Chemical Studies On Canned Meats

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CHEMICAL STUDIES ON CANNED MEATS

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and

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CONTENTS

Chapter I

SOME CHEMICAL CHANGES OF MUSCLE PROTEINS IN CANNING[1]

Some changes take place in proteins and extractive matters of meats simply by heating in the case of canning. In this Chapter it is described on the study of the decomposition occurring in the muscle proteins.

The materials were prepared from muscles by removing substances soluble in water, alcohol and ether. The solutions of various pH values were added to the muscle proteins. The mixtures were sealed tightly in glass tubes and heated at 130-140°C. The purpose for adding the solutions of various pH values to the muscle proteins and heating them is to find out the changes of the muscle proteins in different hydrogen ion concentrations, and

1) Y. OKUDA and K. YAMAFUJI: Nippon Nôgeikagaku Kwaisi, 8. 835. 1933. (In Japanese.)

for using of glass-tubes is to learn the chemical changes free from the influence of any metallic can-materials.

(1) **Changes of the Hydrogen Ion Concenttraions.** As the concentration of hydrogen ion of the contents of cans has great influences on etching the tin plated iron sheet of cans and on the chemical changes of the contents which occur during preservation, the experiments were carried out by the electric method for ascertaining the variation of pH value of muscle proteins by heating.

The proteins of whale, rabbit, hen, sea-bream, yellow-tail, carp, bonito, cuttle-fish and spiny-lobster were chosen as experimental materials. Either a slightly acidic or alkaline solution or distilled water was added to the proteins before heating. The results of experiments always showed the tendency of pH to approach towards the neutral value. For example, when the muscle proteins of whale were heated at the pH values of 3.4, 6.2 (adding water) and 8.5, the pH changed to 4.5, 6.6 and 8.1 respectively. Thus, it is considered that these variations were probably due to the volatile basic and acidic substances, such as ammonia and hydrogen sulphide, as well as to the soluble amphoteric electrolytes, such as polypeptide and amino acid produced while heating.

(2) **Changes of the Form of Nitrogen.** When the muscle proteins of whale, rabbit, cow, hen and mackerel were heated in distilled water at 150°C for one hour, about 20 per cent of their protein-nitrogen changed to the forms of peptone, peptide, amino acid and ammonia. The formation of these soluble nitrogenous substances may cause a speedy putrefaction to the opened canned meat. The distribution of nitrogen of the muscle proteins after heating is shown in Table 1.

Table 1

	In per cent of dry matter					In per cent of total N			
	Total-N	Protein-N	Amino-N	Ammonia-N	Residual-N	Protein-N	Amino-N	Ammonia-N	Residual-N
Whale	16.35	13.52	0.52	0.09	2.22	82.69	3.18	0.55	13.58
Rabbit	15.88	11.35	0.78	0.02	3.73	71.47	4.91	0.13	23.48
Cow	16.52	14.31	0.43	0.29	1.49	86.62	2.60	1.76	9.00
Hen	16.86	13.90	0.52	0.31	2.13	82.44	3.08	1.83	12.63
Mackerel	16.81	14.18	0.45	0.34	1.84	84.35	2.68	2.04	10.95

(3) .**Changes in the Elementary Composition of Muscle Proteins.** In order to ascertain what changes take place in the elementary composition of muscle proteins through heating under pressure, and to find out the effects of pH values upon these changes, the muscle proteins of whale, rabbit, hen and sea-bream were heated at the initial pH values of 3.4, 6.2 and 8.5. The reseults of experiments showed the decrease of their nitrogen and sulphur contents and the amounts of the decrease were particularly marked when the substances were heated in the solutions having the greater values of pH. The results are given in Table 2.

Table 2

		C	H	N	S	P
Whale	Original protein	51.60	6.19	16.48	0.74	0.085
	Protein heated at pH 3.4	51.88	6.88	16.28	0.74	0.076
	pH 6.2	51.93	6.87	15.97	0.73	0.086
	pH 8.5	52.54	6.85	15.57	0.70	0.071
Rabbit	Original protein	52.32	7.12	16.30	0.86	0.093
	Protein heated at pH 3.4	52.47	7.13	16.11	0.86	0.078
	pH 6.2	52.55	7.11	15.92	0.83	0.092
	pH 8.5	52.99	7.05	15.38	0.84	0.069
Hen	Original protein	52.53	7.18	16.76	0.85	0.093
	Protein heated at pH 6.2	52.88	7.14	16.33	0.84	0.094
Sea-bream	Original protein	52.79	7.08	16.42	0.95	0.095
	Protein heated at pH 6.2	52.92	7.03	16.07	0.93	0.093

(4) **Generation of Ammonia and Hydrogen Sulphide.** The results of experiments with four kinds of muscle proteins revealed the fact that both NH_3 and H_2S were generated in larger quantities when they were heated in the solutions having the greater values

of pH. This fact agrees with the result of the elementary analysis. When the material of the tin is bad and iron dissolves in the liquid contained in the can, then sulphide of iron preciptates and causes the deterioration and blackening of the canned meats. The amounts of NH_3 and H_2S in mg. generated from 100 g. of muscle proteins are shown in Table 3.

Table 3

NH_3 (mg. in 100 g. of proteins)

pH before heated	Whale	Rabbit	Hen	Sea-bream
3.4	0.15	0.21	—	—
6.2	0.58	1.76	1.36	1.88
8.5	28.44	36.89	—	—

H_2S (mg. in 100 g. of proteins)

pH before heated	Whale	Rabbit	Hen	Sea-bream
3.4	0	0	—	—
6.2	9.37	1.14	0.87	15.62
8.5	27.72	12.89	—	—

(5) **Changes of the Amounts of Arginine, Histidine, Lysine, Cystine, etc.** In order to learn how the distributions of arginine, histidine, lysine, cystine and other nitrogen in the muscle proteins of whale, rabbit, hen and sea-bream change by heating, the quantitative analyses were carried out by the Van SLYKE method before and after the heating. The proteins were heated at three different values of pH to ascertain the effects of solutions of various pH upon the proteins. The results are as follows (Table 4).

Table 4

	Total-N	Ammonia-N	Melanine-N	Cystine-N	Arginine-N	Histidine-N	Lysine-N	Mono-amino-N	Non-amino-N
Whale									
In per cent of protein									
Original protein	16.48	0.69	0.33	0.29	2.49	2.20	1.34	8.02	1.18
Protein heated at pH 3.4	16.28	0.59	0.45	0.16	2.59	2.28	1.16	7.79	1.23
pH 6.2	15.67	0.55	0.44	0.14	2.36	2.36	1.26	7.66	1.21
pH 8.5	15.57	0.45	0.43	0.10	2.49	1.96	1.34	7.45	1.35
In per cent of total N									
Original protein	100	4.29	2.02	1.45	15.08	13.37	8.15	48.66	7.15
Protein heated at pH 3.4	100	3.62	2.79	1.04	15.94	14.03	6.48	47.84	7.67
pH 6.2	100	3.42	2.73	0.87	14.77	14.79	7.88	47.95	7.57
pH 8.5	100	2.91	2.73	0.64	15.97	12.59	8.62	47.85	8.64
Rabbit									
In per cent of protein									
Original protein	16.30	0.74	0.36	0.19	2.49	1.93	1.26	8.17	1.15
Protein heated at pH 3.4	16.11	0.73	0.46	0.15	2.58	1.92	0.94	7.82	1.41
pH 6.2	15.92	0.50	0.38	0.13	2.34	2.17	1.15	7.89	1.34
pH 8.5	15.38	0.39	0.43	0.10	2.49	1.75	1.23	7.59	1.41
In per cent of total N									
Original protein	100	4.56	2.17	0.18	15.28	11.85	7.74	50.15	7.06
Protein heated at pH 3.4	100	4.55	2.83	0.92	16.04	12.53	6.04	48.45	8.78
pH 6.2	100	3.81	2.36	0.79	14.41	13.60	6.92	49.61	8.43
pH 8.5	100	2.57	2.77	0.65	16.16	11.38	8.02	49.32	9.18
Hen									
In per cent of protein									
Original protein	16.76	1.10	0.48	0.18	2.71	1.97	1.36	8.19	0.76
Protein heated at pH 6.2	16.33	0.89	0.63	0.14	2.55	2.04	1.15	7.97	0.97
In per cent of total N									
Original protein	100	6.58	2.85	1.07	16.14	11.73	8.12	49.60	4.53
Protein heated at pH 6.2	100	5.42	3.88	0.85	15.61	12.51	7.04	48.78	5.95

Sea-bream

In per cent of protein									
Original protein	16.42	0.77	0.36	0.28	2.54	2.24	1.47	8.35	0.42
Protein heated at pH 6.2	16.07	0.45	0.48	0.12	2.46	2.36	1.37	8.20	0.51
In per cent of total N									
Original protein	100	4.70	2.17	1.69	15.46	13.61	8.92	50.83	2.55
Protein heated at pH 6.2	100	3.43	2.99	0.77	14.68	14.71	7.93	50.42	3.17

It was found that the total nitrogen, ammonia and cystine nitrogen always decrease by heating, and the higher the value of pH the greater the rate of the decrease, while melanine nitrogen generally increases. The amounts of cystine, arginine, histidine and lysine contained in the proteins before and after heating were calculated in per cent from the above results.

Table 5

		Cystine	Arginine	Histidine	Lysine
Whale	Original protein	2.49	7.74	8.12	6.99
	Protein heated at pH 3.4	1.37	8.04	8.41	6.05
	pH 6.2	1.20	7.33	8.71	6.57
	pH 8.5	0.86	7.74	7.23	6.99
Rabit	Original protein	1.63	7.74	7.11	6.57
	Protein heated at pH 3.4	1.29	8.02	7.09	4.90
	pH 6.2	1.11	7.27	8.01	6.00
	pH 8.5	0.86	7.74	6.46	6.41
Hen	Original protein	1.54	8.42	7.27	7.09
	Protein heated at pH 6.2	1.20	7.92	7.53	6.00
Sea-bream	Original protein	2.40	7.89	8.27	7.67
	Protein heated at pH 6.2	1.03	7.64	8.71	7.14

According to Table 5, the quantities of cystine, arginine, histidine and lysine contained in the proteins after heating showed a tendency of decrease, as compared with those contained in the original proteins. Such tendencies were remarkable on cystine at the higher pH before heating and on lysine at the lower pH.

(6) **Changes of Tyrosine and Tryptophane.** The quantities of tyrosine and tryptophane contained in the muscle proteins of whale, hen, rabbit, yellow-tail, carp, bonito, sea-bream, cuttle-fish and spiny-lobster were determined before and after heating. The amounts of those amino acids decreased by heating, but very little, as it is obvious in Table 6.

Table 6

Proteins	Tyrosine		Tryptophane		pH	
	Before heating	After heating	Before heating	After heating	Before heating	After heating
Whale	5.11	4.97	1.51	1.32	6.2	6.6
Hen	4.81	4.78	1.58	1.59	6.2	6.6
Rabbit	5.49	5 27	1.68	1.57	6.2	6.6
Yellow-tail	4.97	4.69	1.70	1.62	6.51	6.54
Carp	4.71	4.53	1.50	1.47	5.02	5.92
Bonito	4.84	4.60	1.63	1.46	7.17	6.65
Sea-bream	5.00	4.74	1.63	1.56	6.37	6.51
Cuttle-fish	4.83	4.71	1.37	1.29	4.67	5.57
Spiny-lobster	5.05	4.81	1.46	1.34	3.98	5.29

(7) **Changes of Proline.** The experiments carried out by using each 40 g. of gelatine to find out the difference between the quantities of proline contained in the materials before and after heating. It was observed that there was almost no difference between them, and when the pure solution of proline was heated, there was no detectable decomposition. Therefore the amount of proline in muscle proteins may probably be the same.

(8) **Changes of the Forms of Cysteine, Cystine and Sulphur.** When the solutions of pure cysteine and cystine were heated

under the different pH, a part of the one always changed into the other. That is, when the solution of any of the two acids was heated, it was found that the solution contained the both acids, but the sum of the two quantities always decreased. The results of the experiments are as follows:

Table 7

pH before heating	Sample	Used, mg.	Found, mg. Cysteine	Found, mg. Cystine	Sum
1.7	Cysteine	37.5	32.0	3.8	35.8
4.8	Cystine	45.6	2.9	39.9	42.8
6.8	Cysteine	25.1	9.4	6.6	16.0
6.8	Cystine	22.6	2.7	17.1	19.8
8.3	Cysteine	25.8	5.1	5.3	10.4
8.6	Cystine	25.0	2.7	16.2	19.2

The muscle proteins of sea-bream were heated at pH 6.1 (a) and 9.2 (b), and the forms of sulphur were determined. The results obtained are as follows:

Table 8

Mg. per cent. of protein	Total S	Cysteine	Cystine	H_2S S	Sulphide S	Sulphate S	Soluble-organic S
Before heating	690	660	190	—	—	—	—
After heating (a)	—	490	200	6.6	0.4	18	96
,, ,, (b)	—	440	110	20.9	4.6	30	103

In per cent. of total S	Total S	Cysteine	Cystine	H_2S S	Sulphide S	Sulphate S	Soluble-organic S	Protein S
Before heating	100	26.0	7.2	—	—	—	—	—
After heating (a)	—	19.0	7.5	0.9	0.06	2.6	14.0	82.4
,, ,, (b)	—	17.5	4.3	26.9	0.7	4.3	15.0	77.1

Namely, when it was heated in alkaline solutions, the decompositions of cysteine and cystine were especially considerable, and hydrogen sulphide and other sulphides were formed in large quantities.

Chapter II

ON THE CONTENTS OF GASES AND METALS IN STORED CANS[2]

This chapter deals with the contents of gases and metals in the cans which have endured long storage.

As a means to know the changes of canned meats and the state of corrosion of can-materials, gases, such as carbon dioxide, hydrogen, oxygen and nitrogen, sometimes ammonia and hydrogen sulphide, together with metals, such as iron and tin, dissolved from cans were determined with the results shown in Tables 1, 2 and 3.

Table 1

Beef. (+ : present ; -- : absent)

Age of cans (years)	15	7	5	1
No. of analysis	6	7	3	3
Blown cans	+	–	–	--
Corrosion of cans	+++	++	++	+
Putrid oder	—	--	–	–
Appearance of meat	Normal	Normal	Normal	Normal
Contents (g.)	156	159	450	459
Water (%)	61.0	60.5	60.2	59.7
Dry matter ,,	39.0	39.5	39.8	40.3
Gas (c.c.)	79.5	25.9	15.9	10.4
CO_2 (%)	3.4	4.9	3.6	2.8
O_2 ,,	1.3	1.8	3.0	4.7
H_2 ,,	82.2	22.3	22.3	12.2
N_2 ,,	13.2	71.0	71.2	80.4
Fe (mg. %)	191.5	15.6	14.2	13.7
Sn ,,	375.0	219.5	104.5	78.3
pH	5.8	5.6	5.8	5.8

Table 2

Crab

Age of cans (years)	5	3	1
No. of analysis	6	4	6

2) Y. OKUDA and K. KATAI: Nippon Nôgeikagaku Kwaisi, 12. 1059. 1936. (In Japanese.)

Contents (g.)	231	221	224
Water (%)	79.2	78.5	80.0
Dry matter „	20.8	21.5	20.0
Gas (c.c.)	9.5	7.0	11.0
CO_2 (%)	0.3	0.6	0.4
O_2 „	9.6	7.2	10.1
H_2 „	11.6	11.9	8.7
N_2 „	78.5	80.4	80.8
Fe (mg. %)	10.6	11.3	9.7
Sn „	19.9	17.9	15.0
pH	6.9	6.9	7.0

Table 3

Salmon and Tunny

	Salmon		Tunny	
Age of cans (years)	1	7	1	7
Contents (g.)	452	480	404	422
Water (%)	73.7	75.2	62.4	61.1
Dry matter „	26.3	24.8	37.6	38.9
Gas (c.c.)	1.5	5.0	21.5	102.0
CO_2 (%)	0	1.8	13.1	5.5
O_2 „	6.7	10.2	0.7	0.3
H_2 „	35.3	25.0	20.8	73.8
N_2 „	58.0	63.0	65.4	20.4
Fe (mg. %)	13.8	15.9	12.7	49.9
Sn „	24.2	108.7	87.0	214.8

Chapter III

CARBON DIOXIDE AND HYDROGEN GASES PRODUCED AT CANNING AND IN STORAGE[3]

For the purpose of knowing the changes of canned meat and the state of corrosion of can-materials, we determined oxygen, nitrogen, carbon dioxide and hydrogen gases in commercial cans as described in the preceding chapter. In the experiment recorded in this chapter, carbon dioxide was again determined as a means of knowing some chemical changes which occurred in canned meat, and hydrogen gas to know the state of the corrosion of can-material. But in the present case, instead of commercial cans, sealed glass tubes containing 5 g. of meat powder, 0.5 g. each of

[3] Y. OKUDA and K. KATAI: Nippon Nôgeikagaku Kwaisi, 12. 1064. 1936. (In Japanese.)

tin and iron powders, and solutions of different hydrogen ion concentrations were used for the sake of more exact comparison. The tubes were heated at 130° for different hours, to know the influence of heat and pressure upon canned meat and can-material at canning, and preserved at 50° for different periods to know the effect of storage.

The experiments were performed with three kinds of meats, but only the data with beef are described below, as the results with other meats were analogous.

Table 1

Carbon Dioxide (c.c.)

(a) Sulphuric acid was added

Meat powder	Fresh meat				Somewhat spoiled meat			
pH. before and after heating	4.0-4.5				4.0-4.3			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	2.1	2.6	2.1	3.1	2.2	2.1	1.8	2.7
Sn added	1.4	2.6	2.9	2.2	1.1	1.9	2.5	1.8
Fe and Sn added	2.2	2.2	1.9	3.1	2.0	2.1	1.5	2.8

(b) Water was added

Meat powder	Fresh meat				Somewhat spoiled meat			
pH. before and after heating	5.5-5.7				5.5-5.7			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	1.7	1.2	0.8	2.6	1.7	1.1	1.2	2.5

Sn added	1.5	2.4	2.8	2.3	1.2	2.0	2.4	2.0
Fe and Sn added	1.5	0.5	0.9	2.4	1.4	0.8	0.8	2.4

(c) Sodium hydroxide was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	8.5-7.9				8.2-7.9			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	0.9	0.5	0.2	1.8	1.1	0.3	0.2	2.0
Sn added	0.9	1.2	1.3	1.6	1.0	1.4	1.8	1.8
Fe and Sn added	0.9	0.3	0.2	1.4	1.2	0.5	0.2	2.0

Table 2

Hydrogen (c.c.)

(a) Sulphuric acid was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	4.0-4.5				4.0-4.3			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	18.6	48.2	57.7	32.5	19.9	55.0	60.1	30.2
Sn added	0.3	0.2	0.2	0.3	0.3	0.3	0.1	0.3
Fe and Sn added	19.7	49.3	57.8	32.8	23.7	54.1	63.3	27.8

(b) Water was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	5.5–5.7				5.5–5.7			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	5.2	32.1	36.0	7.4	5.9	34.9	41.1	8.1
Sn added	0.2	0.2	1.2	0.3	0.2	0.1	0.5	0.2
Fe and Sn added	5.2	33.4	33.0	8.7	5.6	40.0	41.6	9.6

(c) Sodium hydroxide was added.

Meat powder	Fresh meat				Somewhat spoiled meat			
pH, before and after heating	8.5–7.9				8.2–7.9			
Hours of heating	1			3	1			3
Days of storage	0	30	60	0	0	30	60	0
Fe added	0.5	16.4	21.5	1.2	1.8	22.9	27.1	5.2
Sn added	0.2	0.1	0	0.2	0	0	0.1	0.2
Fe and Sn added	0.9	17.2	21.2	0.8	1.4	22.1	27.8	5.1

Chapter IV

PROTEIN, FAT AND NUTRITIVE VALUES OF STORAGED CANNED MEATS[4]

1. Protein

a) The experiments were carried out with canned beef of different ages of storage, from 2 to 15 years. The meats were

[4] Y. OKUDA: Represajo de la Bulteno Scienca de la Fakultato Terkultura, Kjuŝu Imperia Universitato, Vol. 8, No. 1. Julio, 1938. (In Japanese.)

dried, pulverized, and analysed with the following results which are described in per cent of dry matter.

Table 1

Age of cans	Total nitrogen	Crude protein	Crude fat	Ash
15	10.86 %	67.88 %	8.89 %	10 94 %
10	11.29	70.56	9.16	8.85
7	10.28	64.25	12.22	13.24
5	10.42	65.13	12.56	12.07
2	10.72	67 00	9.50	11.79

b) Crude proteins were obtained from canned and fresh beef by boiling with water faintly acidified with acetic acid, and by extracting several times with alcohol and ether. Ash and nitrogen contents of the proteins were determined as mentioned below.

Table 2

Age of Cans	In dry matter		In ash and moisture free substance
	Ash	Total nitrogen	Total nitrogen
15	1.78 %	15.37 %	15.65 %
10	0.91	15.77	15.91
7	0.95	15.77	15.92
5	0.56	15.48	15.57
2	0.38	15.58	15.63
Fresh meat	0.25	15.78	15.82

From the result of experiments we see that the nitrogen content of the proteins obtained from canned and fresh meats is nearly equal, while their ash content is higher the older the cans. This result concerning the ash content is in accord with the fact set forth in Chapter II, namely that the dissolved quantities of iron and tin arising from the corrosion of can-materials is in proportion to the age of cans.

c) Each protein was subjected to analysis by the Van SLYKE method with the following results.

Table 3

In ash and moisture free proteins

Age of cans	15	10	7	5	2	Fresh meat
Total-N	15.65	15.91	15.92	15.57	15.63	15.82
Amide-N	0.97	0.98	1.00	1.00	1.03	1.06
Insoluble-Humine-N	0.07	0 07	0.07	0 08	0.08	0.07
Soluble-Huimine-N	0.34	0.24	0.32	0.25	0.25	0.13
Arginine-N	2.07	2.10	2.04	2 07	2.05	2 05
Cystine-N	0.14	0.14	0.14	0.15	0.14	0.14
Histidine-N	1.03	0.94	1.11	1.04	1 08	0.92
Lysine-N	1.80	1.94	1.80	1.80	1.82	2 03
Mono-amino-N	8.59	8.86	8.76	8.78	8.65	8.92
Non-amino-N	0.63	0.50	0.57	0.36	0.50	0.49
Sum	15.64	15.77	15.81	15.53	15.60	15.81

In per cent of total nitrogen

Age of cans	15	10	7	5	2	Fresh meat
Total-N	100	100	100	100	100	100
Amide-N	6.20	6.16	6.28	6.42	6.59	6.70
Insoluble-Humine-N	0.45	0.44	0.44	0.51	0.51	0.44
Soluble-Humine-N	2.17	1.51	2.01	1.61	1.60	0.82
Arginine-N	13.23	13.20	12.81	13.29	13.12	12.96
Cystine-N	0.89	0.88	0.88	0.96	0.90	0.88
Histidine-N	6.58	5.91	6.97	6.68	6.91	5.82
Lysine-N	11.50	12.19	11.31	11.56	11.64	12.83
Mono-amino-N	54.89	55.69	55.03	56.39	55.34	56.38
Non-amino-N	4.03	3.14	3.58	2.31	3.20	3.10
Sum	99.94	99.12	99.31	99.73	99.81	99 93

From the analytical results we see that no remarkable quantitative difference was to be observed among the protaines obtained from the canned meats of different ages and the fresh meat. This fact brought out the conclusion that the proteins obtained from them have nearly equal nutritive value. This conclusion parallels that obtained from feeding experiments performed long years age[5].

2. Fat

(a) The iodine value and acid value were determined in the fats obtained from canned beef of different ages of storage, from 2 to 15 years, with the following results.

Table 4

Age of cans	Acid value	Iodine value
15	30.45	49.08
10	25.47	48.10
7	13.67	45.85
5	11.40	43.65
2	10.44	45 98

From these results we see that the acid value increases appreciably with the length of the storage of the cans.

(b) We examined two groups of cans of beef both of which had been stored for 6 years. One of these was normal, but the other swollen abnormally, becoming convex at the ends, by the pressure of hydrogen gas evolved from can-materials by corrosion. For the purpose to comparing the chemical properties, fat was obtained by extracting with ether, dehydrating with anhydrous sodium sulphate, and evaporating the ether in carbon dioxide gas at diminished pressure. The results of determination of these fats together with that of the fat of fresh beef are shown in the following table:

5) U. SUZUKI, Y. OKUDA, T. OKIMOTO and T. NAGASAWA: Tokio Kagakukwaisi; 40, 385, 1919. (In Japanese.)

Table 5

	Fresh meat	Canned meat	
		Normal	Blown
Acid value	11.61	16.14	11.09
Saponification value	199.0	197.5	197.3
Ester value	187.39	181.36	186.21
Iodine value	47.96	46.39	44.08
Acetyl value	9.36	9.25	10.58
Hehner value	93.51	93.05	94.16
Reichert-Meissl value	1.54	1.56	1.53
Vitamin A	—	—	—

3. Nutritive Value

As far as the experiments performed, the proteins obtained from canned meats of different ages of storage have nearly the same composition and similar nutritive value as already described[5]. In the present feeding experiments, we compared the nutritive value of meat-powders obtained by simply drying the total contents of cans. In every case albino rats of the same litter and of the same sex were fed with the foods containing 7 per cent of muscle proteins in the form of meat-powder.

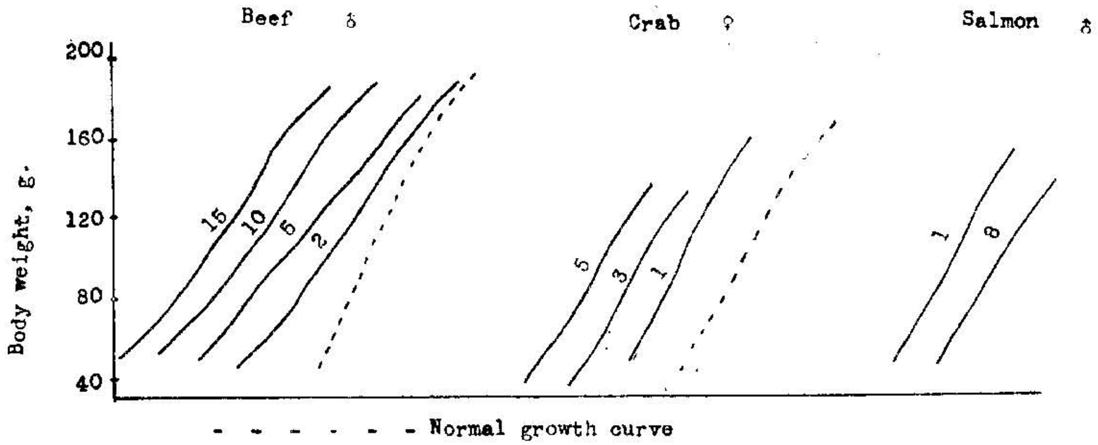


Table 6

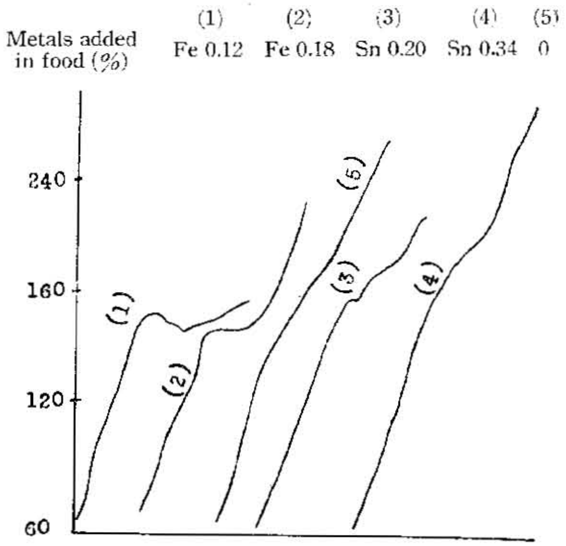
		Canned beef				Canned crab			Canned salmon	
Age of cans		15	10	5	2	5	3	1	8	1
Sex of rats		♂	♂	♂	♂	♀	♀	♀	♂	♂
Food mixture	Meat powder, g.	11.0	10.7	11.2	11.0	9.4	9.2	9.0	9.8	9.7
	Starch, g.	64.0	64.3	63.8	64.0	65.6	65.8	66.0	65.2	65.3
	Cane sugar, g.	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Agar-agar, g.	1.0	1.0	1.0	1.0	1.0	1,0	1.0	1.0	1.0
	McCollum salts, g.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	Butter, g.	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
	Orizanin, c.c.	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Initial body weight, g.		50	50	46	42	36	32	46	4.4	46
Finale ,, ,,		185	188	180	186	135	132	160	136	154
Increased ,, ,,		135	138	134	144	99	100	126	92	108
Increase per day, g.		1.2	1.2	1.2	1.3	1.7	1.7	2.1	1.5	1.8
Period of experiment		4 months				2 months			2 months	

According to the experimental results, in spite of the great difference of ages of storage, the meat-powders from the same kind of cans differed only slightly in nutritive. All albino rats fed with the foods containing 7 per cent of protein in the form of meat-powders showed a rate of growth a little lower than normal.

The above mentioned results were obtained in the case of experiments with the cans of superior quality, whereas in the case of materials of inferior quality the nutritive value of aged cans was much lower than that of new ones. This discrepancy may be ascribed to the difference both in the contents of the cans and in the can-materials.

To examine the injurious action of iron and tin, which form the can materials, and which came into the meat-powder by dissolving, two or three times as much iron or tin as present in ordinary meat-powders was mixed into the basal food in the form of their chlorides. The basal food contained 22 per cent of casein, 53 of starch, 5 of cane sugar, 4 of McCollum salt, 15 of butter, 1 of agar-agar and 4 c.c. of oryzanin. With these foods male albino rats of the same litter were fed for two months.

The results are shown in the following graph. From this we see that the injurious action of an excess of iron is greater than that of tin.



Chapter V

SUMMARY

I. Chemical Changes of Muscle Proteins in Canning

(1) The muscle proteins of some hens, various fishes and certain animals were prepared as samples for the purpose of studying what changes take place in the muscle proteins at the time of canning meats under pressure and heating. The materials were sealed in glass-tubes and heated at 130-140°C for one hour, and changes of materials were studied.

(2) The hydrogen ion concentration of all of the proteins showed a tendency to approach toward the neutral point.

(3) About 20 per cent of the protein nitrogen was transformed by heating to peptone, peptide, and amino acid nitrogens.

The formation of soluble nitrogen compounds, such as these, is considered to cause a speedy putrefaction of contents of an opened can.

(4) As the results of elementary analyses of carbon, hydrogen, nitrogen, sulphur and phosphorus, it was found that the quantities of nitrogen and sulphur contained in the proteins generally decreased by heating, and the changes were more marked the higher the values of pH. There was no appreciable change in phosphorus when the solution was neutral, but its amount decreased when solution was acidic or alkaline, and hence the percentage of carbon increased.

(5) The quantities of NH_3 and H_2S generated by heating were greater in proportion to the values of pH of the solutions. This results explains the fact that, when the tin of cans are bad and the pH of the contents is high, the contents of the can deteriorate more readily and the colour changes to black.

(6) As the results of the analyses of the proteins by the Van SYLKE method, the decrease of the total nitrogen, ammonia nitrogen and cystine nitrogen and the increase of melanine nitrogen were detected especially when the pH value increased. The quantities of cystine, arginine, histidine and lysine contained in the materials showed a tendency of decrease in all three cases and the same tendencies were very remarkable on cystine at the higher value of pH and on lysine at the lower.

(7) Tryptophane by the May-Rose method and the tyrosine by the Folin-Denies method were quantitatively analyzed, and the decrease of these substances by heating were very insignificant.

(8) The test for proline was made by the Fisher-Bechner method, but no decomposition by heating was observed.

(9) Cysteine and cystine were analyzed quantitatively by the OKUDA-KATAI method, and it was found that a part of any one of these acids always changed to the other acid by heating. But the sum of the two always decreased, and the decomposition of both of these acids was remarkable at the higher value of pH, and the decomposition of cysteine was greater than that of cystine.

(10) A part of the protein-sulphur changed by heating to hydrogen sulphide, other sulphides, sulphuric acid and soluble

organic sulphur, and the quantities of these substances generated were greater at the higher pH of the solutions, as in the case of the decompositions of cysteine and cystine.

II. On the Contents of Gases and Metals in Storaged Cans

The experiments were chiefly carried out with canned beef of different ages of storage, from 1 to 15 years, were as follows:

1) Among gases contained in cans examined, the quantity of nitrogen was the largest in the majority of the cans, but in some old cans the amount of hydrogen was frequently more than that of nitrogen.

2) The proportion of oxygen as compared to that of nitrogen was much smaller than it is in the air.

3) The content of carbon dioxide in cans was larger than that in the air, but it did not increase appreciably during the storage of the cans.

4) Free ammonia and hydrogen sulphide showed only traces.

5) The concentration of hydrogen ion of the canned meats showed almost no change in storage.

6) The contents of iron and tin in both canned beef and fish were nearly proportional to that of hydrogen in the cans which was produced by corrosion of can-materials. But in the case of crab meat packed in the cans which are covered inside with lacquer, almost no increase of the contents of iron, tin and hydrogen was observed.

7) Unusual increase of hydrogen gas in some very long-stored beef-cans sometimes gave rise to the so called "blown" cans, in which the ends become convex, and are apparently analogous to the spoiled cans dilated by the pressure of carbon dioxide produced by the action of bacteria upon the contents.

III. Carbon Dioxide and Hydrogen Gasses Produced at Canning and in Storage

In the present case, instead of commercial cans, sealed glass tubes containing a certain meat, tin and iron powders, and solutions of different hydrogen ion concentration were used.

1) The production of carbon dioxide during canning increased a little more, as a rule, in the presence of iron than in the presence of tin alone. And also the longer the time of heating the more was the increase.

2) The production of carbon dioxide during storage, gradually increased in the presence of tin alone, but decreased in the presence of iron. The decrease seems to be due to the fact that carbon dioxide produced by gradual oxidation acts on iron to make iron carbonate and hydrogen.

3) The production of carbon dioxide seems to have some relation with the hydrogen ion concentration of meat-juice and the kind of meats, but the relation with the freshness of the meat is not definite.

4) The production of hydrogen is chiefly due to the presence of iron but only slightly to that of tin. In the presence of iron, the production had an intimate relation with the hydrogen ion concentration of meat-juice, the stronger being the concentration the more the production. The production increased proportionally to the length of time of heating in canning, and to the period of storage of cans.

5) The kind and freshness of meats have more or less influence upon the production of hydrogen from can-material.

6) The quantity of carbon dioxide produced was generally very small as compared to that of hydrogen.

IV. Protein, Fat and Nutritive Value of Storaged Canned Meats

The present investigation deals with the chemical changes of the proteins and fats, and also the nutritive value of meats in cans which have endured long storage. The results of the experiments carried out with canned meats of different ages of storage were as follows :—

1) The proteins obtained from fresh and canned beef aged from 2 to 15 years contained nearly equal amounts of nitrogen but differed greatly in amounts of ashes. The ash-content was the more the older the cans.

2) The results of analyses of the proteins by the Van SLYKE method showed no remarkable difference each other. The analogy of the chemical composition of those proteins indicates the similarity of the nutritive value of them. This result agrees with that of feeding experiments performed by us long years ago.

3) Acid value, saponification value, ester value, iodine value, acetyl value, Hehner value, and Reichert-Meissl value were examined in the fats obtained from fresh and canned beef of different ages of storage, but no definite conclusions were obtained, except that the longer the time of storage the higher was the acid value.

4) Carr-Price test for vitamin A was negative in all of the fats examined.

5) The nutritive value of the meat powders obtained from canned beef from 2 to 15 years old, and from canned crab from 1 to 5 years old showed only slight differences, when feeding experiments were performed with albino rats.

6) When the great excess of iron and tin in the form of their chlorides was administrated to the rats, the injurious action of iron was greater than that of tin.

In conclusion the authors wish to express their thanks to Messrs. U. ENDO, S. NAGATAKE and S. SIGEMATU for their analytical works and also to "Hattori-Hokokwai" for a research grant which has defrayed a part of the cost of this investigation.