STUDIES ON BLACKENING OF CANNED PRAWNS

I. INFLUENCE OF COPPER AND IRON ON PRODUCT BLACKENING

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A linear relationship was observed between the copper content and intensity of blackening in commercially canned prawn meat. Average copper and iron contents of unblackened canned prawn meat were 9.6 and 32.5 ppm on dry weight basis respectively. In the blackened product copper content ranged from 15.8 to 63.9 ppm and iron content between 43.7 and 71.45 ppm depending on the intensity of blackening. But incorporation of copper in the above range to experimental cans produced blackening while iron upto 250 ppm did not impart any blackening under standard conditions of canning.

INTRODUCTION

Blackening of canned seafoods and black staining of the can interior have been the subject of research for many years. The occurrence of this phenomenon in canned protein foods including fish and shell fish products have been investigated by many workers (Piggot and Dollar, 1964; Thompson 1963; Thompson and Waters 1960; Pigott and Stanby, 1956; Tanikawa, 1958; Machida, 1911; Oshima, 1927; Kaneko, 1951; Arakawa, 1928; Sekine, 1926; Tanikawa *et. al*, 1966, 1967). Most of the workers concluded that blackening developed due to the formation of black sulphides of iron and/or copper. Thompson and Waters concluded that blackening of canned prawns was caused by the formation of sulphide of iron which is already present in the meat or introduced from the can body due to electrochemical reaction, while Kaneko and Tanikawa *et. al.* explained that hydrogen sulphide required for the black sulphide formation in canned protein foods found its origin in the sulphur-containing amino acids by the thermal degradation and/or by bacterial action. Board *et. al.* (1965) reported that as little as 0.5 ppm of copper present as impurity in the brine caused product blackening in canned meats. The above investigations reveal that copper and iron independently or in combination may be the causative agents

of blackening which are controlled by various factors such as the processing conditions, raw material quality, pH, vacuum and bacterial action.

A more detailed investigation of the problem with particular reference to prawn was deemed necessary, as this commodity forms a major portion of the world export/import trade in fishery products. Data on the pre-shipment quality control inspection of canned prawn for export from India reveal that more than 50 percent of the total detention at source, is due to blackening of the meat and can interior.

The present communication deals with the investigations carried out on the effect of heavy metals such as copper and iron on the blackening of canned prawns. Data on the distribution of copper and iron in commercial samples of canned prawns have been collected and the influence of the metals on the development of product-blackening has been studied and discussed.

Materials methods

a) *Collection of samples*: Canned prawn meat showing different intensities of blackening and of normal colour, were collected from random samples brought to the laboratory for pre-shipment quality control inspection. On the basis of the intensity of black discolouration, the meat, in general was classified into four groups viz. (1) normal (without blackening), (2) slightly blackened, (3) moderately blackened and (4) heavily blackened. In cases, where only some individual pieces were blackened in a can, the affected and the unaffected portions were analysed separately.

Fresh prawns collected from the trawlers of the Institute operating off Cochin were used for all experiments where blackening was induced in canned meat.

b) *Preparation of cans for producing blackening artificially:*

Fresh prawns *(M. dobsoni)* of medium size after beheading were peeled and deveined manually and washed thoroughly in potable water. The washed meat was blanched in 7 % brine (w/v) containing 0.1 % critic acid (brine to meat ratio being, 750 ml for 1 kg) for two minutes after reboiling. After draining off the brine, the blanched meat was immediately cooled under a fan.

100g of the blanched meat was packed in sulphur resistant lacquered cans (301 x 206)with 100ml of 3% brine containing 0.2% citric acid with or without copper and/or iron in different concentrations as required. Copper was added as copper sulphate solution and iron as ferrous ammonium sulphate solution. After steam-exhausting for 10 minutes, the cans were double-seamed and autoclaved at 115.3°C for 18 minutes.

c) *Estimation of iron and copper:*

The prawn meat samples after drying were digested with $HClO_4$ – HNO_3 mixture (1:7). From the digest, copper was estimated by sodium diethyldithiocarbamate method (I. S. I, 1963) and iron by o-phenanthrolein method (Sandell, 1944). Analar grade chemicals and redistilled water were used in the preparation of the reagents. Double-distilled carbontetrachloride was used for the colorimetric estimation of copper.

Results and discussion

The iron and copper contents of the canned prawn meat in some typical commercial samples showing different degrees of blackening are presented in Table I.

The averages given for copper and iron contents were calculated from results obtained for 100 samples in each case. Canned prawn meat without any discolour-

TABLE I IRON AND COPPER CONTENTS IN COMMERCIAL SAMPLES OF CANNED PRAWN SHOWING VARYING INTENSITIES OF BLACKENING

(Values expressed as ppm in dry meat)

Sample No.	Normal		Mild Blackening		Moderate Blackening		Heavy Blackening	
	Iron	Copper	Iron	Copper	Iron	Copper	Iron	Copper
1	17.15	8.872	14.45	19.26	40.21	24.38	39.10	70.57
2	23.58	9.118	22.68	10.08	18.32	25.35	83.20	81.43
3	38.12	12.72	35.38	18.32	86 26	23.62	34.85	35.09
4	48.52	10.92	26.34	15.92	49.26	24.50	24.36	42.44
5	63.74	6.026	20·29	13.93	21.37	31.41	135.20	37.54
6	41.34	3.538	47.48	17.66	47.60	29.78	34.57	52.35
7	56.20	12.49	23.03	14.55	26.43	30.70	115.77	91.96
8	26.46	11.98	62.53	19.30	49.62	27.80	136.80	163.80
9	41.97	9.959	89.93	15.39	29.47	23.84	78.18	39.06
10	19.36	3.850	32.86	18.55	50.12	25.86	45.83	85.55
Maximum	63.74	12.49	89.93	19.30	86.26	31.41	136.80	163.80
Minimum	17.15	3.54	14.55	10.08	18.32	24.38	34.36	35.09
Average (from 100 samples each)	32.53	9.672	43.71	15.82	47.96	27.97	71.45	63.95

ation shows 3.5 to 12.5 ppm of copper on dry weight basis (D. W. B.) The ranges for mildly, moderately and heavily blackened meats are 10 0 to 19.3, 24.4 to 31.4 and 35.1 to 163.0 ppm of copper D.W.B. respectively. The corresponding ranges for iron in unblackened and the blackened products of different intensities are 17.2 to 63.7, 14.5 to 89.9 18.3 to 86.2 and 34 4 to 136.8 ppm respectively. The results indicate that either copper/iron, or both are responsible for blackening.

Some of the commercial cans which showed partial blackening of the product were analysed after separating out the black portion from the rest. The results show comparatively higher distribution of copper in the affected portion while the iron contents are more or less same in both the blackened and unblackened portions as seen from Table II.

TABLE II IRON AND COPPER CONTENTS OF BLACKENED AND NONBLACKENED PORTIONS OF CANNED PRAWN MEAT COLLECTED FROM THE SAME CAN

Sample No.	Blackened portion		Unblackened portion	
	Iron	Copper	Iron	Copper
	(Expressed as ppm in dry meat)			
1	83.20	81.43	78.11	10.74
2	89.78	81.43	37.80	7.29
3	76.21	64.32	77.21	8.21
4	47.44	71.34	48.21	9.81
5	78.91	59.26	70.11	10.14
6	93.21	69.80	81.32	11.61
7	52.38	41.26	50.21	5.38
8	92.37	54.62	97.20	8.29

This clearly indicates that copper might be the actual causative agent for blackening.

The comparative merit of copper over iron as a blackening agent is also corroborated by the data from experiments in which blackening was artificially developed (Tables III, IV and V).

TABLE III CHANGE IN COPPER CONTENT AND INTENSITY OF BLACKENING OF CANNED PRAWN MEAT OWING TO THE ADDITION OF INCREASING LEVELS OF COPPER TO FILLING BRINE

Copper added in the filling brine (ppm)	Colour of the canned meat	Iron content of the dry meat (ppm)	Copper content of the dry meat (ppm)
0	Normal colour	32.48	12.88
1	Very slight blackening	32.92	17.28
2	Mild blackening	32.21	19.86
3	| to	32.15	24.35
4	v	32.43	27.11
5	Moderate Blackening	32.09	31.23
6	| to	32.25	
7	v Heavy blackening	32.13	38.92
8	,,	32.40	43.54
9	,,	32.21	47.08
10	,,	32.10	52.44

TABLE IV IRON ABSORBED BY THE MEAT BY THE ADDITION OF DIFFERENT CONCENTRATIONS OF IRON TO FILLING BRINE.

Iron adedd in filling brine (ppm)	Colour of the canned meat	Iron content of the dry meat (ppm)	Copper content of the dry meat (ppm)
0	No blackening	32.48	12.36
1	,,	42.02	11.98
3	,,	52.69	12.11
5	,,	60.49	12.38
10	,,	79.52	12.15
20	,,	113.90	12.21
30	,,	155.40	12.10
40	,,	208.30	12.38
50	,,	235.70	12.38
60	,,	250.00	12.22

Table III shows the effect of addition of copper on blackening. Incorporation of as little as 2–3 ppm of copper (in the filling brine) imparts slight but visible blackening to the meat. Further addition of copper increases the intensity of blackening proportionately. When the copper level in the dried meat exceeds the critical level (15 ppm, D. W. B) blackening is initiated. The intensity of blackening as shown in Table III compares well with that shown by the commercial samples (Table I) depending on the copper content of the tissue.

Table IV shows the amount of iron retained by the meat with the increase in the added concentration of iron in the filling brine. Meat containing up to 250 ppm of iron (D. W. B.) does not show any blackening under standard canning conditions.

Studies with different combinations of iron and copper (Table V) indicate that intensity of blackening developed is governed only by the amount of copper and not by iron. For example under the fixed levels of 5 and 10 ppm of copper added in the filling brine, the intensity of blackening developed in each case remains the same irrespective of the amount of iron added.

A statistical diagnosis of Tables III and IV indicates a highly significant linear relationship between the copper/iron added to the filling brine and copper/iron absorbed by the meat (Figs. 1 and 2).

The correlation coefficients for the copper and iron series are 0.9984 ($P < 0.001$) and 0.9900 ($P < 0.01$) respectively.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. A. N. Bose, Director, Central Institute of Fisheries Technology, Ernakulam, for the

TABLE V BLACKENING DEVELOPED IN CANNED PRAWN MEAT UNDER FIXED LEVE OF COPPER AND VARYING LEVELS OF IRON ADDED IN THE FILLED BRINE

(Values of copper and iron expressed as ppm in brine)

Series I			Series II			Series III		
Copper	Iron	Nature of the product	Copper	Iron	Nature of the product	Copper	Iron	Nature of the product
0	1	No blackening	0	0	—	10	1	+ + +
0	3	,,	5	1	+ +	10	2	+ + +
0	6	,,	5	2	+ +	10	4	+ + +
0	10	,,	5	3	+ +	10	5	+ + +
0	20	,,	5	5	+ +	10	7	+ + +
0	30	,,	5	7	+ +	10	9	+ + +
0	50	,,	5	8	+ +	10	10	+ + +
0	100	,,	5	9	+ +	10	15	+ + +
0	200	,,	5	10	+ +	10	20	+ + +

+ + = moderate blackening; + + + = heavy blackening; — = No blackening.

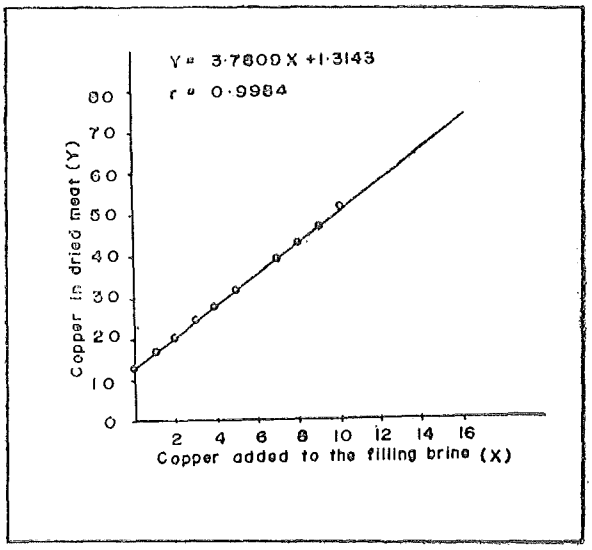

Fig. 1 Statistical co relation benween copper added to the brine and copper absorbed by the meat.

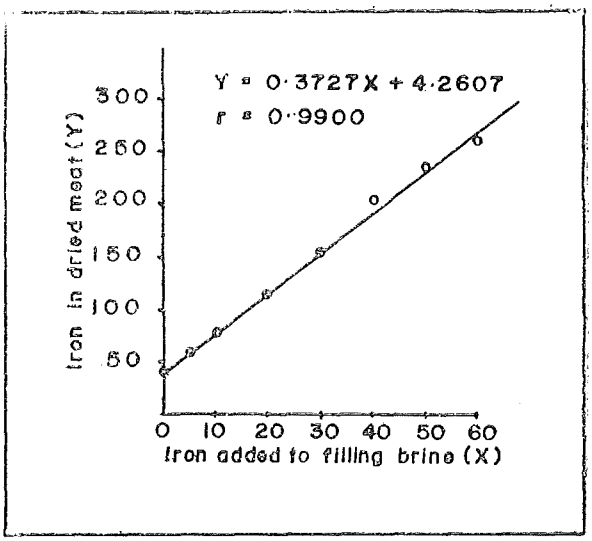

Fig. 2 Statistical co relation between iron added to the brine and iron absorbed by the meat.

valuable suggestions rendered during the conduct of the work. They thank Mr. H. Krishna Iyer for assistance in the statistical analysis of the data.

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