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D9

THE DEPLETION OF ADDED SODIUM NITRITE IN MEATS

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It has long been known that the amount of nitrite actually required for colour development is very small. We have been able to produce normal-tasting hams, for instance, by adding only 1/10 the normal amount of nitrite (about 15 ppm.).[1] More recently our work on the relationship between nitrite content and toxinogenesis by C. botulinum[2] has led us to examine more fully the losses of nitrite that occur during cooking and storage of cured meat products. Our experience, for instance, shows that canned hams contain only a fraction as much nitrite after several months storage as was present directly after canning. There was a rapid reduction of nitrite during retorting and then a further slower depletion on storage.

Other investigators have noted a similar depletion with time [3],[4],[7]. Dyson Rose [3] of the National Research Council, for instance, noted that there was a progressive destruction of nitrite (which was independent of bacterial contamination) which he attributed to be due to the reducing systems of fresh pork. The pH of the product influenced the depletion rate. He worked on fresh pork extracts in the temperature range of 60-120°F (15.6 - 48.9°C). Morris[4] noted a correlation of nitrite content with production of gaseous pressure, due presumably to oxides of nitrogen, during canning. This was later confirmed in tests in our laboratories. Walters and Taylor[5] used differential absorption monometry to show that a gas having the solubility characteristics of nitric oxide was produced when pork muscle was incubated with nitrite at a concentration of 2500 ppm. at 37°C. Gas was passed through water, alkali, then alkaline

sulphite using a Warburg apparatus. The gas passed by alkali but trapped by alkaline sulphite was presumably NO. This was later confirmed by mass spectrometry. Kueck[7] in a patent on a process for canned meat reported data showing rate of depletion of nitrite in canned meat held at various temperatures.

Although there has been some work reported in the literature, it has (with the exception of Kueck) been under very specific and sometimes unrealistic conditions. Dyson Rose for instance worked on aqueous pork extracts at 60-120°F (15.6 - 48.9°C) while Walters and Taylor used abnormally high levels of nitrite (2500 ppm.). We felt therefore that a general investigation into the area of nitrite depletion was warranted. Recent emphasis on the importance of nitrite level in papers by Silliker and by Pivnick et al.[6],[2] in which they demonstrated that nitrite has an inhibitory effect on bacterial growth and toxingenesis after processing, has made this investigation seem more urgent.

In our work, fresh ham meat was ground through a 1/4" plate, then chopped in a silent cutter together with normal amounts of salt brine, phosphate and nitrite. The product was then vacuum canned in small cans (211 x 103) to allow for rapid temperature change (see Graph I) and held at various temperatures. Samples were selected at intervals and analysed for nitrite using the α-napthylamine sulphanilic acid method.[8] Graph II shows the effect of temperature on the rate of depletion of nitrite. Nitrite concentration is plotted on the log scale and time on the linear scale of semi-log graph paper.

A straight line fits most of the data plotted in this manner. These straight lines are characteristic of a reaction in which the rate is proportional to the concentration of the reactant and the slope of such a curve can be defined by specifying its half life. For instance at 190°F (87.8°C) a half life of 4 hours was found for the ham being examined. If this ham originally contained 200 ppm. nitrite and was held at 190°F (87.8°C), it would contain 100 ppm. after 4 hours, 50 ppm. after 8 hours, 25 after 12 hours, etc. As the level of nitrite decreases, the rate of depletion decreases

in the same manner as radioactivity decays until at low levels almost no change occurs. Note that for some samples there appears to be a divergence from the straight line relationship as the concentration drops, indicating that other factors besides temperature and concentration contribute to the rate of depletion.

At room temperature the rate of depletion becomes unusually rapid and is probably due to bacterial contamination. The rapidly increasing slope of the curve seems consistent with an increasing rate of bacterial consumption of nitrite as the bacterial population multiplied. This contention is also supported by the fact that if the nitrite-containing meat is first sterilized to an F_o value of 3 and then held at room temperature, a normal curve of about the expected slope is obtained. This is shown in Graphs II and III.

Examination of Graphs II and III indicates that the slope of the curves or the depletion rate is not greatly altered by sterilization.

Graph IV shows the effect of different levels of added nitrite. The lines showing nitrite concentration with respect to time were essentially parallel over the range of 88-340 ppm. added when the meat was held at 170°F (76.7°C).

Graph V shows the effect of the pH of the meat on the depletion rate when held at 170°F (76.7°C) and 212°F (100°C). The effect appears to be quite pronounced; particularly at 170°F (76.7°C). More work is planned using a wide range of pH. All the preceding data shown in Graphs I and IV were obtained on meat with a pH in the region of 5.9. Note that here, too, as in Graph II there appears to be a considerable deviation from straight line relationship for some samples as the nitrite level becomes low.

If the half life is plotted on the log scale and temperature on the linear scale of semi-log graph paper a reasonably straight line is obtained as shown in Graph VI. This indicates that for a given nitrite concentration the reaction rate is exponentially related to the temperature and doubles for approximately every 22°F (12.2°C) increase in temperature. Thus, at 100°F (37.8°C) the half life was about 80 hours whereas at 122°F (50°C) it was about 40 hours. This,

of course, was for ham meat in the pH region of 5.9. This line might easily be shifted up or down depending on the pH of the meat being used, but it seems probable that the same relationship between temperature and half life would exist at other pH values.

In summary then it appears that the rate of nitrite depletion is proportional to its concentration and doubles for every 22°F (12.2°C) increase in temperature in the absence of nitrite-consuming bacteria, and that it is not greatly affected by heat coagulation of the meat.

This statement is at present based on rather limited experimental data. Although numerous time-temperature conditions were used, only 4 separate ham emulsion preparations were made. Future investigations should include some effort to determine what variability exists between hams. Preliminary studies using high and low pH hams show that the half life is affected by pH. More work will be undertaken along these lines. Other investigators do not appear to have found a relationship between bacterial contamination and depletion rate. This may well be due to the specific conditions which they used, or to a difference in microbial flora. This point should be further studied, possibly with the aid of antibiotics. In Graph II the lines for 190°F (87.8°C) and 150°F (65.6°C) show a distinct departure from straight line relationship at the low nitrite levels. This may be due to an analytical error or it may be a characteristic of this reaction. Some support is lent to this latter possibility by recent analyses of canned meat which were several years old and still contained about 10 ppm. of nitrite. This must be studied further taking special care with the analysis since at this level the method is particularly sensitive to impurities.

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(1) Barnett, H.W., Nordin, H.R., Bird, H.D. and Rubin, L.J. "A Study of Factors Affecting the Flavour of Cured Ham". XI European Meeting of Meat Research Workers, Beograd, 1965.

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(6) Silliker, J.H., Greenberg, R.A., and Schack, W.R., "Effect of Individual Curing Ingredients on the Shelf Stability of Canned Comminuted Meats". Food Tech., 12, 551, (1958).

(7) Kueck et al., U.S. Patent No. 3,192,053. June 29, 1966. Process for Canned Meat.

(8) A.O.A.C., Official Methods of Analysis. 10th Ed., Sec. 23,013, p. 347.

SUMMARY

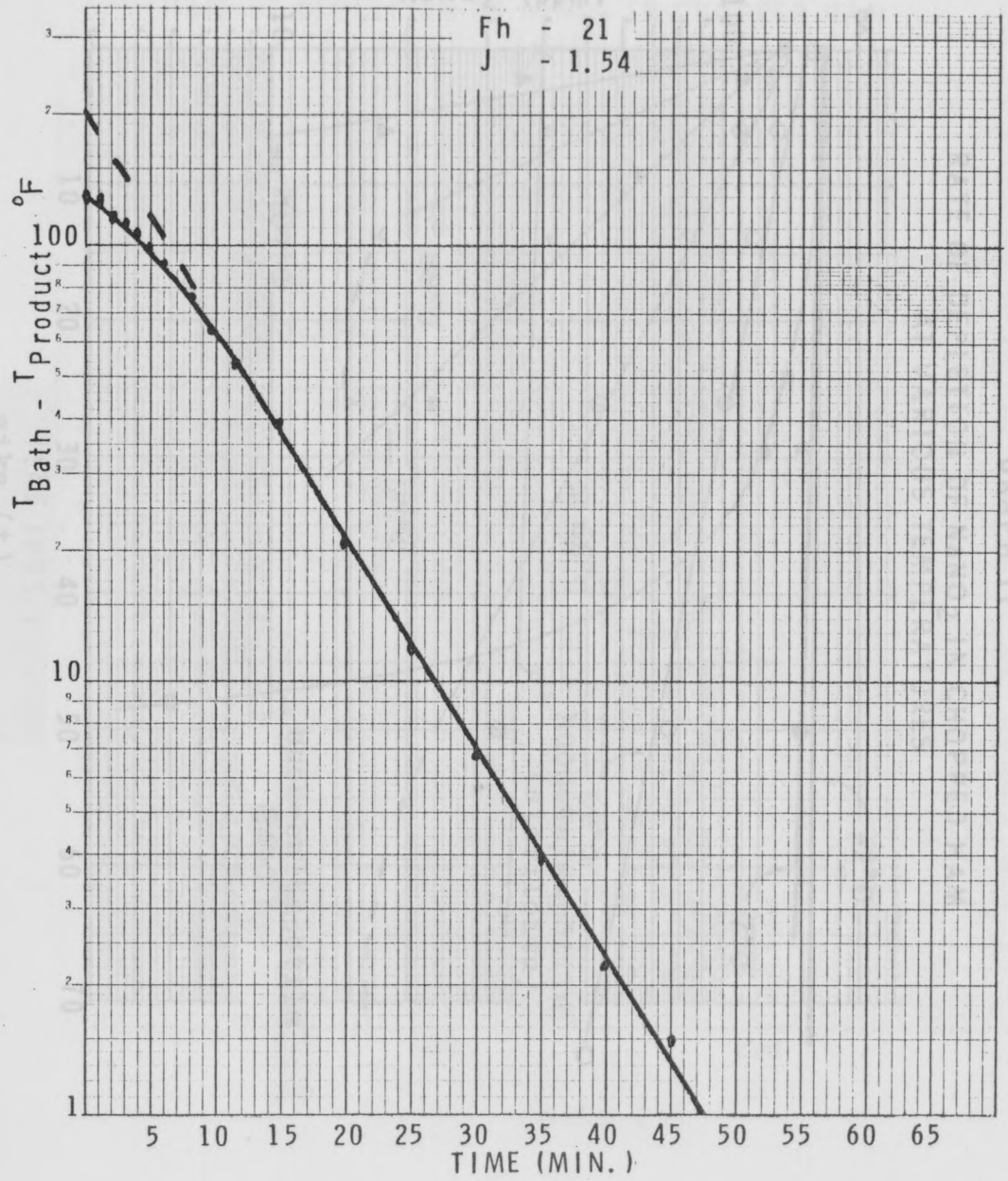
The concentration of added sodium nitrite in meat is progressively reduced during curing, cooking, and storage. The rate of this depletion appears to be exponentially related to temperature and for ham meat at pH 5.9 doubles for every 22°F (12.2°C) increase in temperature over the range studied. Thus the "half life", i.e. the time required for the nitrite to be depleted to one-half its original value, ranged from 500 hours at 40°F (4.4°C) to only 2 hours at 220°F (104.4°C). This relationship appeared to be independent of initial nitrite concentration under the range of conditions tested. The rate of nitrite depletion was unusually rapid at room temperature unless the product was first sterilized, indicating that bacterial consumption was probably a factor. Preliminary studies have indicated that the rate of nitrite depletion is higher at lower pH values.

RÉSUMÉ

La concentration de nitrite de sodium dans la viande diminue progressivement durant le vieillissement, la cuisson et l'entreposage. La vitesse de diminution paraît être liée exponentielement à la température, et pour le jambon au pH 5.9 se double chaque 22°F (12.2°C) augmentation de température dans la région étudiée. Alors la "demi-vie", le temps requit pour le nitrite de diminuer de la moitie de sa valeur originale, était de 500 hr. à 40°F (4.4°C) à 2 hr. à 200°F (104.4°C). Cette relation paraît être indépendante de la concentration initiale de nitrite dans les conditions essayées. La vitesse de diminution de nitrite était plus rapide que prévue à température ambiante, à moins que le produit soit stérilisé avant, indiquant que la consumation de nitrite par les microbes était probablement un facteur. Des études préliminaires ont indiqué que la vitesse de diminution de nitrite est plus grande à des valeurs de pH inférieurs.

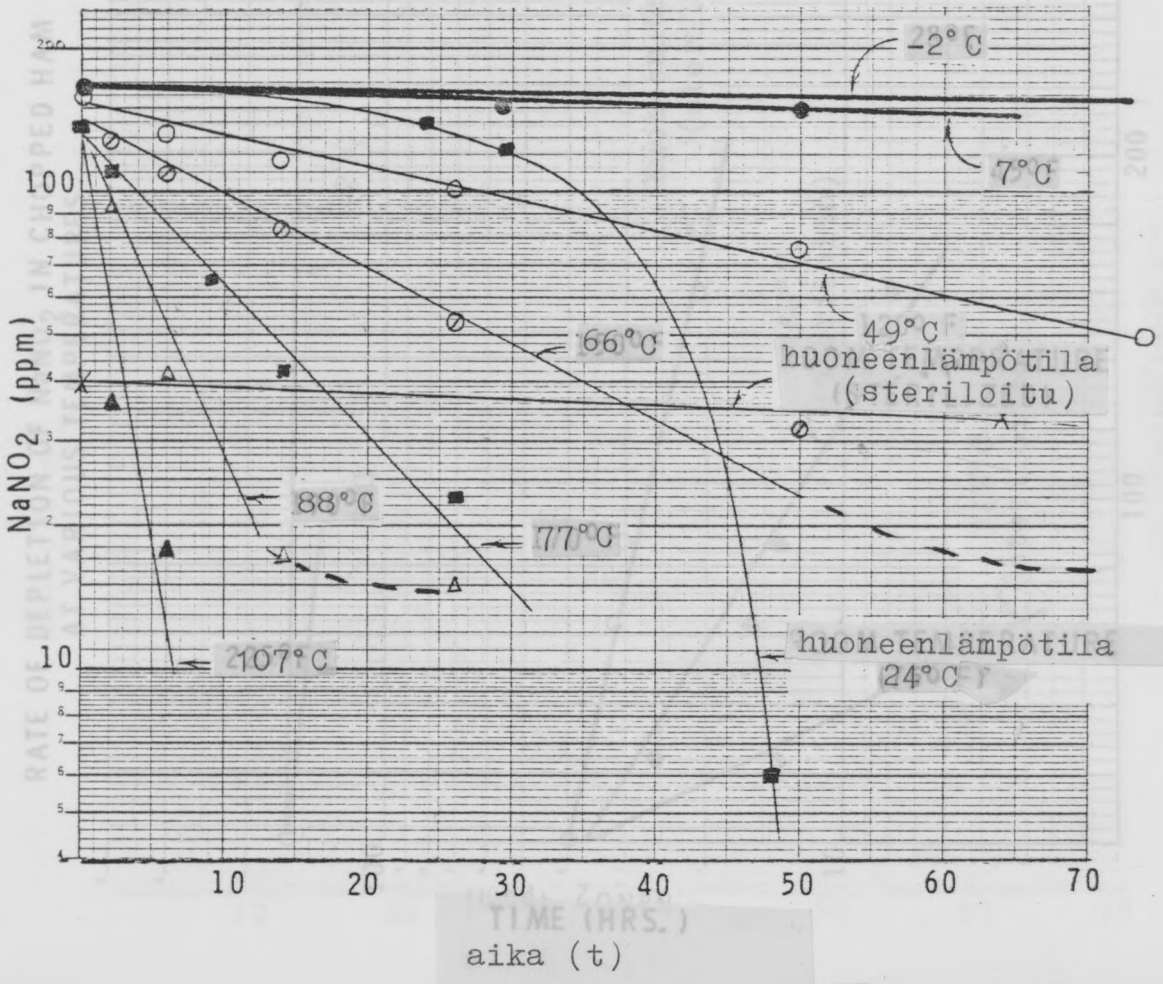
GRAPH I

HEATING OF EMULSION
IN 103 X 211 CANS
IN 170°F OIL



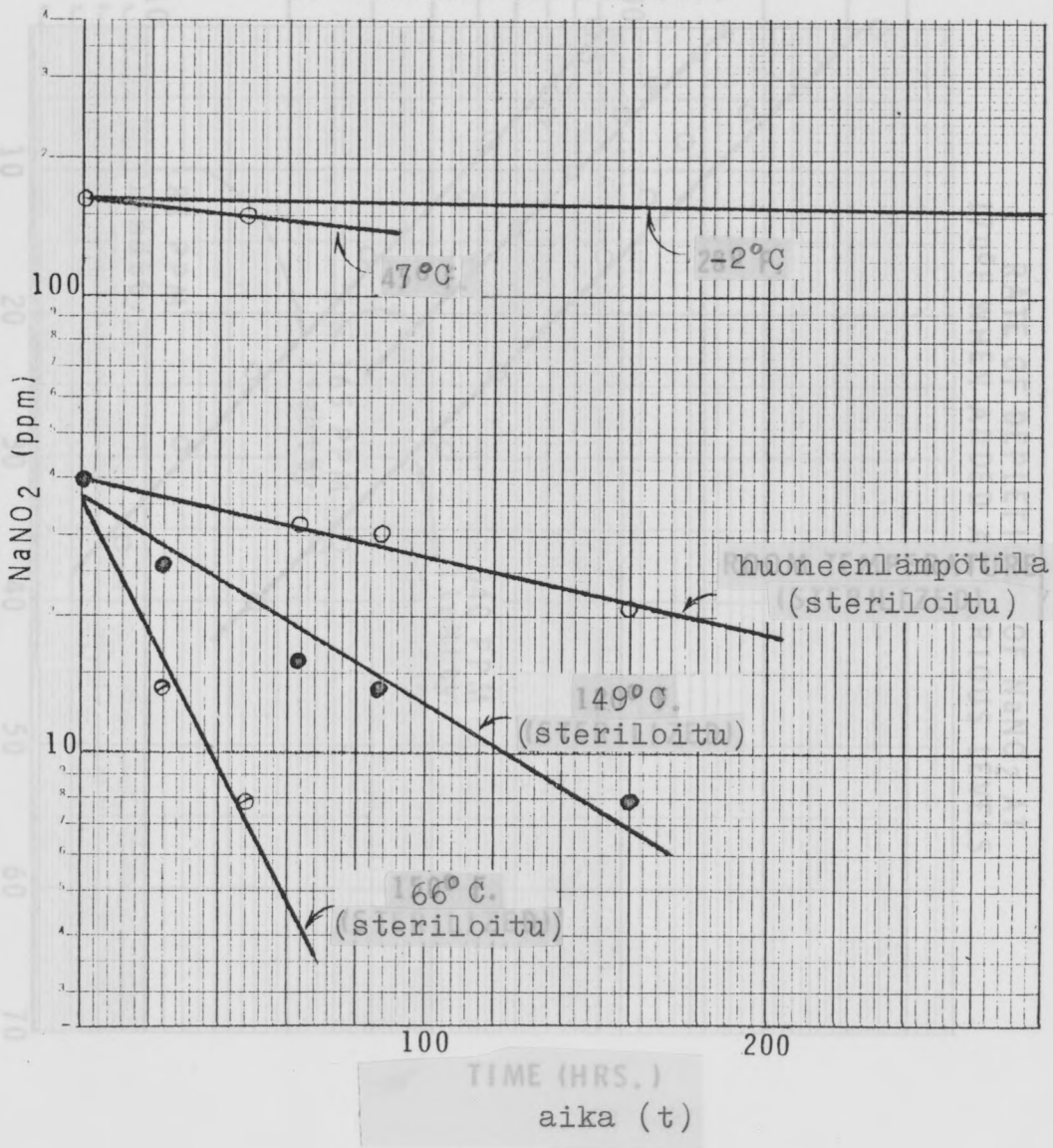
GRAPH 11

RATE OF DEPLETION OF $NaNO_2$ IN CHOPPED HAM AT VARIOUS TEMPERATURES



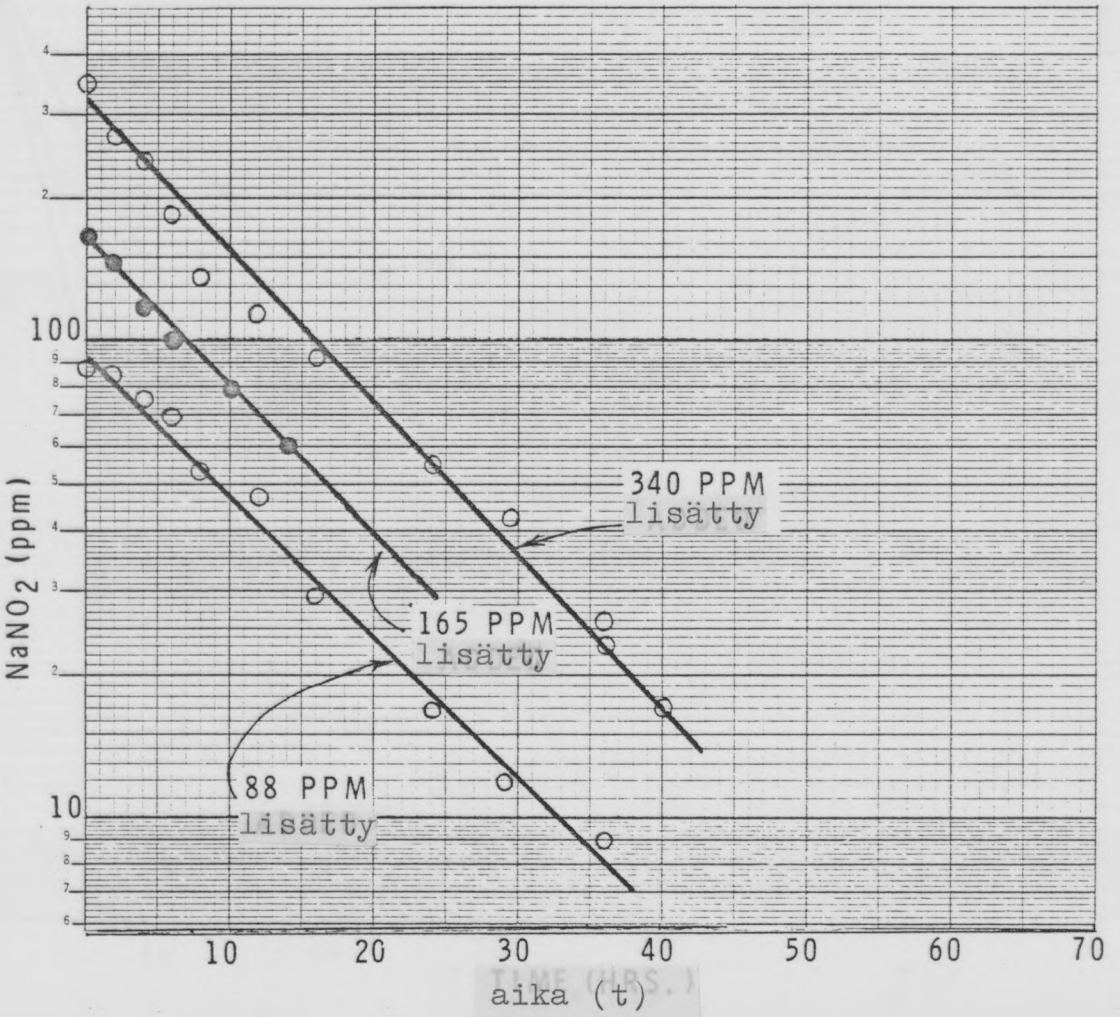
GRAPH 111

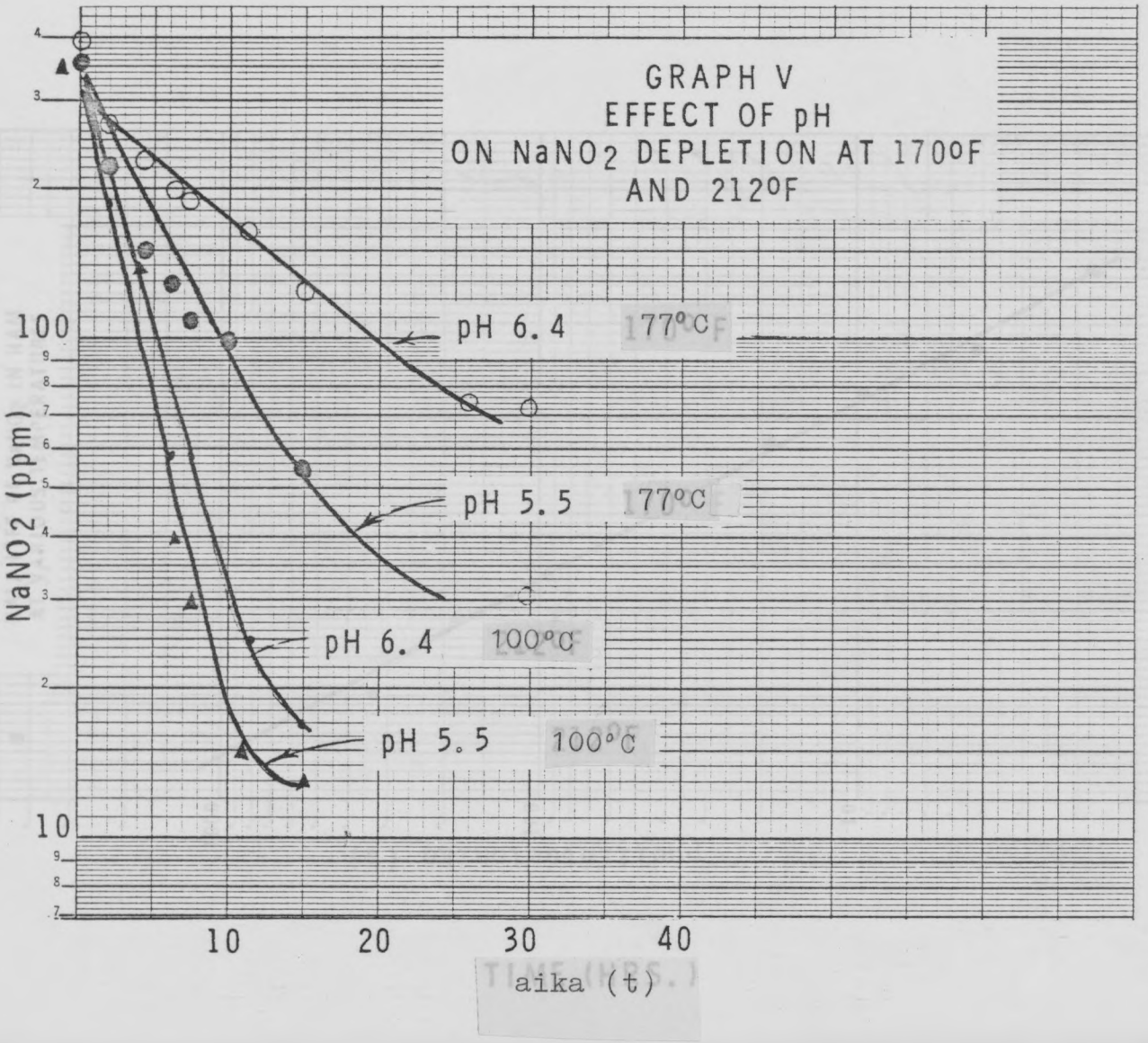
RATE OF DEPLETION OF $NaNO_2$ IN CHOPPED HAM
AT VARIOUS TEMPERATURES

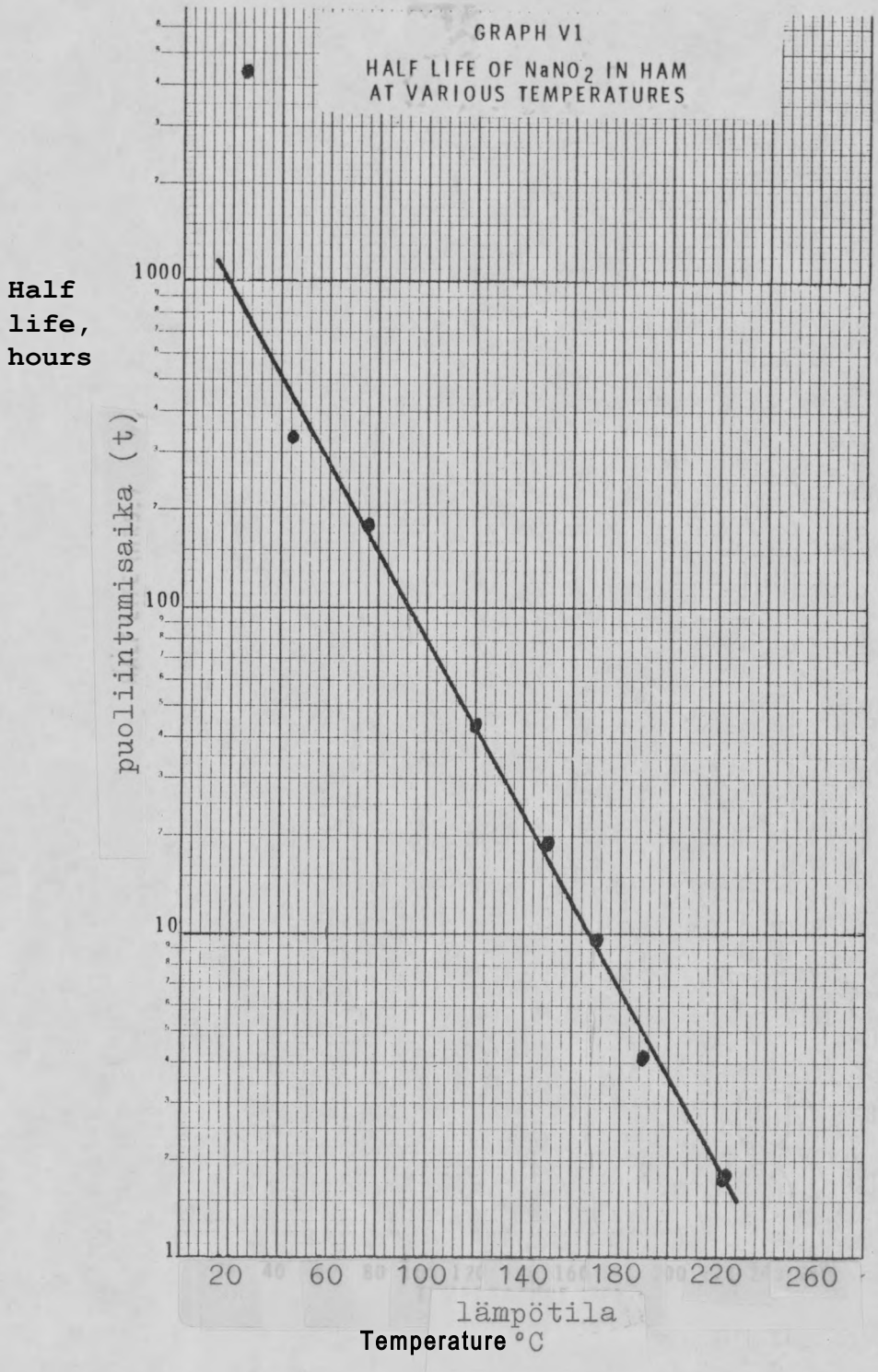


GRAPH 1V

RATE OF DEPLETIONS OF $NaNO_2$ AT
170°F WHEN ADDED AT VARIOUS LEVELS




GRAPH V
EFFECT OF pH
ON NaNO2 DEPLETION AT 170°F
AND 212°F
pH 6.4 77°C
pH 5.5 77°C
pH 6.4 100°C
pH 5.5 100°C
NaNO2 (ppm)
100
10
10
20
30
40
aika (t)


GRAPH V1
HALF LIFE OF $NaNO_2$ IN HAM
AT VARIOUS TEMPERATURES
Half life, hours
puolintumisaika (t)
1000
100
10
1
20
60
100
140
180
220
260
lämpötila
Temperature °C