ADSORPTION OF TIN BY PROTEINS AND ITS RELATION TO THE SOLUTION OF TIN BY CANNED FOODS

by

B.C. GOSS

Adsorption of Tin by Proteins and Its Relation to the Solution of Tin by Canned Foods

A DISSERTATION

PRESENTED TO THE

FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

B. C. GOSS

Accepted by the Department of Chemistry, June, 1914.

Adsorption of Tin by Proteins and Its Relation to the Solution of Tin by Canned Foods

B. C. GOSS

ADSORPTION OF TIN BY PROTEINS AND ITS RELATION TO THE SOLUTION OF TIN BY CANNED FOODS

The presence of tin in foods which have been packed in tin cans has long been known and a great amount of work has been done on this subject, especially since 1878, when Menke published an article on "Tin in Canned Foods."[1] This work has, however, been almost entirely concerned with the mere presence of tin, determination of total tin present and with methods for recovering it.[2-14] The general procedure is to destroy first the organic matter. This is done by wet or dry oxidation or a combination of the two.

In the dry oxidation, the food is evaporated and the dry mass charred and oxidized in a muffle furnace, a small amount of potassium nitrate or nitric acid assisting in the operation. The tin is left in an insoluble form as stannic oxide. It is then rendered soluble by fusion with sodium carbonate and sulfur or with caustic potash, giving, respectively, sodium sulfostannate or potassium stannate. Also the stannic oxide may be reduced to metallic tin by a stream of hydrogen gas at red heat or fused with potassium cyanide and the metal dissolved in hydrochloric acid.

The moist incineration processes involve oxidation of organic matter by nitric acid, hydrochloric acid and potassium chlorate, sulfuric acid and potassium sulfate or by a mixture of nitric and sulfuric acids. In the latter two cases the tin is left in soluble form, as stannic sulfate, without any volatile compounds being formed which might cause a loss of part of the

[1] *Chem. News*, **38**, 5.
[2] *Analyst*, **1880**, p. 218.
[3] *Chem. News*, **48**, 257.
[4] *Chem. Ztg.*, **24**, 263.
[5] *Z. Nahr. Genussm.*, **3**, 246.
[6] *Chem. Ztg.*, **23**, 854.
[7] *Arch. Hyg.*, **45**.
[8] *Z. Nahr. Genussm.*, **7**, 676.
[9] U. S. Dept. Agr., Bureau of Chemistry, *Bull.* **107**, 61.
[10] Report No. 7, Local Government Board, Gt. Britain (**1908**).
[11] U. S. Dept. Agr., Bureau of Chemistry, *Bull.* **137**.
[12] *Ibid.*, **67**.
[13] *J. Ind. Eng. Chem.*, **5** (1913), 3.
[14] *8th Intern. Congr. Appl. Chem.*, **18**, 35.

tin. Having destroyed the organic matter and having the tin in solution, the amount may be determined either gravimetrically or by one of several volumetric methods, all of which depend upon the conversion of stann*ous* to stann*ic* salts. We have adopted, for the purpose of this investigation, the method worked out by H. A. Baker, now of the American Can Company,[1] and used with slight variations by the Bureau of Chemistry, American Can Company and the National Canners' Association.

A new method may be mentioned here which was tried for determining the tin in our solutions. We have found that the organic matter may be easily and quickly destroyed by perchloric acid at its boiling point where the approximate composition[2] is $HClO_4.2H_2O$, or, especially by a mixture of perchloric and nitric acids from which the nitric acid may then be easily driven off. The salts of perchloric acid are perfectly stable, readily soluble and not reduced by electrolysis so it was thought that the tin might be very accurately determined by electrolysis of this perchloric acid solution. We found that by using a mercury surface of 200 cm^2. as the cathode, with which the tin is easily amalgamated while the overvoltage of the hydrogen is at a maximum, tin ions could be completely and quickly removed from large volumes of dilute solution. In the removal of the mercury by distillation, however, difficulties were encountered, owing to the tendency of the tin to oxidize and stick to the walls of the flask. We expect to do more work along this line.

Little or no exact information has been obtained regarding the mechanism of the solution of the tin by the canned food nor the condition in which it is present. Bigelow and Bacon[3] compared the acidity of a large number of canned foods with the total tin present, and there appears to be little relation between the two. For example, beets packed in plain tin cans were found, 6 months after packing, to contain 72.8 mg. of tin per 100 mg. of acid, while cherries contained only 1.5 mg. of tin per 100 of acid. J. P. Atkinson noticed that if tin salts were added to meats, only a third to a half of the tin could be recovered by electrolysis even after an artificial gastric digestion.[4] We have noticed that in the electrolysis of a pulped

[1] 8th Intern. Cong. Appl. Chem., **18**, 35.
[2] *J. Am. Chem. Soc.*, **34** (1912), 1480.
[3] *J. Ind. Eng. Chem.*, **3** (1911), 832.
[4] J. P. Atkinson, Bureau of Health, New York (unpublished).

food sample over a mercury cathode only a part of the tin was deposited, even after a much longer time than is usually necessary. Evidently the tin is not entirely in solution. Some evidence on this point was found in the experiments of Unger and Bodlander, confirmed by Buchanan and Schryver, in which the food was roughly separated into liquid and solid portions by a sieve and each analyzed separately for tin[1,2]. The solid portion, of course, still contained large amounts of liquid but the results showed an unequal distribution of tin between the liquid and solid portions.

It is obvious from this brief review of the situation that the first question to be settled is exactly the one of how much tin is in true solution in the various kinds of canned foods as well as the total amount of tin present.

EXPERIMENTAL

We have succeeded in making a satisfactory separation of the tin which is in true solution from the combined tin by means of dialysis. Owing to the ease with which tin salts hydrolyze, precautions had to be taken to avoid hydrolysis during the dialysis. The following scheme was adopted. The bottom was cut off from a wide, two-liter bottle and replaced by a film of collodion which was made by pouring out the collodion upon a dish of mercury and before entirely hard, pressing it upon the glass.[3] This makes a membrane which is very strong and capable of being used for several determinations before requiring replacement and, therefore, owing to ease of preparation, strength, and the short time required for dialysis, it was chosen in preference to gold-beaters' skin and thin parchment which were also tried. The acidity of the sample of food was determined directly on removal from the can by titrating 20 cc. of the filtered juice, using phenolphthalein as indicator, against $N/10$ sodium hydroxide. If the juice was too darkly colored, azolitmin on a spot plate was used.[4] Information regarding the character of the acid was obtained in most cases from the work of Bigelow and Dunbar, "Acid Content of Fruit Juices."[4] In most berries the acidity is due chiefly to citric acid while in the stone fruits, such as cherries, plums, peaches, apples,

[1] Beckurts, *Jahresber.*, **45**.

[2] Report No. 7, Local Government Board, Gt. Britain (**1908**).

[3] Bigelow and Gemberling, *Amer. Chem. J.*, **29** (1907), 1576.

[4] Bigelow and Dunbar, "Acid Content of Fruits" (unpublished).

apricots and most pears, the predominating acid is malic.

One liter of an acid solution of the same kind and strength as that of the liquid of the canned food was placed in a high crystallizing dish and the dialyzer suspended in this solution. A weighed sample of the pulped fruit was placed inside and constantly stirred so as to present a fresh surface to the membrane. A battery of 8 dialyzers was stirred from a central revolving shaft. It was found that in about 48 hours the equilibrium was established, although in some cases a longer time was allowed, and after this interval the dialyzer was raised and the volume of the contents inside and out measured. The large volume of the solution outside the membrane was evaporated and transferred to a Kjeldahl flask and the residue of pulp inside to another: 100 cc. of concentrated nitric acid were added to each and the mixtures let stand. If the food sample contained much sugar, rapid oxidation began almost at once and the flasks were left until brown fumes ceased to come off when 50 cc. of concentrated sulfuric acid were added and heat applied, thus avoiding too violent action. After heating until dense fumes of sulfuric acid appeared, the flasks were cooled and in case the solution was not colorless, small portions of nitric acid were added successively and heating repeated. The finally clear solution, from which all nitric acid had been expelled, was cooled, diluted with water and the acid neutralized with concentrated ammonia, testing with litmus paper and then the solution was acidified slightly with hydrochloric acid, heated to boiling and hydrogen sulfide passed in until the tin was all precipitated. The precipitates were allowed to settle and filtered in pairs, by suction, through asbestos, using false bottom Gooch crucibles. The precipitates were washed with hot water which had been saturated with hydrogen sulfide. The tin sulfide was dissolved in Erlenmeyer flasks by boiling with concentrated hydrochloric acid, to which successive small portions of potassium chlorate were added and the chlorine expelled at the end of the addition of a gram of aluminum foil. The flasks, four at a time, were placed upon a hot plate and attached to a carbon dioxide generator. After all the air had been displaced by carbon dioxide, the tin was reduced to the stannous condition by the addition of about 2 g. of aluminum foil. The solutions were boiled for a

few minutes after the aluminum disappeared and then cooled in ice-water, still in an atmosphere of carbon dioxide, removed one at a time, tubes and stoppers washed down with air-free water and titrated with $N/100$ iodine solution, using starch as indicator. Each time a series of titrations was made the iodine was standardized against a tin solution, 1 cc. of which contained 1 mg. of tin. Knowing the amount of tin in the solution outside the membrane, from the relative volumes of the acid solution and of the food pulp, the total amount of tin which was in true solution was calculated and, by difference, the tin which was in an insoluble form. The determinations were carried out in pairs and the average of results given. In some cases, as that of rhubarb, the agreement was exceptionally close, the pair yielding, respectively, 8.9 and 9.17 mg. of insoluble tin in a 75-g. sample. Where a large percentage of the tin was in an insoluble form, however, the agreement was not so close, due partly at least to the impossibility of getting two samples having just the same proportions of liquid and solid, and therefore in which the insoluble tin compound was equally distributed. A determination of the total tin in the sample of food used was also made in the usual way.

It will be noticed that in Table I the foods examined are arranged in the order of their increasing acidity as shown in column 9. It is obvious that neither the total tin nor the tin which is in solution are directly proportional to the acidity and it is evident that the amount of tin which is removed from the can is dependent also upon other factors. In calculating the amount of tin in solution in the pulp, from the concentration of tin outside the membrane after dialysis and the volume of the pulp it was assumed that the tin in actual solution was free to diffuse throughout the whole volume of the pulp; that is, that the space occupied by the solid particles of the food did not lessen the volume over which the soluble tin could distribute itself. In order to determine the maximum possible error which might arise from this source, the volume of the solids was determined in the case of two of the foods which contained the highest percentage of tin in solution, for it would be in such foods that the error must be greatest. A weighed sample of rhubarb, similar to the one used in the dialysis, was sucked dry of liquid in a Buchner funnel and the solid residue immersed in a measured amount of water,

TABLE I

No.	Food Sample Used	Age Years	Sample Grams	Time of Dialysis Hours	Vol. of Acid Cc.	Vol. of Pulp Cc.	Mg. Tin in Solution	Mg. Tin in Pulp		Acidity (Per cent) by Titration	Mg. Tin per Kg. Total	Mg. Tin per Kg. In Solution	Mg. Tin per Kg. Insoluble	Per cent of Tin In-soluble
1	Beets (Bur. Chem. F 21644)	5	100	72	970	205	45.6	37.7	Citric	0.074	833	552	281	33.9
2	Beets (enamel) (New York State)	1	...	...	...	...	...	...	Citric	0.080	11	....	...	....
3	Pumpkin (Bur. Chem. F 21040)	5	100	56	905	235	24.6	59.0	Citric	0.085	836	310	526	63.0
4	String beans (Maryland)	1	50	168	1010	150	1.8	5.9	Citric	0.090	154	42	114	73.5
5	Squash (Bur. Chem. F 22642)	3	100	72	995	270	5.2	24.8	Citric	0.112	300	66	234	78.0
6	Tomatoes (N. Y. State)	1	100	53	975	170	3.78	3.24	Citric	0.39	70	44	26	37.1
7	Black cherries (enamel)	5	100	56	970	200	1.5	7.5	Malic	0.51	90	18	72	83.3
8	Pickled peaches (N. Y. State)	1	...	...	...	...	...	...	Malic	0.52	39	....	...	....
9	White cherries (N. Y. State)	1	75	120	950	195	4.68	5.7	Malic	0.58	138	74.7	62.7	45.7
10	White cherries (N. Y. State)	1	75	144	940	150	4.9	5.4	Malic	0.58	138	74.7	61.4	44.9
11	Strawberries (Bur. Chem. F 22617)	5	100	50	970	265	14.5	27.1	Citric	0.70	416	185	231	55.5
12	Red cherries (Bur. Chem. F 22614)	5	100	58	950	230	5.9	16.3	Malic	0.71	222	73	149	67.2
13	Raspberries (Bur. Chem. F 21623)	5	...	...	...	...	...	...	Citric	0.71	316	....	...	....
14	Raspberries (enam.) (Bur. Chem. F 21626)	5	100	72	935	240	2.6	15.4	Citric	0.75	180	32.7	147	81.6
15	.....	..	...	...	...	...	...	...	.....	...	....	....	...	....
16	Gooseberries (Maryland)	1	50	48	980	150	4.0	6.56	Citric	1.2	212	92	118	56.2
17	Rhubarb (Bur. Chem. F 22634)	5	75	72	745	190	103	35.4	Citric & oxalic	1.5	1847	1725	122.2	6.62
18	Rhubarb (Bur. Chem. F 22634)	5	75	144	900	190	109	29.5	Citric & oxalic	1.5	1847	1741	118.7	6.38
19	Currants (enamel) (N. Y. State)	3	...	...	...	...	...	...	Citric	2.2	110	....	...	....
20	.....	..	...	...	...	...	...	...	.....	...	....	....	...	....

noting the increase in volume. This was found to be only 0.3 cc. so that the volume of the pulp inside the membrane through which tin could diffuse was 189.7 instead of 190.0 cc. Calculating the amount of tin in solution, on this basis, in the pulp we found 26.22 instead of 26.26 mg., a difference of 0.04 mg., which is negligible. Next to rhubarb, beets contain the highest percentage of tin in solution, and the difference found in the amount of tin in solution in the pulp, when the volume of the solid in the pulp was taken into consideration, was 0.02 mg. out of a total of 9.63 mg. From these results we have concluded that the volume actually occupied by the solid in the pulp may be neglected and the tin in the solution in the pulp calculated as if it were equally distributed over the total volume inside the membrane.

It will be observed from Table I that rhubarb, which was the first of the fruits examined, showed a small percentage of tin in an insoluble form, while pumpkin, squash, string beans and other foods high in proteins, contained a large amount of tin which was no longer in solution. We expected then that in the case of the berries, which are rather strongly acid and contain almost no protein matter, the greater part of the tin would be found in solution as was determined for rhubarb. When we came to examine raspberries, however, we were much surprised to find so high a percentage of the tin, about 81 per cent, in an insoluble form. The same was true in varying degrees for other similar fruits, strawberries, gooseberries, currants, cherries, etc. Since there appeared to be some relation between the amount of protein matter and the part of the tin which was insoluble, and since the only proteins in berries are in the nuclei of the seeds, some of these seeds were analyzed for tin.

The whole raspberries, containing 180 mg. of tin per kg., were pulped and pressed through cloth, the seeds being removed from the solid residue by washing and decantation in a large crystallizing dish. In this way perfectly clean seeds, free from pulp, were obtained. These were then washed with boiling water, dried in air and the tin determined in the usual way. The tin in the seeds ran 805 mg. per kg. In other words, most of the tin which is in an insoluble form was found in the seeds. In strawberries, this retention of tin is even more marked. The seeds of strawberries were found to contain, roughly, six times as much tin, weight for weight, as the whole fruit—the

seeds gave 2630 mg. per kg. as compared to 416 for the whole fruit. The fact that the larger part of the tin in the berries mentioned is combined and insoluble in the seeds is of fundamental importance in determining the physiological action of tin in canned foods, for the seeds, and with them the adsorbed tin will be eliminated, to a large extent at least, directly in the feces.

On the basis of these experiments, it would appear that the amount of soluble tin salts, rather than the total tin present in a can of food, should be limited, since it is the part of the tin adsorbed which determines the physiological action. A few typical determinations on fruit seeds appear in Table II.

TABLE II—ADSORPTION OF TIN BY SEEDS OF FRUITS

No.	Food Sample	Age Yrs.	Acidity Per cent	Total Tin Mg. per Kg.	Per cent Insoluble Tin	Seeds Mg. per Kg.
1	Red cherries.....	5	Malic 0.70	222.0	67.2	448.0
2	Black cherries (enamel).	5	Malic 0.51	90.0	83.3	321.0
3	Red raspberries (enamel)	5	Citric 0.71	180.0	81.6	805.6
4	Strawberries.....	5	Citric 0.70	416.0	55.5	2630.0
5	Tomatoes.....	1	Citric 0.39	70.0	37.1	106.5

We have already mentioned the fact that beets and rhubarb, the first of the foods examined, contain almost no protein and that in these foods we found large amounts of tin in solution. The foods high in proteins, such as string beans, squash and pumpkin, next to be investigated, showed a high percentage of tin in an insoluble form. In berries, we found that the greater part of the tin was concentrated, with the protein, in the seeds. It seemed from these results that there was some connection between the amount of protein in the food and the percentage of tin in solution as well as the total amount of tin removed from the inner surface of the can.

In order to get further evidence on the part played by proteins in determining the action of canned foods on the tin can, the following experiments were carried out: Coagulated globulins, prepared by heating the 10 per cent sodium chloride extract from dried, pulverized pea beans (soup beans), were washed and suspended in water in contact with tin plate of 392 sq. cm. surface and the tubes sealed. After two weeks, an average of 0.6 mg. of tin was found combined with the protein. Also, it was found that proteins, sealed with dilute acid solutions in contact with tin, greatly increase the amounts of tin going into solution (Table III). In these experiments a coil of tin plate, having

TABLE III—INFLUENCE OF AGAR JELL, PROTEINS, ETC., ON SOLUTION OF TIN BY CITRIC ACID

	Time (Mo.)	Mg. Tin Dissolved
Citric Acid (5%)	2	17.9
	7	20.5
Citric Acid (5%) + Agar Jell	2	18.3
	4	25.0
	7	25.3
Citric Acid (5%) + Proteins	4	32.7
	4	34.6
Citric Acid (2%)	7	11.7
Citric Acid (2%) + Agar Jell	7	16.9
Citric Acid (2%) + Crushed Peas	7	35.5
Citric Acid (2%) + String Beans	7	32.5

a surface of 392 sq. cm., was sealed in contact with a constant volume of citric acid solution (100 cc.), a part of the tubes containing citric acid alone, the others having coagulated proteins, agar jell, etc., added. All were kept at the same temperature.

The simple first reaction of the acid in the can of food is complicated by the presence of large amounts of colloidal proteins which undoubtedly affect the solution of tin. Albumins, globulins and other proteins are negative colloids and are precipitated by an ion of opposite charge. This is especially true of the heavy metal ions, of which tin is an example, and this precipitation is irreversible. It is known that when a sol is thus precipitated, the precipitating ion is firmly adsorbed and carried down with it. Linder and Picton first observed this in the case of arsenious sulfide sol and barium chloride.[1] In such cases the solution remaining is found to be strongly acid and in the same degree in which the precipitate contains the metal ion. These precipitates hold the metal ion very firmly and no amount of washing will remove it. In some respects they appear to be true chemical compounds, but the composition is too variable to admit of this view. For example, precipitates formed by the action of copper salts on albumins contain all the way from 1.4 to 20 per cent of copper oxide.[2]

These facts observed for other heavy metals agree closely with the facts observed in the combination of tin with food materials. After a small amount of tin has been dissolved from the surface of the can, adsorption and precipitation take place. When the tin ion is removed from solution by the proteins, the acid ion is liberated and more tin dissolved. In this way the tin would be constantly removed from solution and a small concentration of acid could ultimately dissolve a very large amount of tin. If the cell walls surrounding the colloidal proteins were unbroken,

[1] *Chem. Soc. Jour.*, **67** (1895), 63.

[2] W. W. Taylor, "Chemistry of Colloids," p. 118.

the proteins could not diffuse out into the solution, but the tin could enter and adsorption take place. Since practically all of the action of the food on the container takes place after processing, which involves heating to a rather high temperature, most of our proteins have been coagulated, but this seems to have little or no effect on the removal of tin from solution, and coagulated proteins were found to take up large quantities of tin. Beans were pulverized with sand, extracted first with water, obtaining a solution of proteoses and albumins, and then with a 10 per cent sodium chloride solution which removed large quantities of globulins. These solutions and egg albumen were used for the following tests: Small volumes of each of the above solutions were added to an excess of 2.5 and 5 per cent stannic chloride and stannic ammonium chloride solutions and the precipitate which was formed filtered, washed several times in boiling water, dried at 110° C. and the percentage of tin in a weighed sample determined gravimetrically. Parts of the same protein solutions were coagulated by heat and the coagulated proteins suspended in the same tin solutions for two days. The results show a varying percentage of tin which, however, is uniformly high. It was also noticed that if the precipitate was filtered and washed and one part of it dried and the percentage of tin determined, while the other part was put back in the solution and let stand, it continued to adsorb more tin. For example, 40 cc. of dilute globulin solution in 10 per cent NaCl were added to 400 cc. of 5 per cent stannic ammonium chloride; a white precipitate formed which was warmed to complete the coagulation and let stand for a day, then filtered, washed and dried; 0.409 g. gave on analysis 0.227 g. of tin or about 55.5 per cent. A part of the same precipitate was left in contact with the solution for a week before filtering, when 0.777 g. showed 0.441 g. of tin or 60.6 per cent. Using a 5 per cent stannic chloride solution the percentage of tin in one case ran to 69.2. As might be expected, the percentage of tin increases with the concentration of the solution. This is shown in Table IV.

TABLE IV—ADSORPTION OF TIN BY COAGULATED PROTEINS

	Original concentration Gm. of Tin ($SnCl_4$) per cc.	Final concentration Gm. of Tin per cc.	Per cent Tin in Dried Protein
A	0.000310	0.0000019	4.92
B	0.000517	0.0000465	9.90
C	0.001610	0.0009730	20.50
D	0.004680	0.0041600	35.60

Stannic chloride solutions, of varying concentrations, were made up and concentrated hydrochloric acid added to each to prevent hydrolysis. A constant weight of coagulated protein, 1.5 g., was suspended in 350 cc. of each solution and left for a week, after which a portion of the clear liquid was withdrawn with a pipette and analyzed for tin, and the protein was filtered off, washed with several portions of boiling water, dried at 110° C., and the percentage of tin determined. It will be noticed that in each case tin was left in solution.

Experiments were made with the insoluble tin compound from several of the canned foods which, although but slightly acid, contained large amounts of tin and it was found that here, too, the tin is very firmly bound. Squash is a good example of this. Samples of squash, which had been packed in tin cans and contained 300 mg. of tin per kg., were boiled for about 5 hours with water and the three protein solvents, 10 per cent NaCl solution, 70 per cent alcohol and 2 per cent HCl, and filtered through hardened filters. In the first three cases—water, alcohol and salt solutions—only 32.5, 32.8 and 35.8 per cent, respectively, of the tin was found in solution. The hydrochloric acid seems to break up the tin compound slowly on boiling and after 5 hours 25.4 per cent of the tin was still found combined with the solid residue. The question as to whether the tin which is adsorbed by these proteins passes through the processes of digestion without being absorbed is of first importance. We have mentioned this point in regard to the tin which was found combined in the seeds of berries and in addition have performed the following experiments to obtain further information.

Artificial gastric digestions were carried out upon the solid residue obtained by boiling canned squash, which contained 300 mg. of tin per kg. with water and filtering. This solid residue contained about 67 per cent of the total tin in the squash sample. The gastric juice, pepsin in 0.35 per cent HCl, was added to the squash and the mixture kept in a thermostat at 36° C. for 24 hrs., after which it was transferred to a dialyzer and the tin in solution determined in the usual way. Less than 10 per cent of the tin was found in solution. Both gastric and tryptic digestions were kindly carried out for us by Dr. E. N. Harvey, of the Biology Department, on the tin protein complex, prepared by allowing the freshly coagulated protein

to stand in contact with tin solutions, after it had been allowed to dry, and in each case only a trace of tin was found in solution. It appears from the above results that the tin protein combination which is formed is very stable, and in most of the foods containing the larger amounts of tin, the greater part is in an insoluble form. The possibility suggests itself that the part of the tin which is so firmly adsorbed will be eliminated directly in the actual digestive processes and not figure in the physiological action as determined for soluble tin salts.

The work of J. P. Atkinson on the electrolysis of metallic salt solutions to which chipped beef had been added is of interest in this connection. A known amount of the metal in the form of a soluble salt was added to finely divided beef and then submitted to artificial gastric digestion for 24 hrs. at 37° after which the solution was electrolyzed for 45 to 50 hrs. A few typical results follow:

Metal	Added Gram	Recovered Gram	Difference Gram	Per cent Recovered
Mercury	0.0500	0.0121	—0.0379	24.1
Mercury	0.0500	0.0217	—0.0283	43.4
Tin	0.0330	0.0051	—0.0279	15.5
Tin	0.0330	0.0063	—0.0267	19.1
Zinc	0.0500	0.0561	+0.0061	100.0
Nickel	0.0492	0.0497	+0.0005	100.0
Iron	0.0500	0.0497	—0.0003	99.7

It appears that the metals of relatively low toxicity are least firmly bound and he suggests that this may offer an explanation of the relative toxicity of metals, in that they interfere with the metabolism of the cell. Iron, being so easily separated, adds to this view. It was found that the toxicity of mercury as the bichloride was greatly diminished by adding it to chopped meat and submitting it to an artificial gastric digestion. One mg. of mercury as bichloride will kill a 250-g. guinea pig in 4 hrs. if injected subcutaneously, toxic symptoms beginning in a few minutes. The same quantity of mercury, after combining it with tissue as described above, produced no toxic symptoms and death did not follow until the fifth day. Rabbits also were injected without apparent harmful effects.

Résumé and Conclusions

It has been shown that the solution of tin by canned foods is neither dependent upon, nor proportional to, the acidity alone and, also, that in the foods of relatively slight acidity which dissolve large amounts of tin, the greater part of the tin is in the form of an insoluble and stable complex. The explanation which

agrees most closely with the observed facts is that we are dealing here with adsorption phenomena; that the tin, after being dissolved from the lining of the can, is being constantly removed from solution by the proteins, carbohydrates and other highly porous solid phases in contact with the solution. Whether we regard this as an adsorption of tin ions, or whether we consider the tin salt to be first hydrolyzed and the resulting stannous hydroxide adsorbed, in either case the acid would be regenerated and able to attack more tin. The former explanation seems to be the more probable; i. e., the tin ions are adsorbed, since tin is taken up equally well by proteins even from concentrated acid solution. It will be seen from the above results that while in several respects the observed phenomena appear to be true adsorptions, in one important respect they differ. While a true adsorption is an equilibrium and can be approached from either side, being reversible, this removal of tin is not a reversible action, for if the tin protein complex is transferred to an aqueous solution containing no tin, it does not lose tin to the liquid phase. A number of cases similar to this are known and have been called by W. W. Taylor, "Pseudo-adsorptions."[1] The removal of heavy metal salts from solution by charcoal is an example of this type of action; the first stage may be an adsorption, since the salts of heavy metals are strongly adsorbable, but a secondary reaction must have taken place and the final state cannot be put down to adsorption alone.

The author wishes to express his appreciation and thanks for the very valuable assistance and advice given by Dr. G. A. Hulett in connection with this work.

Laboratory of Physical Chemistry, Princeton, N. J.
and Bureau of Chemistry, Washington, D C.

[1] W. W. Taylor, "Chemistry of Colloids," p. 252.