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THE USE OF ASCORBIC ACID IN MEAT CURING

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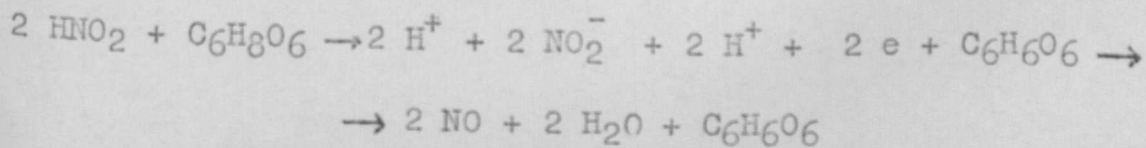
(Director: Prof. Dr. W. Csiszár)

An acid medium and reducing condition are required in meat to enable curing ingredients to form the pink pigment of cured meat from the blood and muscle haemoglobin. This pigment does not become grey or brown during cooking or baking. The acidity of fresh meat is due to the production of lactic acid from glycogen. Reducing conditions are provided by the natural reducing agents of the meat and by enzymes which are chiefly of bacterial origin. The quantity and quality (and, consequently, also the effect) of the reducing agents and enzymes may be different in various meats. In order to speed reduction and make the cured meat pigment more stable, some foreign countries (especially the United States of America) have used ascorbic acid and sodium ascorbate in curing. In this article experiments are discussed which, owing to our research work relating to the discoloration of the cured colour (Vas and Bocsó, 1948) were carried out with these materials in 1949\*, 1955-56 and 1957.

The effect of the ascorbic acid during and after curing.

Ascorbic acid - pure vitamin C - is a strong reducing agent, consequently it can be very easily oxidized. It is, therefore, used as an antioxidant in the food industry although, in fact, it is not a true antioxidant but only a synergic agent of phenolic antioxidants. Its use in the meat industry is likewise connected with its strong reducing power.

In the acid meat nitrous acid is formed from nitrite, produced from nitrate or added as such, and, under the influence of the reducing agents in the meat, this nitrous acid is converted into nitric oxide. The nitric oxide converts the similarly reduced myohemoglobin into a pink pigment, nitric oxide myohemoglobin, which does not turn grey even on heating. With its strong reducing and weak acid properties ( $K = 6,2 \cdot 10^{-5}$ ;  $pK = 4,21$ ) ascorbic acid hastens this procedure while being itself oxidized to dehydro-ascorbic acid (when sodium ascorbate is used only the reducing effect is manifested).



The ascorbic acid reduces not only the nitrous acid but also the oxidized blood and muscle pigment (the met-myohemoglobin)

\* In the Department of Mycology and Meat Industry of the National Chemical Institute/Budapest, II, Keleti Karoly St. 24/ and in the master butcher E. Siklosi's butchery/Budapest, II, Keleti Karoly St. 13.

respectively; otherwise the pigment of cured meat could not be formed from this pigment since, as is well-known, nitric oxide can form the cured colour only from reduced myohemoglobin. At higher temperatures (in the smokehouse) the effect of the ascorbic acid is particularly strong, and when curing with nitrite it renders the procedure of reduction independent of the natural reducing agents of the meat. The excess ascorbic acid remaining in the meat or in the meat product can protect it against colour deterioration and other changes due to oxidation. On the other hand, the cured colour formed in this procedure is also more stable because in the presence of ascorbic acid its formation is more complete. Therefore, by decreasing the effect of the oxidizing enzymes, the ascorbic acid may have not only a colour-protecting effect but smell- and flavour-protecting effects also.

### Laboratory and plant experiments and their conclusions

#### Laboratory experiments

In the laboratory experiments the effects of different concentrations of ascorbic acid in ground meat and in 0,5 % hemoglobin solution, and in the presence of different concentrations of nitrite or nitrate, were investigated. In some experiments lactic acid and hydrogen peroxide were also added to the hemoglobin solution.

As a result of the first laboratory experiments in 1949 I could state that when ascorbic acid is used as a colour-protecting agent it not only protects the colour of the cured meat but also hastens the curing procedure, especially when curing with nitrite. It may also have a colour-protecting effect when curing with nitrate. The reddening of the ground meat is delayed at higher nitrite concentrations; if, after the addition of the nitrite ascorbic acid is also added to the meat, the sequence of reddening is inverted. Our former experiments have proved that, within limits, the less nitrite is added to the ground meat the slower is the colour deterioration. On the other hand, my recent experiments have shown also that the protective effect of the ascorbic acid lasts longer if less nitrite is added. It should be stated that, beside the appropriate temperature and time, sufficient nitrite is also needed for the development of a stable pigment of cured meat. On the other hand, nitrite in higher quantity may have a colour-deteriorating effect. When using ascorbic acid the quantity of nitrite can be reduced and the quantity of nitrite is also less in the finished product. Without ascorbic acid the product quickly lost its colour with 0,006 % nitrite calculated to the meat; using 0,05 % ascorbic acid the cured colour became more stable/Tables 1 and 2.

My experiments performed with Hb-solutions have shown that the protective effect of ascorbic acid depends also on the quantity of nitrite. When 0,004 % nitrite was used the protective effect of 0,019 % ascorbic acid lasted for several days. In the presence of roughly the same quantity of ascorbic acid (0,033 %), 0,007 % nitrite gave rise to a change of colour to brownish green after 16-21 hours (Table 3). The rate of the colour deterioration caused by the hydrogen peroxide is proportional to the quantity of the nitrite (this fact is shown also by our above-mentioned experiments performed in 1947). The nitric oxide liberated from the 0,007 % nitrite sterilized the Hb-solution so that it remained undamaged even for two weeks: 0,004 % nitrite was less effective.

After heating at 73-76°C for three hours a solution containing 0,2 % potassium nitrate and 0,09 % ascorbic acid, prepared with boiled distilled water and held in a closed flask, contained ascorbic acid in unchanged quantity. The ascorbic acid was not oxidized by the potassium nitrate.



Knowing the quantity of ascorbic acid added to the ground meat or remaining in it, and of the nitrite, the study of the pH and pH values can yield information about the velocity of the curing process and, in the finished product, about the protection against oxidation changes.

Higher concentrations of ascorbic acid (e.g. 0.3 %) turn fresh meat first purple (reduced myohemoglobin) and then rapidly pale brown (choleoglobin, met-myohemoglobin).

#### Plant experiments

In one phase of our plant experiments finely chopped sausage was made with ascorbic acid or sodium ascorbate while curing both with saltpetre and nitrite. The highest concentration of ascorbic acid or sodium ascorbate used was 0.45 % calculated to the meat. The ascorbic acid or its salt was added either dry or dissolved in water (about 15%): in some experiments it was added while making the "meat-dough", 1 - 2 minutes after the addition of the curing salt, and in some experiments not until the next day, i.e. immediately before mixing ready the product (before adding the lard). The vitamin can also be added together with the spices; in several countries mixtures of spice and ascorbic acid are commercially available. The effects of ascorbic acid and sodium ascorbate, separately, used together with the dried milk and condensed phosphate (Plasmal) were also investigated. The temperature of smoking the products was generally recorded. The usual method of cooking and cooling was not changed.

In the other phase of our plant experiments the effects of the ascorbic acid and ascorbyl palmitate were tested with dry smoked sausages (Gyulai sausage and salami). The quantity added with the spices amounted to 0.016 - 0.096 % calculated to the stuffing; otherwise the manufacturing process was not changed. The curing agent throughout was saltpetre.\*

In our experiments with finely chopped sausages we observed that, in presence of sufficient nitrite, ascorbic acid accelerates the process of reddening at lower temperatures also but especially in the smokehouse. If when using ascorbic acid the temperature of the smokehouse rises too quickly, sudden decomposition of the nitrite may easily cause undesirable changes of colour and consistency. This is particularly likely in the presence of higher concentrations of nitrite, and if the ascorbic acid has not been kept together with the chopped water-in-meat emulsion of the product for some time before smoking. Of course, in this case as well as when ascorbic acid is not used, the principle is valid that the temperature of the smokehouse may be increased depending on the thickness of the smoked goods, i.e. the thinner the product the more rapid the increase can be. Moreover, while smoking the fact has to be taken into consideration that when ascorbic acid is used the colour of the product can develop much more quickly, before the middle reaches the temperature necessary for pasteurization. Preliminarily contact with ascorbic acid and careful smoking, as well as the presence of normal or lower quantities of nitrite (this quantity may be decreased when using ascorbic acid), present the

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\* My experiments with finely chopped sausage were carried out in the plant of the Meat Industrial Enterprise of Kispest in 1955-56 and in March 1957 with plant manager L. Balazs's assistance, and with dry smoked sausages in the Salami Factory of Budapest in the second half of 1956 and in January and November of 1957, with production manager F. Kovacs's collaboration. Thanks are due for the help of these two enterprises.



irregular colour and consistency. In such cases an even higher concentration of ascorbic acid can be added to the product. As is well-known, if the product contains a higher quantity of nitrite, and if the smoking is not carefully done, irregular colour and consistency (nitrite burn) can also be obtained without ascorbic acid.

In order to accelerate curing ascorbic acid needs a certain quantity of nitrite. When curing with nitrate the quantities of nitrite formed are uncertain; therefore when curing with nitrite (and to some extent in case of mixed curing too) the effect of the ascorbic acid is more certain. Although ascorbic acid increases the slight reduction of nitrate in the meat at the temperature of smoking, and its colour-improving effect, this is not sufficient to obtain a complete cure.

Although a higher quantity of ascorbic acid may be added to the product, to accelerate the curing and protect the colour, smell, and flavour, it is sufficient to add to the product 0,05 % ascorbic acid calculated to the meat, and good results can be obtained even with smaller quantities.

In our experiments at least 50%, and in some experiments even up to 76%, of the added ascorbic acid or sodium ascorbate remained unchanged in the freshly smoked goods.\* Consequently, the products may also serve as a source of vitamin C (Tables 4 and 5). Mention must be made of the fact that when using higher concentrations of ascorbic acid the absolute loss was likewise higher.

In the United States of America cooked, cured, comminuted meat food products may be produced with at most 46,9 gm. ascorbic acid or 54,7 gm. sodium ascorbate per 100 kg fresh meat or meat by-product; at most 56,1 gm. may be used to 100 litres of curing solution; while the surface of cured pork and beef products and comminuted meat food products may be sprayed with a solution containing not more than 5% ascorbic acid (Meat Inspection Branch Memorandum No. 217, 15 June 1955).

The quantity of ascorbic acid and sodium ascorbate permitted in the United States increases the permanence of the colour by about 25% and, in the case of goods packed under vacuum, by 24-28 hours (private communication of the Meat Institute and Meat Inspection Branch of the United States). The improvement of colour appears - as observed by ourselves too - either while smoking or only later, during the storage. Under the influence of ascorbic acid the smell and flavour of the stored products remains more agreeable. In several cases the improvement of the smell and flavour can be observed on the fresh product too.

The ascorbic acid and sodium ascorbate used together with the condensed phosphate (Plasmal) and dried milk made more stable the smell and flavour of the products having otherwise good consistency and particularly good flavour due to the dried milk.

In dry sausages the ascorbic acid may likewise have an improving and protective effect on the colour, smell, and flavour. The fresh Gyulai sausage produced with ascorbic acid or ascorbyl palmitate<sup>xx</sup> had

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\* In this respect I mention my letter of the 29th August, 1956, written to the Vitamin Division of the Chemical Works F. Hoffmann - La Roche & Co. (Basel) and my proposition of the 11th May, 1957, submitted to the Meat Industrial Enterprise of Kispest and the Meat Industry Management of the Ministry of Provision.

<sup>xx</sup> Thanks are due to the Directorate and Vitamin-Division of the Chemical Works Hoffmann - La Roche (Basel and Nutley) for their courtesy in placing at my disposal the sodium ascorbate and ascorbyl palmitate used in my experiments.



a very fragrant smell and taste; the flavour of the product made several months earlier was better than that of the control products, and the rancidity of the fat was less noticeable. In one of the salamis containing a significant quantity of ascorbic acid, the colour-protecting effect of the ascorbic acid was very considerable. In another series, in which only insignificant quantities of ascorbic acid could be detected when tested 6 months after production and in which only the values of the redox potential were more negative - in proportion to the added quantities of vitamin - than those of the control products, the goods containing ascorbic acid had a fresher and more aromatic smell and, though in a lesser degree according to some tasters, their flavour was also better than that of the control goods. The samples made with ascorbic acid had not such a brown border under the skin as the control pieces but the slices were not more colour-fast than the otherwise sufficiently colour-fast control pieces (Table 6, 11-14). It should be mentioned that before testing the conserved sausages were not stored in a refrigerator but in the usual storeroom and afterwards at room temperature.

The permanence of the colour of the cured meat can be increased by spraying a 5% solution of ascorbic acid on the surface. If afterwards the meat or the meat product is packed, possibly under vacuum, into an airtight envelope then the colour-protecting effect is, of course, more intense.

In the case of stuffed goods both ascorbic acid and ascorbate may be used, especially the latter if a slower effect is adequate. The ascorbic acid must not be mixed with dry curing ingredients or concentrated solutions of curing ingredients containing nitrite because it reacts very quickly with the nitrite. Due to its slower effect the sodium ascorbate may be used in curing solutions also (for curing bacon, ham etc.) 1 kg sodium ascorbate corresponds to 888 gm. ascorbic acid, therefore the quantity to be used of the former is about 11% more.

From the ground test products, the ascorbic acid and its salt, respectively, was extracted at low temperature with boiled, distilled water and determined by titration with 2-6-dichlorophenolindophenol. The tougher, less juicy products, were first rubbed together in a mortar with granulated sugar and crystalline citric acid (15 gm. granulated sugar and 1 gm. crystalline citric acid were added to 10 gm. ground product).

#### The use of ascorbic acid in relation to food hygiene and food supervision.

Ascorbic acid is identical with the vitamin C naturally present in foodstuffs and playing an important role in the organism, therefore its use in the meat industry is not perilous from a hygienic point of view. As proved by our experiments, even with 0,05 % or less ascorbic acid calculated to the quantity of the meat, ascorbic acid can remain in the finished product. This fact is important especially in winter when the consumption of sausages is higher and, in consequence of lack of fresh vegetables and fruits, the human organism is insufficiently supplied with vitamin C.

When using at most 0,05 % ascorbic acid calculated to the meat, the cured colour normally formed during smoking is usually more vivid and may be more stable - it nevertheless fades gradually and hence cannot disguise the deterioration of the meat. According to experiments it cannot make the stale meat appear as fresh.

It is particularly worth mentioning that when using ascorbic acid the quantity of the nitrite used to the curing may be decreased and the quantity of the nitrite found in the finished product is also smaller.

Recently in the United States of America the use of iso-ascorbic acid (D-araboascorbic acid) and sodium isoascorbate has become widespread (products of Merck & Co. Inc. and of Pfizer & Co. Inc.). These compounds likewise have an antioxidant effect and some biological effect but their effect against scurvy is negligible. Their advantage is that they are cheaper than the normal compounds, but when the normal compounds are used the products may contain extra vitamin C.

#### Summary

In the presence of the required quantity of nitrite ascorbic acid or sodium ascorbate accelerates the development of the curing colour and makes this colour more attractive and stable. Its use may also have an advantageous effect on the smell and flavour of the product and, during storage, the deterioration of the flavour and the development of rancidity in the fat can be retarded.

When ascorbic acid or sodium ascorbate is used the quantity of nitrite necessary for curing may be decreased, and the quantity of the nitrite remaining in the finished product is diminished also.

The required effect may be obtained with 0,05 %, or even less, ascorbic acid calculated to the meat.

The use of the ascorbic acid can also have advantages in the case of dry sausages.

In order to promote the formation of the colour, in the case of finely chopped sausages, it is advantageous to allow the meat-dough to stand together with the vitamin for several hours or overnight, though good results can also be achieved if the vitamin is added only while mixing the product.

In our experiments a significant percentage of the vitamin, added during preparation, has remained in the finished product.

From a hygienic point of view the use of both the normal and the iso compounds is without any risk.



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Table 1.

pH- and prH-values, nitrite and ascorbic acid content of  
comminuted meats cured with nitrite

Marks of samples	I	II	III	IV
Substances mixed into the meat				
Salt %/	2,5	2,5	2,5	2,5
Sodium nitrite /mg./100gm./	6	6	10	20
Ascorbic acid /mg./100gm./	0	50	50	50
pH <sup>x1</sup>	5,40	5,39	5,39	5,40
prH <sup>x1</sup>	25,6	23,1	22,8	22,8
nitrite <sup>x1, y</sup>	+r	r	+	++
pH <sup>x2</sup>	2,66	2,93	2,91	2,95
prH <sup>x2</sup>	24,9	23,1	22,7	22,4
nitrite <sup>x2, y</sup>	0	0	0	0
ascorbic acid /mg./100gm./ <sup>x2</sup>	0	7,0	21,2	26,8
ascorbic acid/percentage of the quantity mixed into the meat/	-	14,0	42,4	53,6

<sup>x1</sup> Stored overnight. 5 gm. meat + 50 ml. distilled water.

<sup>x2</sup> After heating. 10 gm. meat pounded in a mortar with 15 gm. crystallized sugar and 1 gm. crystallized citric acid, then filled up to 200 mls.

y With the reagent Griess-Ilosvay. The increasing amounts are marked with the signs: r, +, +r, ++





Table 3.

Effect of nitrite, lactic and ascorbic acid on 0,5 percent hemoglobin solutions

Serial number	Media	pH	prH	Time after preparation	Color after 16-21 72 120 hours following the preparation			Microbiological decomposition odour after 2 weeks
1. Hemoglobin-/Hb-/solution		7,75	26,0	3h.15min.	-	-	-	positive-stinking
2. Hb-sol. + 7 mg. NaNO <sub>2</sub>		7,60	25,5	3h.25min.	-	-	-	positive-stinking
3. Hb-sol. + 0,05 ml. lactic acid		4,00	25,4	3h.45min.	-	-	-	positive-stinking
4. Hb-sol. + 33 mg. ascorbic acid		5,72	22,1	15min	Above: red liquid, at the bottom: pale-brown sediment			positive-stinking
5. Hb-sol. + 7 mg. NaNO <sub>2</sub> + 0,025 ml. lact. acid		5,10	25,0	3h.30min.	-	+	++	positive-less stinking than 1, 2.
6. Hb-sol. + 7 mg. NaNO <sub>2</sub> + 0,05 ml. lact. acid		3,90	24,8	3h.40min.	++++	++++	++++	negative-not stinking
7. Hb-sol. + 4 mg. NaNO <sub>2</sub> + 0,05 ml. lact. acid		3,90	25,5	3h.48min.	++++	++++	++++	negative-not stinking. Pos.-stinking <sup>x</sup>
8. Hb-sol. + 7 mg. NaNO <sub>2</sub> + 0,05 ml. lact. acid + 33 mg. asc. acid		3,80	21,5	3h.50min.	+	++	+++	negative-not stinking
9. Hb-sol. + 4 mg. NaNO <sub>2</sub> + 0,05 ml. lact. acid + 19 mg. asc. acid		3,80	20,8	3h.58min.	-	-	-	negative-not stinking. Pos.-stinking <sup>x</sup>

<sup>x</sup> After 6 weeks

Figures used for marking the deterioration of the colour:

Fair curing effect or without essential changes:	-
Fading or browning	-
Greenish-yellow or greenish-brown	+
Green	++
Intensively green	+++
Very intensively (exceedingly) green	++++



Table 4.  
Ascorbic acid and sodium ascorbate content of cooked smoked sausages prepared with ascorbic acid or sodium ascorbate

Serial number	mixed into the meat	corresponding in the finished product	Recovered in the finished product.			mixed into the meat	corresponding in the finished product	Recovered in the finished product		
			gm/100kg	percent of the mixed	on days after preparation			gm/100kg	percent of the mixed	on days after preparation
			gm/100kg					gm/100kg		
1.	89	50	31	62	2nd					
			28	56	13th					
			33	66	44th					
	44.6	250	165	66	2nd					
			154	62	13th					
			222	89	44th					
2.	39	50	28	56	2nd	100	56	34	60	2nd
			30	60	6th			29	51	6th
	178	100	67	67	2nd	200	111	55	49	2nd
			49	49	6th			55	49	6th
3.	46	26	19	72	2nd					
	82	46	35	76	2nd					
4.						38	21	14	66	2nd
5.						57	32	24	75	2nd
6.	74	41	26	63	3rd					
	74	41	30	73	3rd					
7.						64	36	22	61	2nd
8.	39	22	13	58	2nd					
	50	28	18	64	2nd					
9.	46	26	16	61	3rd					
10.	46	26	17	65	2nd					
11.	92	53	37	70	2nd					

x the meanwhile occurred drying considered.

Table 5

Data of examination of cooked, smoked, larged sized sausages/sausages of Paris/  
made with ascorbic acid. (See Table 4, Serial Number 1)

Date of Examina- tion		0/without asc. acid	1./50 gm. asc. acid for 100 kg. finished product	2./250 gm. asc. acid for 100 kg. finished product
27th Nov. 1955	Colour, exter- nal/casings/	yellowish- brown	fairer than 0	as 1.
	Colour, internal /plane section/	fairly pink	brighter than 0	as 1.
	Odour	agreeable	more agree- able than 0	as 1.
	Taste	One cannot find a distinct difference between the samples		
	Water content /per cent/	69,7	70,3	70,4
	Ascorbic acid /per cent/	0	0,030 <sup>x</sup> 0,032	0,170 <sup>x</sup> 0,160
9th Dec.	Colour, internal /plane section/	fair	brighter than 0	brighter than 1.
	Odour	a little stale	better than 0	better than 1.
	Water/per cent/	65,0	64,2	63,6
	Asc.acid/per cent/	0	0,028	0,154
	pH	5,82	5,72	5,67
	prH	25,7	23,8	22,3
28th Dec.	Exterior/casings/ Colour/plane sect./	a white mould red	as 0 darker red than 0	as 0 darker red than 1.
	Odour	stale	better than 0	only barely stale. nearly agreeable
	Consistency	compact	more compact than 0	more compact than 1.
10th Jan. 1956	Colour/plane sect./	dark red	darker red than 0	darker red than 1
	Odour	stale	more agreeable than 0	more agreeable than 1.
	Water/per cent./	37,2	36,8	35,4
	Asc.acid/per cent/	0	0,033	0,222
	pH	6,25	6,25	6,08
	prH	24,5	22,4	20,6

x Date of examination of the National Institute of the Science of Provision  
and Alimentation.



Table 6.

Data of examination of smoked pork sausages/Gyulais, Salamis/made with ascorbic acid

Serial number	Date of manufacture examination	Ascorbic Acid		pH	pH	Nitrite
		mixed into the stock	recovered in the finished product.			
		gm./100kg.	gm./100kg. per cent of the mixed			

Gylulai sausages

1.	9th July, 1956	24th July, 1956.	16	very few <sup>a</sup>		
2.	24th "	17th Spt.'56	32	few <sup>a</sup>		
3.			48	few <sup>a</sup>		
				4,3	9,0 <sup>b</sup>	
4.	18 Jan.'57	6 Feb. '57	64	much <sup>a</sup>		
5.			96	much <sup>a</sup>		
				11,2	11,7 <sup>b</sup>	
6.	Nov. '57	16 Dec. '57	0			3,03 26,4
		18th				3,00 25,7
		13 Feb. '58				2,97 23,9
7.		5 Dec. '57	32	very few <sup>c</sup>		
		14th		2,2	6,7	
		16th		1,2	3,6	2,8 24,6
		18th		12,1	37,8	3,0 23,9
		13 Feb. '58		very few <sup>c</sup>		2,9 23,4
8.		5 Dec. '57	48	7,0	14,6	
		14th		3,7	7,6	
		16th		2,1	4,4	2,85 24,6
		18th		6,6	13,7	3,00 24,2
		13 Feb. '58		very few <sup>c</sup>		2,89 23,3
9.		5 Dec. '57	64	14,0	21,9	
		14th		10,1	15,8	
		16th		21,9	34,2	3,0 23,8
		18th		19,5	30,5	3,0 24,5
		13 Feb. '58		very few <sup>c</sup>		2,93 22,8

SalamisDelicate Salami

10.	Oct. 1956	6 Feb. '57	64 <sup>a</sup>	28,9	45,2 <sup>b</sup>	
				very much <sup>a</sup>		

Hungarian Winter Salami

11.	Nov. 1957	19 May '58	0			3,1 26,9 traces
12.			32	very few <sup>c</sup>		3,07 26,2 0
13.			48	" "		3,1 25,9 0
14.			64	" "		3,1 25,7 0

<sup>a</sup> Estimation with dichloro-phenol-indophenol paper according to the method of Grüu and Böhm.

<sup>b</sup> Determination quantitative in other part of the sample.

<sup>c</sup> No more decidedly determinable with dichloro-phenol-indophenol-solution.

<sup>d</sup> The other samples /32 and 48gm. ascorbic acid mixed into 100kg stock/ are missed.

Note: For the determination of ascorbic acid, pH and pH 10gm. ground sausage were pounded in a mortar with 15 gm. crystallized sugar and 1 gm. crystallized citric acid, then filled up to 200mls. with freshly boiled and cooled distilled water. For the determinations the filtered solutions were used.