IODATE AS IODIZING AGENT IN CURING SALT

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SUMMARY

In Germany 20 to 30 % of the consumption of salt comes from meat products and 80 to 90 % of them are produced with curing salt. According to recommendations of our institute curing salt can be iodized now in Germany by addition and mixing with iodate. Before the regulations for iodized curing salt, we investigated the problems connected with it and found: iodine in the form of iodate is stable in curing salt. There are no sensoric nor technological problems when using iodized curing salt in meat products. After production of different meat products we found losses of inorganic iodine of 20 to 30 %. These losses come from reactions of iodine with fat and protein, only traces of iodine were volatile. During manufacturing of meat-products most of the iodate will be reduced to iodide, in meat-products iodide and nitrite coexist and do not react to volatile iodine. The content of nitrosamines in raw sausages is not influenced by the addition of iodine.

INTRODUCTION

Already in ancient Rome goitre was characteristic for the people from north of the alps. Until today goitre is wide-spread in Germany with an increasing tendency from north to south. This was found still in the seventies and eigthies in german recruits (figure 1). More accurate investigations in Germany showed a pronounced lack of iodine for consumers in mountainous areas, especially in the alps. Iodine had been discovered in 1811, already in 1820 it had been postulated that goitre shows the lack of this element in nutrition. For more than 70 years in Switzerland, 40 years in Sweden and 30 years in Austria common salt is iodized generally and the effect of iodizing against illness of the thyroid gland is very clear. Comparing the supply of iodine in Germany with the advised minimum amount of uptake indicates an alarming deficit (table 1).

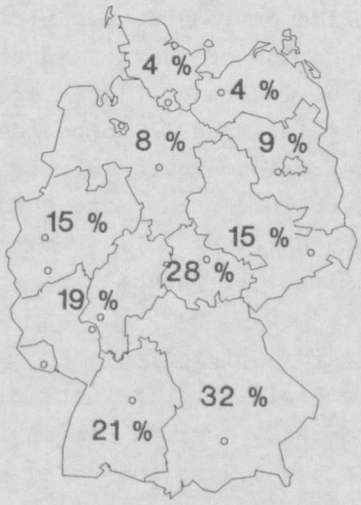


Figure 1: Frequency of goitre in german recruits

Table 1: Supply with iodine in µg/day

adults in Germany (on an average)	30-70
recommended minimum, adults (WHO)	150-200
recommended maximum (WHO)	500
non-toxic maximum (USA)	> 1000

Table 2: Iodation of salt in European countries (1990)

		amount of iodine (mg/kg)	kind of iodine
Austria	(A)	15.3	KI, KIO_3
Belgium	(B)	-	-
France	(F)	25	iodide, iodate
Germany	(D)	15-25	KIO_3, $NaIO_3$
Greece	(GR)	7.6-15.3	KI
Great Britain	(GB)	11.5-23	KI
Italy	(I)	24-42	KI, KIO_3
Netherlands	(NL)	17.6-22.2	KI, KIO_3
Switzerland	(CH)	15.3	iodide
Spain	(E)	51-69	KI, KIO_3
Recommendation of the European Salt Industries to the Europ.Commission		10-30 mg/kg	iodide, iodate

Normal nutrition behaviour in Germany shows a lack of about 100 µg iodine per day. This chronic lack causes several kinds of illnesses. The financial disadvantage only will be more than 1 billion DM per year. Consuming daily 5 g iodized salt (with a content of 20 µg iodine per g of salt) the lack just could be compensated, but even with a consumption of a maximum of 20 g of iodized salt the recommended maximum (WHO) for iodine will not be surpassed. As indicated by legislation in other European countries the lack of iodine in food is a problem in those countries too. Table 2 shows the content and which kind of iodine (iodide or iodate) is permitted. The

amounts of iodine in salt are similar for most countries and in the same range as in Germany: 15-25 mg iodine per kg of salt. The great range indicates the difficulties when preparing a homogenous mixture with such low concentrations or it has to be considered as an additional guard against possible losses. In contrast to other countries in Germany iodate has to be used exclusively. In this form the iodine is stable against oxidation, additional stabilizing agents for iodide as used in other countries will not be needed and only in this form curing salt and iodine can be mixed.

Naturally occuring inorganic and organic bound iodine

Iodine in nature occurs organically bound or in its inorganic form as sodium or potassium iodide or iodate. Technically important sources contain iodate (IO_3^-). Oxidation of iodide or reduction of iodate can result in volatile iodine. Because of the high volatility of iodine we were afraid of greater losses during the manufacturing of meat products.
Only few organic compounds with iodine we know from literature. Best known is thyroxin (tetra-iodo-thyronin), tri-iodo-thyronin and mono- and di-iodo-tyrosine, precursors of thyroxin. Furthermore there was described iodo-cresol 1984 in an experimental cake mix (SEVENANTS et al). From this hints of literature we conclude that iodine has a uncommon high affinity to phenolic compounds as cresole or the amino-acid tyrosine.

Analysis of iodine

The limit for titrimetric determination of inorganic iodine in the presence of starch is 1 mg iodine/l. Iodized common salt contains 15-25 mg iodine/kg, meat-products with 2 % salt contain 0.4 mg iodine/kg and after extraction (10 g substance in 200 ml) the concentration of iodine is 0.02 mg/l. Such low concentrations can be analysed by two methods, both using the catalytic effect of iodide in oxidations. We used a method, working in the range until 20 ppb (µg/l). It can be carried out in every laboratory with a spectrophotometer and there is only need for usual chemicals. In the reaction thiocyanate, forming a red colour with iron-III-salts, is oxidized by nitrite and nitrate in acid solution and iodide will catalyze this reaction. The other method, working in the same range of concentration, is known as 'Sandell-Kolthoff-Reaction'. There the reaction of cerium (-IV) with arsenic (-III) is catalysed by iodide. We used both methods but prefer the first one.

Methods:

The method of 'Sandell-Kolthoff' was first described in 1934. The calibration curve for iodide is logarithmic, decreasing with the concentration of iodide. The calibration curve for the reaction we used was linear and decreasing. This reaction was first described by IWASAKI et al (1957), later by SCHWEIKINA (1975) and MOXON and DIXON (1980).

Table 3: Chemicals and solutions for analysis:

	g/l	Mol/l	quantity in reaction in moles
Ammonium-iron-III-sulfate-12-hydrate solve in 400 ml (hot) water, add	77	0.16	$0.32 * 10^{-3}$
167 ml Nitric acid, (65%, density 1.4 g/l, and water to 1 litre	152	2.412	$4.82 * 10^{-3}$
Potassium-thiocyanate	0.23	0.00237	$2.37 * 10^{-6}$
Ascorbic acid, 1%-solution	10	0.05678	$56.8 * 10^{-6}$
Sodium-nitrite (fresh daily)	20.7	0.300	$0.3 * 10^{-3}$
iodide, max. 20 ppb			$0.63 * 10^{-9}$
Standards:			
Potassium-iodide, dried	5.232	0.0315	
resp. potassium-iodate	6.744	0.0315	

The standards of iodide or iodate in 1 litre of water have a concentration of 4 g iodine/l (4000 ppm). Other standards we made were: 10 ml/1000 ml//5 ml/1000 ml with concentrations of 40 ppm (40 mg iodine/l) and 0,2 ppm (200 ppb = 200 µg iodine/l) and the final standards of 0, 4, 8, 12, 16 and 20 ppb (µg iodine/l).

Procedure of the analysis:

4 ml of each standard, sample and control are mixed; the concentration of iodide shall not exceed 20 ppb. To every sample 1 ml of ascorbic acid solution, 1 ml KSCN and 2 ml of iron-III-salt will be added and mixed on a Vortex-Mixer. After 90 sec 1 ml of sodium-nitrite is

added and mixed again. After exactly 20 min the extinction is measured photometrically at 450 nm. There should be a constant ambient temperature.
We found that without ascorbic acid iodate is not reduced to iodide and cannot be determined. So we could distinguish between the inorganic forms of iodine: iodide and iodate.

RESULTS AND DISCUSSION

Content of iodine in curing salt

For our attempts we used an iodized curing salt. In this salt we found 19.8 ppb iodine per kg curing salt. After some months we found almost the same content of iodine as iodate but iodide only in minor amounts. From this fact we conclude that iodate is stable in curing salt for a long time. More accurate analysis showed an inhomogenous distribution of iodine in the bags, due to the constant total content of iodine in curing salt this however seems to be of no relevance.

Iodized meat products and sausages

Investigations of the technological and sensoric properties of several meat products, manufactured with iodized salt and with curing salt, showed no negative effects. Recoveries of inorganic iodine normally were 70 to 90 %. The results for several meat products are summarized in table 4. Best recoveries were in raw sausage, lowest in cooked ham. The most analyses were made from frankfurter type sausages and raw sausages. In frankfurter type sausages, manufactured in tins, we varied the addition of ascorbate (with/without), the addition of iodine (half/full concentration), the temperature of heating (75, 110, 120°C) and the time of analysis (0, 4, 12 weeks). The statistical calculations showed a small influence only of temperature and storage time (table 5).

Table 4: Recoveries of total iodine in cured meat-products

cooked ham	70.7 ± 2.0 %
liver-sausage	75.1 ± 6.0 %
frk.type saus.	76.9 ± 6.6 %
raw sausage	85.3 ± 13.0 %

Table 5: Relevant statistic factors for the recovery (76.9 ± 6.6 %) of inorganic iodine in frankfurter type sausages:

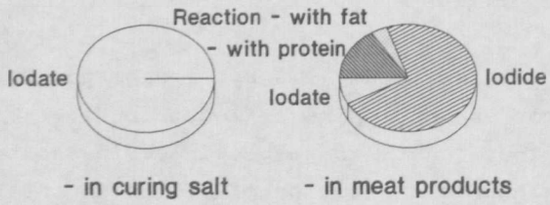
influence of:	
amount of iodine (half/full)	no influence
ascorbic acid (with/without)	no influence
temperature (75°, 110°, 120°C)	*
storage-time (0, 4, 12 weeks)	*

There is a remarkable influence of storage time for the recovery of iodine in raw sausage: the amount of recovered iodine decreases with time.
Analysis showed that most of iodate in meat-products changed to iodide. This conversion was complete in frankfurter type sausages, in raw sausages iodate remained partially (10-20%). The fast and complete reaction in sausages of frankfurter type in the unheated minced meat in comparision with the uncomplete reaction in raw sausage may be caused by the more intensive mixing of different phases (fat-/water-soluble parts). On the other side iodate is stable in processed meat-products: we found that a solution of iodate, added to homogenized frankfurter type sausages did not react to iodide even when heated to 100°C.

Losses of iodine

Because of losses of inorganic iodine we collected and washed the air above the blender with potassium hydroxide. We could find only traces of iodine, so the lost iodine must have reacted otherwise e.g. to organic compounds. Ashing of the samples, as described in literature, gave no reproduceable results, different kinds of ashing were unsuccessful. After extraction of iodine we ashed the fat and protein, remaining in the filter. The distribution of iodine to the fractions of fat and protein were 1:4. From this result we conclude that

Figure 2: Reactions of Iodate
Scheme of Distribution

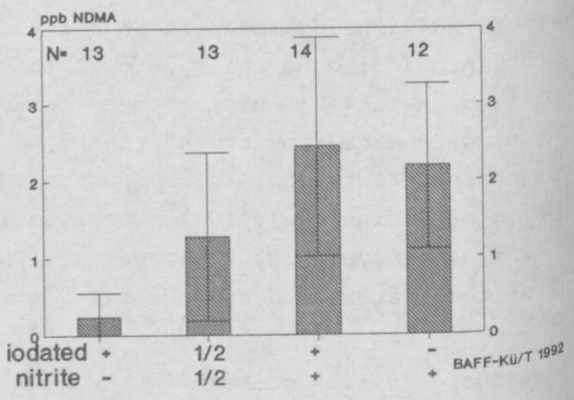


organic iodine is bound mostly to the protein-fraction, a schematic description of this fact shows figure 2. This result has been confirmed by investigations with radioactive iodate (I-131). Iodide was transformed to iodate and manufactured in the usual manner. Only traces of iodine were volatile when manufactured in meat products. In dependence from the products 4 to 37 % of I-131 was non-extractable with water and most of it was found in the protein fraction. We suppose that besides inorganic iodine the element is bound mostly to tyrosine or thyroxin and so it is at the consumer's disposal in an optimal way.

Nitrosamines

We know from literature that reactions of secondary amines with nitrite lead to cancerogenic N-nitrosamines and are catalyzed by iodide. Raw sausages contain most nitrosamines. We produced raw sausages and analysed the content of N-nitrosamines. In the products we found only N-nitroso-dimethylamine (NDMA) but no N-nitroso-piperidine (NPIP) or N-nitroso-pyrrolidine (NPYR). The results are summarized in figure 3. There is statistically no difference between cured raw sausages produced with or without iodine. But it can be seen very clearly, that the content of nitrosamines is correlated with the amount of the nitrite used.

Figure 3: N-Nitroso-dimethylamine-
concentrations in raw sausage



CONCLUSIONS

Iodine - as iodate in table salt or curing salt - is not lost as volatile iodine when used in meat products. In frankfurter type sausages iodate will be converted to iodide completely, in raw sausage to the major part. There are losses of 20 to 30% of inorganic iodine because it is bound organically. In this form iodine is available to the consumer too. In meat-products iodide and nitrite coexist and react scarcely with each other. There is no greater formation of nitrosamines in iodized meat products.

Producers of meat-products are asked to use iodized curing salt for their products. In this way the lack of iodine in our nutrition can be compensated.

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