A C T A A L I M E N T A R I A P O L O N I C A

Vol. VI (XXX), No. 4 1980

JANINA GRABOWSKA
HALINA ZIMIŃSKA
ZENON ZIEMBA

# EFFECTS OF HEAT TREATMENT ON THE CONTENTS OF HYDROGEN SULPHIDE AND ODOUR OF KRILL MEAT

Department of Chemistry and Food Technology, Technical University, Gdańsk

Key words: hydrogen sulphide, krill meat odour, acidification of meat

The canned krill meat possese highly undesirable odour due to large amount of hydrogen sulphide formed during heat treatment. This quality deterioration can be avoided by acidifying the meat prior to heating. From the final quality point of view the most favorable range of the equilibrium pH was 6 to 5.5.

Volatile compounds of sulphur as well as volatile carbonyls and fatty acids are the components of a typical odour of meat after treatment [3, 4, 5, 7, 8, 10, 11, 13, 14]. Hydrogen sulphide is one of the most volatile, reactive and odorous compounds. It turns up in meat in quantities largely exceeding the threshold value [1, 8, 11]. In spite of this, it is not usually detected as a separate distinct odorous factor. Only when there are greater concentrations of it in meat some negative smell turns up (e.g. the smell of boiled eggs — [11]). A negative correlation was observed between the contents of $H_2S$ in canned sterilized meat and the desireability of odour [12].

In canned krill meat the intensity of hydrogen sulphide was unusually high, which caused the authors to examine effects of heat treatment on the contents of $H_2S$ and defining the possibilities of formation of that compound under different processing conditions.

## MATERIALS AND METHODS

The raw material was provided by the "DALMOR" company (Gdynia; 9) and obtained from deep-frozen krill, stored prior to peeling, 6 to 18 months. The krill meat was white and odourless. The chemical composition is given in Table 1.

A C T A A L I M E N T A R I A P O L O N I C A
Vol. VI (XXX), No. 4 1980

JANINA GRABOWSKA
HALINA ZIMIŃSKA
ZENON ZIEMBA

# EFFECTS OF HEAT TREATMENT ON THE CONTENTS OF HYDROGEN SULPHIDE AND ODOUR OF KRILL MEAT

Department of Chemistry and Food Technology, Technical University, Gdańsk

Key words: hydrogen sulphide, krill meat odour, acidification of meat

The canned krill meat possese highly undesirable odour due to large amount of hydrogen sulphide formed during heat treatment. This quality deterioration can be avoided by acidifying the meat prior to heating. From the final quality point of view the most favorable range of the equilibrium pH was 6 to 5.5.

Volatile compounds of sulphur as well as volatile carbonyls and fatty acids are the components of a typical odour of meat after treatment [3, 4, 5, 7, 8, 10, 11, 13, 14]. Hydrogen sulphide is one of the most volatile, reactive and odorous compounds. It turns up in meat in quantities largely exceeding the threshold value [1, 8, 11]. In spite of this, it is not usually detected as a separate distinct odorous factor. Only when there are greater concentrations of it in meat some negative smell turns up (e.g. the smell of boiled eggs — [11]). A negative correlation was observed between the contents of $H_2S$ in canned sterilized meat and the desireability of odour [12].

In canned krill meat the intensity of hydrogen sulphide was unusually high, which caused the authors to examine effects of heat treatment on the contents of $H_2S$ and defining the possibilities of formation of that compound under different processing conditions.

## MATERIALS AND METHODS

The raw material was provided by the "DALMOR" company (Gdynia; 9) and obtained from deep-frozen krill, stored prior to peeling, 6 to 18 months. The krill meat was white and odourless. The chemical composition is given in Table 1.

Table 1. Chemical composition of krill meat

| Content in meat % | Water | Proteins | Lipids | Carbohydrates | Minerals | pH |
|---|---|---|---|---|---|---|
| | 76.2 | 21.6 | 1.9 | 0.016 | 0.86 | 7.6 |
| By dry mass % | — | 88.6 | 7.8 | 0.07 | 3.5 | |

The studies were performed within a model system. The krill meat consisted for 64% of the canned stuff and the remaining 36% were water and salt. Acidity of the meat was modified with 0.2 n hydrochloric acid. The steel tin, cans lacquered inside (99×26 mm) were. Pasteurization in water (70° to 100°C/-$T_R$) and sterilization — in overheated water $T_R$ = 108, 116, 126°C. The profile of temperature data in the geometric centre of the canned product, during heating or cooling, in the course of pasteurisation or sterilization was controlled with the use of thermocouples. Effects of the time-temperature combinations were expressed by means of the heat dose $F_0$:

$$F_o = \int_0^{\tau} 10^{\frac{T-121\cdot 11}{10}} d$$

where the limits of the integer calculus 'o' and 'τ' are bound with the initial and final occurences of the temperature $T = T_R - 10$ in the case of pasteurisation and T = 90°C in the case of the sterilisation.

The canned krill meat odour was characterized by defining the quality of the odour notes. The intensity of the basic odour notes hydrogen sulphide, boiled fish, seaweed-like and rancid, were evaluated according to a 10 point scale. The assesment was performed by 4 judges with formerly established high levels of sensoric sentitivity [2], but without any previous training in the meat quality assessment.

Only one of those persons was experienced in methods of sensoric analysis of food products, mostly fish and meat. On account of the above the group assessment was arrived at during discussions. The odour evaluation was performed immediately after opening a con of krill without taking the contents out.

The level of $H_2S$ was determined in the fluid part of the canned product by means of the colour reaction with N,N'-dimethylo-phenylodiamine in the presence of $FeCl_3$ [6].

## RESULTS AND DISCUSSION

Due to the similarity of the chemical composition and nutritional values of krill meat to other sea products it is being considered to use

krilil as protein feed consumed by man. One of the forms of krill meat to be used is canned product. Initial work revealed, however, the development of an unpleasant smell of hydrogen sulphide in such cans. Systematic studies of the effects of heating on the quantity of sulphur compounds and on the odour of canned krill meat were performed. On the basis of these investigations it was observed that during heating of the standard raw material (storaged in deep-freeze for 6 months before peeling) to 70°C no hydrogen sulphide appears and the odour of canned

Table 2. The content of hydrogen sulphide in canned krill meat as influenced by freezing storage time

| Heating temperature °C | Storage time in −30°C before peeling (months) | | |
|---|---|---|---|
| | 6 | 12 | 18 |
| | μgS/100 g of meat | μgS/100 g of meat | μgS/100 g of meat |
| 70 | 15 | 27 | 36 |
| 80 | 16.5 | 27 | 36 |
| 90 | 18 | 32.4 | 40.5 |
| 100 | 35.2 | 48.6 | 121.5 |

krill produced under such conditions is described as "seaweed-like" and boiled fish. Only when 70°C is exceeded hydrogen sulphide collects in quantities dependent on the temperature level, time of its operation and quality of the meat (Fig. 4). The dependence of the hydrogen sulphide concentration on the combination of temperature and its duration, expressed in terms of $F_0$ heat rate takes on the form of an exponential curve (Fig. 1).

The sensoric assessment of the canned meat odour with different levels hydrogen sulphide content of (Table 2 and Fig. 3) proved that the hydrogen sulphide note appears when concentration of $H_2S$ in cans reaches ca 20 μgS/100 g meat. In the case of krill storaged for 6 months it takes place at 90°C while after 12 months of storage — at 70°C (Table 2). In canned meat heated to higher temperature the content of hydrogen sulphide increases thus intensifying the olfactory effects. The dependence is in accordance with Weber-Fechner equation [2] (Fig. 3). The maximum intensity of odour points was arrived at when concentration of hydrogen sulphide was the range of 450-600 μgS/100 g meat (Fig. 3). This level of $H_2S$ was always present in canned krill heated for one hour at 100°C and in sterilization temperatures. For this reason the meat with natural acidity from krill storaged for 6 months in deep freeze before peeling is unfit for sterilized canning. In order to utilize it for such purpose it is necessary to apply a technique impeding the production of $H_2S$.

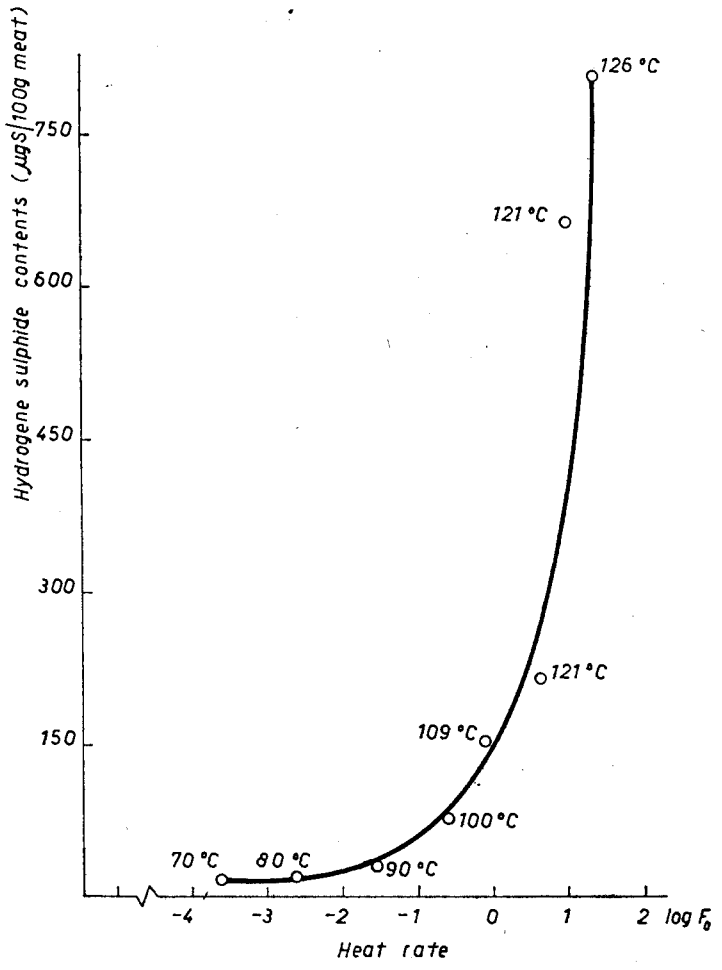


Fig. 1. The content of $H_2S$ in canned krill meat heated to different temperature levels $T_R/C$ (the pH of krill meat was 7.6 and storage time before peeling 9 months in -30°C)

An effective procedure of preventing excessive production of $H_2S$ during heating was acidification of meat. The higher the level of acidity in meat the lower the quantity of $H_2S$ and the relationship is of expotential character (Fig. 4). In pasteurized krill meat of pH below 7 the quantiy of $H_2S$ is lower than the level sensorily detectable (Fig. 5). In the case of sterilized canned krill meat (at $F_0$ ca 5, regarded as bacteriologically necessary) it is indispensable to increase acidity below pH = 6,0 (Fig. 4) in order to eliminate the $H_2S$ odour note. Acidification alters the odour characteristics of canned meat. The odour of canned krill meat of natural acidity was described as hydrogen sulphide-like or boiled fish-like, while increasing of acidity by one unit of pH is enough to remove such odours.

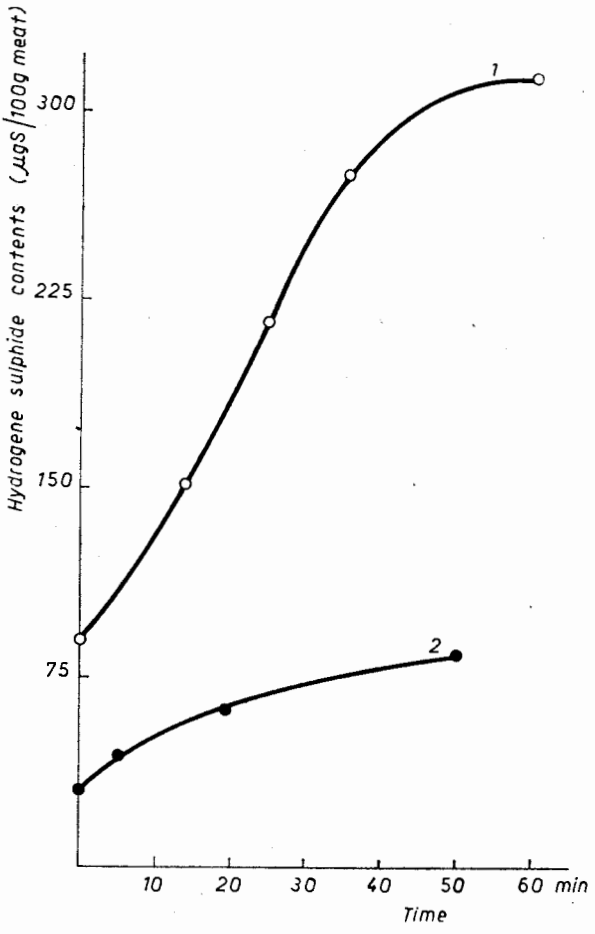


Fig. 2. The influence of heating time in 100°C on $H_2S$ content in canned krill meat; 1 — come-up time 54 min, 2 — come-up time 20 min

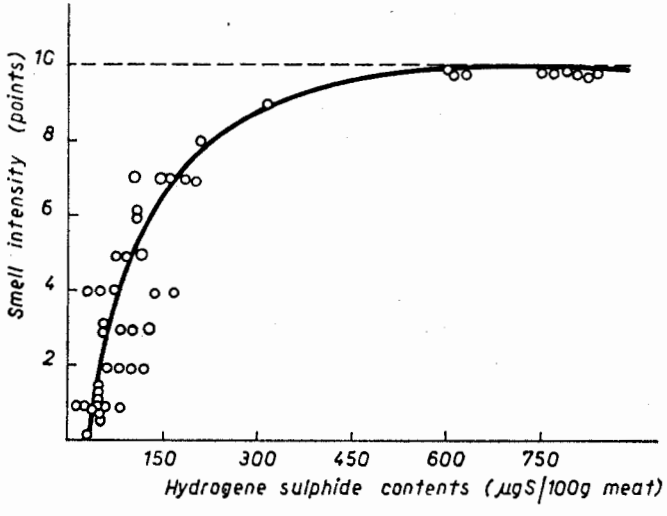


Fig. 3. The relation of hydrogen sulphide odour intensity and its content in canned krill meat

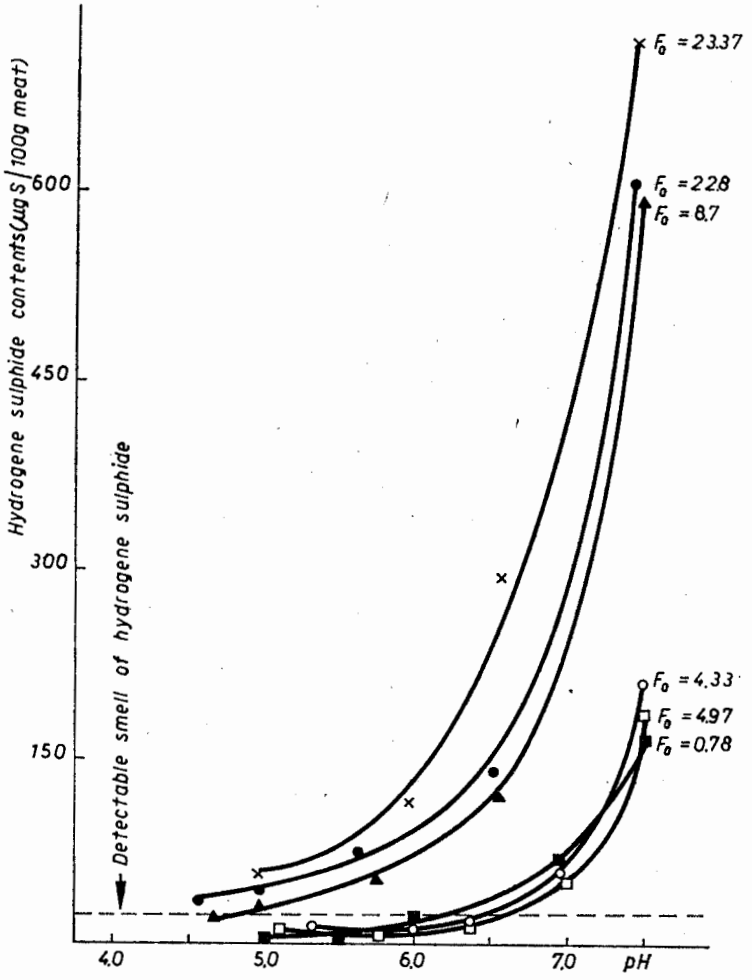


Fig. 4. Changes in hydrogen sulphide content as a function of pH of krill meat by different various value

They are replaced by a seaweed-like odour that dominates in canned meat with pH ranging between 5.5 and 6.8. Further acidification accounts for the fact that gradually the seaweed odour disappears and the most characteristic feature of the odour range is rancidity (Fig. 6).

## CONCLUSIONS

1. The dependence of the level of concentration of $H_2S$ in canned krill meat on heating temperatures takes the form of an exponential curve.

2. The intensity of the $H_2S$ odour changes depending on the content of the compound in krill meat according to Weber-Fechner equation.

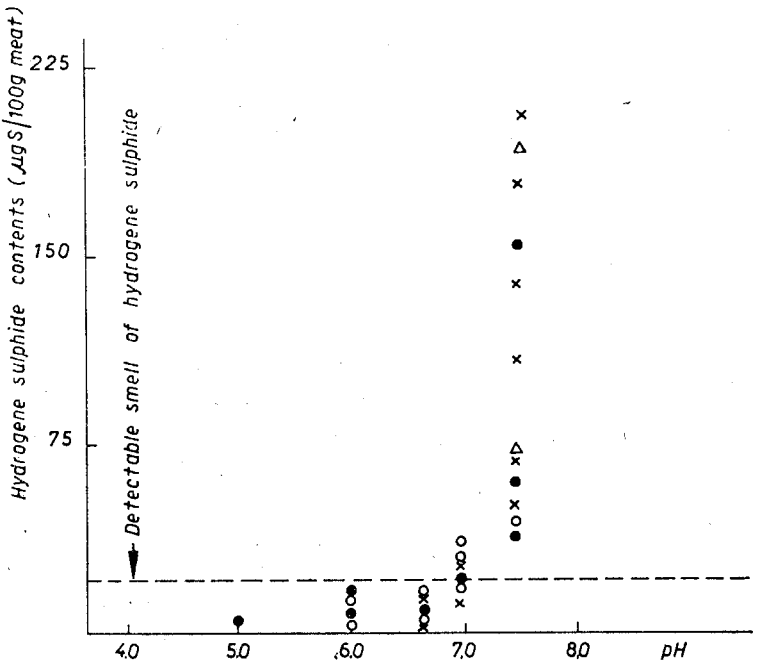


Fig. 5. The content of hydrogen sulphide in krill meat of various pH heated 30 min at 70-100°C

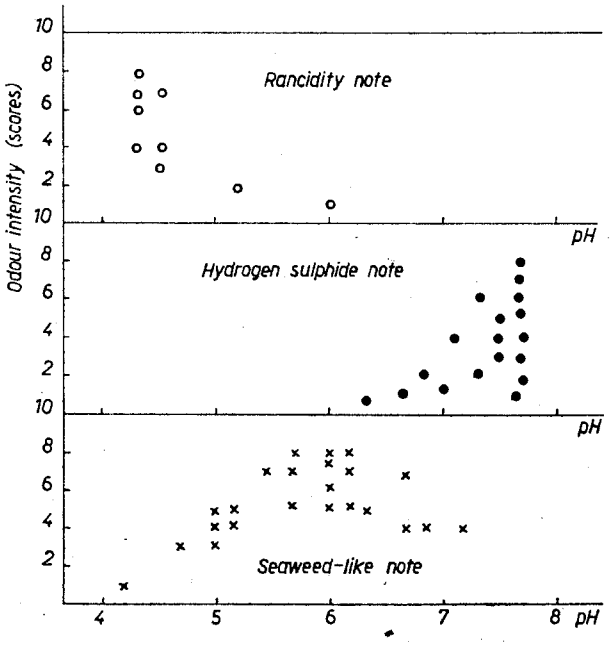


Fig. 6. The intensity of three main odour components of canned krill meat as influenced by the pH of the material

3. Krill meat stored in deep-freeze for about 6 months before peeling is unfit for canning due to large amounts of hydrogen sulphide that are produced.

4. The most effective procedure to prevent excessive production of $H_2S$ during heating is acidification of the meat. The optimal land of acidification is about pH 6.

LITERATURE

1. Baryłko-Pikielna N., Mielniczuk Z., Daniewski M.: Roczniki Instytutu Przemysłu Mięsnego i Tłuszczowego 1976, 13, 67.
2. Baryłko-Pikielna N.: Zarys analizy sensorycznej żywności, WNT, Warszawa 1975, 285.
3. Gruenweld D. S., Patnaik R. K.: Agric. Food Chem., 1971, 19, 775.
4. Hughes R. B.: J. Sci. Food Agric., 1964, 15, 290.
5. Khayast A.: J. Food Sci., 1977, 42, 601.
6. Mc Lay R.: J. Sci. Food Agric., 1967, 18, 605.
7. Mecchi E. P., Pippen E. L., Lineweaver H.: J. Food Sci., 1964, 29, 393.
8. Parr L. J., Levett G.: J. Food Technol., 1963, 4, 283.
9. Patent P-192426.
10. Persson T., von Sydow E.: J. Food Sci., 1974, 39, 406.
11. Pippen E. L., Mecchi E. P.: J. Food Sci., 1969, 34, 443.
12. Przeździecka T., Żółtowska A.: Roczniki Instytutu Przemysłu Mięsnego, 1967, 4, 107.
13. Ziemba Z., Mälkki Y.: Lebensm.-Wiss. u. Technol., 1971, 4, 118.
14. Żółtowska A.: Roczniki Instytutu Przemysłu Mięsnego, 1967, 4, 91.

*Manuscript received: March, 1979*
*Authors address: 80-233 Gdańsk, Majakowskiego 11*

*J. Grabowska, H. Zimińska, Z. Ziemba*

WPŁYW OBRÓBKI CIEPLNEJ NA ZAWARTOŚĆ SIARKOWODORU W MIĘSIE KRYLA

Instytut Chemii i Technologii Organicznej oraz Żywnościowej, Politechnika Gdańska, Gdańsk

Streszczenie

Mięso kryla po obróbce cieplnej w naczyniach hermetycznych ma nieprzyjemny zapach spowodowany wydzielaniem się siarkowodoru.

W celu ustalenia warunków zapobiegających powstawaniu siarkowodoru mięso kryla ogrzewano w puszkach w temperaturze 70-121°C. Kwasowość mięsa zmieniano 0.2 n kwasem solnym w zakresie $4.0 < pH < 7.5$.

Natężenie wyróżników występujących w profilu zapachowym konserwy określano w skali 10-punktowej. Wyniki oznaczeń sensorycznych korelowano z zawartością w warstwie wodnej siarkowodoru.

Stwierdzono, że w konserwach z mięsa otrzymanego z kryla po 6-miesięcznym przechowywaniu w warunkach zamrażalniczych zapach siarkowodoru pojawia się po ich ogrzewaniu w temperaturze 90°C, a po 12-miesięcznym przechowywaniu już w 70°C. Zależność stężenia siarkowodoru od temperatury ogrzewania ma charakter krzywej wykładniczej.

Obniżenie kwasowości środowiska poniżej wartości pH 6.0 zapobiega powstawaniu niepożądanego zapachu w badanych temperaturach.