Chemical studies on the Freshnes of whale Meat III

Effect of Hydrogen-Ion Concentration on Decrease in Freshness and Titration Curve of Whale Meat with HCl and Na_2CO_3

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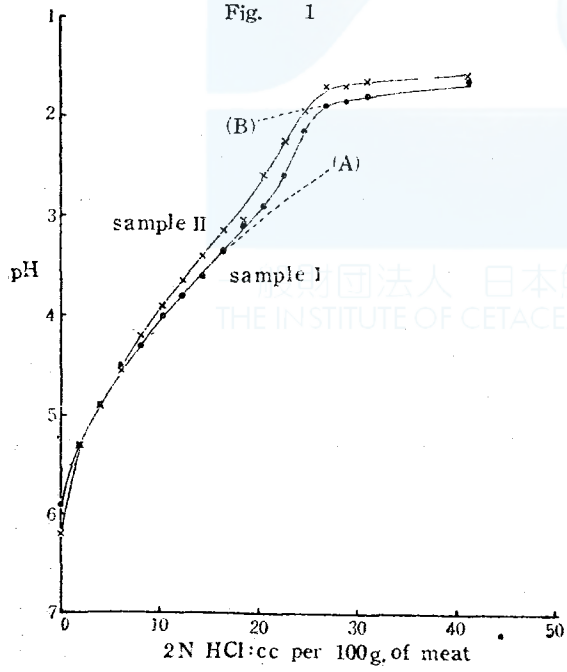
In order to find out the effect of pH on decrease in freshness of whale meat, buffer solution of pH 2; 4.2; 5.9 and 7.7 was added to minced whale meat and left standing for 144 hours at room temperature and the changes in the quantity of volatile basic nitrogen and formol titrating nitrogen were studied. At pH 2 and 4.2, it was observed that formol titrating nitrogen increased slightly but volatile basic nitrogen showed almost no increase. At pH 5.9 and 7.7, both nitrogens showed a very large increase. That is, decrease in freshness may be stopped at pH lower than 4.2, pH 4.2 is very nearly the same as the growth limit pH of bacteria on the acidic side.

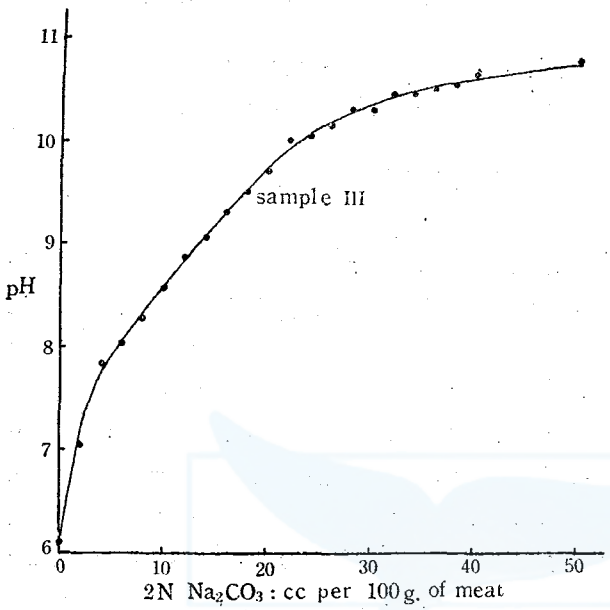
From this result, the author planned a storage experiment on whale meat at pH outside the growth range of bacteria. However, Nakae[1] reports that, with the object of industrial treatment of sardine, he was successful in preventing spoilage of sardine by storage at pH below 3.2 by using HCl. HCl was used in the author's experiment and first of all, in order to find out the required quantity of HCl, 2*N* HCl was used and titration curve of whale meat was obtained (Fig. 1). At the same time, titration curve by 2*N* Na_2CO_3 was obtained because it was necessary for other experiment (Fig. 2). Samples in all cases were baleen whale meat.

Fig. 1



Nakae[2] obtained titration curve with HCl on many kinds of fish and reports that generally there is less buffer action

Fig. 2



between pH 6—4 and appears strongly between the pH 4—3 range. According to the result obtained by the author, with whale meat, buffer action is weak between pH 2—3 and pH 5—7.7 range and appeared relatively strongly at other parts. As can be observed from Fig. 1, buffer capacity was somewhat small until up pH of about 3, in Sample II which is high in fat content and low in other constituents when compared with Sample I which has the opposite content of the various constituents.

Titration curve with HCl clearly indicates that it is composed of two types of curves. For example, in the curve of Sample I there is a curve having an extension (A) and a curve with extension (B) and it shows that there is a combination of both curve in between. That is, it is assumed that curve (A) and curve (B) each indicates a separate reaction. Therefore, according to the graph, a reaction shown by curve (A) only takes place up to pH of about 3.5, next, the reaction shown by curve (B) begins and gradually reaction of curve (A) diminishes and reaction of curve (B) only takes place at pH lower than 2. The same can be said for Sample II. Thus, it is very interesting to note that clearly, two reactions takes place one after the other so it might be able to clarify a part of the chemistry of decrease in freshness by investigating this further.

If pH 3 is assumed to be the objective pH for storage, from the above results, about 200 c.c. of 2*N* HCl will be required per 1 kg. of whale meat. Thus, when a lump of whale meat is soaked in half its quantity of water which also contains the aforementioned percentage of HCl, removed after 5 days and boiled together with water, decomposition of the fleshy part was great and also, the meat had an acidic taste. Therefore, this method

can be applied for studying the quantity of volatile basic nitrogen only because actually it is accompanied by the aforementioned changes so it is inappropriate to apply this in practical cases.

Gratitude is expressed to Dr. Tsutomu Maruyama for his kind instructions and review, and appreciation is expressed to Mr. Ryusuke Fukazawa for his assistance in the expriment.

Experiment

Changes in volatile basic nitrogen and formol titrating nitrogen in whale meat at time of adding buffer solution.

To 2 g. each of minced baleen whale meat 18 c.c. of buffer solution of pH 2, 4.2 (mixed solution of HCl—NaAc); 5.9, 7.7 (mixed solution of phosphate) was added and after standing for 144 hours at room temperature in summer, 30 c.c. of absolute alcoholic *N*/100 H_2SO_4 was added to stop further changes and the following analysis made.

Volatile basic nitrogen— The above mixture is made slightly acidic, boiled mildly on a water bath to evaporate the alcohol and made to about 20 c.c., 1 g. of MgO added and as previously reported[3], volatile basic substance was collected into *N*/50 H_2SO_4 by the aeration method and titrated back with *N*/50 NaOH.

Formol titrating nitrogen— The above mixture is made slightly acidic, heated in a mildly boiling water bath for 15 minutes, drained off and washed 3 times by heating for 5 minutes in water bath with 10 c.c. of distilled water each time. 1 c.c. of 20% sulfosalicylic acid is added to the filtrate and washing and left standing for one night. It is then filtered, washed, filtrate and washing made to 40 c.c. and 25 c.c. of this is titrated by the usual method.

The result obtained was as follows:

	Volatile basic Nitrogen (mg/100 g.)	Formol titrating Nitrogen (mg/100 g.)
At start	43.4	100
pH 2	41.0	131
pH 4.2	44.1	154
pH 5.9	361	555
pH 7.7	More than 389	969

Titration curve.

The sample whale meat were three kinds of baleen whale meat (frozen) and their composition were as follows:

	Moisture %	Crude Protein %	Crude Fat %	Ash %
Sample I	72.65	21.48	3.97	1.02
Sample II	63.80	19.57	15.13	0.85
Sample III	76.89	20.70	1.65	0.95

a) Titration curve by HCl.

Samples I and II were used. These were minced with a meat grinder, variable quantity of 2*N* HCl and distilled water added to 10 g. of minced meat and the total quantitiy made in to 20c.c. of slushy substance. It is left standing for one night and pH determined with Yokogawa type antimony electrode hydrogen ion meter. However, pH of the sample with 0 c.c. HCl added was determined one hour after addition of distilled water.

The following result was obtained. From this, the curve in Fig. 1 was obtained.

2*N* HCl (c.c. per 100g. of meat)	0	2.05	4.11	6.16	8.22	10.27	12.32	14.38	16.45	18.49
pH Sample I	5.9	5.3	4.9	4.5	4.3	4.0	3.8	3.6	3.35	3.1
pH Sample II	6.2	5.3	4.9	4.55	4.2	3.9	3.65	3.4	3.15	3.05

2*N* HCl (c.c. per 100g. of meat)	20.54	22.59	24.65	26.70	28.76	30.81	41.08
pH Sample I	2.9	2.6	2.15	1.9	1.85	1.8	1.65
pH Sample II	2.6	2.25	1.95	1.7	1.7	1.65	1.60

b) Titration curve by Na_2CO_3

Sample III was used, treated in the same manner as a) and the following result was obtained. From this, the curve in Fig. 2 was obtained.

2*N* Na_2CO_3 (c.c. per 100g. of meat)	0	2.0	4.0	6.0	8.0	10	12	14	16	18	20
pH (Sample III)	6.1	7.05	7.85	8.05	8.3	8.6	8.9	9.1	9.35	9.55	9.75

2*N* Na_2CO_3 (c.c. per 100g. of meat)	22	24	26	28	30	32	34	36	38	40	50
pH (Sample III)	10.05	10.1	10.2	10.35	10.35	10.5	10.5	10.55	10.6	10.7	10.85

References

1) Nakae and co-workers: J. Fermentation Technology **21**, 630, 635 (1943).

2) Nakae: Ibid, **21**, 661 (1943).

3) This periodical No. 1, page 21.