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Some Fundamental Relationships of Cooking Losses,
Temperature and Time

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There is no need to stress the necessity of investigations into the basic relationships of cooking losses, time and temperature. In studies concerned with the water binding and holding capacity of meat described in related literature the samples to be examined were treated generally at various temperatures for the same periods of time /1-9/. No attention was paid however to the basic relationships of cooking losses, time and temperature.

The problem involved may be approached theoretically in two different ways: One of the methods is the setting up of a hypothesis and expressing it in mathematical terms. Mathematics furnishes means for the expression of the fundamental laws and principles in a relatively short and precise manner whenever relationships of variable factors are involved. The mathematical solution then can be verified by actual experimentation. A characteristic example of this is Michaelis' and Menten's reaction kinetical law. In this case the equation was evolved from the simple hypothesis related to the process of enzyme reaction. It is proved that the results of enzyme-kinetical measurements will fit mathematical models.

However so far nobody succeeded in establishing models related to cooking losses in meats and meat products which may be expressed in mathematical form. This could be attempted only if more detailed knowledge as to colloid-chemical and other changes occurring on the heat treatment of meats were available.

When pure mathematical consideration fails or when pure theory cannot be applied readily to the problem in question, empirical relationships must be established for experimental data. The thinking process is reversed and instead of experimental verification of a postulated theoretical relationship, an empirical relationship is established from experimental data available.

Materials and Methods.

In the experiments m. quadriceps femoris of pigs was used. Samples were obtained directly from the slaughterhouse, after the pig halves had been in cold storage for 48 hours.

The muscle trimmed of excessive fat and connective tissue was passed through the disk of a meat grinder with perforations of 2 mm diameter. The ground meat was thoroughly mixed and divided into two lots. 2,5 % NaCl was added to one lot /samples marked: s/ and 2,5 % NaCl and 0.4 % $\text{Na}_4\text{P}_2\text{O}_7$ /samples marked: p/ to the other. Each lot was thoroughly homogenized and stored in a refrigerator for 24 hours. Hereafter 20 g samples of the meat were packed in 15,5 x 10 cm

cellothene /cellophane and polyethylene/ bags. The samples were rolled flat and sealed. The thickness of the sample, pouch included, did not exceed 1,2 mm.

During heat treatment of sausages the temperature of the emulsion in each location within the casing is, among others, a function of the temperature environment, time and the coordinates of space. It may be calculated that the thin layer of meat in the pouch reached the constant temperature of the cooking water within 20 seconds. By this method the cross section of the sample could be kept during the whole processing period at a known and constant temperature. Cooking was carried out in an ultrathermostatically controlled waterbath. Great care was taken to ensure the water to be in direct contact with the whole surface of each pouch, during the whole cooking period. After t cooking period the samples were removed from the water-bath and immediately chilled in running water. When reaching room temperature the cooking losses were determined. Preliminary experiments in the temperature range between 50°C to 90°C proved that the water soluble components of the meat did not diffuse through the film into the cooking water.

The determination of cooking losses is the step in the experimental procedure that needs the greatest care. It was done in the following manner: each pouch was opened, the juice drained and the residual meat was placed on a filter paper. Both sides of the

sample were blotted. This process, taking about 25 to 30 seconds, was repeated with a dry filterpaper. Then the residual meat was weighed. To achieve greater accuracy, determination was always carried out by the same person.

Cooking loss /y/ is expressed as follows:

$$\text{Cooking loss \%} = 100 - \frac{\text{weight after cooking}}{\text{weight before cooking}}$$

Results of the studies related to the experimental error are shown in Table 1. Results were obtained by the following procedure: at the given temperature /T/ for each time /t/ applied, two parallel samples were tested / $t_{\text{max}} = 360 \text{ min/}$ and the error mean square was established by analysis of variance. As shown in Table 1. the experimental error variance as changing with temperature is not uniform. The difference in the behavior of the samples treated in various ways did not show any regularity /no addition, sodium chloride added, phosphate added/. No gross error is therefore committed if experimental error variance is considered independent of cooking loss or in other words of temperature and time.

Table 1.

Experimental error variance $D^2/y/$ as a function of temperature
 /T/. /DF= Degree of freedom./

T	No addition		2.5 % NaCl /s/		2.5 % NaCl+0.4% Na ₄ P ₂ O ₇ /p/	
	D ² /y/	DF	D ² /y/	DF	D ² /y/	DF
50°	0.14	12	0.24	11	0.5	12
55°	0.32	11	0.21	11	0.08	11
60°	1.73	12	0.52	12	0.32	12
65°	0.26	11	0.65	11	0.355	11
70°	0.54	12	0.75	12	0.63	12
75°	0.336	11	0.385	11	0.20	11
80°	0.59	11	0.42	11	0.20	11
90°	0.29	9	0.78	10	1.87	10
mean	<u>0.541</u>	89	<u>0.494</u>	89	<u>0.503</u>	90

The pooled experimental error variance of samples treated with NaCl and with the combination of NaCl and Na₄P₂O₇ respectively, amounts to about 0.5 %. Thus the experimental error is $\sqrt{0.5} \approx 0.71$.

Mathematical considerations

An attempt was made to fit experimental points by means of a usual graphical method to one of the simpler functional relationships. It was established that, of the various functional

relationships /exponential, parabolic etc./ they were best fitted to the $y = \frac{at}{b+t}$ type hyperbola, or in transformation $\left[\frac{t}{y} \text{ vs. } t \right]$ the experimental points approximated a straight line /y= % cooking loss, t= cooking time, a and b = constants dependent on temperature/.

Since the true experimental error is considered independent of temperature and time, hyperbolic regression at constant temperature is expressed by the solution of the following optimum value problem:

$$f = \sum_1^n \left(\frac{t}{y} - \frac{at}{b+t} \right)^2 = \min \dots \dots \dots \text{I.}$$

To solve the problem, the partial derivatives belonging to a and b have to equal 0.

$$\frac{\partial f}{\partial a} = 0 \text{ and } \frac{\partial f}{\partial b} = 0$$

The solution is as follows

$$a = \frac{\sum \frac{yt}{b+t}}{\sum \frac{t^2}{(b+t)^2}} \dots \dots \dots \text{II.}$$

$$\sum \frac{yt}{(b+t)^2} \cdot \frac{2t^2}{(b+t)^2} - \frac{2t}{b+t} \sum \frac{t^2}{(b+t)^3} = 0 \dots \dots \dots \text{III.}$$

Since it is almost impossible to solve this problem by manual labour, the numerical values of a and b in equations II. and III. were computed with the 803 electronic computer

/NCR Electronics, National Cash Register Co., London/. Equations II, and III, in a series of experiments consisting of n= 10 - 15 experimental values were computed through iteration in 10 seconds.

The standard error of constants a and b may be determined as follows:

$$D^2/a = \left(\frac{a}{y_i} \right)^2 D^2/y = D^2/y \frac{a^2 \sqrt{\frac{y^2}{b+t/2}}}{\sqrt{\sum y^2 \frac{y^2}{b+t/2} - \left(\sum \frac{y^2}{b+t} \right)^2}} \dots\dots\dots IV.$$

$$D^2/b = \left(\frac{b}{y_i} \right)^2 D^2/y = D^2/y \frac{\sqrt{y^2}}{\sum y^2 \frac{y^2}{b+t/2} - \left(\sum \frac{y^2}{b+t} \right)^2} \dots\dots\dots V.$$

Where D /a/ and D /b/ are the standard errors of a and b respectively, and D/y/ is the experimental error. The y values occurring in equations IV. and V. do not represent experimental data, but stand for points on the regression hyperbola.

For the determination of the hyperbolic regression linear transformation $\left(\frac{1}{y} \text{ vs. } \frac{1}{t} \right)$ could not be used, since in this case the standard deviation about the regression curve is not independent of time and in the direction of increasing t values it widens in a "funnel-like" shape. This means that the application of the least squares procedure becomes too elaborate.

The standard deviation of experimental points about the regression curve - the lack of fit term - is expressed as follows

$$S = \frac{\sum (y_i - Y_i)^2}{n - 2} \dots\dots\dots \text{VI.}$$

where y_i applies to the experimental values and Y_i to the regression curve and n = the number of measurements.

If therefore some estimate of experimental error variance is available /Table 1./ and if the hypobolic regression is suitably chosen, comparison of S with the experimental error variance enables the researcher to obtain some conceptions of the goodness of fit of the postulated equation, that is to say, its representational adequacy in the particular circumstances of the experiment.

Equations IV., V. and VI. were also computed in the electronic computer. The approximation of experimental values by $y = \frac{at}{b+t}$ regression curve means that at $t = 0$ the value of y equals 0 and losses increasing $/y/$ with increasing cooking times are of monotonic character.

Results and Discussion.

Table 2. and Figures 2. and 3. show the results of a series of experiments. In Table 2. the a and b values/ \pm standard error/ and the lack of fit terms $/S/$ are given. The processing times and temperatures were as follows: 60 minutes at

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55° C, 360 minutes at 60, 65, 70, 75 and 80° C, respectively and 300 minutes at 90° C. The hyperbolic regression is valid only within the given experimental range, and extrapolation would be hazardous.

Table 2.

a and b constants /± standard error/ as related to temperature. The lack of fit terms belonging to various temperatures /S/.

T	n	s /pH= 5.91/			p /pH=6.24/		
		a	b	S	a	b	S
55°	2	14.57	16.00	-	14.78	33.3	-
60°	6	18.81±0.61	12.18±2.2	0.681	15.27±0.3	16.92±1.62	0.146
65°	8	24.02±0.41	6.58±0.7	0.617	19.44±0.47	8.43±1.17	0.719
70°	8	27.60±0.64	3.22±0.6	1.795	23.06±0.42	5.34±0.63	0.671
75°	7	28.80±0.81	2.61±0.61	2.424	23.25±1.1	4.38±1.34	3.971
80°	7	29.62±0.45	2.11±0.30	0.777	25.21±0.73	4.29±0.82	1.771
90°	8	30.74±0.58	1.40±0.2	1.483	25.40±0.69	2.68±0.46	1.911

The lack of fit terms /S/ were derived of Equation VI, standard errors of Equations IV. and V. n= number of experimental points. s= meat with 2.5 % NaCl added, p= meat with 2.5% NaCl and 0.4% Na₄P₂O₇ added.

In Table 2, the lack of fit terms /S/ are also shown. Since the experimental error variance is about 0.5 /Table 1./ the lack of fit terms for samples marked s processed at 60, 65 and 80° C, and for samples marked p processed at 60, 65 and 70° C respectively are not substantially larger than the experimental error variance. Thus in this case the experimental data and predicted equation fit well. The experimental values obtained for samples marked s at 70, 75 and 90° C and for samples marked p at 75, 80 and 90° C, respectively do not fit equally well. Thus prediction through the regression hyperbola may not be considered free of bias in each case. In the absence of mathematical models based on preliminary hypothesis, however, the regression hyperbola may be used for calculation. If the experimental values were shown only graphically without taking into consideration any theoretical relationship, we would have to give up the advantage furnished by mathematics. Mathematical relationships offer such systematizing principles which help to orientate in the complex problems involved, even if these, necessarily simplified, may furnish only gross approximation. The $y = \frac{at}{b+t}$ relationship may be given a graphic interpretation /Figure 1./. Now if $t \rightarrow \infty$, $y = a$ and a is the asymptote of the hyperbola. Thus the value of a may be considered as the "boundary loss". The smaller the b values are the more the hyperbola approximates a near stationary region, i.e. the "boundary loss" /a/. Broadly speaking b therefore may be considered as the

"slope" of the curve.

/With increasing slope decreases b , and vice-versa./

From data contained in Table 2. and Figures 2. and 3. the following conclusions may be drawn.

1. In the cooking loss-time relationship, at constant temperature, two phases may be distinguished. In the first phase cooking loss /as a function of time/ shows a steep rise, which slowly diminishes in the second phase and approximates a near stationary region. This region is determined by the asymptote / a value/ of the hyperbola.

2. The "boundary loss" / a / is not independent of temperature, and in the experiments described, showed a monotonic increase with increasing temperature. The "boundary loss" in meats processed at a lower /constant/ temperature did not reach that of meats cooked at higher /constant/ temperatures, but after reaching the near stationary region, the curves become approximately parallel. /This law is valid, however, only within the time limits as applied/. For this reason, the "boundary loss" of meats cooked at various temperature levels is not identical. This characteristic is **not** at all obvious. It could be presumed that meat samples cooked at lower and higher temperatures, asymptotically approximate the same "boundary loss" /similarly to the viable cell count of suspensions processed at temperatures above

60° C and approximating 0/. However with cooking times as applied in practice /8 to 10 hours/ this is not the case. Cooking losses occurring on the application of extremely long cooking times were not investigated.

3. The b value decreases with increasing temperature. Less time is needed therefore at higher temperatures to reach the near stationary region.

4. It may be seen in Figure 4. that the difference between the a and b values of samples s and p respectively, /at a given temperature/ is not independent of the cooking temperature. At lower temperatures /55°C/ the difference between "boundary losses" is smaller, than at higher temperatures. In relation to b values the situation is the reverse. The difference is large at lower temperatures and it is small at higher ones. From all these it may be concluded, that the cooking loss reducing effect of $\text{Na}_4\text{P}_2\text{O}_7$ is not independent of the temperature. At low temperatures, where the cooking losses are small, the effect of phosphate is negligible. However in samples processed at high temperatures greater losses occur but these are substantially reduced by the addition of phosphate.

It may also be proved that at given temperature the difference in the cooking losses belonging to samples s and p respectively /measured at equal times/ has extreme value.

$$\Delta y = y_s - y_p = \frac{a_s t}{b_s + t} - \frac{a_p t}{b_p + t} \dots\dots\dots \text{VII.}$$

The maximum of Δy is by $\frac{d \Delta y}{dt} = 0$.

The t_{opt} value belonging to Δy_{max} is obtained from Equ. VIII.

t_opt = (b_s sqrt(a_p b_p) - b_p sqrt(a_s b_s)) / (sqrt(a_s b_s) - sqrt(a_p b_p))VIII.

The Delta y_max values, thus calculated, show monotonic increase with increasing temperature /Table 3./. Hence the relative efficiency of phosphate as related to cooking losses is higher at higher temperature levels.

Table 3.

Delta y_max - temperature relationship

Table with 3 columns: T, Delta y_max, t_opt /in minutes/. Rows include temperatures from 55 to 90 degrees.

Since in general practice the temperature of the meat product, processed at constant environmental temperature is affected by both time and space coordinates the question arises, what laws

may be established in relation to cooking losses, if instead of thin experimental samples, products of larger diameter are examined? Investigations were not yet extended in this direction. It is intended to approach this problem by applying the samples of minute thickness as in the present experiments and varying the temperature of the waterbath according to a predetermined program. If the temperature is increased gradually cooking losses may follow the curve, as shown in Figure 5. This would mean that cooking losses are of additive character and to a given y value belongs an identical physico-chemical condition of the material /affecting the cooking loss/ independently of the thermal history of the y value /for instance: higher temperature and shorter time, or lower temperature and longer time/. This means further, that if the temperature of the waterbath varies according to some continuous $T = T/t$ function the cooking losses may be derived from

$$\frac{dY}{dt} = \left/ \frac{\partial Y}{\partial t} \right/_{y=Y} \dots\dots\dots IX$$

where y is related to the cooking loss measured at constant temperature, or in other words to the isotherms and Y to the heat treatment according to $T = T/t$ program /Figure 6./

Equ. IX. is shown graphically in Figure 6. It may be derived from the differential equation that the tangent $\frac{dY}{dt}$ of curve $Y = Y/t$ is always equal to the tangent $\frac{\partial Y}{\partial t}$ of the corresponding isotherm at $y = Y$. It may be proved by mathematical means that the

above differential equation at the known $y = \frac{at}{b+t}$ relationship leads to the Riccati type differential equation. It is intended to solve Riccati's differential equation, in the knowledge of the experimental values, with the aid of an analogue computer.

In the evaluation of the results obtained with the method described, difficulties and problems were also encountered. The results of one experimental serie is given in Table 4.

Table 4.

a and b constants /± standard error/ as a function of temperature. S= lack of fit term /Equ.VI./, n= number of /experimental/ points.

T	S /pH= 5.85/			P /pH= 6.28/			n
	a	b	s	a	b	s	
55°	16.2±0.67	37.2±7.09	0.62	14.2±1.4	113.5±34.0	0.83	6
60°	14.7±0.72	14.5±3.66	0.89	12.7±1.28	30.4±11.8	1.74	6
65°	22.4±0.71	9.2±1.65	1.61	18.3±1.01	21.3±5.41	1.96	8
70°	24.4±0.83	4.1±1.01	2.84	18.7±0.81	11.3± 2.62	1.85	8
75°	28.9±0.72	4.0±0.67	1.76	21.3±0.56	8.9± 1.22	0.81	7
80°	28.3±0.32	2.9±0.25	0.36	21.5±2.5	11.0± 6.39	14.6	7
90°	24.4±0.45	1.7±0.23	0.25	18.4±0.38	3.7± 0.37	0.14	4

As shown in Table 4, a values do not increase with increasing temperature in a monotonic way. In samples marked s the "boundary loss" value at 90° seems to be smaller than that at 80° C. Wierbiczki et al. /2/ came also to the conclusion that in general, the amount of moisture lost, increases with increasing temperature, but not uniformly so. "It is highly significant that in the temperature range of 55° - 65° C minima occur in these curves indicating that reactions are taking place to counteract loss of water by the proteins". All this proves that the investigation of the quality of meat and the time-temperature relationship of cooking losses needs special attention. It is conceivable that even the $y = f / t /$ relationship may vary on, certain occasions, according to the quality of raw meat and therefor the regression hyperbola may not be suitable to describe the relationships. When cooking losses of fresh chilled meat were investigated sometimes they were found as small as 2-6% and thus the it became practically impossible to determine exactly the constants a and b of the hyperbola or to establish any relationship. It may be concluded therefore that the method discribed above is suitable only in the case of relatively large cooking losses where the relative error of the method is not too high.

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----- isotherms $y = \frac{a \cdot t}{b+t}$ /
_____ cooking loss curve as pertaining
to T/t function $Y/t/$ /.

Fig. 1

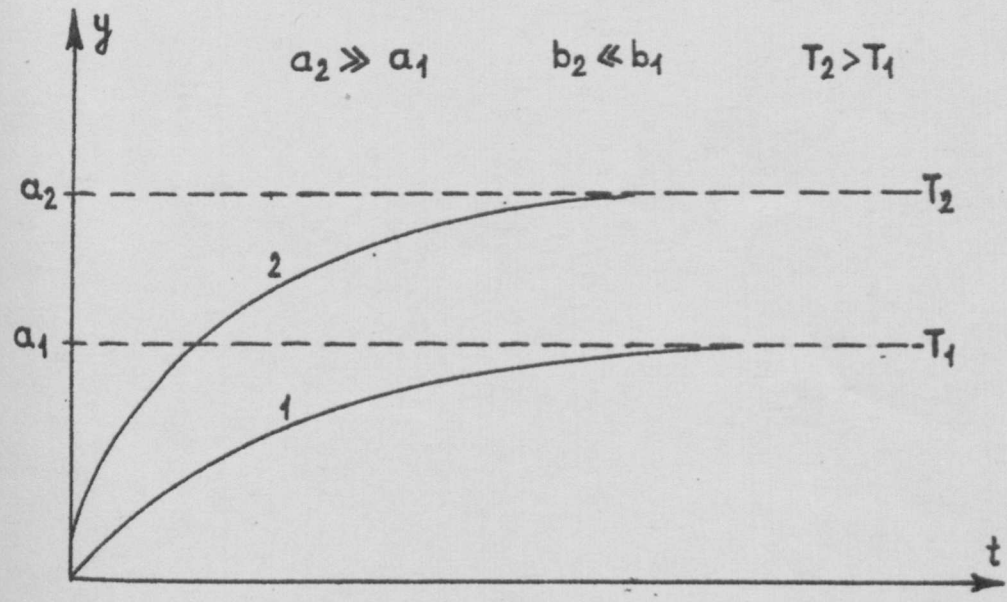
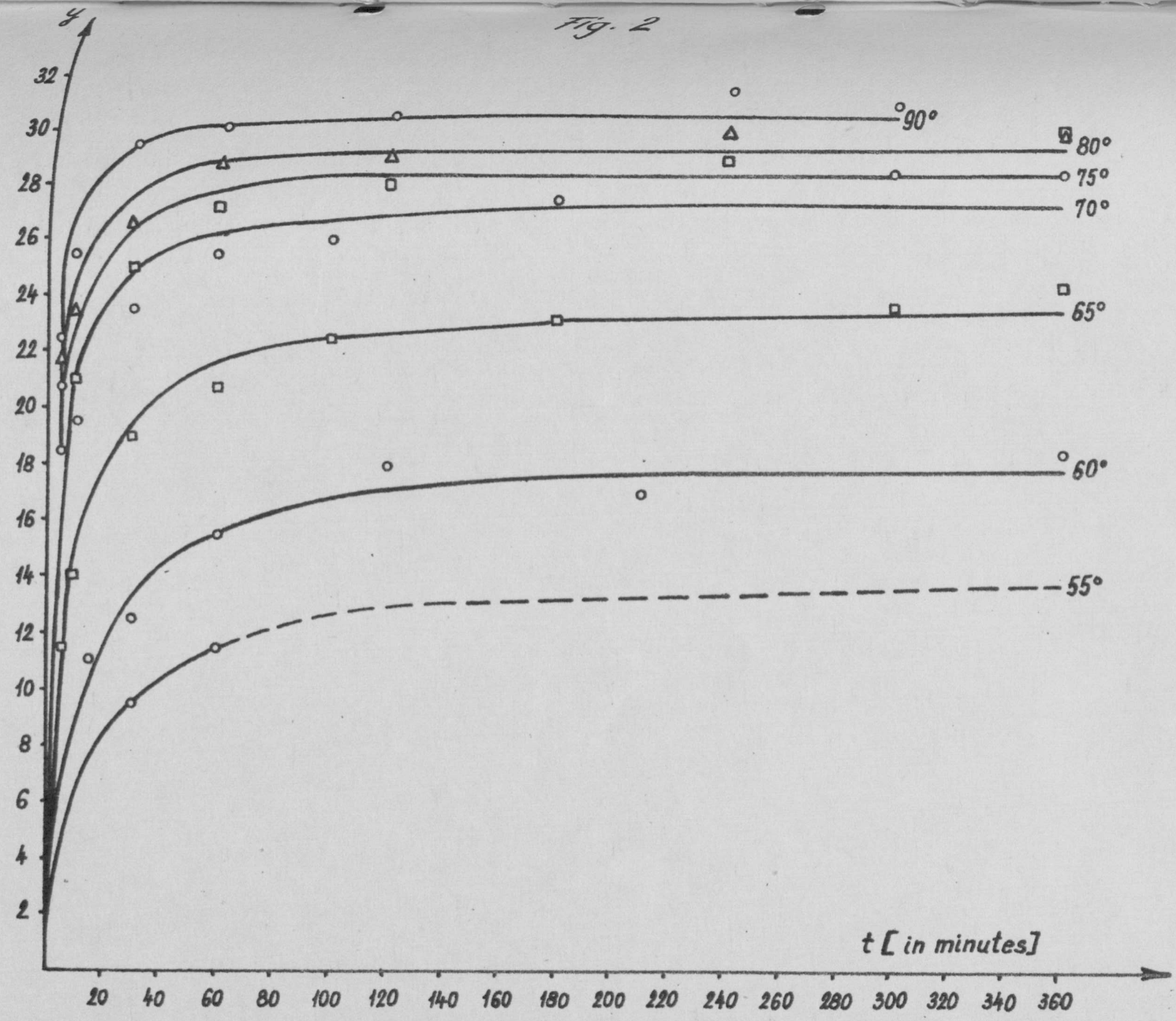
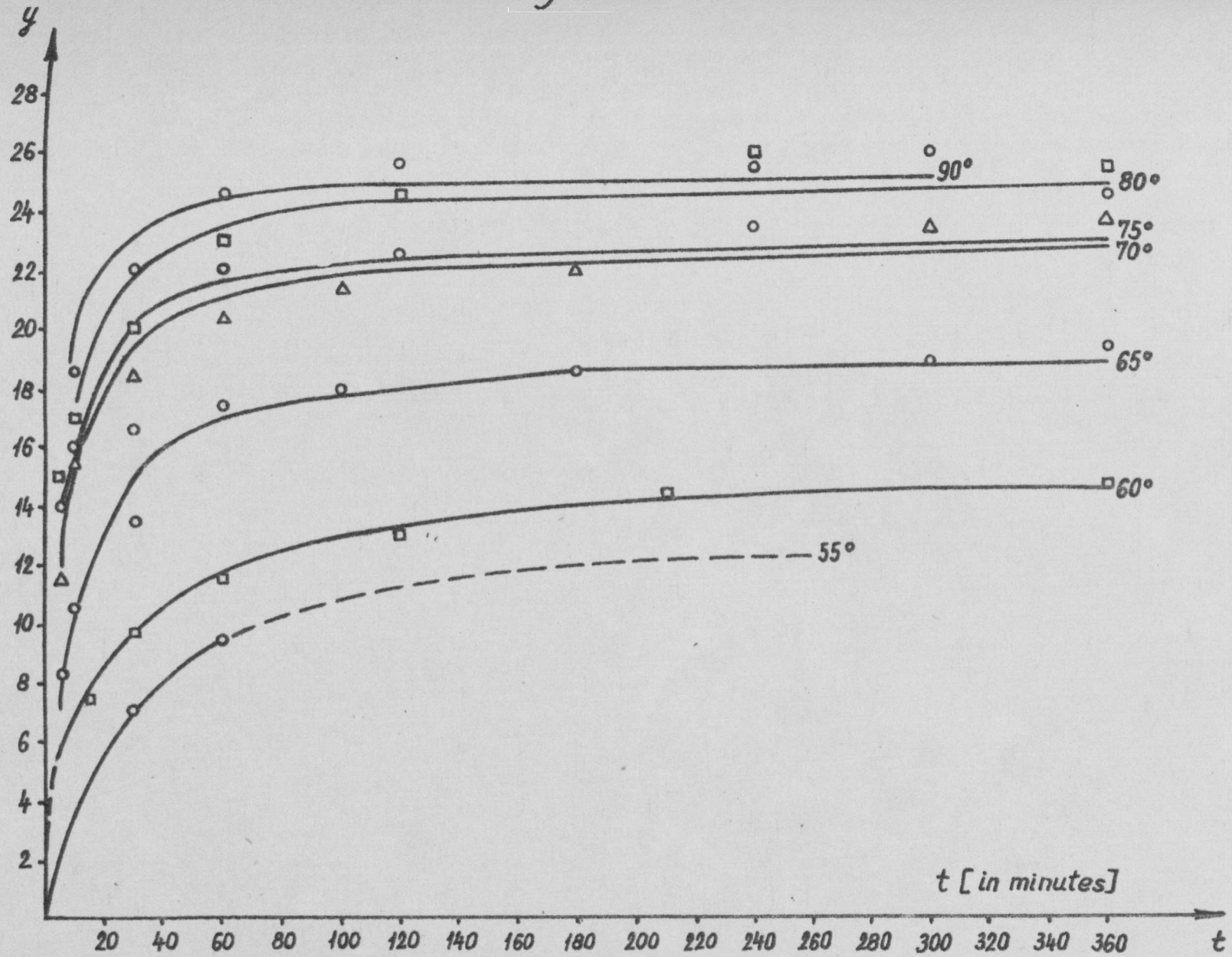


Fig. 2



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Fig. 3



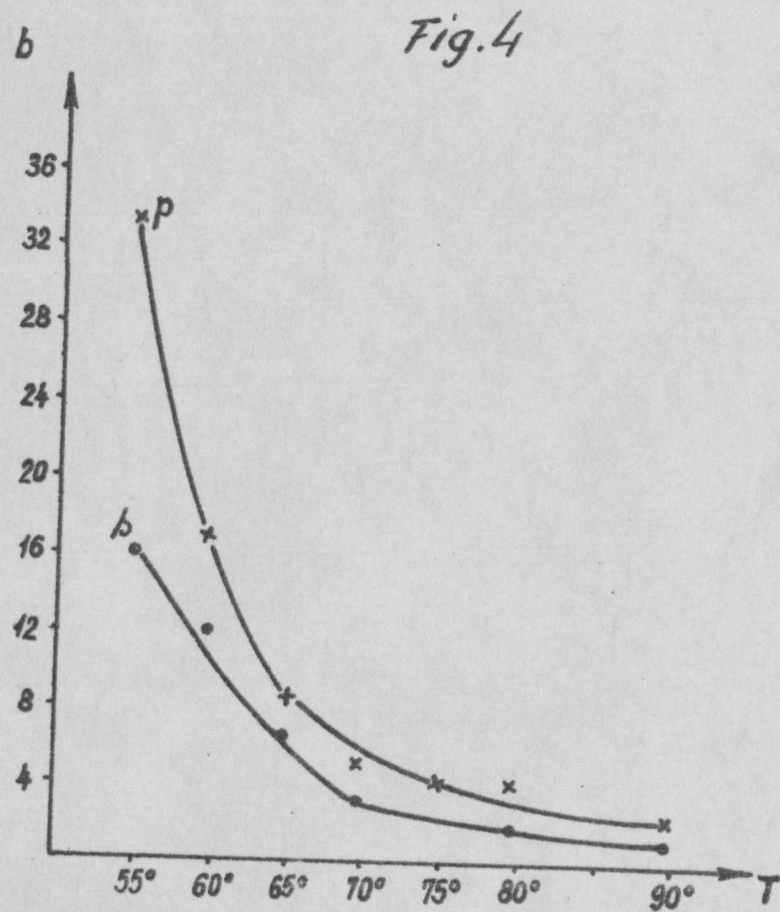
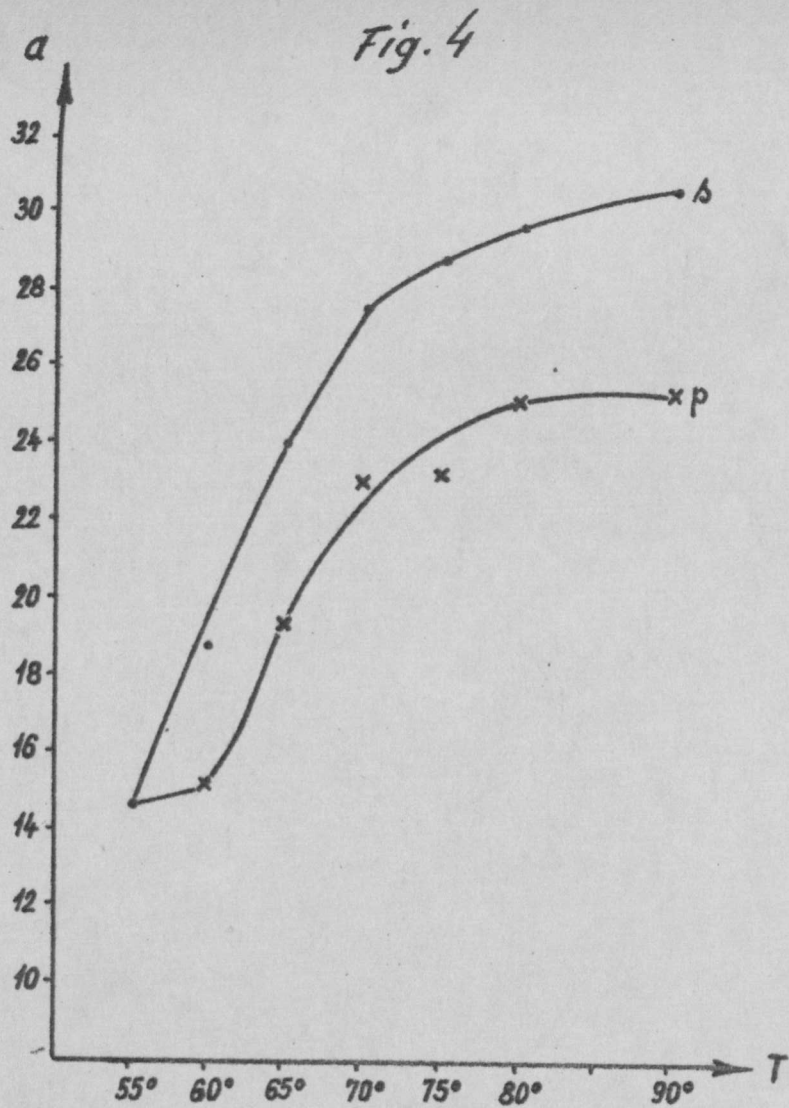


Fig. 5

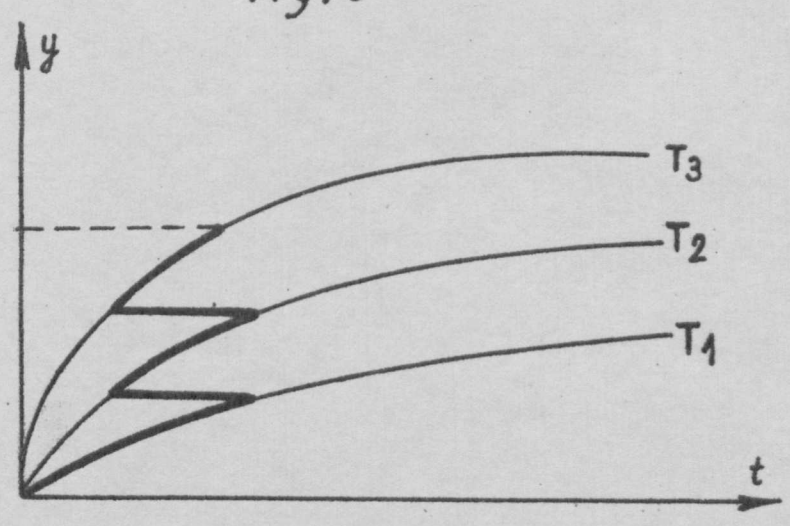
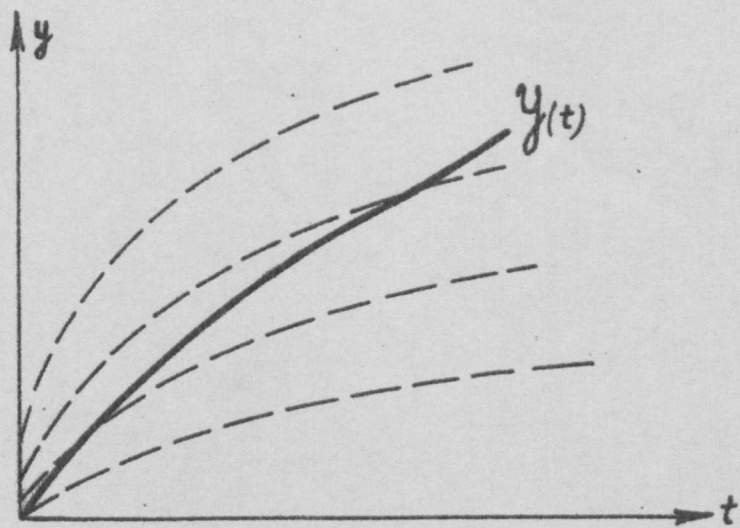


Fig. 6



Grundlegende Zusammenhänge zwischen Gewichtsverlust, Temperatur und Zeitdauer beim Kochen

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Es werden die Zusammenhänge zwischen Gewichtsverlust, Temperatur und Zeitdauer beim Kochen untersucht. Verfasser stellen fest, dass die Messpunkte zwischen dem Kochverlust /Y/ und der Kochzeit /t/ bei konstanter Temperatur sich der Regressionshyperbel $y = \frac{a \cdot t}{b+t}$ ziemlich gut anpassen. Die Konstanten a und b und damit die Änderung des Kochverlustes in Abhängigkeit von der Zeit können anschaulich erklärt werden. Es wird die Untersuchungsmethode eingehend beschrieben, der Fehler der Bestimmung analysiert und die Art der Anpassung, ferner der Zusammenhang der Konstanten a und b in Abhängigkeit von der Temperatur erörtert. Auf das Verhalten des mit und ohne Phosphat wärmebehandelten Fleisches und auf die Probleme der Änderung des Gewichtsverlustes des bei nicht konstanter Aussentemperatur gekochten Fleisches wird auch eingegangen.

Some Fundamental Relationships of Cooking

Losses, Temperature and Time.

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Summary.

The object of the investigations was to establish relationships of cooking losses time and temperature. It was found that at a given temperature the experimental points between cooking losses /y/ and time /t/ fit quite well the $y = \frac{at}{b + t}$ type regression hyperbola.

Constants a and b and thereby the cooking loss as changing with time may be graphically interpreted. A detailed description is given of the experimental procedure. Experimental error and goodness of fit are analysed and the temperature relationship of a and b constants is given. The behaviour of meat on addition of phosphate was studied. Problems related to cooking losses in meat as caused by processing at not constant temperatures were touched upon.

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НЕКОТОРЫЕ ОСНОВНЫЕ ВЗАИМНЫЕ СВЯЗИ ИМЕЮЩИЕСЯ МЕЖДУ
ПОТЕРЕЙ В ВЕСЕ ПРИ ВАРЕНИИ, ТЕМПЕРАТУРОЙ И
ПРОДОЛЖИТЕЛЬНОСТЬЮ ВАРЕНИЯ.

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А Н Н О Т А Ц И Я

Исследовали взаимную связь имеющуюся между потерей в весе при варении, температурой варения и продолжительностью варки. Установили, что между потерей в весе при варении на постоянной температуре (Y) и продолжительностью варки (t) точки измерения довольно хорошо прилегают к регрес-

сиейной гиперболы типа
$$y = \frac{a \cdot t}{b+t}$$

Константам "a" и "b" и образованиям потерь в весе во времени, можно дать наглядное понятие. После подробного описания процесса исследования, анализа ошибок определения и доброты прилегания, обсудили зависимость температуры константов "a" и "b". Проанализировали тоже поведение мяса термообработанного с фосфатом и без фосфата.

Доклад затрагивает проблемы образования потери в весе при варении мяса, варенных при непостоянной внешней температуре.