FACTORS INFLUENCING THE LOSS OF IODINE FROM IODIZED SALT[1]

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INTRODUCTION

The prevalence of goiter in certain sections of the United States has resulted in the general use of iodized salt for both man and animals. The State of Montana lies in one of these so-called "goiterous" regions, and in order to prevent goiter and its associated conditions of weakness in farm and ranch animals, the veterinary department has recommended the use of stock salt containing 1 ounce of potassium iodide to 100 pounds of the salt.[3] This salt is frequently prepared in large quantities and stored in convenient places on the range. After it has been in storage for several months or longer, stockmen have noted that brown specks appear scattered throughout the mass. The question was accordingly raised whether these brown specks were due to discoloration by iodine which had been freed from combination with the potassium. If the discoloration were due to iodine then some iodine would also escape into the atmosphere and the remaining salt would contain less of it. The study to be reported in this paper concerns itself with the loss of iodine from iodized salt, the factors which influence its loss, and methods for preventing it.

HISTORICAL

It is a common observation that solutions of potassium iodide become yellow or brown with age. The brown color of these solutions is due no doubt to the formation of free iodine resulting from the decomposition of potassium iodide. Concerning the mechanism or the dynamics of the change, little definite information is available. Exposure of the solution to sunlight apparently hastens the decomposition.

It is probable that the same factors which operate to liberate iodine from solutions of potassium iodide will operate in a similar way to produce free iodine in an iodized salt. Fellenberg (*5*)[4] finds that iodized salt in ordinary storage in a grocery store loses iodine. Since he found that the purer the salt the lower the loss of iodine, McClendon (*13*) suggests that the loss is probably due to the presence of nitrites or nitrates which oxidize the iodide to iodine, which then volatilizes into the air. Fellenberg (*5*) has determined the impurities likely to be present in salt. He found no correlation between the

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[3] Since the beginning of these experiments, unpublished results of the veterinary department indicate that stock salts carrying as low as 0.02 per cent of KI are effective in preventing goiter.

[4] Reference is made by number (italic) to "Literature cited," p. 183 .

Mg, Ca, SO_4, Fe, and Al content of the salt and the quantity of iodine lost during storage.

Since iodine should not escape so readily from an alkaline medium, this same investigator (*5*) prepared an alkaline iodized salt by the addition of 0.693 gm. of potassium carbonate per kilogram of the salt. In several instances this alkaline salt retained more of its iodine than ordinary iodized salt when the two salts were stored under comparable conditions. Fellenberg (*5*) also investigated the distribution of iodine stored in containers of such a nature that he could obtain upper, middle, and lower layers of the salt. He found that in every case the iodine content was lowest in the middle layer and greatest in the lowest layer. This phenomenon he attributed to the solubility of the potassium iodide in the moisture of the salt and its transportation to the surface by capillarity. At the surface it concentrates owing to the drying out of the salt. Fellenberg also states that slightly moist salt retains its iodine better than dry salt and, further, that iodized salt loses its iodine as it drys out.

Fellenberg (*4*) determined the hydrogen-ion concentration of solutions of stored salt from time to time. If iodine were lost from the salt then the remaining salt should be more alkaline, due probably to the formation of potassium bicarbonate. Fellenberg, however, observed no significant changes in hydrogen-ion concentration.

Exposure to air and light are likely to affect the rate of loss of iodine from materials containing it. Several workers have detected iodine in the atmosphere. Chatin (*2*) was able to classify regions as goiterous or nongoiterous according to the iodine content of the air. Gautier (*11*) found appreciable quantities of iodine in sea air, less in air at Paris, and none in mountain air. The iodine which this last worker detected was all present as organic iodine. Fellenberg (*8*) has determined the influence of exposure to light and air on the loss of iodine from materials containing it. He stored sea water from two sources for periods of two to seven weeks in darkness and in daylight, in still air and in moving air. Only the sea waters which were exposed to a current of air appeared to lose any iodine. Whether stored in darkness or in daylight made no difference in the quantity of iodine lost.

Another means by which iodine could be liberated from materials containing it is by the action of molds or bacteria. This means is of special significance in the case of stock salts which may be scattered or kept in blocks on the ground or fed in troughs which become contaminated with soil.

Fellenberg, Geilinger, and Schweizer (*10*) found that certain agencies in the soil act on potassium iodide to liberate iodine. When a strip of moist starch paper was suspended in a beaker containing soil with added potassium iodide, it turned blue in a short time, indicating the liberation of iodine. The evolution of iodine into the atmosphere occurred more readily in unfertilized than in fertilized soils. This might indicate that the nitrites or nitrates of the soil were not responsible for the reaction. It is quite likely, however, that iodine was also liberated in the fertilized soils but reacted with and was bound by the organic matter.

Concerning the mechanism by which the iodine was liberated, Fellenberg, Geilinger, and Schweizer (*10*) state that the reaction was due neither to bacteria nor enzymes but to inorganic catalysts.

The ferric ion seems the most likely catalyst. Corresponding soils containing ferrous iron liberated some iodine, but the reaction was less rapid. In the case of soils of low iron content the liberation of iodine was more rapid at the higher hydrogen-ion concentrations.

Fellenberg and Geilinger (*9*) also found that *Bacillus coli*, *Aspergillus niger*, and various molds bound free iodine when cultured in neutral media. These microorganisms were not specific or active, but purely passive in their ability to react with free iodine. The iodine merely combined with the protein of the microorganism as it would with any nonliving protein.

EXPERIMENTAL

ANALYTICAL PROCEDURE

The best method of determining minute quantities of iodine which may be present in a material are those developed by Fellenberg (*4*, *6*, *7*) and by McClendon (*13*). The quantity of potassium iodide used in iodized salt, however, is sufficiently large so that other methods were found more convenient. The iodized salts on the market in this country contain several hundredths of a per cent of potassium iodide, while the stock salt recommended by the veterinary department of the Montana Experiment Station contains 0.0625 per cent.

For the determination of such quantities of iodine as these, a modification of Kendall's method (*12*) was found most suitable. According to this method the iodide is oxidized to iodate by means of bromine. The excess bromine is then expelled by boiling, the last traces being removed by treatment with salicylic acid. After acidification with H_3PO_4, potassium iodide is added and the liberated iodine titrated with standard thiosulphate solution. The thiosulphate solution used was approximately 0.01 normal. One cubic centimeter of such a solution is equivalent to 0.0002116 gm. of original iodine. Throughout all the work the thiosulphate solution was checked against a standard solution of potassium biniodate. This method may be used when large quantities of sodium chloride are present. When relatively small quantities of bromides are present, however, low results are obtained.

THE SALTS USED

The iodized salts were prepared from three types of commercial salts varying in size of particle. On the market these salts are known as table salt, hay salt, and stock salt. The salts were obtained from a salt manufacturer of Salt Lake City, Utah.

In the preliminary work attempts were made to prepare the iodized salts by adding potassium iodide to the salts in the form of a powder. Using this method it was found extremely difficult to obtain duplicate samples which would contain the same quantity of iodine. This was particularly true of the coarse stock salt. Since preliminary experiments indicated that some other method of preparing the iodized salt would have to be found, in order that uniform samples might be obtained, experiments were performed in which an aqueous solution of potassium iodide was added to the salt. It was thought that by this method the potassium iodide would be distrib-

uted more uniformly throughout the mass of salt and that on drying it would adhere to the salt particles. In any case the evaporation of the water would leave the potassium iodide more finely divided than by the previous method. By following this procedure it was possible to obtain more concordant results. It was accordingly adopted.

RESULTS

In giving the results which were obtained when the various iodized salts were stored under different conditions, each of several variables in the conditions of storage will be considered separately. Among the factors which were thought important as affecting the rate of loss of iodine from iodized salt were the moisture content as determined by the humidity of the surrounding atmosphere, the acidity or alkalinity which might be superimposed upon the salt, and the method of preparation of the salt, as, for example, whether the potassium iodide were added as a powder or crystallized from the brine with the sodium chloride. Salts iodized with potassium iodate were also prepared and stored under the same conditions as salts iodized with potassium iodide.

The work was also extended to include observations on the loss of iodine from iodized salt exposed to direct sunlight and to rain. The effect of heat alone on the loss of iodine was also studied.

Storage of Dry Iodized Salt in Pasteboard Cylinders

Samples of hay salt and stock salt were prepared, containing approximately the quantity of iodine recommended by the veterinary department. The original salts were moistened with a solution of potassium iodide, and then before storing in the covered pasteboard cylinders the iodized salts were dried by spreading out in a thin layer at room temperature. Periodically for a year the iodine contents of the salts were determined. The results are given in Table 1. A study of this table shows that no significant changes in the iodine content of the salts had taken place. Hence, it is safe to conclude that iodized salts kept in this manner will retain most of their iodine for storage periods of considerable length. Fellenberg (*5*) reached similar conclusions in regard to iodized salt prepared for human consumption and kept on the shelves of a store until sold.

Table 1.—*The loss of iodine from iodized salts stored in pasteboard cylinders*

Date	Storage period	KI content	
		Hay salt	Stock salt
	Weeks	*Per cent*	*Per cent*
Oct. 5, 1925	0	0.0565	0.0610
Nov. 28, 1925	8	.0546	.0612
Feb. 4, 1926	17	.0553	.0597
May 7, 1926	31	.0570	.0603
June 30, 1926	38	.0563	.0610
Sept. 5, 1926	48	.0572	.0623
Oct. 18, 1926	54	.0571	.0615

Storage of Iodized Salt Under Semisheltered Conditions

Samples of iodized stock salt were stored in such a way as to allow free circulation of air through them. One sample in an open glass jar was placed in an open shed. Another sample in a burlap bag was stored in the loft of a barn. The iodine contents of these salts were determined after various intervals of time. The results obtained are given in Table 2. These data indicate that considerable losses of iodine occurred under these conditions of storage. The salt stored in the burlap bag appeared to lose iodine more rapidly than the one stored in the glass jar. Thus, after about 13 months the salt stored in the burlap bag had lost 14.4 per cent of its iodine, while that stored in the glass jar had lost only 6.1 per cent. Since air would circulate much more freely in the salt stored in the burlap bag and remove the free iodine more rapidly with consequent shifting of the conditions back to where more iodine would be liberated, it is possible that this may account for the greater loss of iodine from the salt subjected to more aeration.

Table 2.—*Loss of iodine from samples of iodized salt stored under semisheltered conditions*

Stored in open jar in shed					Stored in burlap bag in barn loft				
Date	Storage period	KI	Loss per 10-gram sample	Loss	Date	Storage period	KI	Loss per 10-gram sample	Loss
	Weeks	*Per cent*	*Mgm.*	*Per cent*		*Weeks*	*Per cent*	*Mgm.*	*Per cent*
Sept. 29, 1925	0	0.0605	0	0	Oct. 26, 1925	0	0.0629	0	0
Nov. 30, 1925	9	.0606	0	0	May 20, 1926	29	.0589	.40	6.8
Feb. 3, 1926	19	.0594	.11	1.8	July 20, 1926	38	.0572	.57	10.0
June 25, 1926	39	.0590	.15	2.5	Nov. 22, 1926	56	.0550	.79	14.4
Sept. 10, 1926	50	.0575	.30	5.2					
Nov. 14, 1926	60	.0570	.35	6.1					

Storage of Iodized Salts in Atmospheres of Different Relative Humidities

Since iodized salts prepared on the range are likely to be stored under conditions differing in the relative humidity of the surrounding atmosphere, an experiment was devised to study this factor. The iodized salts were stored in desiccators in which the relative humidity was controlled by some substance or solution contained in the desiccator. The following relative humidities were maintained: 100, 50, 20, and 0 per cent. The 100 per cent relative humidity was maintained by having water in the desiccator, the 50 and 20 per cent by solutions of KOH, and the 0 per cent by solid $CaCl_2$. Potassium hydroxide was used for the intermediate relative humidities, as it would remove any free iodine from the atmosphere and hence would not allow the reaction by which iodine was liberated to stop or slow up because an equilibrium had been reached.

TABLE 3.—*Loss of iodine from iodized salts stored in atmospheres of different relative humidities*

Date	Storage period (weeks)	Percentage of KI at—			
		100 per cent relative humidity (over water)	50 per cent relative humidity (over KOH solution)	20 per cent relative humidity (over KOH solution)	0 per cent relative humidity (over $CaCl_2$)
Oct. 2, 1925	0	0.0630	0.0615	0.0688	0.0650
Nov. 27, 1925	8	.0563	.0621	.0644	.0637
Feb. 3, 1926	18		.0617	.0629	.0622
May 7, 1926	31	.0587	.0613	.0626	.0588
June 29, 1926	38		.0618	.0620	.0630
Sept. 3, 1926	48		.0615	.0620	.0635
Oct. 5, 1926	53		.0610	.0593	.0622
Feb. 8, 1927	71	.0517			

The data which were obtained are given in Table 3. These data indicate that iodized salt stored over water loses considerable iodine. After May 9, 1926, it was impossible to sample this salt as it had taken up so much water. On February 8, 1927, the whole mass of salt was dissolved in water and the iodine content determined. The salt stored in an atmosphere of 100 per cent relative humidity lost nearly 20 per cent of its iodine during storage from October, 1925, to February, 1927. The salt stored over the solution of KOH of such concentration as to give 50 per cent relative humidity lost no iodine during storage, while the two salts stored in drier atmospheres, i. e., over the more concentrated solution of KOH and over $CaCl_2$, lost small quantities of iodine. Further observations concerning the loss of iodine from very dry iodized salts will be given later. Fellenberg obtained similar data when he stored dry and moist iodized salts.

STORAGE OF ACID AND ALKALINE IODIZED SALTS

It is known that when free iodine is introduced into an alkaline solution it reacts with the alkali to form the iodide. On the other hand, iodine is readily liberated from acid solutions of the iodide. Hence iodized salts rendered alkaline may retain their iodine better than neutral or iodized salts rendered acid. In order to test the validity of this idea, one iodized salt was rendered acid by the addition of 1 per cent of KH_2PO_4 while another was rendered basic by the addition of 1 per cent of $NaHCO_3$. These salts were stored in a bell jar at ordinary humidity and the iodine content determined periodically. The results obtained are given in Table 4. The data in this table show that the salt rendered acid lost about one-third of its iodine during storage for aproximately one year. The salt rendered alkaline not only did not lose but actually showed an increase in iodine content when stored for a year. Since the two salts were stored under the same bell jar, the basic salt apparently absorbed a small quantity of the iodine liberated from the acid salt. That iodine was liberated from the acid salt and not from the basic salt was shown qualitatively. A piece of paper was placed in each salt. The paper placed in the acid salt became dark brown, while that in the basic salt showed no discoloration.

TABLE 4.—*The influence of added acid or alkaline salts on the loss of iodine from iodized salts*

Date	Storage period	KI content	
		Salt containing 1 per cent KH_2PO_4	Salt containing 1 per cent $NaHCO_3$
	Weeks	*Per cent*	*Per cent*
Oct. 2, 1925	0	0.0610	0.0622
Nov. 28, 1925	8	.0622	.0631
Feb. 4, 1926	18	.0509	.0630
May 7, 1926	31	.0468	.0640
June 28, 1926	38	.0451	.0645
Sept. 3, 1926	48	.0428	.0648
Oct. 13, 1926	54	.0410	.0649

The effect of the alkalinity in preventing loss of iodine from iodized salt is not in entire agreement with certain work of Fellenberg. He found that the addition of 0.693 gm. of K_2CO_3 to a kilogram of salt did not always prevent the loss of iodine, although in some cases it did. Fellenberg did not work with an acid salt. It is possible that a slight loss of iodine from the alkaline salt would have been found in the writers' experiments also if the atmosphere had not been so rich in iodine liberated from the salt which had been rendered acid. Data will be presented later, however, to show that the addition of $NaHCO_3$ distinctly reduces the loss of iodine from iodized salt.

POTASSIUM IODIDE LEACHED FROM IODIZED SALT BY RAINS

In order to study the effect of exposure to climatic conditions, particularly rain, on the loss of potassium iodide from salts containing it, a large deep funnel containing 2,240 gm. of the salt was set up out of doors. A bottle was placed under the funnel in order to catch the solution which would seep through the salt. It was thought that almost all the potassium iodide which was present in the salt would be removed by the first rain (on account of the great solubility of KI in water), and thereafter the residual salt would be practically iodine free. Such was not the case, however, as the data in Table 5 indicates. After several rains resulting in the collection of 667 gm. of leachings the salt still contained more than 20 per cent of its original potassium iodide. One would expect, moreover, to obtain more iodine in the first rains than in later rains. The rate of rainfall, however, appears to regulate this. The first rains were very hard, while those which came later were slower.

The reason that more potassium iodide is not removed is probably because the rain washes channels down through the salt and the channels once formed allow most of the water to pass through. The remainder of the salt was protected by air which was unable to escape through the wetted salt surrounding it. Hence the water does not come in contact with the potassium iodide in the body of the salt but only with that along the channel. The formation of these channels in the salt layer was checked up in the laboratory. Salt was placed in long tubes and water from a burette allowed to drip slowly on the salt. The effect of the water as it seeped through the tube was then noted.

TABLE 5.—*Potassium iodide leached from iodized salt by rain*

Date	Rainfall	Weight of leachings	Total solids in leachings	KI extracted	Percentage of original KI extracted
	Inches	*Grams*	*Per cent*	*Mgm.*	
July 29, 1925 [a]	0.31	114.0	14.0	109.0	8.5
Do		37.9	26.1	62.0	4.8
Aug. 3, 1925	.03				
Aug. 13, 1925	.01				
Aug. 14, 1925 [a]	.64	109.2	20.7	214.5	16.7
Aug. 15, 1925	.01	196.0		292.5	22.7
Aug. 20, 1925	.01				
Aug. 27, 1925	.38				
Aug. 28, 1925	.21	210.7	25.0	321.0	25.0
Total	1.60	667.8		999.0	77.7

[a] Collected in two portions.

At the end of the experiment the salt remaining in the funnel was dissolved in water, and the potassium iodide in an aliqout of solution was determined. The leachings contained 77.7 per cent and the residual salt 22.4 per cent of the original potassium iodide, respectively, making a total of 100.1 per cent. This indicates that all of the iodine is accounted for in the leachings and in the residue and that very little could have been liberated by sunlight or other climatic factors. The experiment was, however, too crude to enable one to make accurate observations concerning the effect of sunlight in liberating iodine from iodized salt.

THE EFFECT OF METHOD OF CRYSTALLIZATION ON THE LOSS OF IODINE FROM IODIZED SALT

In most of the study which has been recorded the iodized salts were prepared by moistening the sodium chloride with a solution containing the proper quantity of potassium iodide. It was thought that it might be possible to prepare iodized salt in which the potassium iodide would be either occluded or held in solid solution within the crystals of sodium chloride. If such were possible the rate of loss of iodine should be slower than when the potassium iodide is merely coated on the outside of the sodium chloride crystals, as is probably the case when the salts are iodized by adding a solution of potassium iodide. In following out this idea an iodized salt was dissolved in water and, by evaporation of the water, it was recrystallized. The salt was then dried and stored, in one instance, in a pasteboard carton and, in another instance, in a canvas bag. The same iodized salt but not recrystallized was stored in an open glass jar. The iodine content of the three salts was determined perodically. The results are given in Table 6. A study of the data in this table indicates that the recrystallized salt stored in the pasteboard carton lost no iodine during storage for a year. This is in agreement with the data in Table 1 in which several salts were stored in the same manner. A sample of the same recrystallized salt stored in a canvas bag lost about the same quantity of iodine (a slightly greater percentage) as did the iodized salt not recrystallized. Hence, it would appear that no advantage attends recrystallizing the salt in this manner.

TABLE 6.—*Comparison of losses of iodine from ordinary iodized salt and iodized salt recrystallized*

Recrystallized iodized salt stored in pasteboard carton			Recrystallized iodized salt stored in canvas bag			Iodized salt (not recrystallized) stored in open glass jar		
Date	Storage period	KI content	Date	Storage period	KI content	Date	Storage period	KI content
	Weeks	*Per cent*		*Weeks*	*Per cent*		*Weeks*	*Per cent*
Oct. 19, 1925	0	0.0794	Oct. 19, 1925	0	0.0798	Aug. 18, 1925	0	0.1205
Jan. 19, 1926	13	.0794	Dec. 21, 1925	9	.0762	Oct. 19, 1925	9	.1150
May 7, 1926	29	.0797	Feb. 3, 1926	15	.0751	Dec. 21, 1925	18	.1137
June 30, 1926	36	.0797	May 1, 1926	28	.0743	May 8, 1926	38	.1138
Sept. 7, 1926	46	.0792	June 30, 1926	36	.0720	June 30, 1926	45	.1130
Oct. 18, 1926	52	.0794	Sept. 3, 1926	46	.0720	Sept. 5, 1926	55	.1132
			Nov. 22, 1926	57	.0705	Nov. 1, 1926	63	.1125

In order to determine further whether mixed crystals of potassium iodide and sodium chloride were formed, the following experiment was performed: Seventy grams of iodized salt was dissolved in just sufficient water to dissolve it, and about half the water evaporated. The salt which separated out was then placed in a Büchner funnel and sucked dry. Then enough water was added so that a pasty mush was formed. This mush was stirred for a few minutes and finally the water was drawn off by suction. This process was repeated. If a solid solution of potassium iodide in sodium chloride had been formed during the recrystallization then the mother liquor as well as the crystals remaining on the filter should contain considerable quantities of potassium iodide. If a solid solution had not been formed then the potassium iodide should all be dissolved in the mother liquor due to its relatively greater solubility. The salt remaining on the filter was found to contain practically no potassium iodide, hence it may be concluded that mixed crystals had not been formed. Since the recrystallized salt used in the storage experiment had been prepared in this manner, there is no reason to expect that it would retain its iodine to any greater degree than salt iodized in the ordinary way. Since sodium chloride and potassium iodide are of similar crystal structure it might be possible to prepare mixed crystals containing the two salts if proper conditions were maintained during crystallization. The preparation of solid solutions of several of the alkali halides is recorded in the literature. Such mixed crystals of potassium iodide and sodium chloride would probably contain much more iodine than is present in iodized salt, and would have to be used for iodizing salt. There is the possibility that salts iodized with mixed crystals of potassium iodide and sodium chloride would lose their iodine at a slower rate than salt iodized with potassium iodide. In view of the relatively small losses of iodine from salts stored under even only moderately favorable conditions this possibility did not seem worthy of investigation.

THE EFFECT OF SUNLIGHT ON THE LOSS OF IODINE FROM IODIZED SALT

Since in the feeding of iodized salts to stock the salts are likely to be exposed to sunlight for various periods of time, and since it is known that sunlight hastens the decomposition of potassium iodide,

a study was made of the effect of sunlight on the rate of loss of iodine from iodized salts. The salts were stored in open crystallizing dishes on the sill of a south window and determinations of the iodine content were made periodically. Four salts were used in this study, (1) a salt iodized with finely divided KIO_3, (2) a salt iodized with KI solution, (3) and (4) two iodized salts which had been recrystallized according to the method used in the preceding section. The results obtained are given in Table 7. The most significant conclusion that can be drawn from these data is that salts iodized with KIO_3 retain their iodine when exposed to sunlight, while salts iodized with KI lose considerable portions of it. Thus, the salt which originally contained 0.0620 per cent of KI contained only 0.0165 per cent at the end of 63 weeks. The recrystallized salts show no advantage over ordinary iodized salts in regard to retaining their iodine when exposed to sunlight. Salt (4) was stored in a crystallizing dish of 4⅜ inches diameter while the other salts were stored in dishes of 7½ inches diameter. Hence, a smaller surface of the salt was exposed to the light. This probably accounts for the smaller loss of iodine in this case.

TABLE 7.—*Loss of iodine from several iodized salts stored on the sill of a south window. Salt (1) was iodized with KIO_3 powder; salt (2) with KI solution; salts (3) and (4) were iodized with KI and recrystallized*

Date	Storage period	KI content			
		Salt 1	Salt 2	Salt 3	Salt 4
	Weeks	*Per cent*	*Per cent*	*Per cent*	*Per cent*
July 30, 1925	0	0.0630	0.0620	0.0528	----------
Oct. 5, 1925	10	.0628	.0495	.0270	0.0780
Nov. 28, 1925	17	.0620	.0399	.0179	.0745
Feb. 4, 1926	27	.0613	.0355	.0173	.0729
May 7, 1926	40	.0627	.0299	.0072	.0694
June 28, 1926	48	.0630	.0280	.0065	.0663
Sept. 3, 1926	57	.0633	.0250	.0049	.0621
Oct. 13, 1926	63	.0636	.0165	.0040	.0588

Since the surface exposed to the light appeared to be a factor in determining the quantity of iodine lost from an iodized salt, this factor was subjected to further study. Ten gram samples of iodized salt were weighed out on watch glasses and some of the watch glasses containing the salt were placed in dark cupboards, others were placed on the roof in direct sunlight, and still others were placed on the roof in the sunlight but covered with other watch glasses. The data which were obtained are given in Table 8. The losses in iodine which occurred are relatively large. Thus, exposure of the salt for two days resulted in a loss of 40 per cent of the iodine. When the watch glass containing the salt was covered the loss was less, or only 14.9 per cent. In the experiment in which one day's exposure was allowed the sky was somewhat cloudy. This may account for its lower loss in proportion to the loss for two days. The losses in all cases, however, are relatively large.

TABLE 8.—*Effect of exposure to sunlight on the rate of loss of iodine from iodized salt*

Treatment	Exposure of a salt for 1 day	Exposure of another salt for 2 days
Control (stored in dark cupboard), per cent KI	0.1662	0.0530
Exposed to direct sunlight, per cent KI	.1505	.0316
Difference	.0157	.0214
Loss, per cent	9.4500	40.300
Control (stored in dark cupboard), per cent KI	.1662	.0530
Exposed to sunlight but kept under glass, per cent KI	.1557	.0451
Difference	.0105	.0079
Loss, per cent	6.4900	14.900

EXPOSURE OF IODIZED SALTS TO VARIOUS CONDITIONS OF TEMPERATURE AND LIGHT

In the data which have been recorded thus far it has developed that losses of iodine were prevented when the salts were iodized with KIO_3 and when salts iodized in the ordinary way had added to them 1 per cent of $NaHCO_3$. It would have been most desirable to expose such salts to direct sunlight in order to determine their efficiency in retaining iodine under such a condition. Such experimentation as was carried out in the preceding section was, however, very difficult, as in many cases the watch glasses containing the salts were upset by wind or rain and the whole experiment had to be repeated. In the experiments to be described in this section, artificial conditions of heat and light were therefore set up with the idea of paralleling as closely as possible natural conditions of exposure to sunlight. An attempt was also made to determine what wave lengths of light were responsible for the decomposition of potassium iodide. The results which were obtained, when several salts were exposed to varying degrees of heat and light, are given in Table 9. Salts A, B, and C were iodized with potassium iodide, C being the neutral salt, while A contained 1 per cent of added $NaHCO_3$ and B 1 per cent of KH_2PO_4. Salt D was a neutral salt iodized with KIO_3. Ten gram portions of each of the salts were weighed out into small evaporating dishes and exposed to the different degrees of light or heat.

TABLE 9.—*Exposure of several iodized salts to various conditions of light and heat. Salt A contained 1 per cent $NaHCO_3$; salt B, 1 per cent of KH_2PO_4; salt C was the neutral salt; and salt D was a neutral salt iodized with KIO_3*

Treatment	Percentage of KI in—			
	Salt A	Salt B	Salt C	Salt D
	Per cent	*Per cent*	*Per cent*	*Per cent*
None	0.0568	0.0561	0.0569	0.0600
Exposure to ultra-violet light for 10 minutes	.0562	.0550	.0567	.0595
Exposure to infra-red light for 30 minutes	.0568	.0551	.0568	.0595
Exposure to electric light for 70 hours	.0551	.0443	.0520	----------
Exposure to electric light for 100 hours	.0555	.0405	.0511	.0603
Exposure to electric light for 167 hours	.0550	.0387	.0497	----------
Exposure to heat on hot plate at about 80° C. for 70 hours	.0543	.0424	.0395	.0590
Exposure to heat on hot plate at about 80° C. for 77 hours	.0556	.0416	.0394	.0602
Exposure to electric light for 167 hours, last 67 hours on hot plate at about 80° C	.0545	.0346	.0351	----------

In one instance the salts were exposed for 10 minutes to ultraviolet light generated by an apparatus used by a local physician. The salts were placed about 4 feet from the source of the light. A study of the data in Table 9 indicates that none of the salts lost significantly great quantities of iodine. The salt with the acid reaction, however, showed the greatest loss. It is likely that the time of exposure was not long enough to allow the decomposition to proceed very far. The apparatus was such, however, that the light could not be generated for longer periods of time without injury to the apparatus.

When portions of the same salts were exposed to infra-red rays (also produced by a physician's apparatus) for a period of 30 minutes at a distance of 3 feet from the source of light, only very slight losses of iodine occurred. It is significant, however, that again the salt rendered acid with KH_2PO_4 lost the greatest quantity of iodine. It is also probable in this case that exposure to the light for longer periods of time would have given more significant results, but again this was not possible.

Portions of salts A, B, C, and D were next exposed to the light from a 750-watt electric light bulb, the dishes containing the salts being placed 10 inches from the filament. One series was exposed for 70 hours, another for 100 hours, and a third for 167 hours. At the end of these periods of exposure the iodine contents were determined. The data show that the salt containing the iodate lost none of its iodine; salt A, rendered alkaline with $NaHCO_3$, lost very little; while the neutral and acid salts lost considerable quantities which increased as the time of exposure to the light was increased. Also the acid salt lost appreciably more than the neutral salt. This result might be expected as the instability of the iodides in acid solution is well known.

The effect of heat alone on the loss of iodine from the same series of salts was next investigated. The dishes containing the salts were placed on a hot plate with the heat turned "low." The temperature attained by the salt was found to be about 80° C. A study of the data in Table 9 shows that the salt iodized with iodate again lost none of its iodine and that the loss from the salt rendered alkaline was relatively slight. Salts B and C again lost considerable quantities of their iodine. It is interesting to note that in this experiment the neutral salt lost more of its iodine than the one rendered acid with KH_2PO_4. This behavior occurred in two instances when the salts were exposed to heat alone; hence it is not likely that it is due to experimental errors. The explanation for the phenomenon is at present unknown.

Salts A, B, and C were next exposed to heat and light simultaneously. Salt D was omitted from this experiment as it had already been shown to be stable when exposed to either heat or light alone. Salt A again showed itself to be very stable. It lost only slightly more iodine than when exposed to light alone for the same time. In every case the losses of iodine from the salt rendered alkaline with $NaHCO_3$ are slight. Salts B and C lost about 60 per cent of their iodine. The losses in the case of these two salts were greater than when they were exposed to light alone for the same period of time. Thus the iodine content of the neutral salt decreased from 0.0569 per cent to 0.0497 per cent when exposed to light alone, while when

kept at 80° C. for the last 67 hours of the 167-hour exposure to light it decreased further to 0.0351 per cent. The acid salt showed similar decreases from 0.0561 per cent to 0.0387 per cent and to 0.0346 per cent, respectively. From these data it is evident that both light and heat are factors affecting the rate of loss of iodine from iodized salt.

The experiments of Fellenberg (*5*) as well as some of those of the present writers, showed that iodized salts which were kept perfectly dry lost more iodine tkan moist salts. The factor of dryness and the effect of heat alone on the salt may be linked together in some way, as the salt kept at 80° C. on the hot plate was certainly dry.

Concerning the mechanism of the reactions which take place when iodine is liberated in solutions of potassium iodide or from iodized salt, little definite information is available. Since iodine is set free, the solution or the salt, as the case may be, should have an alkaline reaction due to an excess of base. To test out this idea, a solution of KI which had stood in the laboratory for several years and had become a dark brown was decolorized by the addition of finely divided silver. The silver reacted with the free iodine to form silver iodide, and when filtered the solution became water clear. The resultant solution was red to phenolphthalein and when titrated with standard acid it was found to be 0.013 normal in its alkalinity; with methyl orange the alkalinity was 0.016. Why such an alakline solution does not cause the combination of iodine and alkali to reform the iodide is not known unless the iodine exists in some complex combination, which is probably the case.

Fellenberg (*4*) attempted to measure the decomposition of iodized salt by determining the hydrogen-ion concentration of a solution of the original salt and then that of the salt after storage. An increase in alkalinity would indicate loss of iodine. He found that solutions of the salts prepared before and after storage showed no significant difference in hydrogen-ion concentration. The quantity of KI in the iodized salts which he used was, however, so low [5] as to render difficult the determination of any slight changes which may have taken place. In the writers' work it was found that whenever any appreciable loss of iodine occurred there was also a resulting change in hydrogen-ion concentration. Thus, at the end of the storage period when drops of indicators were placed upon small portions of the salt, the salt stored in an atmosphere of 100 per cent relative humidity (Table 3), which had lost a considerable quantity of iodine, was shown to be more alkaline than the same salt which was stored in an atmosphere of 50 per cent relative humidity.

This same fact was shown in another set of experiments. The hydrogen-ion concentrations of the series of salts listed in Table 9 as being exposed to the light of the 750-watt electric light bulb were determined before and after exposure to the light. The results are given in Table 10. A comparison of the values for iodine lost as given in Table 9 and changes in P_H as given in Table 10 shows the relation which exists. The salts which lost the most iodine show the greatest change in the hydrogen-ion concentration of their solutions. With the hydrogen electrode it was impossible to determine the hydrogen-ion concentration of solutions containing the iodate.

[5] The salts with which Fellenberg worked contained five parts of KI per million parts of the salt. This quantity of KI was in accordance with the recommendations of the Swiss Goiter Commission.

Colorimetric determinations indicated, however, that the acidity of the salt iodized with KIO_3 had not been changed by exposure to the light.

TABLE 10.—*The hydrogen-ion concentration of solutions of several iodized salts. Salt A contained 1 per cent of $NaHCO_3$; salt B, 1 per cent of KH_2PO_4; salt C was the neutral salt; salt D was a neutral salt iodized with KIO_3*

Salt	Hydrogen-ion concentration in terms of P_H [a]		Salt	Hydrogen-ion concentration in terms of P_H [a]	
	Original	Final		Original	Final
A	7.13	7.25	C	6.54	7.02
B	2.62	3.50	D		

[a] The hydrogen-ion concentrations were determined before and after the salts had been exposed to electric light for 100 hours.

RELATION BETWEEN THE QUANTITY OF IODINE PRESENT IN AN IODIZED SALT AND THE QUANTITY LOST

In order to determine whether a certain proportion of iodine was lost from an iodized salt or whether an absolute quantity of it was lost, two salts were prepared containing widely different percentages of iodine. These salts were stored and their iodine content determined periodically. The results which were obtained are given in Table 11. The data in this table indicate that a certain percentage of the iodine is lost and not an absolute quantity of it. Thus, during the same storage periods the sample containing originally 0.1205 per cent of KI lost 0.08 mgm. of KI per gram of salt, while that containing originally 0.0288 per cent lost 0.02 mgm. of iodide per gram of salt. Of KI lost, the sample containing 0.1205 per cent of KI lost 6.65 per cent, while that containing 0.0288 per cent lost 6.95 per cent.

TABLE 11.—*Relation of quantity of KI present in an iodized salt to that lost during storage*

Date	Iodized salt of high KI content		Iodized salt of low KI content	
	KI present	KI lost	KI present	KI lost
	Per cent	*Per cent*	*Per cent*	*Per cent*
Aug. 18, 1925	0.1205		0.0288	
Oct. 19, 1925	.1150	4.57	.0282	2.08
Dec. 21, 1925	.1137	5.65	.0280	2.78
May 8, 1926	.1138	5.57	.0281	2.43
June 30, 1926	.1130	6.23	.0274	4.85
Sept. 5, 1926	.1132	6.06	.0275	4.51
Nov. 1, 1926	.1125	6.65	.0268	6.95

Table 12 gives results from which similar conclusions may be drawn. In this case two series of salts containing different quantities of iodine were exposed to electric light for 100 hours. The quantity of iodine lost apparently depends on the quantity present.

TABLE 12.—*Relation of quantity of KI present in an iodized salt to that lost by exposure to electric light for 100 hours. Salt A contained 1 per cent of $NaHCO_3$; salt B, 1 per cent of KH_2PO_4; salt C was the neutral salt*

KI content	Salts of high KI content			Salts of low KI content		
	Salt A	Salt B	Salt C	Salt A	Salt B	Salt C
Initial KI content, per cent	0.0568	0.0561	0.0569	0.0114	0.0112	0.0114
Final KI content, per cent	.0555	.0405	.0511	.0106	.0084	.0095
Difference	.0013	.0156	.0058	.0008	.0028	.0019
Per cent loss	2.29	27.80	10.20	[a] 7.00	25.00	16.7

[a] A single determination, others in duplicate.

DISCUSSION

From the data which have been given it is evident that iodized salts show considerable variation in the degree to which they retain their iodine when stored for extended periods of time. It appears that when air is able to circulate freely over the salt or through it the loss of iodine is greater than when circulation of air is prevented. On this basis coarse-grained iodized salts should lose their iodine more rapidly than fine-grained salts. In several instances this has been found to be true. The data indicate quite clearly that when circulation of air is prevented, loss of iodine for all practical purposes does not occur even when the salt is stored for periods longer than a year, provided the salts are not too damp and provided they are not exposed to light of too great intensity. Salts may be stored in atmospheres up to at least 50 per cent relative humidity without serious loss of iodine. In fact, iodized salts stored in atmospheres of 50 per cent humidity appear to retain their iodine more effectively than salts stored in drier atmosphere.

Exposure of ordinary iodized salts to sunlight results in setting free very considerable quantities of the iodine which is present. In one instance 40 per cent of the iodine of an iodized salt was lost when a thin layer of the salt was exposed to direct sunlight for two days. This loss of iodine by the action of light may be reduced either by iodizing the salt with KIO_3 or by rendering it alkaline with 1 per cent of $NaHCO_3$. It is possible that a smaller quantity of $NaHCO_3$ might have been sufficient, but investigations with the addition of other quantities were not made in this study. Concerning the advisability of replacing KI with KIO_3 there may be a question. Crespolani (*3*) states that small quantities of KIO_3 are changed in the intestine to KI, and hence utilized in the same way as KI. The principal agency in the reduction which takes place is thought to be peptones in acid solution. He administered as much as 2 to 3 gm. at a dose. When such large doses were administered, however, some KIO_3 was excreted unchanged in the urine. Mellor (*14, p. 598*), on the other hand, states that care must be exercised in the choice of KI for medicinal purposes as it may contain some KIO_3, which, according to him, is a poison. It is not believed, however, that the small quantity of KIO_3 which would be taken internally in iodized salt would have any ill effects on the organism. In this regard McClendon in a private communication states that KIO_3 may be administered orally to human beings to the extent of ¼ gm. per

kilogram body weight. He advises against its injection into the system. Crespolani (*3*) also states that intravenous, intramuscular, or subcutaneous injection of iodates does not result in their reduction to iodides. From this he concludes, as has already been stated, that the reduction occurs in the alimentary canal. The use of KIO_3 to replace KI in iodized salt must, however, be a subject for further research.

According to Chapline and Talbot (*1*), the best way in which to feed salt to sheep is at the camp each night. Only what will be eaten is fed each time; hence there is no danger of losing iodine by exposure to sunlight. When, however, the salt is kept in a trough in the open sunlight for days or weeks at a time, considerable quantities of iodine will be lost before the salt has been eaten. The same is true of blocks or cubes of salt kept on the range. The iodine in the surface of the cubes may entirely disappear between the times when stock remove the outer surface. It would appear, therefore, that the use of iodized salt in blocks would not be a desirable practice.

At the beginning of the work it was reported that iodized salts containing brown spots were found, but no such spots have come under the observation of the writers. Van de Vorst (*15*) states that brown spots developed in postassium iodide due to the growth of a certain fungus. Such fungus growth might have caused the brown spots reported by the veterinary department.

CONCLUSIONS

Iodized salts stored in atmospheres of relative humidities of 50 per cent lose smaller quantities of their iodine than salts stored under similar conditions at other humidities.

Iodized salts rendered alkaline by the addition of $NaHCO_3$ lose practically none of their iodine during storage, while neutral salts or salts rendered acid lose appreciable quantities.

Salts iodized with KIO_3 lose none of their iodine when stored for extended periods.

Exposure of iodized salts to sunlight effects a loss of iodine from neutral or acid salts, only a slight loss from salt rendered alkaline, and practically no loss from salts iodized with KIO_3.

Exposure to heat alone effects losses of iodine from acid, neutral, and alkaline iodized salts and from salt iodized with KIO_3 in precisely the same order as did exposure to sunlight.

Exposure to light and heat simultaneously effects greater losses of iodine from salts of neutral or acid reaction than exposure to light alone or heat alone. In the case of iodized salts of alkaline reaction the losses of iodine are again insignificant or negligible, even though the salts are exposed to light and heat simultaneously.

The quantity of iodine liberated from a neutral salt iodized with KI appears to depend on the quantity of KI present.

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