18	78 ±6 (38)	309 ±20	86 ±9 (72)
Soda	-	-	267 ±35	105 ±7 (61)
Seltzer	-	-	267 ±35	99 ±17 (63)

[1]Mean ±s.d., n=4.
[2]Shrimp were dipped in bisulfite then re-dipped in the corresponding treatment usually for 5 min.
[3]Values in () are the % reduction from control.

CONCLUSIONS

Most typical cooking methods offer little advantage in reducing sulfite levels on shrimp. If there is a reduction in sulfite, it occurs at the higher dipping concentration (2.0%). Higher dip concentration may yield a higher portion of free (SO_2) residual. High intensity cooking such as sauté dramatically reduced the residual bisulfite levels on shrimp at all dip concentrations. It would appear, the CAC standard of 30 ppm SO_2 on cooked product must be re-evaluated.

Thawing, peeling and washing can reduce residual (SO_2) sulfite levels on adulterated shrimp, but the percent reductions are limited. The reductions observed were similar for small (51/60) or large (26/30) shrimp.

Ozone reduced (16%) residual bisulfite on the 2.0% dipped shrimp but failed to lower residual levels at 1.25% dip. Hydrogen peroxide (3%) treatment did significantly lower the residual bisulfite on shrimp but melanosis resulted producing an inferior product. Soda and seltzer water dips also resulted in a reduction of residual bisulfite on shrimp. Unlike the H_2O_2, these treatments do not seem to promote melanosis.

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